SYNTHESES OF VINYL AROMATIC COMPOUNDS BY PYROLYSES OVER CATALYSTS

- LEVI -

SYNTHESES OF VINYL AROMATIC COMPOUNDS BY PYROLYSES OVER CATALYSTS

A Thesis

by

Leo Levi

Submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

McGill University

September 1950

ACKNOWLEDGEMENTS

The author wishes to express his gratitude
for the advice and encouragement received
from his research directors,

Dr. R.V.V. Nicholls

and

Dr. C.B. Purves

during the course of this investigation.

Acknowledgement is also extended
to the
National Research Council of Canada
for a special grant-in-aid of this project
as well as summer maintenance

and to the
Scientific Research Bureau
of the
Ministry of Industry and Commerce,
Province of Quebec,
for the award of a scholarship.

TABLE OF CONTENTS

GENERAL INTRODUCTION

The potentialities of catalysis were foreseen by Ostwald when he prophesied that a scientific knowledge and control of catalytic phenomena would lead to immeasurable results technically (1). This prophecy has been fulfilled, for to-day the importance of catalysis in science and industry is recognized by chemists everywhere.

The petroleum industry in particular has assisted greatly in this development and has made notable contributions. Catalytic methods have been developed for the cracking of complex petroleum molecules into simpler high-grade aviation fuels; for polymerizing smaller hydrocarbon molecules to form larger molecules of high anti-knock value in the gasoline range; for adding simpler saturated molecules to unsaturated molecules to form valuable fuels by processes of catalytic alkylation, and these processes in their turn demanded catalytic processes of isomerization, involving the changing of molecules to other configurations more valuable as fuels.

With the advent of World War II the technical importance of catalysis was further emphasized by the multiple demands made upon chemical industry by the Armed Forces. One of the most pressing of these demands was for the manufacture of synthetic rubber. Considering the eventual curtailment of its natural rubber supply, the United States Government at the outset of hostilities launched a gigantic synthetic rubber program under the auspices of the Office of Rubber Reserve. Two aims of this program were to develop a process by which adequate quantities of an essential raw material, styrene, could be produced, and to find new methods by which styrene as well as styrene homologues could be made, so that auxiliary supplies and improved co-polymers might eventually be created. The more important of these tasks, namely, securing an adequate supply of monomeric styrene for GR-S, was solved with the Dow Process for the catalytic conversion of ethylbenzene to styrene. An interesting account of the research work leading up to this process and a fitting tribute to those who helped in its development has been given by the late Willard Dow of the Dow Chemical Company (2).

The second task, carried on to a large extent at the laboratories of the University of Illinois, showed that nuclear as well as side-chain substituents in the styrene molecule greatly altered the physical and chemical properties of the corresponding co-polymere. For example, butadiene co-polymers of desirable solvent resistance, improved tensile strength, better milling behavior and excellent balance between hysteresis heat rise and flex-cracking resistance were obtained if a properly substitued styrene instead of styrene itself was used in the GR-S recipe (3). On the other hand, attempts to find fundamentally new processes for preparing substitued vinyl aromatics were not successful. The present investigation is primarily concerned with the problem of finding a novel method of styrene synthesis, particularly by a catalytic vapor-phase process.

The catalyst used was activated Morden bentonite, a Canadian clay large quantities of which are readily accessible, and the reactants chosen were an acid anhydride and an aromatic aldehyde. This pair of substances was chosen because in theory styrenes might be obtained on pyrolysis as a result of either the intermediate formation of an α,β-unsaturated acid which would decarboxylate, or of a ketene from the anhydride which would react with the aldehyde, or of a direct condensation product which would break up in a suitable way under the influence of the catalyst. Each of these possibilities was investigated on acetic anhydride-benzaldehyde mixtures, and a mechanism was worked out which explains the experimental results and is in accordance with accepted theories put forward to explain similar reactions. In order to determine the scope of the pyrolysis, the reaction was applied to substituted aromatic and heterocyclic aldehydes and was used successfully for the preparation of a number of vinyl compounds.

HISTORICAL INTRODUCTION

Preparation of Vinyl Aromatic Compounds

A survey of the literature shows that although quite a number of reactions may be resorted to for the synthesis of a particular styrene analogue, only five are available for the preparation of a large number of vinyl-substituted aromatics. A brief characterization of the essential features of these reactions is of both theoretical interest and industrial importance.

In each case the overall reaction will be indicated by the appropriate chemical equation and by a short description of the basic experimental procedure. Those styrenes, which have been prepared by applying the essential features of the reaction under discussion, will then be tabulated.

I. Decarboxylation of Cinnamic Acids

$$ArCH{=}CHCOOH \dashrightarrow ArCH{=}CH_2 + CO_2$$

The starting materials may be obtained by heating an aldehyde of the aromatic series with the anhydride of an aliphatic acid in the presence of the sodium or potassium salt of the acid at 175-180°C. under reflux for five hours. They may also be synthesized by condensing malonic acid with aromatic aldehydes (5). This reaction is usually carried out in alcoholic solution at 100°C. and in the presence of dry ammonia, or a primary or secondary amine, usually piperidine. The initially formed unsaturated malonic acid derivative usually undergoes decarboxylation in the course of the condensation and gives an α,β-unsaturated aromatic acid. Yields may be improved and the process period reduced from about four hours to two hours by using pyridine as solvent and a small amount of piperidine as a promoter (6).

Decarboxylation is carried out in the liquid phase. The acid is heated above its melting point in the presence of a trace of a polymerization inhibitor, and the corresponding styrene is isolated from the distillate. Some cinnamic acids tend to sublime without undergoing decarboxylation, and more favorable conversions are obtained if the reaction vessel, usually a Claisen flask, is immersed in a heating bath which completely surrounds the bulb and extends a short distance up the neck. This arrangement also decreases polymerization losses caused by excessive heating and refluxing.

If carried out in the presence of a basic solvent, such as quinoline, and copper powder or a copper salt, such as copper sulfate, as catalyst the reaction affords quite attractive yields in many cases. Losses from polymerization may be further reduced by dropping the quinoline solution of the acid slowly upon the hot copper powder at such a rate that no appreciable quantity of liquid is present in the reaction vessel at any given moment. Although the presence of both the copper salt and the basic solvent is generally reported to be necessary for efficient decarboxylation, 4-vinylguaiacol may be obtained in practically theoretical yields from ferulic acid in the presence of quinoline alone (7).

In spite of technical improvements and rather general applicability, the method is of no immediate industrial interest because the starting materials are not available in commercial quantities.

TABLE I

Styrenes Obtained by Decarboxylation of Cinnamic Acids

Vinyl Compound	% Yield	Reference
p-Acetoxystyrene	37	8
p-Aminostyrene	almost quantitative	9
m-Bromostyrene	56	10
o-Chlorostyrene	50	10
m-Chlorostyrene	67	10
p-Chlorostyrene	50-54	10
o-Cyanostyrene	28.9	11
m-Cyanostyrene	51	12
2,4-Dichlorostyrene	20	10
3,4-Dichlorostyrene	22	10
3,4-Dihydroxystyrene	75	13 14
3,4-Dimethoxystyrene	10	10
p-Dimethylaminostyrene	0	10
α-Ethoxystyrene		15, 16
p-Ethylacetoxystyrene	34	8
β-Ethylstyrene		17
o-Fluorostyrene	65.5	11
p-Formylstyrene	52	18
o-Hydroxystyrene	57	19
	50	20
	quantitative	21
Isopropylstyrene		17
Isopropyl-β-ethylstyrene		17
Isopropyl-β-methylstyrene		17
α-(2-Isopropyl-5-methyl)-phenoxystyrene		22
p-Isopropyl-α-methylstyrene		23
o-Methoxystyrene	67	10 11, 34
m-Methoxystyrene	27	24
p-Methoxystyrene	75	10 17

....

TABLE I (cont'd)

Styrenes Obtained by Decarboxylation of Cinnamic Acids

Vinyl Compound	% Yield	Reference
α-Methoxystyrene		25
3-Methoxy-4-acetoxystyrene	0	7
(4-Vinyl guaiacolacetate)	25	26
3-Methoxy-4-hydroxystyrene	74	27
(Vinyl guaiacol)	almost quantitative	7
	19	28
β-Methylstyrene		17
p-Methoxy-β-methylstyrene		17
p-Methylacetoxystyrene	50	8
p-Methyl-α-methylstyrene		23
α-(α-Naphthoxy)styrene		29
m-Nitrostyrene	0	10
	60	35
α-Phenoxystyrene	almost quantitative	29
α-(2,4-Dimethyl)phenoxystyrene		30
α-(o-Methoxy)phenoxystyrene		31
Styrene	almost quantitative	10
	38-41	32
	45.5	33
α-p-Tolyloxystyrene		29
α-o-Tolyloxystyrene		29
p-Vinylstyrene (p-Divinylbenzene)	45	18

II. Simultaneous Decarboxylation and Dehydrohalogenation of β-Aryl-β-Halopropionic Acids

$$\mathrm{ArCHBrCH_2COOH} \xrightarrow[\mathrm{Na_2CO_3}]{} \mathrm{ArCH{=}CH_2} + \mathrm{CO_2} + \mathrm{HBr}$$

The starting materials are usually synthesized by heating an α,β-unsaturated acid or its ester with glacial acetic acid saturated at 0°C. with hydrogen bromide. The reaction is carried out in a closed bomb at a temperature of 100°C. and usually interrupted after thirty minutes, longer reaction times or higher temperatures being avoided in order to prevent the excess hydrogen bromide from attacking the addition product. The crude β-aryl-β-halopropionic acid obtained on cooling may either be purified or heated directly with an excess of sodium carbonate. Steam distillation serves to isolate the corresponding styrene from the reaction mixture.

This method is of little practical value. The introduction of a molecule of hydrogen bromide into an unsaturated aromatic acid, which itself is prepared by a relatively involved synthesis, is followed by its removal together with a molecule of carbon dioxide. Furthermore, dehydrohalogenation is not the only reaction taking place, for in addition to the vinyl compound there also is obtained the corresponding β-phenyl-β-hydroxypropionic acid as well as its lactone, and invariably some of the β-aryl-β-halopropionic acid escapes decarboxylation.

TABLE II

Styrenes Obtained by Simultaneous Decarboxylation and Dehydrohalogenation of β-Aryl, β-Halopropionic Acids

Vinyl Compound	% Yield	Reference
p-Bromostyrene		36
p-Chlorostyrene		36
Isopropylstyrene		17, 44, 45
Isopropyl-β-ethylstyrene		17, 44, 45
Isopropyl-β-methylstyrene		17, 44, 45
o-Methoxystyrene		34, 17
p-Methoxystyrene		34, 17
o-Methoxy-β-ethylstyrene		34, 17
o-Methoxy-β-methylstyrene		34, 17
p-Methoxy-β-ethylstyrene		17, 44, 45
p-Methoxy-β-methylstyrene		17, 44
β-Methylstyrene		17
o-Methylstyrene		37
m-Methylstyrene		38
p-Methylstyrene	51	39
o-Nitrostyrene	10	40
m-Nitrostyrene	30	41
p-Nitrostyrene	29	42
Styrene	65	43 17

III. Dehydrohalogenation of α- or β-Haloethyl Aromatic Compounds

$$\left.\begin{array}{l}\mathrm{ArCHClCH_3}\\ \mathrm{ArCH_2CH_2Cl}\end{array}\right\rangle\text{---- Base ---}\rightarrow \mathrm{ArCH{=}CH_2} + \mathrm{HCl}$$

This method consists in heating the halogenated ethylbenzene with a dehydrohalogenating agent, such as pyridine, quinoline, ethanolamine or alcoholic potassium hydroxide and isolating the monomer from the reaction mixture by conventional procedures. In some cases dehydrohalogenation is carried out in the vapor phase.

The starting materials may be conveniently obtained by (a) halogenating alkylated aromatics formed by Friedel-Crafts type of reactions, (b) interacting aromatic compounds with hydroxyhalides, or (c) treating α-phenylethyl alcohols with hydrogen chloride.

Although the general nature of this method is evident, a serious limitation with respect to practical applicability arises from the fact that both the rate and extent of side chain halogenation are greatly influenced by the nature of the nuclear substituents present. Furthermore, careful control of conditions is necessary to have halogenation proceed in the side chain exclusively. If halohydrins are used as halogenating agents, dehydrohalogenation leads to the formation of positional isomeric styrenes which are separated only with difficulty. Conversion of α-phenylethyl alcohols to the corresponding phenylethyl halides as intermediates in styrene synthesis is no longer resorted to because direct dehydration to vinyl aromatic compounds can be achieved quite efficiently. (Method IV).

The disadvantages pointed out are encountered to a lesser extent in the synthesis of halogenated ethylbenzenes by the chloroethylation process. This reaction, discovered by Quelet and Ducasse, is a feasible method for the preparation of a number of α-chlorinated ethylbenzenes - and therefore of substituted styrenes - provided the aromatic nucleus is activated by the presence of strongly o-, p-directing groups, such as a methoxy or phenoxy group or both. The reaction itself is easily carried out. The phenolic ether, paraldehyde and concentrated hydrochloric acid are brought together at a temperature of 0-10°C. A rapid stream of hydrogen chloride is passed for about one hour into this mixture, which is then poured onto crushed ice and extracted with petroleum ether. After washing, drying and removal of the ether, the chlorinated ethylbenzene is heated at a temperature of 100-110°C. for five to six hours in the presence of pyridine, and the cooled reaction mixture is acidified with concentrated hydrochloric acid. After extraction with ether, purification of the extract and removal of the solvent the residue is fractionated to yield the monomer.

Unfortunately, chloroethylation cannot be considered a practical route for the preparation of styrene derivatives used in making synthetic rubber, not only because it is limited to phenolic ethers, but also because in chloroethylation, just as in chloromethylation, two competing reactions are operative. Choosing anisole as an example, the overall reaction may be shown to proceed as follows:

$$CH_3OC_6H_5 + CH_3CHO + HCl \dashrightarrow CH_3OC_6H_4CHClCH_3 + H_2O$$

$$CH_3OC_6H_5 + CH_3OC_6H_4CHClCH_3 \dashrightarrow (CH_3OC_6H_4)_2CHCH_3 + HCl$$

The latter of these two reactions leads to the formation of a diarylethane by-product and in fact it is so serious that for obtaining optimum yields of the chlorinated ether chloroethylation can be allowed to proceed only until the concentration of the α-chloroethylanisole has increased to the point where the two reactions are consuming anisole at about equal rates. Extending the reaction time beyond this point results in an increase of the by-product involving two aromatic nuclei.

A further limitation imposed on this reaction is the relatively low temperature at which it must be carried out in order to avoid pronounced tar formation from the paraldehyde. Hence, only the most highly reactive aromatic nuclei undergo chloroethylation and even these give relatively low yields of monomers. The phenolic ethers which react best give styrene yields ranging from 35-50 per cent when based on unrecovered starting material. A single halogen in the aromatic nucleus causes sufficient deactivation to prevent reaction. Attempts to chloroethylate o-, m-, and p-chloroanisole and o-, m-, and p-bromoanisole were unsuccessful. The only value of this method lies in that it may be tried for the preparation of styrene derivatives which are difficult to obtain by other syntheses.

TABLE III

Styrenes Obtained
by
Dehydrohalogenation of α- or β-Haloethyl Aromatic Compounds

Vinyl Compound	% Yield	Reference
3-Bromo-2-methyl-α-methylstyrene	18	46
3-Bromo-4-methyl-α-methylstyrene	45	46
Chlorostyrene	92	47
	90	48
m-Chlorostyrene	92.5	49
p-Chlorostyrene	almost quantitative	50
4-Chloro-α-methylstyrene	16	46
3-Chloro-2-methyl-α-methylstyrene	26	46
3-Chloro-4-methyl-α-methylstyrene	48	46
2,3,4,5,6,-Pentachlorostyrene	60	51
	87	52
o-Cyanostyrene	57	53
p-Cyanostyrene	55	53
3,4-Dimethoxystyrene	6	54
		69
2,4-Dimethylstyrene		55
2,5-Dimethylstyrene	78	55
2,3-Dimethyl-α-methylstyrene	8	46
3,4-Dimethyl-α-methylstyrene	72	46
p-N,N-Dimethylsulfonamidostyrene	67	56
Divinylbenzene	82	48
p-Ethoxystyrene		57
β-Ethylstyrene		58
p-Ethylstyrene	70	55
4-Ethyl-α-methylstyrene	18	46
		23
p-Fluorostyrene	71.5	59
5-Isopropyl-4-methoxy-2-methylstyrene	49	54
		60,79,80
4-Isopropyl-α-methylstyrene	73	46
		57
o-Methoxystyrene	80	57
	40	61

....

TABLE III (cont'd)

Styrenes Obtained
by
Dehydrohalogenation of α- or β-Haloethyl Aromatic Compounds

Vinyl Compound	% Yield	Reference
m-Methoxystyrene		57
p-Methoxystyrene	32.8	54
	high	57
	40	62
		63, 64
2-Methoxy-5-isopropylstyrene	30	65
2-Methoxy-5-methylstyrene	34	54
		60, 79, 80
4-Methoxy-3-methylstyrene	38	54
		60, 79, 80
3,4-Methylenedioxystyrene		57, 66
α-Methylstyrene	77	46
β-Methylstyrene		67
Methylstyrene	90	68
p-Methylstyrene	73	55
	15	70
4-Methyl-α-methylstyrene	60	46
		57
p-Nitrostyrene	68-73	71
p-Phenoxystyrene	17	54
Styrene	75-80	72
		55, 73
	53	74
1,3,5-Trimethylstyrene		55
1,2,4-Trimethylstyrene		55, 78
o-Vinylstyrene		75
m-Vinylstyrene		75
p-Vinylstyrene		76, 77

IV. Dehydration of α- or β-Arylethyl Alcohols

A. Dehydration of α-Arylethyl Alcohols

$$ArCHOHCH_3 \dashrightarrow ArCH{=}CH_2 + H_2O$$

This method for preparing substituted styrenes has received particular attention during the last few years in connection with the synthetic rubber program of the United States Government. The alcohols may be obtained by (1) Grignard reactions, involving (a) substituted benzenes (aryl bromides or aryl iodides) or (b) aromatic aldehydes; also (2) by reductions of ketones, obtained by (a) acetylation of substituted benzenes, and (b) by oxidation of substituted ethylbenzenes.

1(a). The dry ether solution of the substituted benzene is added slowly to an equimolar amount of magnesium turnings covered with dry ether. This operation usually requires two to three hours per mole of benzene solution because heating only to a gentle reflux is to be maintained during addition. In many instances the reaction does not begin spontaneously and is started by heating under reflux after a small volume of the benzene solution has been added. A few crystals of iodine may serve to catalyze the reaction. The mixture is then heated on a steam bath under reflux for an additional one to two hours, whereafter a solution of freshly distilled acetaldehyde in dry ether - cooled in ice to prevent loss of aldehyde by vaporization - is added as rapidly as the condenser capacity permits. Usually about 1.5 mole of aldehyde is used per mole of benzene solution. After the addition is complete the mixture is kept under reflux for one more hour, then cooled in ice and the organic magnesium compound decomposed by the slow addition of a 25 per cent aqueous solution of ammonium chloride or dilute hydrochloric acid. The ether solution which separates is decanted and combined with the ether portions used to extract the aqueous layer. After washing, drying and removal of the solvent the residual oil is rectified to yield the carbinol.

1(b). A solution of methyl iodide in dry ether is added to an equimolar quantity of magnesium turnings covered with dry ether at such a rate that the solution keeps gently refluxing. After continued stirring for about one hour an equimolar amount of freshly distilled aromatic aldehyde dissolved in dry ether is added dropwise, and the reaction mixture heated for an additional two to three hours, whereafter the complex formed is decomposed with iced dilute hydrochloric acid and the carbinol isolated in the same manner as previously indicated.

2(a). Acetyl chloride or acetic anhydride is added slowly to a mixture of the substituted benzene and anhydrous aluminum chloride. Equimolar quantities of reactants are usually taken. After heating on a steam bath until copious fumes of hydrogen chloride can no longer be observed - in most instances about four hours per mole of reactant - the product is decomposed with iced hydrochloric acid, and the oily material which separates on standing is extracted. After a conventional purification the residue is fractionated under reduced pressure. The Perrier modification of the Friedel-Crafts reaction (81), in which the hydrocarbon is added to a pre-formed complex of aluminum chloride and acetyl chloride in carbon tetrachloride, is reported to be advantageous for the preparation of acetone derivatives of alkylbenzenes. Less tar formation is encountered during the acetylation process than when the usual order of addition is employed, and therefore higher ketone yields are obtainable (82).

Reduction of the ketone to the corresponding carbinol is carried out by dissolving the former in absolute isopropyl alcohol, adding aluminum isopropoxide (mole ratio about 1:2) and heating the mixture under gentle reflux on a steam bath for a period of about four hours (per mole of ketone), during which time the acetone formed and most of the excess solvent distil off. The progress of the Meerwein-Ponndorf reaction may be followed by testing the distillate for acetone with a 0.1 per cent solution of 2,4-dinitrophenylhydrazine in hydrochloric acid. The residue is collected in an ice bath and hydrolyzed with dilute hydrochloric acid. The organic layer is extracted in the usual fashion and rectified.

The ketone may also be reduced to the corresponding carbinol by high pressure hydrogenation over a copper chromite catalyst at about 100-150°C. Higher temperatures are avoided since at about 180°C. complete reduction to the corresponding arylethane occurs. Not all ketones however are efficiently reduced by this treatment, and the Meerwein-Ponndorf reduction is the more general method.

2(b). The synthesis of α-arylethyl alcohols starting with substituted ethylbenzenes is a rather novel method which has not been applied to a great extent as yet. It consists in oxidizing an ethyl aromatic compound with air in the presence of chromium oxide as catalyst to give the corresponding acetophenone which is then hydrogenated to the analogous carbinol by standard procedures.

Comparing the two fundamental methods used for the synthesis of styrenes via carbinols the route preferably chosen is the one going by way of ketone reduction, probably because it avoids Grignard reagents whose use, of necessity, involves a certain amount of hazard.

Dehydration of the alcohols to styrenes may be carried out in the liquid as well as in the vapor phase. The liquid-phase process appears to be quite sensitive to the reaction conditions since considerable variations in yields of monomers are reported by various workers. The most commonly used reagent is potassium acid sulfate. The alcohol is introduced slowly - to prevent excessive foaming and polymerization -

into a flask containing about 1 per cent of the finely powdered fused dehydrating agent and a trace of polymerization inhibitor, such as p-tert.-butylcatechol, sulfur or hydroquinone. The flask is immersed in an oil bath maintained at a temperature of about 175-230°C. and is attached to a total-condensation partial-take-off fractionating column fitted with a receiver. The addition of one mole of carbinol usually requires one to two hours. Distillation is carried out under reduced pressure, and the organic layer obtained from the distillate which contains water, monomer and unchanged starting material, is rectified after it has been subjected to appropriate purification.

Substituted α-arylethyl alcohols which have a strongly electronegative group, such as, a nitro- or trifluoromethyl group, in the meta position are more efficiently dehydrated in the presence of phosphoric acid or anhydride. In a few instances slow distillation under reduced pressure causes dehydration to occur. Tertiary arylmethylcarbinols are best dehydrated over acetic anhydride in the presence of a trace of sulfuric acid. Yields of styrenes are in general satisfactory. If, however, the dehydration is carried out by heating the carbinol under reflux and in bulk and isolating the monomer by subsequent fractionation, considerable loss of product through polymerization is inevitable.

Dehydration in the vapor phase is the more efficient process. Activated alumina, thoria or tungsten oxide are the catalysts most frequently used. The optimum temperature ranges from 250-450°C. Although some disproportionation occurs during pyrolysis to give the corresponding ethylbenzenes and acetophenones (11, 54, 83, 84)

$$2ArCHOHCH_3 \xrightarrow[250-450^\circ C.]{Al_2O_3} ArCH_2CH_3 + ArCOCH_3 + H_2O$$

the yields of styrenes reported are in general higher than those obtained by any of the liquid-phase reactions.

TABLE IV

Styrenes Obtained
by
Dehydration of α-Arylethyl Alcohols

Vinyl Compound	% Yield	Method	Reference
p-Acetoxystyrene (p-Vinylphenylacetate)	45	2(b)	85
p-Aminostyrene	20	2(a)	82
p-Benzylstyrene	83.3	2(a)	11
o-Bromostyrene		1(b)	86
m-Bromostyrene	low	1(b)	87
	51	1(b)	87
p-Bromostyrene		1(a)	88
		1(b)	88
	40-44	1(a)	89
		1(b)	89
p-Bromo-β-methylstyrene		1(b)	88
	60, 80	1(b)	89
	60, 80	1(a)	89
p-Bromo-β-ethylstyrene	85	1(a)	89
	85	1(b)	89
2-Bromo-4-trifluoromethylstyrene	72.8	1(a)	90
d-p-sec.-Butoxymethylenestyrene	47	2(a)	91
m-sec.-Butylstyrene	61	1(a)	92
m-tert.-Butylstyrene	40.4	1(a)	92
	61.4	1(a)	92
p-n-Butylstyrene	70	2(a)	93
p-tert.-Butylstyrene	76	2(a)	82
p-Carbethoxystyrene (Ethyl-p-vinylbenzoate)	5	2(b)	94
	21	2(b)	94
p-Carbomethoxystyrene (Methyl-p-vinylbenzoate)	49	2(b)	94
o-Chlorostyrene	80-94	1(b)	95
	70	1(b)	96
m-Chlorostyrene	84	2(b)	49
	80-94	1(b)	95
	83	1(b)	96
	23	1(b)	97
p-Chlorostyrene	60	2(a)	97
	86	1(b)	96
	80-94	1(b)	95
	30	1(b)	98
o-Chloro-α-methylstyrene	50	1(b)	99

....

TABLE IV (cont'd)

Styrenes Obtained
by
Dehydration of α-Arylethyl Alcohols

Vinyl Compound	% Yield	Method	Reference
m-Chloro-α-methylstyrene	42	1(b)	99
p-Chloro-α-methylstyrene	77	1(b)	99
2,3,4,5,6-Pentachlorostyrene	61	1(b)	51
p-Cyanostyrene	71	2(a)	82
	29	2(a)	100
p-Cyclohexylstyrene	87	2(a)	82
	18	1(a)	92
2,3-Dichlorostyrene	44	1(b)	101
		1(b)	102
2,5-Dichlorostyrene	37	1(b)	96
		1(b)	102
3,4-Dichlorostyrene	83	2(a)	96
	87	2(a)	82
	63.7	1(b)	101
		1(b)	102
3,5-Dichlorostyrene	43	1(b)	101
		1(b)	102
2,4-Dichlorostyrene	33	1(a)	101
		1(b)	101
		1(b)	102
2,6-Dichlorostyrene	31.5	1(b)	101
		1(b)	102
3,4-Dichloro-α-methylstyrene	85	1(b)	99
2,5-Dichloro-α-methylstyrene	89	1(b)	99
3,5-Diethylstyrene	83	2(b)	82
3,4-Dimethoxystyrene		1(b)	66
	18	1(b)	54
2,3-Dimethoxystyrene		1(b)	24
2,6-Dimethoxystyrene	60	1(b)	103
p-Dimethylaminostyrene	0	1(b)	104
	45	1(b)	105
	24-30	1(b)	71
3,5-Dimethylstyrene	87	1(b)	106
3,4-Dimethylstyrene	80	2(a)	106
2,4-Dimethylstyrene	71	2(a)	106
2,5-Dimethylstyrene	88.4	2(a)	106
p-Ethoxystyrene	69	2(a)	82
p-2-Ethylhexylstyrene	30	2(a)	93
m-Ethylstyrene	93	2(b)	82

....

TABLE IV (cont'd)

Styrenes Obtained
by
Dehydration of α-Arylethyl Alcohols

Vinyl Compound	% Yield	Method	Reference
p-Ethylstyrene	80	2(a)	107
	83	2(a)	82
	72	2(a)	93
β-Ethylstyrene	78	1(b)	107
		1(b)	108
		1(b)	58
o-Fluorostyrene	76	1(b)	96
m-Fluorostyrene	80	1(b)	96
p-Fluorostyrene	81	1(b)	96
	89	2(a)	110
	62	1(a)	90
4-Fluoro-3-trifluoromethylstyrene	70	1(a)	90
4-Fluoro-α-methyl-3-trifluoromethylstyrene	83	1(a)	90
2-Fluoro-4'-vinylbiphenyl	73.3	2(a)	110
p-n-Heptylstyrene	69	2(a)	93
p-Iodostyrene	60	2(a)	71
p-Isopropylstyrene		1(b)	55
o-Methoxystyrene		1(a)	11
		1(b)	11
		1(b)	86
p-Methoxystyrene	high	1(b)	111
	65	2(a)	82
		1(b)	86
		1(b)	112
3,4-Methylenedioxystyrene		1(b)	57
	82	1(b)	113
β-Methylstyrene	85	1(b)	107
		1(b)	108
o-Methylstyrene		1(a)	114
m-Methylstyrene	50	1(a)	105
		1(a)	114
p-Methylstyrene	83	2(a)	82
	84	2(a)	107
	71.8	2(a)	93
β-Methyl-3-trifluoromethylstyrene	70	1(a)	90
m-Nitrostyrene	25	2(a)	105

....

TABLE IV (cont'd)

Styrenes Obtained
by
Dehydration of α-Arylethyl Alcohols

Vinyl Compound	% Yield	Method	Reference
p-Phenoxystyrene		2(a)	54
		2(a)	82
o-Phenylstyrene	24	1(a)	115
(o-Vinylbiphenyl)	70	2(a)	116
m-Phenylstyrene	55	2(a)	116
(m-Vinylbiphenyl)			
p-Phenylstyrene	82	2(a)	116
(p-Vinylbiphenyl)			
Styrene	75	1(a)	107
	90	1(a)	117
m-Trifluoromethylstyrene	53.7	1(a)	105
	79	1(a)	90
	79	1(a)	110
2,4,6-Trimethylstyrene		2(a)	78
o-Vinylbenzylacetate	55	2(b)	85
(p-Acetoxymethylenestyrene)			
p-Vinylbenzylalcohol	38	2(b)	85
4-Vinylguaiacol		1(b)	27
p-Vinylstyrene	83	2(b)	82
	81	2(a)	118

B. Dehydration of β-Arylethyl Alcohols

$$ArCH_2CH_2OH \xrightarrow[KOH]{} ArCH{=}CH_2 + H_2O$$

The alcohols, usually obtained by way of Grignard reactions from substituted benzenes, are heated with anhydrous potassium hydroxide and the monomers isolated by fractionation; or the alcohols are dropped slowly onto the dehydrating agent in a partially evacuated system and the monomers are collected in a cooled receiver. In general, β-arylethyl alcohols give purer products than the α-isomers (54, 11). Acidic dehydrating agents are not effective and lead to formation of ethers rather than styrenes (119).

Although no longer of importance in styrene synthesis, this method is of historical interest insofar as the first approach to the problem of making monomeric styrene on an industrial scale involved a process leading through ethylbenzene, a mixture of α- and β-chloroethylbenzenes, and β-phenylethyl alcohol (2).

TABLE V

Styrenes Obtained by Dehydration of β-Arylethyl Alcohols

Vinyl Compound	% Yield	Reference
(o-,-p-)Bromostyrene		120
(o-,-p-)Chlorostyrene		120
2,4-Dimethylstyrene		121
p-Ethylstyrene		122
p-Fluorostyrene	22.5	90
o-Methoxystyrene	69.4	11
m-Methoxystyrene	69	54
o-Methylstyrene		123
m-Methylstyrene		123
p-Methylstyrene	high	124 123, 125
p-Phenoxystyrene	77	54
Styrene	almost quantitative	125
		119
m-Trifluoromethylstyrene	72	90
p-Vinylstyrene		127

V. Dehydrogenation of Ethyl Aromatic Compounds

$$ArC_2H_5 \longrightarrow ArCH{=}CH_2 + H_2$$

This reaction is carried out at elevated temperatures, both as a thermal or catalytic vapor-phase process. Most references to conditions, catalysts and yields are contained in the patent literature. Although characterized by high conversions as well as high yields, catalytic dehydrogenation cannot be applied indiscriminately to any ethyl aromatic compound, because substituents are prone to attack by the catalyst. Thus, dehydrogenation studies made on nuclear-substituted chloroethylbenzenes conducted on a pilot plant scale have not been successful (128).

TABLE VI

Styrenes Obtained
by
Dehydrogenation of Ethyl Aromatic Compounds

Vinyl Compound	Reference
3,5-Dimethylstyrene	129
α-Methylstyrene	130, 131
o-Methylstyrene	129
p-Methylstyrene	129
p-Phenylstyrene	132
Styrene	133, 134, 135

Bentonites

Bentonites are naturally occurring clays deposited widely throughout the United States, Russia, Italy, Japan, Germany and Poland. In Canada large beds occur in the Western Provinces, especially near Morden, Manitoba, where the clay is mined and processed by Pembina Mountain Clays Limited. A yield of about 6,000 tons may be recovered from one acre (136). Somewhat smaller deposits are found near Princeton, B.C. and in the Red Deer River Valley near Drumheller, Alta.

Bentonites are generally considered an alteration product of glassy volcanic ash or turf following its deposition in water, the more basic material of the original ash being removed by leaching or solution leaving the colloidal silica and alumina behind as bentonite. These clays are largely composed of montmorillonite, an aluminum hydrosilicate of the general formula $(Mg,Ca)Al_2O_3.5SiO_2.nH_2O$ where n is approximately 5.

X-ray studies have shown (137) that montmorillonite is made up of superimposed layers of silica and alumina built into a lattice-like structure as visualized by Pauling (138). The water normally associated with montmorillonites in nature disposes itself regularly in layers between the silicate skeletons whose characteristic interlayer spacings may be accurately measured. In addition to silica and alumina other metals such as iron, calcium, magnesium, sodium and potassium may be present as oxides. Canadian bentonites contain but small amounts of such impurities which often alter quite drastically the catalytic activity of natural clays.

Morden bentonite, according to analyses carried out by the Department of Mines and Resources (139) shows the following average composition:

TABLE VII

Composition of Morden Bentonite

	Unactivated	Acid Activated	Regenerated
SiO_2	61.70	71.73	72.95
Al_2O_3	22.87	19.66	19.84
Fe_2O_3	4.89	0.87	0.28
CaO	2.13	0.59	0.53
MgO	4.78	4.08	3.68
Other Bodies by difference	3.63	3.07	2.72
	100.00	100.00	100.00
Loss on Ignition(a)	24.94	22.28	2.77

(a) In each case, the ignition was carried out at 1700°C. for 2 hours. The loss includes uncombined moisture and water of hydration.

Compared with data (140, 141, 142, 143, 144) on bentonites of other countries the outstanding characteristics of Morden bentonite are a low silica:alumina ratio, a high percentage of combined water and low percentages of alkaline earth substituents.

The variable composition of bentonites from different sources is clearly reflected in their physical properties. Their colors may vary from white, grey, yellow to green and brown. When wet many are waxy and greasy, others are hard and brittle. A characteristic property of all bentonitic clays however is their remarkable adsorbent power (145).

Bentonites are seldom used in the raw state but are usually activated by boiling with dilute acid for several hours. After filtration and thorough washing the filter cake is broken up, dried and pelleted. This processing greatly enhances their catalytic and adsorbent properties. According to Oulten (146) the acid treatment removes metallic atoms (mostly aluminum) from the lattice leading to the formation of a more porous structure and therefore to a larger surface area for a given particle size. This effect may also be noted during activation of Morden bentonite, for the aluminum as well as the calcium and iron contents of the crude mineral are considerably higher than those of the acid activated clay. In addition, ionic exchange reactions are thought to take place during activation, with calcium, iron, magnesium and aluminum ions of the raw bentonite being replaced by hydrogen ions (147).

Although more fundamental research is necessary for a detailed understanding of the mechanism of activation and of catalysis in general, the enhancement of catalytic activity by such acid treatment is well recognized and explains the widespread present use as well as the promise of aluminum hydrosilicates in industry. Activated bentonites have been used as carriers in organic vapor-phase reactions such as cyclization of aliphatic compounds (148) as catalysts for condensing ethylene and hydrogen sulfide to form mercaptans (149), for sweetening petroleum oils (desulfurizing), (150) for decomposing hydrogen peroxide and isopropyl alcohol (151), and for the refining and bleaching of mineral oils (136). The use of aluminum hydrosilicates in vapor-phase catalysis has recently been very much extented, and this tendency is not surprising since aluminum oxide as well as silica, their chief components, have each been employed in this way for many years with excellent results.

Morden Bentonite as a Vapor-Phase Catalyst

This University in 1942 began to investigate the activity of Morden bentonite in several types of reactions and it was found that the clay, if properly prepared, is an efficient and versatile vapor-phase catalyst. The compounds studied so far and the reactions observed by the various research workers are listed in Table VIII.

TABLE VIII

Morden Bentonite as a Vapor-Phase Catalyst

Class	Compound	Reactions Observed	Reference
Acids	Acetic Acid	Decarboxylation, Dehydration	152
Alcohols	n-Amyl alcohol	Dehydration, Isomerization	152
	Diethyl carbinol	Dehydration, Polymerization	152
	Dimethylethyl carbinol	Dehydration	152
	Cyclohexanol	Dehydration, Isomerization	153
	p-Methylcyclohexanol	Dehydration, Isomerization	153
	Butanediol-2,3	Dehydration, Decomposition	154
	Butanediol-1,3	Dehydration, Decomposition	154
	Butanediol-1,4	Dehydration, Decomposition	154
N-Alkylanilines	N-Methylaniline	Dealkylation, Alkylation, Isomerization	155
	N-Ethylaniline	Dealkylation, Alkylation, Isomerization	155
	N-n-Propylaniline	Dealkylation, Alkylation, Isomerization	155
	N-n-Butylaniline	Dealkylation, Alkylation, Isomerization	155
	N-N-Diethylaniline	Dealkylation, Alkylation, Isomerization	155
Ethers	Anisole	Alkylation, Isomerization	155
Aromatic Hydrocarbons	Ethylbenzene	Dealkylation	152
	Isopropylbenzene	Dealkylation, Dehydrogenation	152
	Isopropyltoluene	C-C Bond Fission	156
	1,1 Diphenylethane	Dearylation, Hydrogenation	157
	Styrene	Hydrogenation	157
Ketones	Acetone	Dehydration, Decomposition	152
	Methyl isobutyl ketone	Dehydration, Polymerization	152
	Butanone-2	Dehydration, Isomerization	154
	Octanone-2	Dehydration, Polymerization	139
	Cyclohexanone	Dehydration, Polymerization, Cracking	152
Aniline + Aliphatic Alcohols	Aniline + Methanol	Alkylation	155
	Aniline + Ethanol	Alkylation	155
	Aniline + Propanol-1	Alkylation	155
	Aniline + Butanol-1	Alkylation	155

Ionic and Free Radical Mechanisms in Catalysis

Although catalysis in both organic and inorganic reactions was recognized more than a hundred years ago, our knowledge of catalytic phenomena is to-day still largely unco-ordinated, and no single theory has been formulated to interpret adequately the heterogeneity of a vast number of experimental facts. From the various viewpoints on the intricate mechanism of catalysis, two, however, slowly crystallized into well-founded concepts that have been generally accepted. We are to-day agreed that catalytic reactions in the liquid as well as in the vapor phase may proceed by either an ionic or a free radical mechanism.

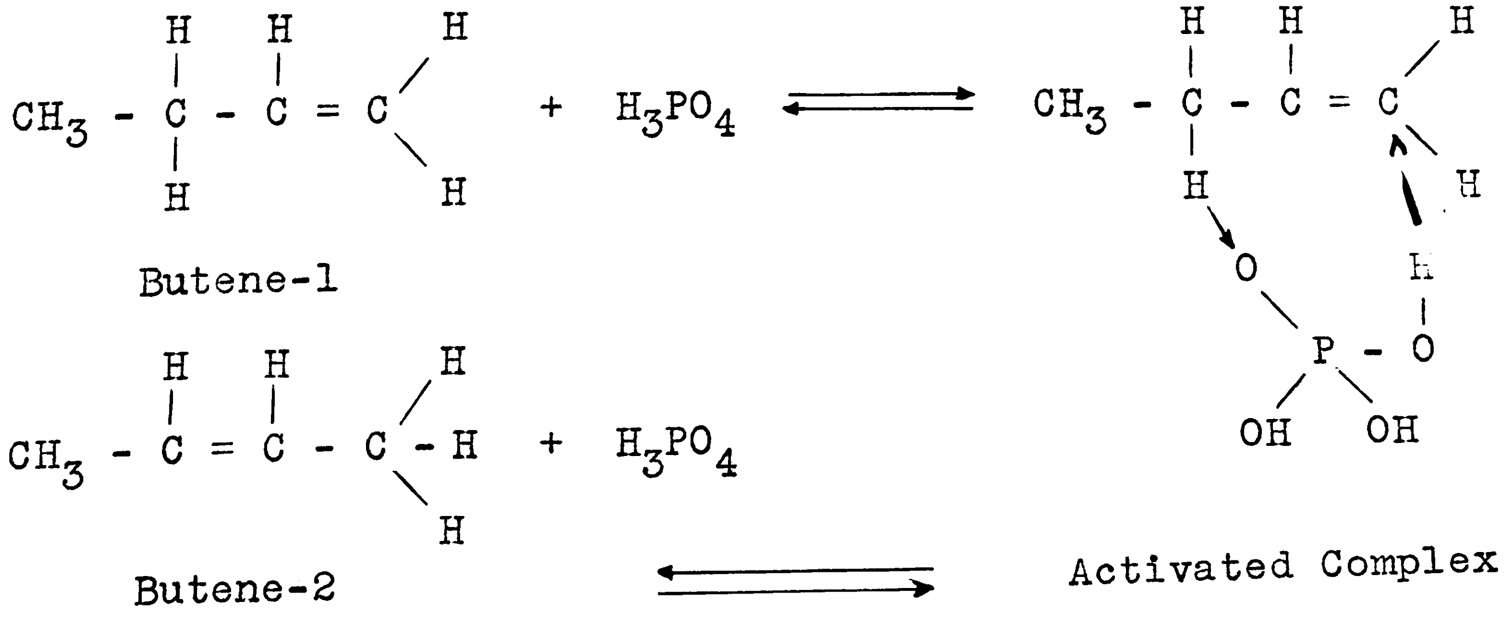
These theories need not be reviewed here in any detail, but it seems desirable to give a brief account of the features which are of primary importance for an understanding of the role played by hydrous aluminum silicates in vapor-phase catalysis.

The Ionic Mechanism

Achalme (109) in 1912 approached the problem of how catalysts act by considering their electronic characteristics, and on the basis of experimental work concluded that a substance acts as a catalyst if it is capable of either supplying electrons to a system or removing electrons from it. About ten years later, this concept of electron transfer was more clearly defined by G.N. Lewis in his electronic theory of acids and bases (158), according to which an acid is a substance capable of accepting a share in a lone electron pair from a base to form a covalent bond, and a base is a substance capable of donating a share in a lone electron pair to an acid. Acidic behavior therefore does not depend upon the presence of any particular element, such as oxygen as Lavoisier had believed, or a proton as Brønsted and Lowry had postulated. A common Friedel-Crafts type catalyst, such as aluminum chloride, may be shown to exhibit typical acidic properties and not to differ fundamentally from H-acids in its catalytic behavior. In fact, it may often be replaced by such acids - hydrogen fluoride, sulfuric acid or phosphoric acid - in Friedel-Crafts and similar reactions (159).

The concepts of the electronic theory of acids and bases were successfully applied to explain such reactions as alkylation of aromatic nuclei (159, 160, 161, 162), dehydration of alcohols (163), esterification of aldehydes (Cannizzaro reaction) (164, 165), condensation of carbonyl compounds (166, 167), halogenation of aromatic compounds and alcohols (168, 169, 170, 171) and acylation of aromatic esters (172, 173, 174, 175, 176). The common and important feature of all these reactions lies in the formation of intermediate carbonium ions, and it is the function of the catalyst, which may be an H-acid or not, to produce these carbonium ions in high concentrations.

These ideas were not entirely recognized by Turkevich and Smith (177) who made a kinetic study of the double bond migration in normal alkenes, using a variety of catalysts, both liquid and solid, and also determined the rate of exchange of radioactive hydrogen and tritrium in the olefin-catalyst system. They found that isomerization occurred not as the result of the addition of a proton to the double bond with the formation of a carbonium ion but as the result of a two-way hydrogen transfer initiated by the catalyst. Considering, for example, the interconversion of butene-1 to butene-2 in the presence of phosphoric acid, a catalyst molecule is visualized as moving toward a hydrocarbon molecule in such a way that one of the hydroxyl hydrogen atoms of the acid approaches a terminal carbon atom of a butene-1 molecule while the non-hydroxyl or "double bonded" oxygen atom approaches the carbon atom once removed. On breaking away from this activated complex the catalyst may take with it the hydrogen atom once removed but leave a hydrogen on the terminal carbon atom.



The acid therefore acts as both a donor and acceptor of hydrogen atoms, the hydrogen lost by the hydroxyl is gained by the "double bonded" oxygen. Instead of phosphoric acid other acids, such as sulfuric acid, silicic acid or perchloric acid may be used. Similarly, the action of solid catalysts, such as moist aluminum chloride or aluminum bromide, is interpreted as resulting from $HAlCl_4$ or $HAlBr_4$, and the catalytic activity of hydrous aluminum silicates is postulated to result from the presence of silicic or aluminosilicic acid in these catalysts. "The critical demand on the catalyst is that it be able to furnish a hydrogen and accept a hydrogen at a distance of about 3.5 A, which is the distance separating the hydrogen of the first and third carbon atom in an aliphatic chain". This requirement for catalytic activity is met by the acids enumerated, all of which may therefore easily form undistorted activated hydrocarbon-catalyst complexes. Other processes are similarly explained by this "Unitary Theory of Catalytic Hydrocarbon Reactions", which is based upon the spacial inter-relationships of catalyst and substrate and so attempts to explain catalytic specificity. Polymerization, for instance, is visualized as a hydrogen transfer between two olefin molecules, alkylation is formulated as a hydrogen transfer from a paraffin to an olefin and cracking is considered the reverse of alkylation. A carbon-carbon bond is broken as the catalyst (silicic acid or aluminosilicic acid) removes the hydrogen from one carbon and transfers it to a carbon atom once removed.

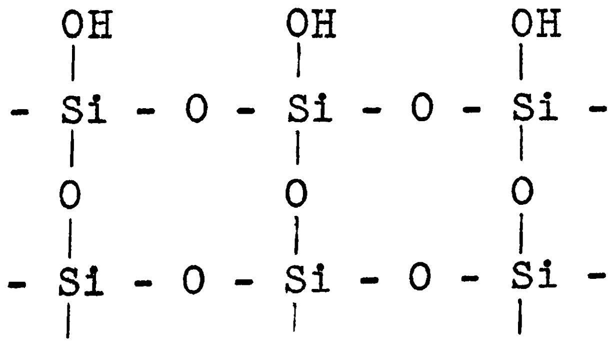
A somewhat similar mechanism was suggested by Ciapetta (178) for the alkylation of saturated hydrocarbons by olefins in the presence of sulfuric acid as catalyst, while a more rigorous treatment of this hydrogen donor-acceptor mechanism with particular reference to vapor-phase catalysis was given by Hansford (179), who used a synthetic silica-alumina catalyst in a number of cracking experiments on n-butane. He noted that relatively small amounts of adsorbed water raised the efficiency of the catalyst considerably, and he concluded that some sort of interaction of this water with the hydrocarbon undergoing catalysis must occur. This was substantiated, for when deuterium oxide instead of water was adsorbed on the catalyst and the same experiments were carried out on n-butane, spectrophotometric analyses showed considerable amounts of deuterium in the cracked products as well as in the unconverted n-butane.

The exchange which had taken place was believed to be ionic in nature because it occurred with adsorbed water, and Hansford therefore postulated that adsorbed water can accept a proton from a hydrocarbon, so that a negative hydrocarbon ion is formed. This ion may rearrange under the influence of the catalyst and at elevated temperatures to form a branched structure (isomerization) or it may decompose (cracking) to a smaller ion of similar structure and a hydrogen deficient fragment. Neutralization of the carbanion with a proton from the catalyst occurs to generate a stable molecule. Thus, an attempt is made to correlate the chemical nature of the catalytic surface and catalytic activity.

The catalytic behavior of clays composed of hydrated aluminum silicates may be explained in the same manner, since they "have the characteristic of attracting to their surface with great force a film of water which is mutual with the adjoining particle" (180). The average thickness of this film amounts to about 3 x 10^{-5} cm. and its stability has been shown not to be influenced by pressures as high as 800 kilograms per square centimeter.

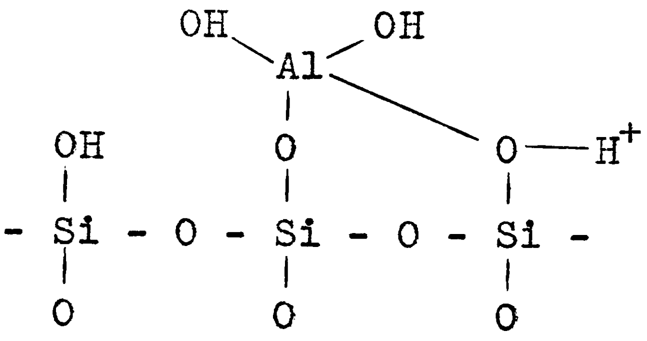
Silica-alumina catalysts, the most effective catalysts used in the petroleum industry, are in general prepared from hydrogels (silica gel) and hydrous oxides (aluminum hydroxide) both of which are only slightly active as cracking catalysts. It becomes therefore necessary to assign to the silica-alumina combination a definite function that is not present in either component alone.

The silica hydrogel which is usually first formed when preparing a synthetic silica-alumina catalyst may be pictured to have the following structure:



$$\begin{array}{ccccccccccc} & OH & & & & OH & & & & OH & \\ & | & & & & | & & & & | & \\ - & Si & - & O & - & Si & - & O & - & Si & - \\ & | & & & & | & & & & | & \\ & O & & & & O & & & & O & \\ & | & & & & | & & & & | & \\ - & Si & - & O & - & Si & - & O & - & Si & - \\ & | & & & & | & & & & | & \end{array}$$

As a result of the deposition of alumina by simple impregnation water is split out between the aluminum hydrate and an hydroxyl group of the silica gel surface,



the aluminum coordinating with the adjacent hydroxyl oxygen. This coordination weakens the attraction of the hydrogen by the oxygen, and the high activity of silica-alumina catalysts toward hydrocarbon reactions taking place at acid surfaces, e.g. alkylation, isomerization, polymerization, cyclization and cracking, is thought to be associated with these hydrogen ions (181, 182, 183, 184, 147).

This interpretation of catalysis received strong support when the presence of hydrogen ions in a clay cracking catalyst of the montmorillonite class (Filtrol) was demonstrated by a physico-chemical titration method (182). A known weight of catalyst was titrated with alkali in the presence of a salt solution and the course of neutralization followed by a glass electrode-calomel cell. A 5 per cent aqueous sodium chloride solution was found to facilitate greatly the exchange of sodium ions for hydrogen ions held at the base exchange centers of the montmorillonite. This investigation also showed that protons exist in the clay over the entire range of catalytically important cracking temperatures - room temperature to about 1560°F. - and that their concentration is zero once the catalyst has started to sinter.

Carrying this work a step further, Thomas (183) assigned a position to this acidic hydrogen within the lattice structure and explained its nature and function. The physical picture given to the catalyst surface differs from that of Hansford, but agrees in that catalytic activity is also thought to be due to the acidic hydrogen ion associated with the catalytic surface. Application of this concept to hydrocarbon reactions taking place in the vapor phase over acidic catalysts showed that many high temperature catalytic processes, e.g. cracking of paraffins, olefins and naphthenes, alkylation and dealkylation of aromatic compounds, polymerization and depolymerization, isomerization and dehydration, may all be regarded as carbonium ion reactions with no fundamental difference from those which occur as acid catalyzed liquid-phase processes (185, 186, 187, 188).

Considerable support for the close relationship between homogeneous and heterogeneous catalysis may be found in the literature. For instance, alkylation of aromatic nuclei and dealkylation of alkyl aromatics may be carried out in the vapor phase over aluminum-silicate catalysts and naturally occurring clays (156, 189, 190, 191, 192) or in the liquid phase in the presence of sulfuric acid (193, 194), hydrofluoric acid (195), metallic halides of the Friedel-Crafts type (152, 194, 196, 197, 198, 199, 200) or phosphoric acid (201). Acylation of heterocyclic nuclei, e.g. thiophene and furan, may be carried out as a liquid phase process using hydriodic acid, hydrogen fluoride or zinc chloride as catalyst, and it may also be achieved in the vapor phase with naturally occurring clays of the montmorillonite family or synthetic aluminum silicate catalysts (202, 203). Secondary and tertiary alcohols may be efficiently dehydrated in both the liquid and the vapor phase in the presence of acidic catalysts, e.g. sulfuric or phosphoric acid and synthetic or natural aluminum silicates (163). Similarly, isomerization and polymerization of olefins may take place in the liquid phase in the presence of typical Friedel-Crafts catalysts or strong acids as well as in the vapor phase in the presence of aluminum silicates or activated clays (204). Gayer (205) used acid activated floridin to polymerize propylene at 350°C. A synthetic silica-alumina catalyst gave similar results. Alkalis and ammonia were found to poison the catalyst. Burk (206) commenting on the mechanism of catalytic polymerizations writes: "Whether the polymerizing action of such materials as clays and silica is also to be attributed to the acid reaction of these materials is an open question". Hay, Montgomery and Coull (207) studied the isomerization of hexene-1 in the vapor phase and found that effective catalysts were those capable of supplying hydrogen ions, such as synthetic silica-alumina catalysts or acid-treated clays. Ciapetta, Macuga and Leum (208) reported an investigation on the catalytic depolymerization of butylene polymers. The catalysts used were attapulgus clay and synthetic silica-alumina, both producing a gas fraction consisting almost entirely of C_4 hydrocarbons. The mechanism of depolymerization is explained in terms of the carbonium ion theory. Similarly, Moldowsky and Bezedel postulate an ionic mechanism for the dealkylation of aromatic hydrocarbons in the vapor phase over an activated bleaching clay (209).

In brief, vapor-phase reactions in the presence of porous solid acidic catalysts appear to be closely allied to similar reactions which always require the presence of an acidic catalyst but which can occur at lower temperatures. Acidic catalysts exist in many forms, including solid metal halides, such as ferric chloride, boron fluoride, stannic chloride or aluminum chloride with or without various promoters and supports, liquid sulfuric acid, phosphoric acid and hydrofluoric acid, porous solids impregnated with acidic substances, acidic mixtures of refractory oxides, such as the present commercial cracking catalysts and acid-treated clays. These substances all register acidity either intrinsically or in contact with water, and they may all be considered as either direct sources of protons required for the formation of carbonium ions or as electron donors which serve to generate positive ions by formation of intermediate addition complexes. The ions formed by either of these two paths then react further to give stable products.

The Free Radical Mechanism

Just as the ionic mechanism was initially utilized to explain the behavior of liquid phase systems, the free radical mechanism was first applied to reactions taking place in solution. Gomberg (210) in 1900 discovered the dissociation of hexaphenylethane into triphenylmethyl free radicals, and about 30 years later Paneth and Hofeditz (211) prepared methyl free radicals. In 1934 Rice and his collegues (212) showed that at temperatures of 800°C. or over the thermal decompositions of the vapors of a whole range of stable organic compounds, such as paraffin hydrocarbons, ethers, alcohols, aldehydes and ketones yield methyl and ethyl free radicals, and attempts were soon made to account for their occurrence and characteristic features. These attempts were extremely fruitful. To-day the free radical chain theory as amplified by Kossiakoff and Rice (213) serves to predict the product distribution of a large number of thermal decompositions (214). A diagnostic test (215) for the existence of a free radical mechanism comprises the addition of traces of nitric oxide to the system and thereby inhibiting markedly the rate of the reaction. Nitric oxide, itself virtually a free radical, will act as a chain terminator by combining instantly with neutral radicals to produce normal molecules. Significantly, nitric oxide does not reduce the rate of a free radical reaction to zero but lowers it to a finite value which often remains constant for at least a tenfold variation in concentration. As the nitric oxide concentration is still further increased however, the reaction velocity rises again and in very high concentrations nitric oxide is regarded as a positive catalyst. Alkyl nitrites may be conveniently used as a source of nitric oxide in vapor-phase reactions since they decompose on heating in accordance with the equation (216)

$$2\ RCH_2ONO \dashrightarrow 2\ NO + RCHO + RCH_2OH$$

The free radical theory was extended from its original field of application to heterogeneous systems when it was noticed that metals, such as nickel, platinum, palladium, copper and iron, can be used to advantage for bringing about at moderate temperatures many chemical reactions which, in the absence of any catalyst, proceed only as high temperature homogeneous gas reactions by free radical mechanisms. These reactions include hydrogenation, dehydrogenation, oxidation and dehydration. It is interesting to see how these processes which appear so different physically may often be explained by the same fundamental theory, namely the formation and reaction of free radicals. Thus nickel and tungsten surfaces can bring about the atomic exchange reaction between hydrogen and deuterium (217), an exchange also found to occur on aluminum silicate surfaces (179) but assumed to be of an ionic nature. Many other substances, such as methane, ammonia and alcohols, undergo deuterium exchange on metallic surfaces, and dissociation to atoms and radicals has also been suggested in these cases (218, 219, 220).

Hydrogenation on metallic surfaces is another type of reaction which affords many examples of free radical mechanisms (221). Bremner and Keys, on the other hand, assumed an ionic mechanism for the hydrogenation of furfuraldehyde over a copper-alumina catalyst (222) which they regarded as a Lewis acid, that is, an electron acceptor. Formation of alkyl radicals on metal surfaces was found to occur during catalytic hydrogenation reactions accompanied by polymerization of olefins (223). Similarly, dehydrogenations of hydrocarbons by means of sulfur or selenium (224, 225) have been shown to be reactions of atomic rather than ionic type, and naturally occurring clays have also been used for this type of reaction. Styrene in 40 per cent overall yields, based on a 50-hour process period, was obtained by passing ethylbenzene over bauxites (226), and the same reaction occurred when Morden bentonite was used as catalyst (152). Greensfelder and Voge (184) who investigated the catalytic cracking of a large number of hydrocarbons, postulated that vapor-phase free radical type reactions occur over catalysts that are non-acidic. For instance, cetane was shown to crack over quartz chips and activated carbon, a non-acidic, highly active catalyst, via free radicals, according to the Rice-Kossiakoff theory. Activated alumina, a weakly acidic catalyst displayed a mixed type of cracking, intermediate to that encountered over strongly acidic oxides and activated carbon with respect to both rate and product distribution.

Colloidal clay particles behave in many ways as true crystals (227) and much evidence has been accumulated to show that catalytic activity is to be found at crystal edges or at interfaces between different crystals at which there is a disorderly array of atoms (228). Another equally important feature of active surfaces is to be seen in the fact that they all possess loosely bound electrons which can be either released to an adsorbed molecule or used to bind it, by a covalence, to the surface. Metals like sodium, potassium, zinc and aluminum liberate electrons even under the influence of ordinary visible light, provided their surfaces are fresh and clean. This property of electron emission is not confined, however, to metals. Significant research being currently carried out at the University of Wisconsin has revealed that naturally occurring clays also possess this property to a very considerable extent (229). Clays of strong catalytic activity were all found to exhibit a marked degree of electron emission, and the quantitative measurement of this property is thought to lead to a desirable method for catalyst evaluation. Although these features of natural clays could be used as a working basis for studies of reaction mechanisms, no fundamental approach has as yet been made in this direction. Morton (157) assumed a free radical mechanism for the pyrolysis of 1,1-diphenylethane over Morden bentonite, and Stinton (139), using the same catalyst, postulated a chain reaction for the dehydration of butanone, supporting his view by studying the effect of nitric oxide addition to the liquid feed. Small amounts caused a marked decrease in conversion, while beyond a certain concentration (1 per cent) conversion increased again. This behavior is characteristic of free radical reaction systems.

EXPERIMENTAL

Apparatus

Apparatus for Catalysis
(Figures 1 and 2)

A reactor system for continuous flow experiments was constructed. It was of simple and efficient design.

The reactor consisted of a 1 1/4-inch inside diameter stainless steel pipe 40 inches long and bearing two short side arms as inlets. It was heated by three coaxial, 550-watt cylindrical heating elements wound on 12-inch alundum cores (Hoskin FD-303 oversize). The uppermost element, covering the preheating section, was operated independently while the two lower ones were wired in both series and parallel to heat the catalyst bed. Control was manual, guided by variable autotransformers. Asbestos high-temperature pipe covering, two inches thick, was used for insulation purposes. A 14-gauge wire chromel-alumel thermocouple, 24 inches long (Fisher Scientific 13-909) and housed in a thin-walled stainless steel well, was used in conjunction with a Hoskins pyrometer (Fisher Scientific 13-906) to record the temperature at any point throughout the preheating section and the greater portion of the catalyst bed, which comprised 220 cc. of activated Morden bentonite supported by a perforated stainless steel liner. A 6-inch section above the catalyst was packed with quartz chips as heat exchangers for more efficient vaporization.

The feed system could be used for charging solids as well as liquid reactants.

When the material to be pyrolyzed was a solid at room temperature it was melted and fed into the reactor from a calibrated cylinder wound with nichrome wire, jacketed and heated about 15°C. above the melting point of the reactant, the temperature being controlled by an external rheostat. Displacement of the melt was achieved by exerting on a mercury reservoir a constant pressure of 10 p.s.i., maintained by the mercury head in a pressure regulator T-tube. The feed rate was adjusted by stopcock manipulation, the required amount of mercury to be delivered in unit time having previously been determined by calibration. This arrangement was found to give a very satisfactory control of liquid input. Steam, which was used in some experiments as a diluent, was generated by feeding water into a vaporizer, the liquid being displaced by dropping mercury at a constant rate from a suitably placed reservoir. Flow rates could easily be observed on a rotameter and conveniently be regulated by stopcock adjustment.

This simple system was also used for the introduction of liquid reactants into the catalyst tube. A constant head of mercury was maintained in the lower reservoir by admitting mercury from the upper one at a rate equal to that with which the feedstock was introduced into the reactor. Purified nitrogen was used in some experiments as carrier gas. It was led through a sulfuric acid trap in order to insure constant flow rates and metered into the reactor through a flow meter after being freed from oxygen and moisture by passage through Fieser's solution (sodium hyposulfite) and a tower containing Drierite.

The apparatus for collection of products was of conventional type. The hot vapors issuing from the catalyst chamber were quenched during passage through a Friedrichs condenser attached to the reactor outlet by means of a Neoprene rubber stopper, and the condensate was collected in a cooled receiver, fitted to the condenser by a ground joint. Gaseous products made their exit from the condenser through a side arm, passed through a cooled trap, a drying tube, a bubbler and a Fisher Precision Wet Test Meter from where they were vented.

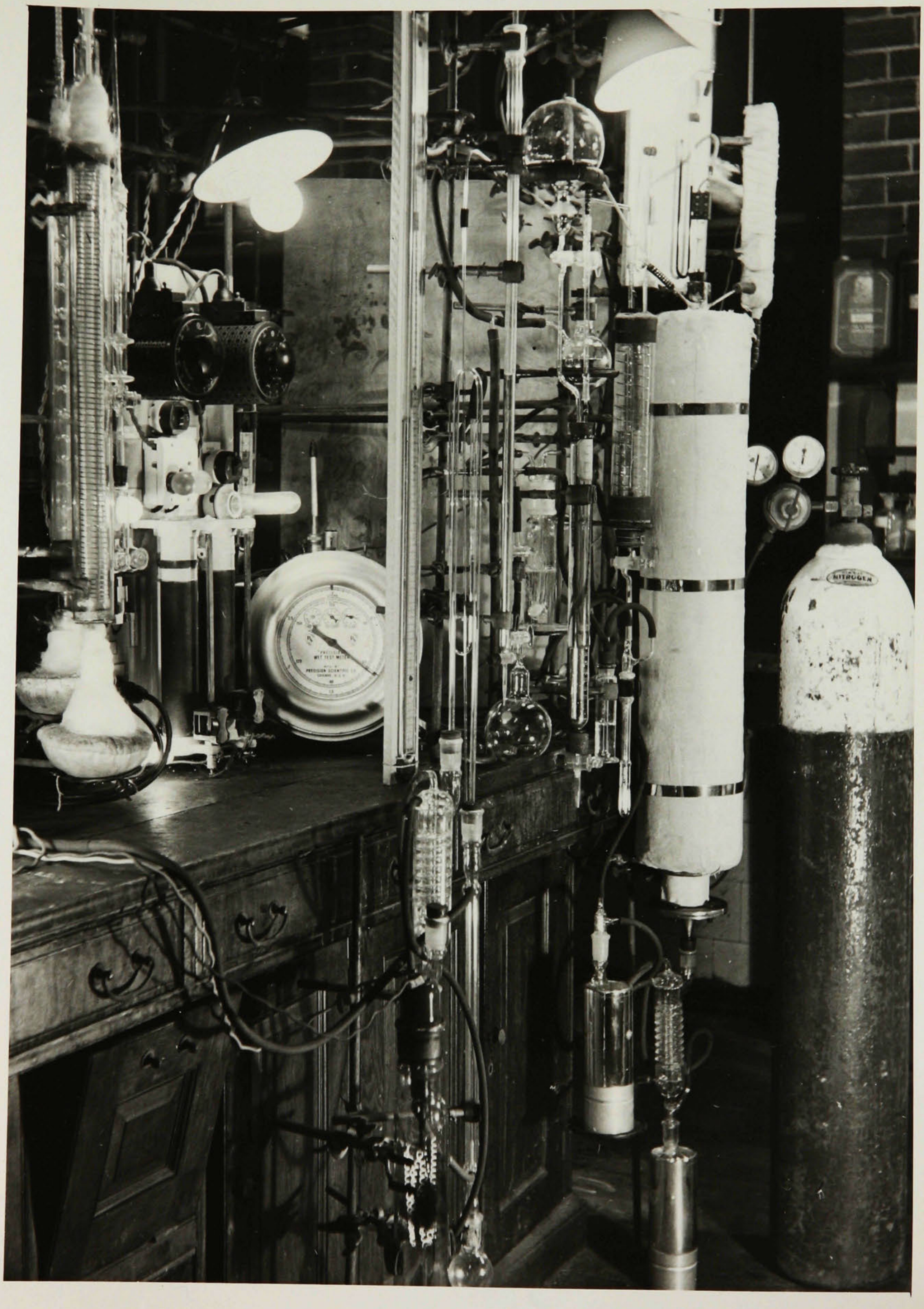
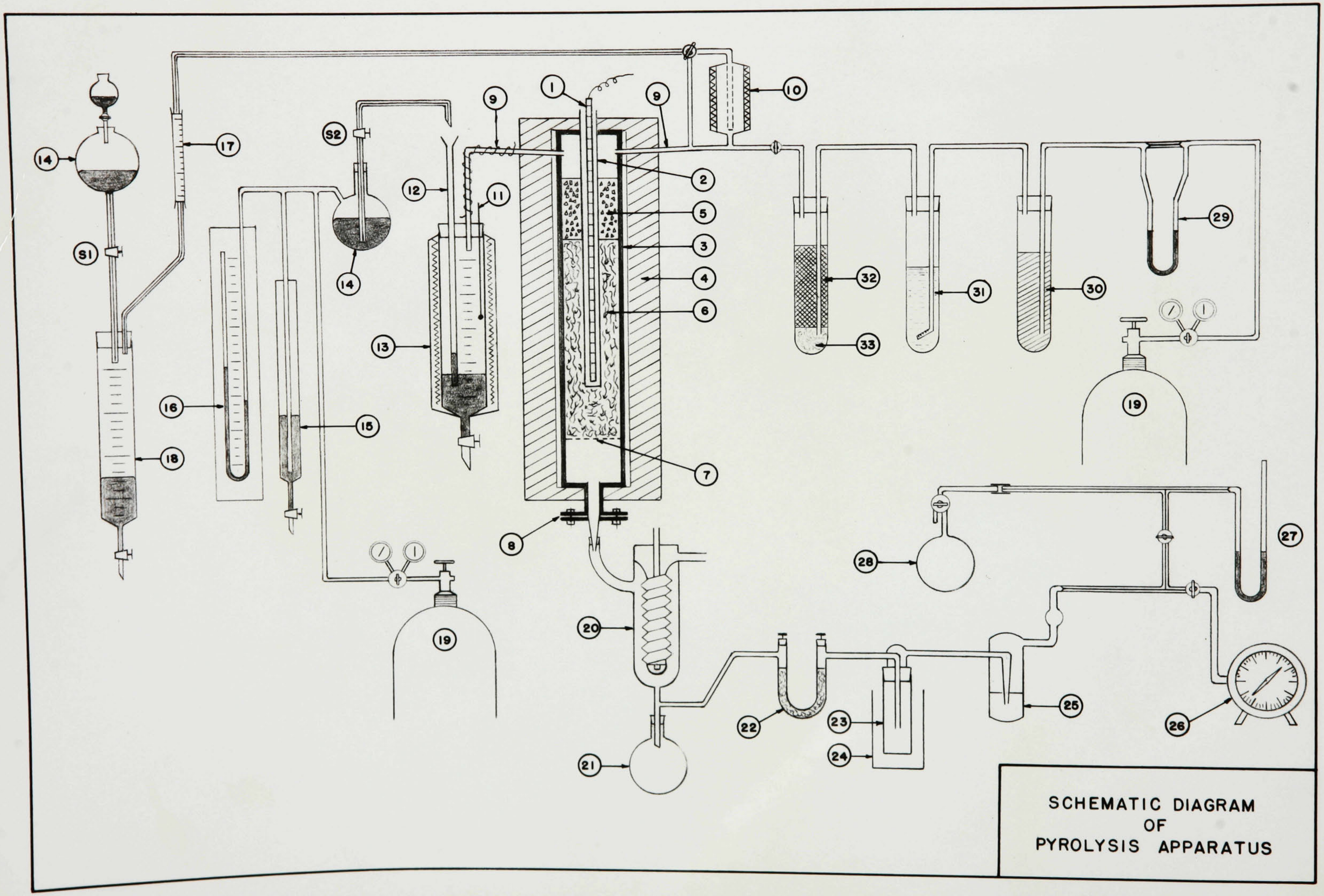


Figure 1

Pyrolysis Apparatus

FIGURE 2



SCHEMATIC DIAGRAM
OF
PYROLYSIS APPARATUS

Legend for Schematic Diagram of Pyrolysis Apparatus

1	Thermocouple
2	Thermowell
3	Reactor Tube
4	Insulation and Heaters
5	Quartz Chips
6	Catalyst
7	Stainless Steel Gauze
8	Asbestos Gasket
9	Inlet Tubes
10	Water Vaporizer
11	Thermometer
12	Mercury Inlet Tube
13	Jacketed 250 ml. Burette
14	Mercury Reservoir
15	Mercury Safety Head
16	Pressure Gauge
17	Rotameter
18	250 ml. Burette
19	Nitrogen Supply
20	Condenser
21	Liquid Receiver
22	Gas Drying Tube
23	Trap
24	Dewar Flask
25	Bubbler
26	Wet Test Meter
27	Manometer
28	Gas Sampling Bulb
29	Gas Flow Meter
30	Sulfuric Acid
31	Fieser's Solution
32	Drierite
33	Glass Wool

Apparatus for Gas Analysis

Use was made of a modification of the standard type of Bone and Wheeler Apparatus consisting of a U-tube, water jacketed and backed by a mirror scale, for measurement of the gas pressure at constant volume. Absorption of gases was carried out in a standard bell-shaped dome, connected to the U-tube by capillary tubing. Mercury was the confining liquid.

The various gases were absorbed, in the order listed, by the following reagents:

Reagent	Gas Absorbed
Conc. potassium hydroxide solution	Carbon dioxide
Bromine water	Unsaturated hydrocarbons
Alkaline pyrogallol solution	Oxygen
Ammoniacal cuprous chloride solution followed by cuprous sulphate, β-naphthol solution	Carbon monoxide

A copper-oxide slow-combustion furnace, kept at 260-270°C., was used for hydrogen determinations and saturated hydrocarbons were determined by burning in oxygen over a glowing platinum coil.

Fractionating Columns

Two columns were available for distillations, a large Stedman column and a small Whitmore-Fenske column, both of which were used for the analysis of liquid products. The

Stedman column was 90 cm. long and of 1.5 cm. inside diameter. It had a rated efficiency of fifty theoretical plates and was specially suitable for the distillation in vacuo of high boiling liquids. It was used for the purification of all starting materials. The small Whitmore-Fenske column had previously been constructed and tested in this department. It was 45 cm. long, had an internal diameter of 1.0 cm. and was packed with single turn glass helices of 0.24 cm. diameter. It had a small hold-up and high efficiency (157). Both columns were heated electrically and controlled by powerstats. They had stillheads of the total-condensation partial-take-off type with stopcocks suitably arranged to regulate the reflux ratio. They could both be operated successfully at atmospheric as well as reduced pressure.

Preparation and Regeneration of the Catalyst

The bentonitic clay, a gift from Pembina Mountain Clays Limited of Winnipeg, Manitoba, was activated according to the method outlined by Gallay (136). The dry material as received was boiled gently for five hours in a 20 per cent aqueous solution of sulphuric acid. The volume of concentrated acid used was one-half the weight of the clay being activated. The mixture was stirred from time to time to keep it thoroughly dispersed, and water lost by evaporation was periodically replaced. After cooling, the slurry was diluted to four times its original volume, filtered and then washed with distilled water until the filtrate gave only a faint test for sulfate ions. The clay was then dried for twelve hours at 110°C., broken up and screened into pellets of from 4 to 8 mesh. Before being used for pyrolytic studies the dried material was placed into the reactor and heated to 500°C. while a slow stream of moist air, generated by applying mild suction to the reactor outlet, was passed over it. During this treatment about 8-12 ml. of water collected, which had a faint greenish tinge, gave a positive test for iron and sulfate ions and was strongly acidic. Such freshly activated catalyst has been reported (156, 157) to behave differently than regenerated catalyst, and in order to compare and co-ordinate the experimental results more readily only those data have been recorded which were obtained with the use of regenerated catalyst.

This catalyst was prepared by a process of re-activation which had to be carried out regularly after each run. It served to restore the efficiency of the catalyst which was impaired during pyrolysis as a result of the formation and gradual accumulation of carbon, resinous sludges and poisons. Removal of these deposits was achieved by heating the catalyst for 7-8 hours to 600-630°C. while a slow stream of moist air was drawn over it. The temperature was not allowed to rise above 700°C. in any part of the reactor, because the catalyst would then sinter and lose its activity. Since regeneration was a strongly exothermic process the air stream was kept below 30 l. per hour for at least 3 to 4 hours after which time it could gradually be increased to 100 l. per hour. This mode of regeneration was found to remove very efficiently all carbonized material and polymeric residues from the catalyst surface, as ascertained by an occasional visual inspection. Catalytic activity tests showed that when generation was properly carried out a single charge completely retained its activity for 8 to 10 consecutive runs.

Operation of the Catalysis Apparatus

The experimental procedure embraced three operations:

(a) The controlled introduction of the charging stock into the catalytic apparatus,

(b) Vaporization of the liquid feed at constant temperature when entering and while passing through the reactor,

(c) Cooling and collection of products including gaseous constituents.

The freshly activated catalyst was placed in the reactor and heated gradually to 500°C. while a slow stream of moist air was passed over it. Then 50 cc. of acetic acid were pyrolyzed and the catalyst regenerated immediately. For all experiments 220 cc. of catalyst (90-94 g.) were used and unless otherwise specified only regenerated catalyst was employed for pyrolytic studies.

Before making a run the reactor was gradually brought to the desired temperature, tested for leaks and thoroughly flushed with nitrogen. Then operation of the feed system was started. After a fore-run of about 20-25 cc. had collected the receiver was changed, time and temperature readings were taken, the gas volume was recorded and the level of the calibrated feed reservoir noted. Readings were taken at 5-minute intervals throughout the run in order to check uniformity of conditions for the entire operation.

After 100 cc. of feed had been passed over the catalyst the volume of gas generated was recorded and the reactor emptied with a slow stream of nitrogen. Liquid products, condensed by passage through a Friedrichs condenser, collected in a cooled receiver, and gaseous products were vented after passage through a Fisher Precision Wet Test Meter. A sample of the gaseous products was collected during the middle of a run in an evacuated sampling bulb connected to the gas line. This operation was carried out very slowly in order to maintain atmospheric pressure in the system. In several experiments a dry-ice acetone trap was used to condense low boiling gases.

Purification of Reagents and Analytical Procedure

Acetic anhydride, obtained from Shawinigan Chemicals Ltd., was distilled over phosphorus pentoxide and the fraction which boiled at 139.1-139.8°C. was used for pyrolytic studies. Its physical constants were:

B.P. (corr.) 139.6°C., n_D^{20} 1.3902, d_4^{20} 1.082

Benzaldehyde, (N.F. Grade) supplied by Merck & Co. Ltd., was extracted with a 5 per cent aqueous sodium carbonate solution, washed with water until neutral, dried over Drierite and distilled under reduced pressure in an atmosphere of nitrogen. The material which boiled at 75-75.7°C. at 16 mm. pressure showed the following physical constants:

B.P. (corr.) 179.2°C., n_D^{20} 1.5453, d_4^{20} 1.046

It was stored in the dark, in small, tightly stoppered amber colored bottles.

Two runs were carried out using equimolar quantities of starting materials, one at a low temperature (200°C.) in order to ascertain whether direct condensation of the reactants did occur, and one at an elevated temperature (650°C.) in order to determine the types of compounds formed and to develop appropriate procedures for analysis. This mode of attack gave very interesting results from the start.

At 650°C. the products formed on pyrolysis consisted of two layers; a lower one, which was easily identified as pure water and an upper one, which consisted of benzene, toluene, ethylbenzene, styrene and unchanged benzaldehyde (Table IX).

Pyrolysis at 200°C., that is, at a temperature just about sufficient to vaporize the aromatic component, gave a single product layer from which only one aromatic compound - disregarding the recovered benzaldehyde - could be isolated. This aromatic compound was the desired product, styrene (Tables XI and XII).

In order to gain information regarding the non-aromatic phase, aliquots of the products were analyzed in the following manner:

1. A 1.0-g. sample of the total liquid products was titrated with 1 N sodium hydroxide solution and the total acidity of the products calculated in terms of acetic acid.
2. A 35.0-g. sample of the total liquid products was carefully fractionated at atmospheric pressure. Distillation started at 110°C. and was continued up to a temperature of 120°C., whereafter an aliquot was titrated against 1 N sodium hydroxide. From the data obtained the total weight of acetic acid in the total liquid products could be calculated. By subtracting the weight of acetic acid thus determined from the total weight of acetic acid previously found and by converting the difference into the acetic anhydride equivalent, the weight of unchanged acetic anhydride in the total liquid products could be calculated.

It was found that the aqueous layer consisted of 11.7 g. of acetic acid and 31.8 g. of acetic anhydride. The total weight of the non-aromatic fraction was therefore 43.5 g. The weight obtained by subtracting the weight of aromatics isolated from the total weight of liquid products would amount to 42.9 g. (Table XI; Run 17). This type of analysis constituted a sound approach toward obtaining information regarding the distribution of acetic acid and acetic anhydride in the non-aromatic fraction of the products, as will become more evident after the pyrolyses of acetic acid and acetic anhydride over Morden bentonite have been reported (Tables XXVI and XXX).

The procedure adopted for isolation of the aromatics consisted in treating the products with dilute aqueous sodium carbonate solution and extracting with ether. The neutralization, an exothermal process, was always carried out after the pyrolyzate had been cooled with ice in order to prevent styrene losses by polymerization. The ether layer was washed with water until neutral, dried over calcium chloride, and after removal of the solvent the residue was fractionated under reduced pressure in an atmosphere of nitrogen. In order to avoid excessive polymerization of the styrene during distillation 2 to 3 per cent of hydroquinone was used as stabilizer, and purified α-methylnaphthalene, B.P. 241-243°C., served as booster for a more complete rectification. In spite of these precautions distillation residues on the average amounted to about 10 per cent (Table X).

TABLE IX

Identification of Aromatic Products from Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture at 650°C.

Compound	Boiling Point °C.		Density d_4^{20}		Refractive Index n_D^{20}	
	Given	Found	Given	Found	Given	Found
Benzene	80.0	80.1	0.879	0.879	1.5017	1.5014
Toluene	110.8	110.5	0.866	0.867	1.4955	1.4957
Ethylbenzene	136.2	136.1	0.867	0.867	1.4959	1.4959
Styrene	145.0	145.1	0.906	0.905	1.5465	1.5468
Benzaldehyde	179.0	179.1	1.046	1.046	1.5455	1.5456

TABLE X

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

Benzaldehyde	51.0 % by wt.
Acetic Anhydride	49.0

Volume Pyrolyzed: 100 ml.
Feed Rate: 2.0 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Weight of Liquid Products	89.1 g.
Gas Evolved	10.4 l.
Weight of Aromatics	48.6 g.

Composition of Aromatics

Benzene	1.3 % by wt.
Ethylbenzene	14.1
Styrene	32.7
Benzaldehyde	42.1
High Boiling Material	9.8

A more accurate analysis of the products could be carried out by distilling the dried aromatics under reduced pressure from a Claisen flask to which 0.2 per cent of p-tert.-butylcatechol had been added as a polymerization inhibitor. Aliquots of the distillate, which had been collected in a dry-ice acetone trap, were then titrated for styrene according to the procedure outlined by Williams (230).

This method, before being adopted for product analysis, was tested on mixtures of known styrene concentrations in the presence of benzaldehyde, toluene, benzene and ethylbenzene, and it was found that styrene could be determined to within ± 0.4 per cent of the theoretical value. An attempt to analyze the products for unconverted aldehyde according to the method of Seyewetz and Bardin (232) was not successful. This method, which is based upon reaction of the aldehyde with excess sodium sulfite and titration of the alkalinity developed against standard sulfuric acid, always gave low results when tested on mixtures of known benzaldehyde concentration in the presence of styrene, ethylbenzene, toluene and benzene, the average deviation from the theoretical value amounting to 3 to 4 per cent. The method was abandoned and the values for the aldehyde reported were obtained by subtracting from the total weight of the distillate all fractions whose percentages had been accurately determined by either titration (styrene) or fractionation at atmospheric pressure (benzene, toluene, ethylbenzene).

RESULTS AND DISCUSSION

Determination of Optimum Conditions for Pyrolysis of Benzaldehyde-Acetic Anhydride Mixtures over Morden Bentonite

Effect of Temperature

Before studying the effect of temperature on the reaction, 100 cc. of an equimolar acetic anhydride-benzaldehyde mixture was passed through the reactor whose central section was filled with 250 cc. of quartz chips as an inert contact material. At a temperature of 400°C. and a feed rate of 2 cc. per min. only 0.6 l. of gas was formed and only unconverted benzaldehyde could be recovered from the aromatic portion of the products.

Similarly, when pyrolyzing acetic anhydride alone under identical conditions, 0.3 l. of gas was evolved and only 5.2 per cent of acetic acid could be isolated from the reaction products by fractional distillation. Hence, both the benzaldehyde-acetic anhydride mixture as well as acetic anhydride were but slightly decomposed, particularly since formation of acetic acid during pyrolysis of acetic anhydride may also take place by hydrolysis if moisture is present in the reactor or if no precautions are taken to exclude moisture during subsequent treatment of the products. In this experiment no such precautions had been taken.

These results show that formation of styrene by pyrolysis of benzaldehyde-acetic anhydride mixtures over Morden bentonite is a heterogeneous reaction which takes place at the catalytic surface exclusively and is uninfluenced by the walls of the reactor system.

A study of the experimental data (Tables XI and XII) shows that the optimum yield of styrene, based upon the total weight of aromatic products isolated, is obtained at a temperature of 500°C. At 200°C., i.e. only 20°C. above the boiling point of the aldehyde, the reaction is particularly clean-cut, leading to the formation of styrene only. At about 250°C. formation of ethylbenzene begins, becoming more and more pronounced with rise in temperature until at and above 600°C. it constitutes the reaction of greatest magnitude. Appearance of ethylbenzene is caused by a disproportionation reaction which accompanies the condensation reaction and which leads to hydrogenation of the side chain of the styrene molecule. This reaction occurs almost invariably during high temperature catalytic reactions leading to the formation of styrenes, particularly when activated alumina or aluminum hydrosilicates are used as catalysts. Marvel and Hein (11) encountered it during the pyrolysis of 1-(p-benzylphenyl)-ethanol and 1-(o-methoxyphenyl)-ethanol, Frank and Adams (54) noticed it during pyrolysis of 1-(4-phenoxyphenyl)-ethanol and Marvel and Overberger (233) found it to be the only reaction occurring during pyrolysis of m-N-methylaminophenylmethylcarbinol. Morton (157) obtained styrene

TABLE XI

Effect of Temperature on Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed:
Benzaldehyde 51.0 % by wt.
Acetic Anhydride 49.0
Volume Pyrolyzed: 100 cc.
Feed Rate: 2.0 cc./min.
Catalyst Volume: 220 cc.

Run No.	Temp. °C.	Liquid Products g.	Gas Evolved l.	Aromatics g.	Gas (Litres per Mole)	
					Feed	Anhydride
17	200	86.9	3.7	44.0	3.6	7.2
15	300	90.2	6.4	46.3	6.3	12.6
16	400	86.5	10.6	47.8	10.4	20.8
14	500	69.5	22.5	45.7	22.0	44.0
18	600	54.0	34.6	39.9	33.9	67.8
20	650	36.2	39.9	29.1	39.1	78.2

TABLE XII

Analysis of Aromatics from Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Run No.	Distillate % by wt.	High Boiling Material % by wt.	Percent by Weight Composition of Distillate					Styrene	
			Benzene	Toluene	Ethylbenzene	Styrene	Benzaldehyde	% by wt. in Aromatics	% of Theoretical Yield
17	97.2	2.8	--	--	--	8.3	91.7	8.1	8.2
15	97.1	2.9	--	--	6.7	30.7	62.6	29.8	30.4
16	96.2	3.8	1.7	--	16.6	39.8	41.9	38.3	39.1
14	95.9	4.1	4.8	2.7	25.8	42.6	24.1	40.8	41.6
18	95.2	4.8	6.8	3.9	39.8	37.9	11.6	36.1	36.8
20	94.6	5.4	9.2	5.4	46.8	31.2	7.4	29.5	30.1

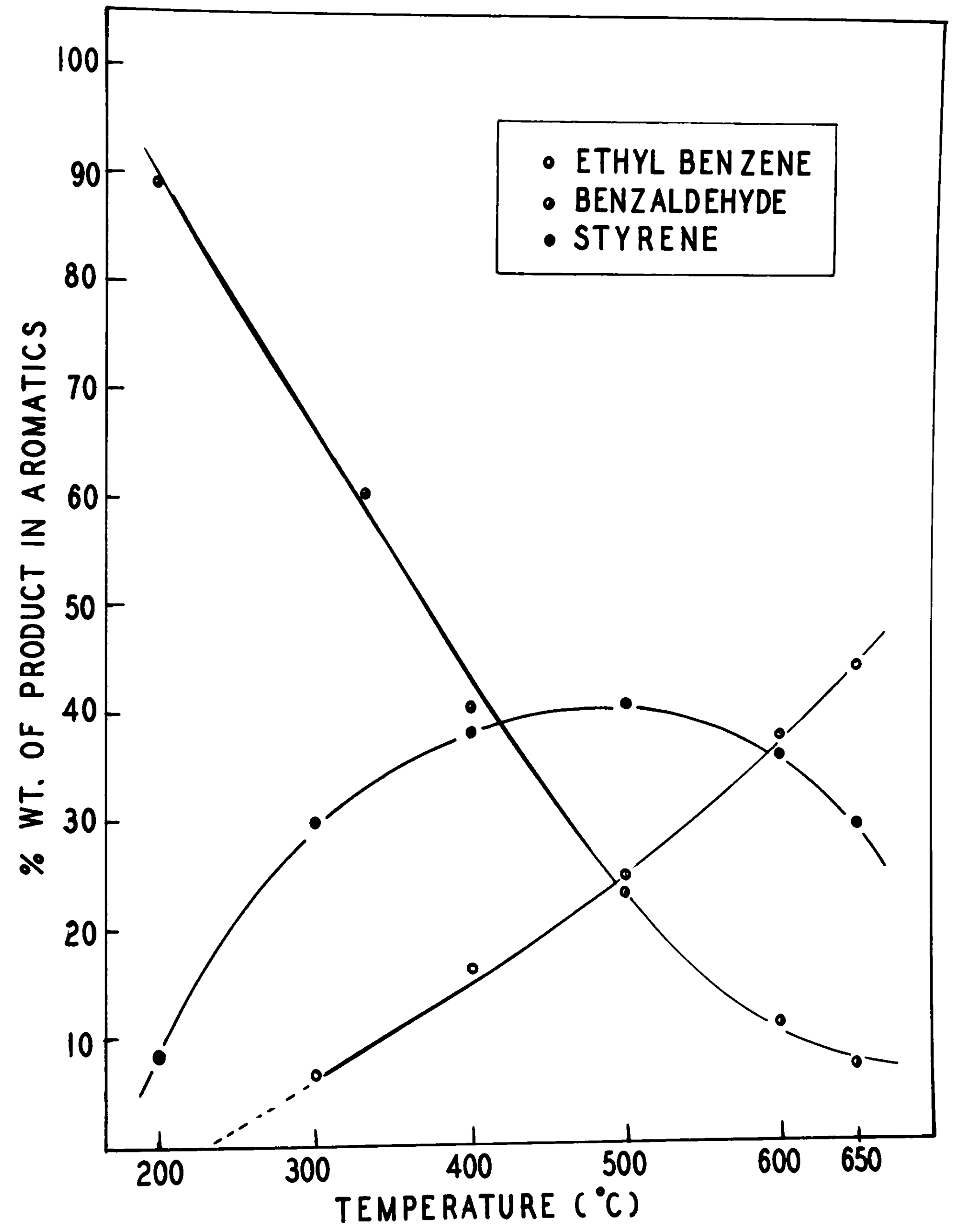


Figure 3

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixtures
Temperature vs. Yield

TABLE XIII

Analysis of Gaseous Products from Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Percent by Volume

Run No.	Temp. °C.	Carbon Dioxide	Alkenes	Carbon Monoxide	Hydrogen	Alkanes
17	200	56.1	12.7	27.1	4.1	--
16	400	41.4	16.4	26.1	10.9	5.2
18	600	28.9	10.6	28.7	25.2	6.6

contaminated with ethylbenzene when pyrolyzing 1,1-diphenylethane over Morden bentonite in an iron tube and showed that pyrolysis of equimolar styrene-benzene mixtures at 500°C. led to the formation of ethylbenzene. He interpreted this hydrogenation as a "reaction between the styrene and any hydrogen formed from side chain decomposition", a reaction also postulated by Han-Ying Li (234) who carried out the same pyrolysis over an acidic white clay at 600°C.

In order to determine the magnitude of this hydrogenation reaction in the stainless steel reactor used throughout this investigation, Morton's experiment was repeated, but instead of taking styrene-benzene mixtures pure styrene was used as feed stock. Furthermore, the pyrolyses were carried out at lower temperatures, namely 300 and 400°C. (Table XIV). The products from the pyrolyses were dried over calcium chloride and fractionated in an atmosphere of nitrogen under reduced pressure, using hydroquinone as polymerization inhibitor. The compounds obtained were identified by determining their main physical constants and comparing the values found with those in the literature. It is to be noted that, in spite of the use of nitrogen as carrier gas during pyrolysis, considerable material losses could not be prevented.

Morton's results were confirmed. Styrene was partly broken down to benzene and partly converted to ethylbenzene. However, from the experimental data one may conclude that

TABLE XIV

Pyrolysis of Styrene over Morden Bentonite

Weight of Styrene Pyrolyzed: 50.0 g.
Feed Rate: 1.0 cc./min.
Catalyst Volume: 220 cc.
Nitrogen: 15 l./hr.

Run No.	Temp. °C.	Products g.	Percent by Weight Composition of Dry Aromatics			
			Benzene	Ethylbenzene	Styrene	High Boiling Material
23	300	38.4	3.3	40.7	48.6	7.4
24	400	41.8	5.2	53.5	33.1	8.2

hydrogenation probably does not solely "depend on the presence of available hydrogen from side chain decomposition", but is also caused by a more complete breakdown of some aromatic nuclei. If hydrogenation of the styrene molecule would involve destruction to carbon and hydrogen of some of the side chains only, one would expect a proportion of benzene much larger than that found in the styrene, ethylbenzene, benzene mixture obtained on pyrolysis. Actually, at both 300° and 400°C. only a small percentage of benzene, as compared to that of ethylbenzene, was isolated from the reaction products. It is of interest to note that Tonks (155) was also forced to assume the total breakdown of some aromatic nuclei in order to account for the products obtained on pyrolysis of anilines over Morden bentonite at temperatures ranging from 300 to 400°C. Another potential source of hydrogen in the reaction under investigation is, of course, the acetic anhydride which is efficiently attacked by the catalyst at a temperature of 300°C. (Table XXVI).

At 400°C. some benzene and at higher temperatures both benzene and toluene are formed. The small amount of benzene obtained at 400°C. may result from a partial breakdown of either styrene or benzaldehyde molecules or both. Toluene, as well as benzene, are known to be products of the pyrolysis of ethylbenzene over Morden bentonite at temperatures above 400°C. (152). They also form when benzaldehyde is passed over the clay at and above 400°C. (Table XV).

TABLE XV

Pyrolysis of Benzaldehyde over Morden Bentonite

Weight of Benzaldehyde Pyrolyzed: 60.0 g.
Feed Rate: 1.0 cc./min.
Catalyst Volume: 220 cc.

Run No.	Temp. °C.	Liquid Products g.	Loss on Drying g.	Total Gas Evolved l.	Percent by Weight Composition of Dry Products			
					Benzene	Toluene	Benzaldehyde	High Boiling Material
25	400	55.1	1.4	0.2	4.1	2.5	89.6	3.8
26	500	51.7	2.4	6.7	9.5	5.3	81.7	3.5
27	600	44.8	3.9	11.2	14.8	8.3	72.8	4.1

Apparently the two reactions occurring in this instance are

$$C_6H_5CHO \longrightarrow C_6H_6 + CO$$

$$C_6H_5CHO + 2H_2 \longrightarrow C_6H_5CH_3 + H_2O$$

Again the hydrogen necessary for conversion of the aldehyde to toluene may form as the result of the total breakdown of some aromatic molecules. Good evidence for the latter reaction was the isolation of water during distillation of the pyrolysis products which had not been thoroughly dried. Furthermore, increase of toluene formation with temperature was found to go parallel with an increase of the material lost by drying the total liquid products prior to distillation.

It is to be noted that recovery of the aromatics obtained by pyrolysis of acetic anhydride-benzaldehyde mixtures is maximal at 400°C. Below this temperature some material apparently remains in the catalyst bed, because insufficient gas is evolved for carrying the pyrolysis products through and out of the reactor, while at higher temperatures severe cracking of the feed stock and all primary reaction products sets in as evidenced by the greatly increased gas evolution.

Effect of Nitrogen as Carrier Gas

The effect of nitrogen diluent on the pyrolysis of equimolar benzaldehyde-acetic anhydride mixtures may be evaluated from the results shown in Table XVI.

By comparison with the data given in Tables XI and XII it is seen that in each case the weight of aromatics isolated from the reaction products exceeds that obtained in similar runs carried out in the absence of any diluent. At the low temperature of 200°C. a still faster stream of the carrier gas appears to be necessary for more complete product recovery. Another beneficial effect resulting from the presence of nitrogen in the system is the increase of the styrene content in the aromatic products. This effect is particularly pronounced at the lowest temperature used. In the absence of the carrier gas most of the material retained in the catalyst bed apparently consists of styrene or styrene polymer. However, while at the low temperature the increased styrene content of the aromatic fraction obtained is caused by the more complete sweep of the reactor during pyrolysis, the increased styrene content of the products from pyrolyses carried out at higher temperatures results primarily from a corresponding decrease in ethylbenzene formation. Evidently, when using nitrogen diluent there is, because of the shortened contact times, not only less chance for reactant as well as product molecules to break down but also less chance for

TABLE XVI

Effect of Nitrogen as Carrier Gas on Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.0 cc./min.
Catalyst Volume: 220 cc.
Nitrogen: 15 l./hr.

Run No.	Temp. °C.	Liquid Products g.	Total Gas l.	Aromatics g.	Distillate from Aromatics % by wt.	High Boiling Material % by wt.
31	200	92.1	16.7	47.1	97.3	2.7
29	300	94.0	19.1	49.7	97.5	2.5
30	400	89.2	24.2	50.3	96.3	3.7
28	500	72.1	36.7	47.1	96.0	4.0

Run	Percent by Weight Composition of Distillate					Styrene	
No.	Benzene	Toluene	Ethylbenzene	Styrene	Benzaldehyde	% by wt. in Aromatics	% of Theoretical Yield
31	--	--	--	16.2	83.8	15.8	16.1
29	--	--	3.1	34.8	62.1	34.0	34.6
30	--	--	11.2	44.3	44.5	42.6	43.4
28	3.1	1.7	18.6	47.5	29.1	45.6	46.5

any hydrogen once formed to effect hydrogenations. For this same reason conversion of the aldehyde in turn is not increased, and benzene not yet formed at 400°C. The main effects of the nitrogen diluent on the reaction, therefore, are carrying the organic vapors more efficiently out of the catalyst bed, thereby insuring more favorable products recovery, shortening the contact times, and reducing the extent of undesirable side reactions, such as hydrogenation of styrene to ethylbenzene and formation of benzene. The desirable conversion of the aldehyde itself, however, is also slightly inhibited. It is evident that these two opposite effects will have to be taken into account in order to secure maximum styrene yields.

A study of the experimental data (Tables XI, XII, XVI) shows that in spite of the higher percentage of styrene in the aromatic products obtained at 500°C. the process is more efficiently carried out at a temperature of 400°C. Thus, the theoretical yield of styrene per single pass based upon the original weight of benzaldehyde amounts to 34.5 per cent at 400°C. (Table XI, Run 16), 35.1 per cent at 500°C. (Run 14) in the absence of nitrogen diluent, and 40.3 per cent at 400°C. (Table XVI, Run 30), 40.4 per cent at 500°C. (Run 28) in the presence of nitrogen diluent. These differences, which lie within the limits of experimental errors, will become more apparent if it is realized that the unchanged benzaldehyde may be recycled with acetic anhydride in each case. When considering the conversion efficiency of the process, it will be found that the 34.5 per cent styrene obtained in the absence of nitrogen diluent at 400°C. represents 57.7 per cent of the theoretical yield obtainable at a conversion of 59.7 per cent. The 35.1 per cent styrene obtained at 500°C. represents only 45.6 per cent of the theoretical yield obtainable at a conversion of 76.9 per cent. Similarly, the 40.3 per cent styrene obtained in the presence of nitrogen diluent at 400°C. represents 70.6 per cent of theory at a conversion of 57.2 per cent while the 40.4 per cent styrene obtained at 500°C. corresponds to only 56.1 per cent of theory at a conversion of 72.1 per cent. Further experiments were therefore performed at 400°C. i.e. at the temperature at which the process may be carried out most economically.

Effect of Space Velocity

An increase in the space velocity, defined as the volume of liquid feed in cubic centimetres per hour per 10 cc. of catalyst, caused the per cent conversion to fall off steadily. Thus at a space velocity of 2.7 the aromatic fraction contained 41.8 per cent of unchanged benzaldehyde, and the conversion efficiency was reduced by 11.3 per cent when the space velocity was increased to 10.9. The effects observed are similar to those noticed when nitrogen was used as a carrier gas, since high space velocities of necessity are equivalent to short contact times. At a space velocity of 1.4, however, conversion fell below that attained for a space velocity of 2.7. Evidently, in this case the long contact time caused carbonization and fouling of the catalyst, a tendency which is especially pronounced at higher temperatures but apparently also operative at very slow feed rates.

It can be seen from the experimental data given in Table XVII and plotted in Figure 4 that formation of styrene is greatly dependent upon the space velocity. Low space velocities (prolonged contact times) favor the more efficient breakdown of the reactant and product molecules during their passage through the catalyst bed and thus enhance undesirable side reactions, while high space velocities favor styrene formation at the expense of possible side reactions but also decrease the conversion efficiency with which the process may be carried out. As a result of the interaction of these reaction trends the styrene yield passes through a maximum. At low space velocities a relatively large proportion of the styrene is converted to ethylbenzene while at high space velocities less styrene is formed because conversion in general is decreased.

TABLE XVII

Effect of Space Velocity on Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Volume Pyrolyzed: 100 cc.
Catalyst Volume: 220 cc.
Nitrogen: 15 l./hr.
Temperature: 400°C.

Run No.	Feed Rate cc./min.	Space Velocity	Liquid Products g.	Total Gas l.	Aromatics g.	Distillate from Aromatics % by wt.	High Boiling Material % by wt.
34	0.5	1.4	82.1	63.0	47.0	94.4	5.6
33	1.0	2.7	85.5	38.3	48.5	95.7	4.3
30	2.0	5.5	88.1	23.0	50.3	96.3	3.7
32	4.0	10.9	93.3	15.4	50.2	96.4	3.6

Run No.	Percent by Weight Composition of Distillate				Styrene	
	Benzene	Ethylbenzene	Styrene	Benzaldehyde	% by wt. in Aromatics	% of Theoretical Yield
34	2.2	15.7	36.5	45.6	34.5	35.2
33	1.5	13.1	41.7	43.7	39.9	40.7
30	--	11.2	44.3	44.5	42.7	43.4
32	--	5.0	39.9	55.1	38.5	39.2

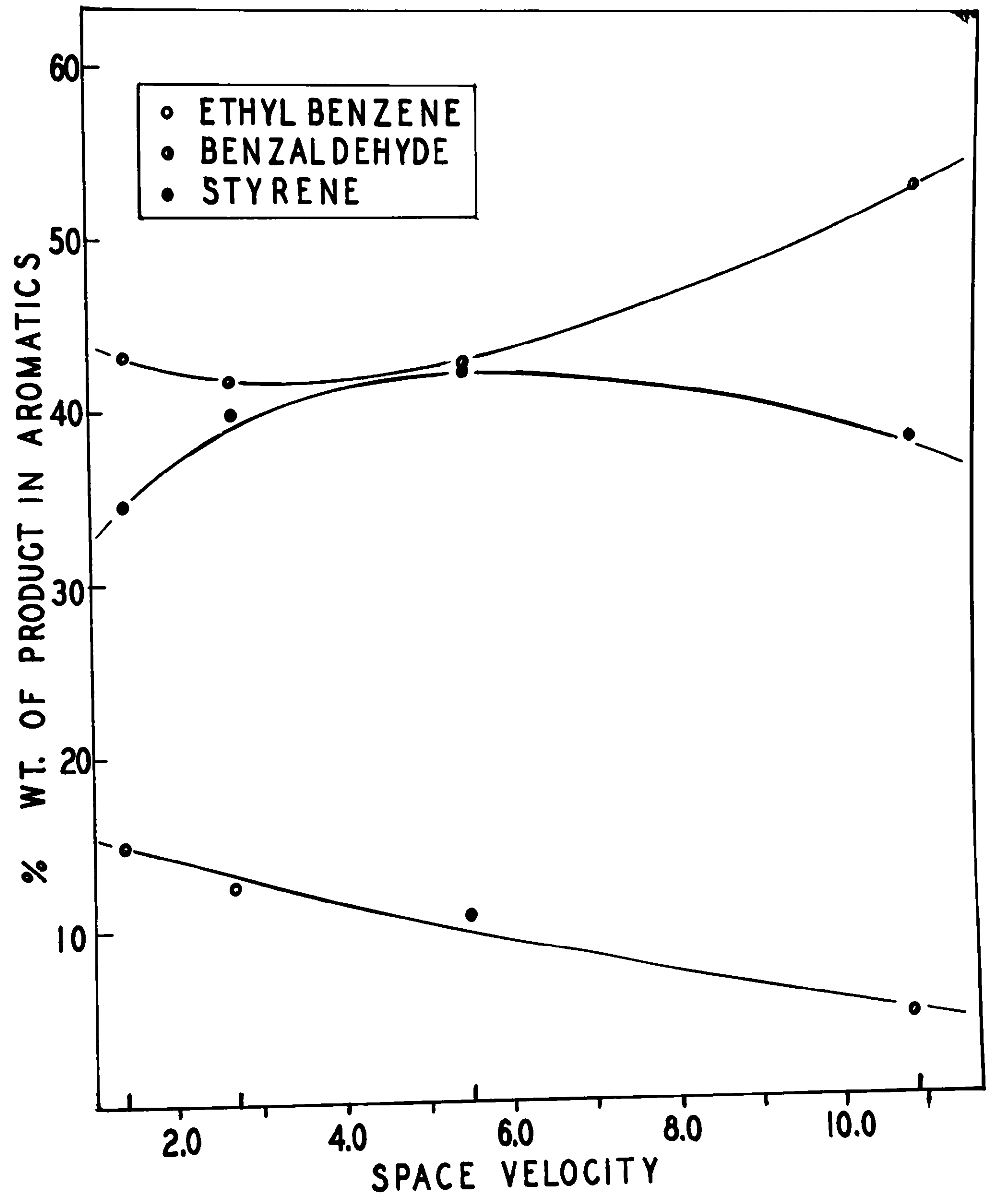


Figure 4

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixtures
Space Velocity vs. Yield

Effect of Ratio of Reactants

The results obtained by varying the ratio of the reactants for the pyrolysis of benzaldehyde-acetic anhydride mixtures are shown in Tables XVIII to XXI.

The experiments were arranged so that the same weight of aldehyde was fed into the reactor in unit time but the weight of acetic anhydride passed over the catalyst in unit time was increased by definite amounts from run to run. A similar series of experiments was carried out in which the same weight of acetic anhydride was fed into the reactor in unit time but the weight of the aldehyde increased progressively from run to run. It was found that styrene yields increased when the acetic anhydride-benzaldehyde ratio was increased. This important result will be further discussed when the mechanism of the reaction is to be explained.

From Tables XVIII and XIX it can be seen that increased acetic anhydride concentrations lead not only to higher yields of styrene in the aromatic products but also to higher conversions. As the concentration of the acetic anhydride in the feed stock is increased from 49.0 to 70.6 per cent the conversion of the aldehyde is increased by 3.3 per cent. This is surprising insofar as the higher conversion (62.0 per cent) is obtained at a feed rate considerably faster than that which gave only 58.7 per cent conversion at the equimolar ratio. The increase in styrene yield caused by the more efficient conversion of the aldehyde is still further enhanced by the progressive decrease of ethylbenzene formation with faster feed rates (Fig.5). This experimental result is renewed proof that the disturbing hydrogenation reaction may be suppressed by shorter contact times. Furthermore, benzene is no longer detected in the reaction products at a feed rate equal to or higher than 2.4 cc./min. But again the limitations imposed by shorter contact times when using increased acetic anhydride concentrations become apparent, since the per cent styrene yield appears to level off and approach a maximum value.

The gas evolution also indicates these reaction trends. The total volume of gas per mole of styrene formed increases with increasing acetic anhydride concentration in the feed because of increased conversion, and particularly because most of the hydrogen gas formed instead of attacking the monomer side chain escapes the reactor as a result of the decreased contact times. Optimum conditions for styrene production therefore appear to be high concentrations of acetic anhydride in the feed stock and fast rates of throughput. Thus, when using a molar ratio of anhydride to aldehyde equal to 3:1 and a feed rate of 3.8 cc./min. the aromatic pyrolyzate was found to contain 53.7 per cent of styrene. This represents 80.8 per cent of the theoretical yield obtainable at a conversion of 61.3 per cent.

TABLE XVIII

Effect of Ratio of Reactants on Pyrolysis of Benzaldehyde-Acetic Anhydride Mixtures over Morden Bentonite

Volume Pyrolyzed: 100 cc.
Feed Rate: 0.01 mole Aldehyde per min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Run No.	Mole Ratio $\frac{\text{Anhydride}}{\text{Aldehyde}}$	Composition of Feed % by wt.		Feed Rate cc./min.	Liquid Products g.	Gas Evolved l.	Aromatics g.	Gas l./mole of Styrene
		Anhydride	Aldehyde					
35	1.0	49.0	51.0	2.0	87.7	10.8	48.4	62.4
37	1.5	59.1	40.9	2.4	87.1	11.3	39.5	70.1
38	2.0	65.8	34.2	2.9	87.0	11.7	34.1	74.1
39	2.5	70.6	29.4	3.4	86.4	12.2	28.8	86.3
41	3.0	74.3	25.7	3.8	86.9	11.8	25.0	91.5

TABLE XIX

Analysis of Aromatic Products from Pyrolysis of Benzaldehyde-Acetic Anhydride Mixtures at 400°C.

Run No.	Distillate % by wt.	High Boiling Material % by wt.	Percent by Weight Composition of Distillate				Styrene	
			Benzene	Ethylbenzene	Styrene	Benzaldehyde	% by wt. in Aromatics	% of Theoretical Yield
35	95.7	4.3	0.9	17.1	38.9	43.1	37.2	37.9
37	96.5	3.5	--	14.0	44.1	41.9	42.5	43.4
38	97.0	3.0	--	9.5	49.7	40.8	48.2	49.2
39	96.3	3.7	--	7.4	53.1	39.5	51.1	52.1
41	97.2	2.8	--	5.0	55.2	39.8	53.7	54.7

Analysis of Gaseous Products - Percent by Volume

Run No.	Carbon Dioxide	Alkenes	Carbon Monoxide	Hydrogen	Alkanes
41	50.2	10.5	18.0	19.2	2.1

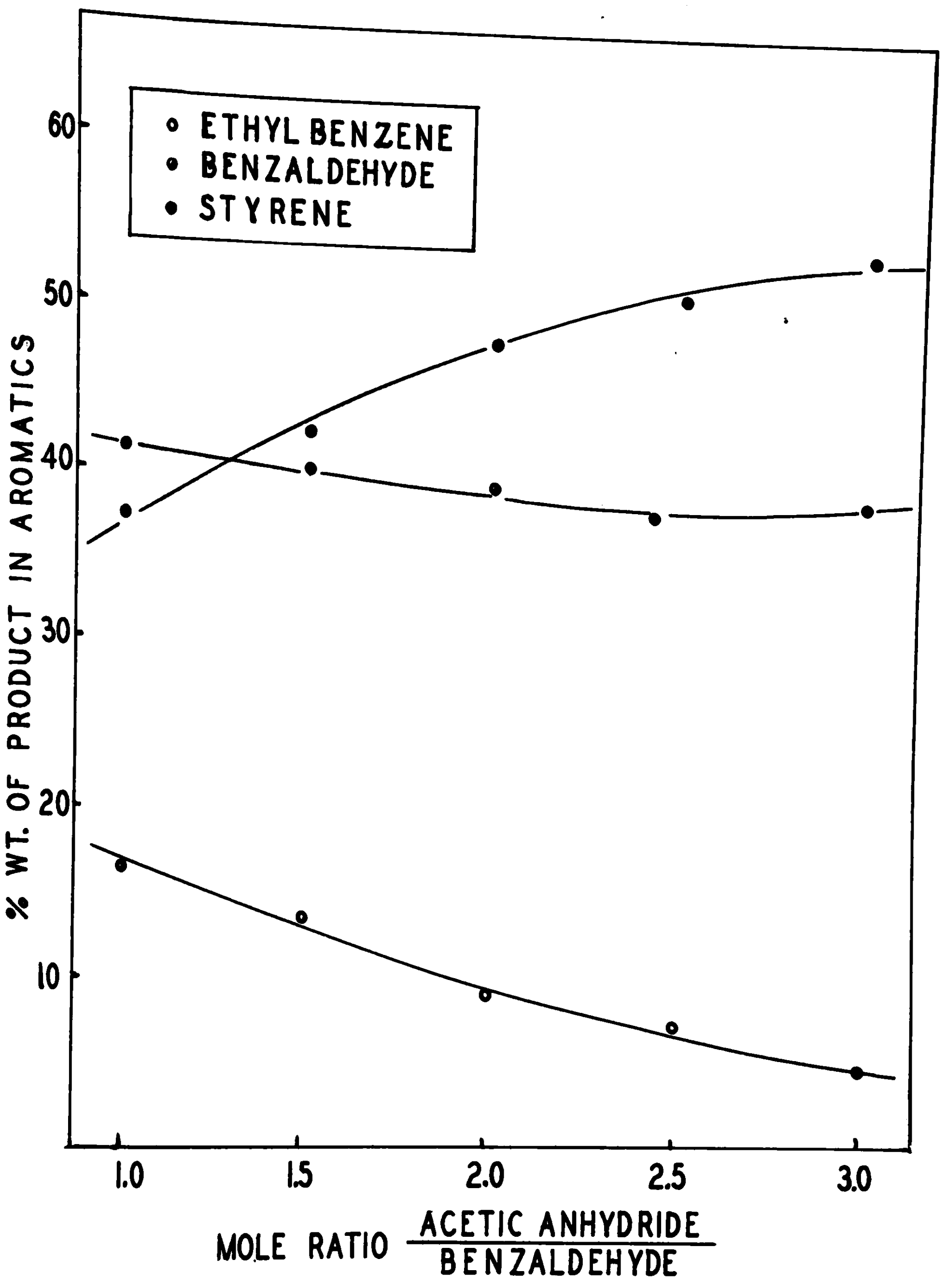


Figure 5

Pyrolysis of Benzaldehyde-Acetic Anhydride Mixtures
Mole Ratio $\frac{\text{Acetic Anhydride}}{\text{Benzaldehyde}}$ vs. Yield

For molar ratios of acetic anhydride to benzaldehyde less than unity the yield of styrene decreases continuously (Tables XX and XXI). Conversion of the aldehyde falls off with increased feed rate, and the rate of gas evolution drops steadily. Further relations between styrene formation, concentration of reactants and contact times are given in Table XXII.

The free space of the catalyst bed was measured by evacuating a 100 cc. sample of catalyst and determining the amount of water required to just cover the material. It was found that 78 cc. of reaction volume were available per 100 cc. of catalyst.

The data calculated show that when the aldehyde concentration is kept constant the styrene yield increases with the vapor space velocity and is directly proportional to the volume of acetic anhydride vapor present in the reactor at any given moment. Although an increase in feed rate of necessity shortens the contact times of both components it is seen that with increasing acetic anhydride concentrations the contact times of the benzaldehyde decrease more rapidly than those of the acetic anhydride. For molar ratios of acetic anhydride to benzaldehyde less than unity and feed rates so adjusted as to keep the acetic anhydride concentration constant the styrene yield is seen to be inversely proportional to the vapor space velocity and also inversely proportional to the vapor volume of the aldehyde in the reactor at any given moment. Again the faster feed rates shorten the contact times of both components but it is seen that with increasing benzaldehyde concentrations the contact times of the acetic anhydride decrease more rapidly than those of the aldehyde. These results will be more fully interpreted when the mechanism of the reaction is to be discussed. Assuming for the moment that reaction requires co-ordination of the anhydride with the catalyst, it follows that increased acetic anhydride concentration will tend to favor reaction, and assuming further that the aldehyde also may co-ordinate with the surface - and thereby block "active centers" at the surface - it follows that increased aldehyde concentrations will tend to inhibit reaction. The co-ordination may be visualized to involve the carbonyl groups of the reactants. Hence, an advantage of 2:1 by the anhydride over that of the aldehyde exists when using molar quantities of reactants.

Accepting the fundamental assumptions made so far, it follows that all experimental conditions tending to facilitate the co-ordination of acetic anhydride molecules with the catalytic surface, such as increasing the acetic anhydride concentration, will be conducive to styrene formation, and all experimental conditions tending to inhibit co-ordination of acetic anhydride molecules with the surface, such as increasing the benzaldehyde concentration, will suppress styrene formation.

Considering the effect of contact time in this way it is evident that if the contact time of the aldehyde is reduced more rapidly than that of the anhydride, styrene formation will be favored, and, conversely, if the contact time of the anhydride is reduced more rapidly than that of the aldehyde, styrene formation will be inhibited. These conclusions are in accord with the data given in Table XXII.

TABLE XX

Effect of Ratio of Reactants on Pyrolysis of Benzaldehyde-Acetic Anhydride Mixtures over Morden Bentonite

Volume Pyrolyzed: 100 cc.
Feed Rate: 0.01 mole Anhydride per min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Run No.	Mole Ratio Aldehyde/Anhydride	Composition of Feed % by wt.		Feed Rate cc./min.	Liquid Products g.	Gas Evolved l.	Aromatics g.
		Aldehyde	Anhydride				
35	1.0	51.0	49.0	2.0	87.7	10.8	48.4
42	1.5	60.9	39.1	2.5	87.0	9.8	60.1
43	2.0	67.5	32.5	3.0	88.6	9.5	67.2
45	2.5	72.2	27.8	3.5	88.9	8.8	71.7
44	3.0	75.7	24.3	4.0	92.2	8.3	75.1

TABLE XXI

Analysis of Aromatic Products from Pyrolysis of Benzaldehyde-Acetic Anhydride Mixtures at 400°C.

Run No.	Distillate % by wt.	High Boiling Material % by wt.	Percent by Weight Composition of Distillate			Styrene	
			Ethylbenzene	Styrene	Benzaldehyde	% by wt. in Aromatics	% of Theoretical Yield
35	95.7	4.3	17.1	38.9	43.1	37.2	37.9
42	95.9	4.1	15.4	37.2	47.4	35.7	36.4
43	96.0	4.0	12.7	34.7	52.6	33.3	34.0
45	95.7	4.3	11.8	32.4	55.8	31.0	31.6
44	95.8	4.2	10.4	29.9	59.7	28.6	29.2

TABLE XXII

Relation between Ratio of Reactants, Vapor Space Velocity and Contact Time

Volume Pyrolyzed: 100 cc.
Catalyst: 220 cc. of Morden Bentonite
Catalyst Free Space: 172 cc.
Temperature: 400°C.

Run No.	Mole Ratio Anhydride/Aldehyde	Feed Rate cc./min.	Vapor Volume cc./sec.		Vapor Space Velocity Vol.Vapor/Vol. Free Space/sec.	Contact Time sec.		Styrene % of Theoretical Yield
			Aldehyde	Anhydride		Aldehyde	Anhydride	
35	1.0	2.0	9.4	9.4	0.109	4.6	4.6	37.9
37	1.5	2.4	9.1	13.6	0.132	3.0	4.5	43.4
38	2.0	2.9	9.2	18.4	0.161	2.1	4.2	49.2
39	2.5	3.4	9.4	23.2	0.190	1.5	3.8	52.1
41	3.0	3.8	9.1	27.3	0.212	1.2	3.5	54.7
42	0.67	2.5	14.0	9.3	0.136	4.4	3.0	36.4
43	0.50	3.0	18.6	9.3	0.162	4.1	2.1	34.0
45	0.40	3.5	23.1	9.3	0.188	3.8	1.5	31.6
44	0.33	4.0	27.7	9.2	0.215	3.5	1.2	29.2

Effect of Process Period

The question of how long a catalyst retains its activity above a certain level is an important one to industry. It cannot yet be answered on the basis of theoretical considerations. The nature of the catalyst as well as the nature of the reaction play an important role and the safest way to decide whether a catalyst is suitable for a particular reaction is to find out by appropriate experimentation. This approach was chosen and the most important variable, the process period, was studied at two different temperatures (Table XXIII).

A total volume of 240 ml. was pyrolyzed - in addition to a fore-run of 25 ml. which was discarded - and product samples each corresponding to 80 ml. of charging stock were collected and analyzed for styrene. It was found that monomer formation decreased with time, particularly during the initial phases of the pyrolysis but appeared to level off somewhat during the later stages. The reduction of catalytic activity was more marked at the higher temperature. Evidently, at more elevated temperatures when relatively large volumes of gases are generated and disproportionation reactions are more pronounced carbonization of the catalyst occurs at a faster rate and catalyst deactivation proceeds therefore more rapidly.

The results obtained are conveniently plotted (Figure 6) so as to indicate the per cent styrene contained in the aromatic fraction at any time. Thus, when pyrolyzing the equimolar mixture for two hours at 375°C. the aromatic fraction isolated will contain about 31.7 per cent of styrene, the overall decrease in styrene yield amounting to about 4.2 per cent during the last eighty minutes of the process period. Similarly, when operating at 525°C. for two hours the aromatic fraction isolated will contain about 30 per cent of styrene and the decrease in styrene yield amount to about 8.7 per cent during the last eighty minutes of the pyrolysis.

The results obtained are in accordance with the decreased gas evolution in unit time, signalling less conversion. Again, the rate at which gas formation falls off is a function of the process period and of the temperature at which the pyrolysis is carried out. The higher the temperature the more rapid the decrease of gas formation, and the longer the process period the more slowly the decrease of gas formation in unit time. Hence, the gas evolution also indicates the more rapid decrease of catalyst activity at more elevated temperatures, and the gradual decrease at any temperature with time.

This work has illustrated the importance of using equal feed volumes for pyrolytic studies when experimental data are to be compared.

TABLE XXIII

Effect of Process Period on Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Volume Pyrolyzed: 240 cc.
Feed Rate: 2.0 cc./min.
Catalyst Volume: 220 cc.

Run No.	Temp. °C.	Feed Volume cc.	Liquid Products g.	Gas Evolved l.	Aromatics g.	Distillate % by wt.	High Boiling Material % by wt.	Styrene	
								% by wt. in Distillate	% by wt. in Products
46	375	80	70.4	7.4	38.8	96.8	3.2	37.1	35.9
	375	80	71.3	5.5	39.3	97.3	2.7	31.6	30.7
	375	80	71.0	4.2	38.9	97.0	3.0	29.5	28.6
47	525	80	52.8	20.6	35.4	95.2	4.8	40.7	38.7
	525	80	53.6	15.7	36.1	95.5	4.5	29.8	28.5
	525	80	53.9	11.9	36.6	95.1	4.9	23.9	22.7

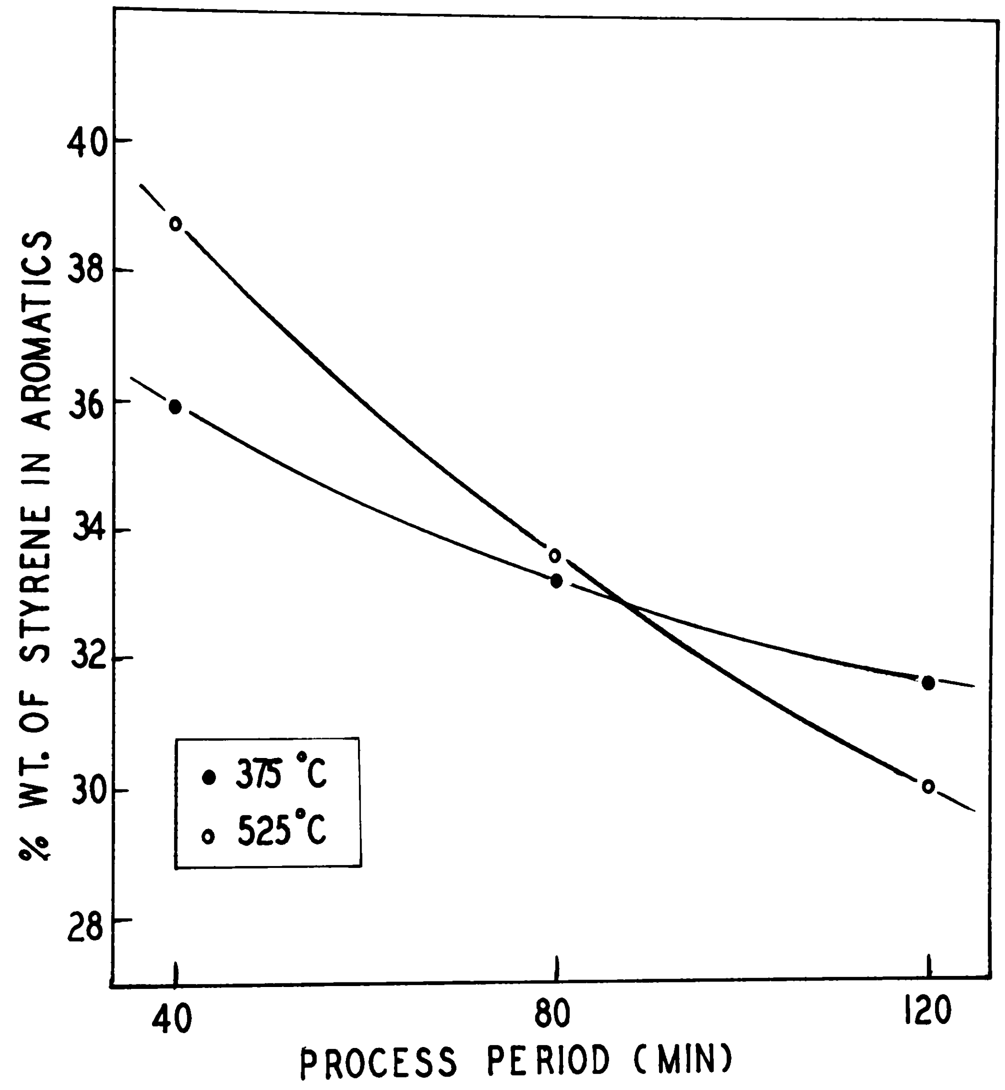


Figure 6

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture
Process Period vs. Yield

Effect of Catalyst Volume

It was found that the per cent conversion of the aldehyde increased steadily with increasing amounts of catalyst (Table XXIV). Only when 220 cc. of catalyst were used could a small amount of benzene be isolated from the reaction products. It appears that a fairly large volume of catalyst is necessary to obtain satisfactory conversion and that a critical volume is required for a normal predictable behavior of the system. When using only 55 cc. of catalyst conversion was extremely low, and the product distribution differed markedly from that obtained when 220 cc. of catalyst were employed. When using 110 cc. of catalyst conversion was still very low but the product distribution resembled more closely that of similar runs with 220 cc. of catalyst. It would therefore appear that a definite amount of catalyst must be taken so that pyrolysis may occur to a certain extent according to a definite pattern.

The weight of the aromatic fraction recovered decreased as the catalyst volume was increased, and since the types of aromatic products obtained when using 55 cc. or 110 cc. of catalyst are the same and nearly equal in molecular weight, the loss of aromatics may be directly related to the volume of catalyst used. This phenomenon is not surprising since catalysis involves processes of adsorption and desorption which are equilibrium processes that seldom go to completion.

TABLE XXIV

Effect of Catalyst Volume on Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.0 cc./min.
Catalyst: Morden Bentonite
Temperature: 400°C.

Run No.	Catalyst Volume cc.	Liquid Products g.	Gas Evolved l.	Aromatics g.	Distillate from Aromatics % by wt.	High Boiling Material % by wt.
49	55	95.7	3.1	51.8	97.2	2.8
48	110	89.0	5.7	49.2	97.0	3.0
16	220	86.5	10.6	47.8	96.2	3.8

Run No.	Percent by Weight Composition of Distillate				Styrene	
	Benzene	Ethylbenzene	Styrene	Benzaldehyde	% by wt. in Aromatics	% of Theoretical Yield
49	--	4.1	4.7	91.2	4.6	4.7
48	--	11.4	18.1	70.5	17.6	17.9
16	1.7	16.6	39.8	41.9	38.3	39.1

Effect of Nitric Oxide

Isoamyl nitrite was added with the acetic anhydride-benzaldehyde mixture into the reactor so as to yield 1 per cent by weight of nitric oxide assuming complete decomposition. This concentration was chosen because it had been used by Stinton (139) to depress most effectively the vapor-phase dehydration of butanone over Morden bentonite.

The aromatic products were analyzed by fractional distillation under reduced pressure and in an atmosphere of nitrogen. No benzene could be isolated, and the high-boiling fraction exceeded 10 per cent (Table XXV). Conversion of the aldehyde, however, was nearly the same as that obtained with similar runs carried out in the absence of nitric oxide (Table X). For this reason no further pyrolyses aimed at detecting the presence of free radicals in the system were performed.

TABLE XXV

Effect of Nitric Oxide on the Pyrolysis of a Benzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

Benzaldehyde	49.1 % by wt.
Acetic Anhydride	47.0
Isoamylnitrite	3.9

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.0 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Weight of Liquid Products	85.6 g.
Total Gas Evolved	10.9 l.
Weight of Aromatics	45.1 g.

Composition of Aromatics

Ethylbenzene	17.7 % by wt.
Styrene	30.2
Benzaldehyde	41.2
High Boiling Material	10.9

Pyrolysis of Acetic Anhydride over Morden Bentonite

Since acetic anhydride was one of the reactants used in this investigation its pyrolysis was also studied. The anhydride, purified as previously described, was passed over activated Morden bentonite at various temperatures and found to be effectively decomposed by the catalyst (Table XXVI). The products were fractionated at atmospheric pressure and found to consist of acetic acid, acetone, water and unchanged acetic anhydride. The actual percentage of water in the products was determined by subtracting from the total weight of distillate collected from 98 to 120°C. the weight of acetic acid as found by titrating aliquots with standard alkali.

At the lowest temperature employed, namely 200°C., 84.6 per cent of the anhydride could be recovered unchanged, while at 400°C., 97.1 per cent had reacted. At the latter temperature the yield of acetic acid was maximal (Figure 7), and it is interesting to note that this temperature was also found to give optimum styrene yields when pyrolyzing acetic anhydride-benzaldehyde mixtures. Since benzaldehyde itself was only slightly attacked by the catalyst at 400°C. - see Table XV - and since experimental evidence had shown that benzaldehyde and acetic anhydride did not react in the absence of the catalyst, it seems reasonable to believe that interaction between the anhydride and the aldehyde during pyrolysis over Morden bentonite is initiated by change in the more reactive anhydride at the catalytic surface.

TABLE XXVI

Pyrolysis of Acetic Anhydride over Morden Bentonite

Volume Pyrolyzed: 100 cc.
Feed Rate: 1.0 cc./min.
Catalyst Volume: 220 cc.

Run No.	Temp. °C.	Liquid Products g.	Gas Evolved l.	Gas l./mole of Feed	Percent by Weight Composition of Pyrolyzate				
					Acetic Acid	Anhydride	Acetone	Water	High Boiling Material
56	200	104.7	0.4	0.4	12.6	84.6	0.5	--	2.3
53	300	92.8	5.7	5.4	61.9	24.4	9.7	1.9	2.1
51	400	75.1	17.3	16.3	72.2	2.9	14.3	8.7	1.9
52	450	64.3	27.8	26.2	63.3	--	19.6	14.9	2.2
54	500	32.4	52.7	49.7	33.1	--	21.3	43.5	2.1
55	600	17.6	70.5	66.5	0.7	--	10.1	86.5	2.7

Composition of Gaseous Products - Percent by Volume

Run No.	Temp. °C.	Carbon Dioxide	Alkenes	Carbon Monoxide	Hydrogen	Alkanes
53	300	25.9	25.4	32.8	9.8	6.1
51	400	29.1	17.3	26.2	22.7	4.7
54	500	24.0	12.8	24.4	32.3	6.5

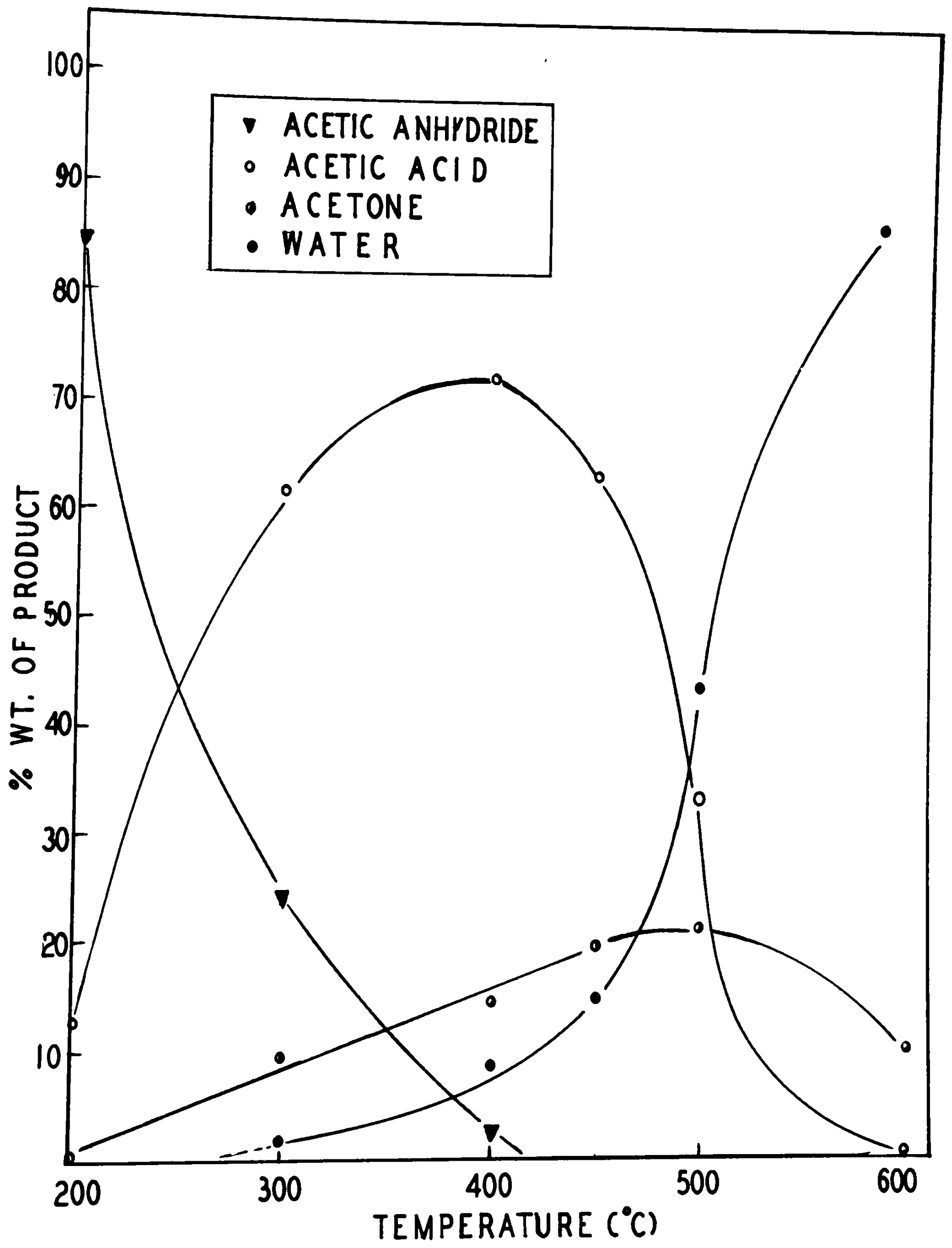
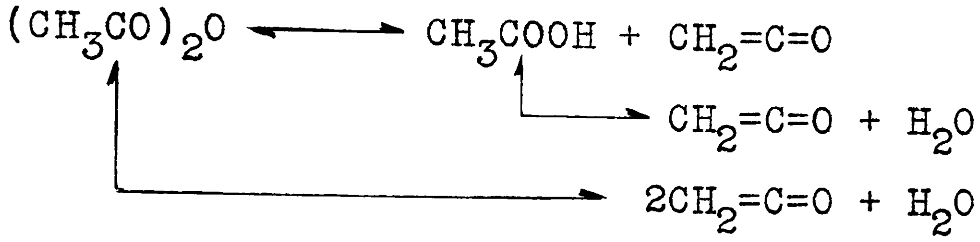


Figure 7

Pyrolysis of Acetic Anhydride
Temperature vs. Yield

In addition to illustrating the maximum in the acetic acid formed, Figure 7 shows that the percentage of water in the products increases steadily with temperature. Formation of water may result from dehydration of the anhydride as well as from its primary reaction product, acetic acid, according to the equations



$$(CH_3CO)_2O \longleftrightarrow CH_3COOH + CH_2{=}C{=}O$$

$$CH_3COOH \longrightarrow CH_2{=}C{=}O + H_2O$$

$$(CH_3CO)_2O \longrightarrow 2CH_2{=}C{=}O + H_2O$$

Dehydration of acetic anhydride as well as of acetic acid often serves to generate ketene. High temperatures, 800-1000°C., are required for thermal decomposition to take place (126). Morden bentonite, which is known to be an efficient dehydration catalyst, apparently brings about this reaction at a much lower temperature.

Figure 7 further shows that the percentage of water formed increased only slowly with increases in the pyrolysis temperature up to 450°C. A much more abrupt increase then set in which remained obvious to 600°C. The reason for this behaviour is to be seen in the interaction of water with unchanged acetic anhydride during passage through the reactor. This interaction will continuously decrease in magnitude as the temperature is raised and more and more of the anhydride is decomposed. Hence, the peculiar shape of the graph illustrating the amount of water contained in the products at any temperature between 300 and 600°C.

One must realize, however, that the catalyst itself which was always activated by passing a stream of moist air through the reactor may also supply some of the water needed for this reaction. It is known that water adsorbed by aluminum-silicate catalysts during activation may subsequently react during pyrolysis (179) and this effect is particularly pronounced at low temperatures (236).

Still another possibility of water removal from the products, particularly at lower temperatures, lies in a potential interaction with ketene. Unfortunately, in none of the runs carried out, could any ketene be detected. A dry-ice acetone trap failed to remove any condensate and no acetanilide could be isolated when passing the product gases through a cooled aniline trap. Hence, ketene may be considered an intermediate reaction product which is further decomposed, possibly to ethylene and carbon monoxide. The high percentage of these two gases, identified by a general gas analysis (Table XXVI), and the isolation of ethylene dibromide when passing the gases into a bromine solution, strongly suggest that this type of decomposition does take place.

The fact that no ketene could be identified in the reaction products does however not eliminate the possibility of acetic acid formation by reaction of the unsaturated gas with water. At lower temperatures in particular, some ketene may react non-catalytically with the water present in the system in preference to being decomposed by the catalyst.

At 450°C. severe cracking of the anhydride and its main reaction product, acetic acid, begins, the gas evolution increases greatly and the water content of the products rises rapidly. Apparently, the intermediate ketene is now decomposed further to carbon monoxide and hydrogen (Table XXVI) as well as carbon. It is to be noted, however, that carbon monoxide may also arise from the interaction of the water formed during pyrolysis and the carbon deposited on the catalyst:

$$H_2O + C \longrightarrow CO + H_2$$

Occurrence of this water-gas reaction was observed by Gleason during pyrolysis of cyclohexanol over Morden bentonite (153). The carbon monoxide, in turn, may react with some of the water present in the system and generate carbon dioxide and hydrogen:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

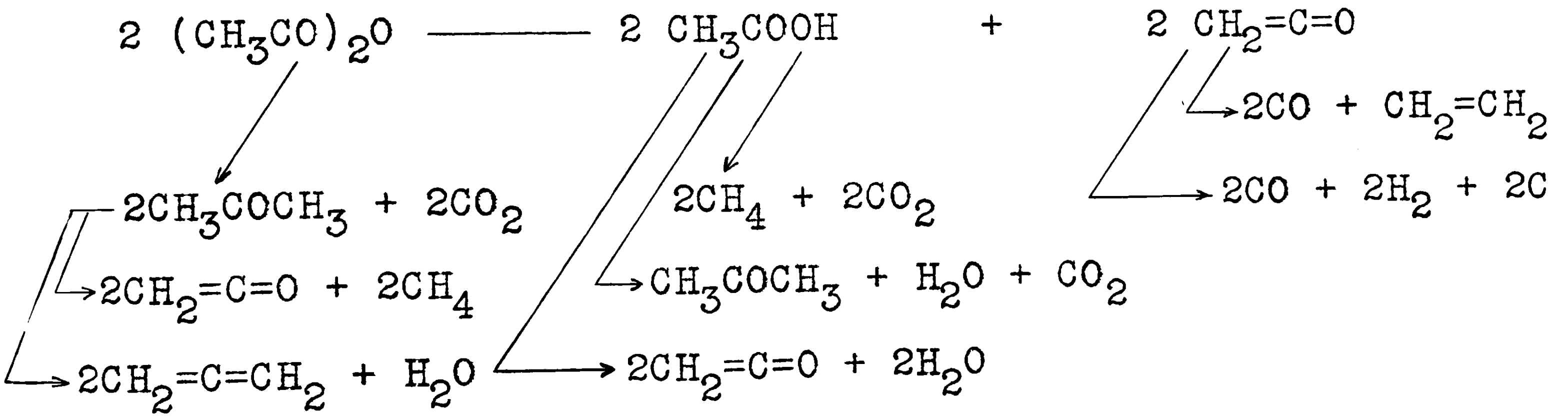
or it may be partly converted to carbon dioxide:

$$2\ CO \longrightarrow CO_2 + C$$

as postulated by Wasson (152). It is evident that the complexity of the pyrolysis increases greatly with temperature because of the interaction of the various reaction intermediates.

A trace of acetone could be detected in the products obtained at 200°C., and ketone yields gradually increased up to a temperature of 500°C. Acetone may be formed by either direct decarboxylation of the anhydride or by decarboxylation-dehydration of its primary reaction product, acetic acid. At 600°C. the acetone formed is further decomposed - possibly to allene and water or to ketene and methane, as found by Wasson (152).

The experimental data suggest that the following reactions may occur during pyrolysis of acetic anhydride over Morden bentonite.



Pyrolysis of Acetic Acid-Benzaldehyde Mixtures over Morden Bentonite

Since acetic acid was found to be the main product of the pyrolysis of acetic anhydride over Morden bentonite, the possibility of styrene formation from acetic acid-benzaldehyde mixtures was investigated.

The acetic acid used was reagent-grade material purchased from Shawinigan Chemicals Ltd. Its physical constants were:

B.P. (corr.) 118.0°C., n_D^{20} 1.3719, d_4^{20} 1.049

A trial run showed that the same compounds as those obtained by pyrolysis of acetic anhydride-benzaldehyde mixtures were formed, and in order to obtain a close comparison with these experiments the standard volume of both catalyst and charging stock was used, the same feed rate (0.02 mole per min.) was employed and the same analytical procedure followed.

The optimum temperature for styrene formation was found to be 400°C. i.e. the same temperature at which highest yields of styrene were obtained when pyrolyzing acetic anhydride-benzaldehyde mixtures.

When carrying out the catalytic reaction at 300°C. the aromatics isolated from the pyrolyzate contained only 3.8 per cent of styrene (Table XXVII). Evidently, insufficient gas was evolved at that temperature to prevent excessive polymerization of the monomer during its passage through the catalyst bed.

TABLE XXVII

Pyrolysis of Equimolar Acetic Acid-Benzaldehyde Mixture over Morden Bentonite

Composition of Feed:
Acetic Acid 36.1 % by wt.
Benzaldehyde 63.9
Volume Pyrolyzed: 100 cc.
Feed Rate: 1.6 cc./min.
Catalyst Volume: 220 cc.

Run No.	Temp. °C.	Liquid Products g.	Aromatics g.	Gas Evolved l.	Gas l./mole of Feed	Distillate % by wt.	High Boiling Material % by wt.	Styrene % by wt. in Distillate	Styrene % by wt. in Aromatics
59	300	86.6	56.6	1.2	1.0	97.8	2.2	3.9	3.8
56	400	88.2	58.7	8.0	6.1	96.2	3.8	21.1	20.3
58	500	69.3	54.5	18.3	14.5	95.7	4.3	24.7	23.6

TABLE XXVIII

Effect of Ratio of Reactants on Pyrolysis of Acetic Acid-Benzaldehyde Mixtures over Morden Bentonite

Volume Pyrolyzed: 100 cc.
Feed Rate: 0.01 mole Aldehyde per min.
Catalyst Volume: 220 cc.
Nitrogen: 5 l./hr.
Temperature: 400°C.

Run No.	Mole Ratio Acetic Acid / Benzaldehyde	Composition of Feed % by wt.		Feed Rate cc./min.	Liquid Products g.	Aromatics g.
		Acetic Acid	Benzaldehyde			
56	1	36.1	63.9	1.6	88.2	58.7
62	2	53.1	46.9	2.2	93.0	44.2
61	3	62.9	37.1	2.7	94.8	35.2
60	4	69.4	30.6	3.3	96.2	29.1

TABLE XXIX

Analysis of Aromatic Products from Pyrolysis of Acetic Acid-Benzaldehyde Mixtures at 400°C.

Run No.	Distillate % by wt.	High Boiling Material % by wt.	Percent by Weight Composition of Distillate				Styrene	
			Benzene	Ethylbenzene	Styrene	Benzaldehyde	% by wt. in Aromatics	% of Theoretical Yield
56	96.2	3.8	1.7	7.9	21.1	69.3	20.3	20.7
62	96.9	3.1	--	5.4	29.7	64.9	28.8	29.3
61	96.5	3.5	--	4.5	34.3	61.2	33.1	33.7
60	96.8	3.2	--	4.6	36.7	58.7	35.5	36.2

At 400°C. a more favorable material balance was obtained and 20.3 per cent of the aromatics consisted of styrene (Run 56). Similar phenomena were observed during pyrolyses of acetic anhydride-benzaldehyde mixtures (Tables XI and XII).

In an effort to improve the monomer yield several runs were carried out by increasing progressively the acetic acid concentration in the feed but keeping the rate of throughput of the aldehyde constant (Table XXVIII). This increase was accompanied by an increase in styrene concentration in the aromatic products (Table XXIX). Thus, when using an acetic acid-benzaldehyde mixture of molar ratio 3:1 the aromatics contained 33.1 per cent of styrene, or 12.8 per cent over that obtained when pyrolyzing an equimolar mixture.

This value compares favorably with that (16.5 per cent) obtained when pyrolyzing acetic anhydride-benzaldehyde mixtures of comparable composition under similar conditions (Tables XVIII and XIX). But, on the other hand, even for a molar ratio of acetic acid to benzaldehyde equal to 4:1 the per cent yield of styrene per single pass accounted for 2.8 per cent less of the aromatics than that obtained under similar conditions with an equimolar acetic anhydride-benzaldehyde mixture (Table XII; Run 16).

Again a limiting value for the styrene yield appears to be approached because the pyrolytic conditions chosen called for faster feed rates with increased acetic acid concentration.

Reducing the rate of throughput but keeping all other variables constant would probably not favor conversion of the aldehyde to styrene but, judging by the results of previous experiments, favor its conversion to ethylbenzene instead.

Pyrolysis of Acetic Acid over Morden Bentonite

Since styrene could be obtained by passing acetic acid-benzaldehyde mixtures over Morden bentonite, the pyrolysis of acetic acid itself was studied in order to throw additional light on the mechanism involved. Wasson (152) had found that decomposition to methane and carbon dioxide was the main reaction taking place in this pyrolysis and that acetone, water and acetic anhydride made up the liquid products. No quantitative determination of the products, however, was made, nor was the reaction investigated systematically over a wide enough temperature range. Of particular interest in the present study was the quantitative determination of acetic anhydride and its relation to styrene yields from acetic acid-benzaldehyde mixtures.

The liquid reaction products were fractionally distilled and the various fractions determined as in the case of the acetic anhydride pyrolyzates. The experimental data given in Table XXX illustrate both strong similarities to, as well as marked differences from, the results for the vapor-phase reaction of acetic anhydride over Morden bentonite.

TABLE XXX

Pyrolysis of Acetic Acid over Morden Bentonite

Volume Pyrolyzed: 100 cc.
Feed Rate: 1.0 cc./min.
Catalyst Volume: 220 cc.

Run No.	Temp. °C.	Liquid Products g.	Gas Evolved l.	Gas l./mole of Feed	Percent by Weight Composition of Pyrolyzate				
					Acetic Acid	Anhydride	Acetone	Water	High Boiling Material
64	300	101.3	0.5	0.3	97.2	--	1.6	--	1.2
63	400	93.8	7.0	4.0	79.9	1.9	6.2	9.8	2.2
65	450	73.4	18.8	10.8	65.0	--	10.1	23.4	1.5
66	500	38.8	45.2	25.9	25.3	--	11.4	61.5	1.8
67	600	29.7	51.6	29.6	0.8	--	8.2	88.4	2.6

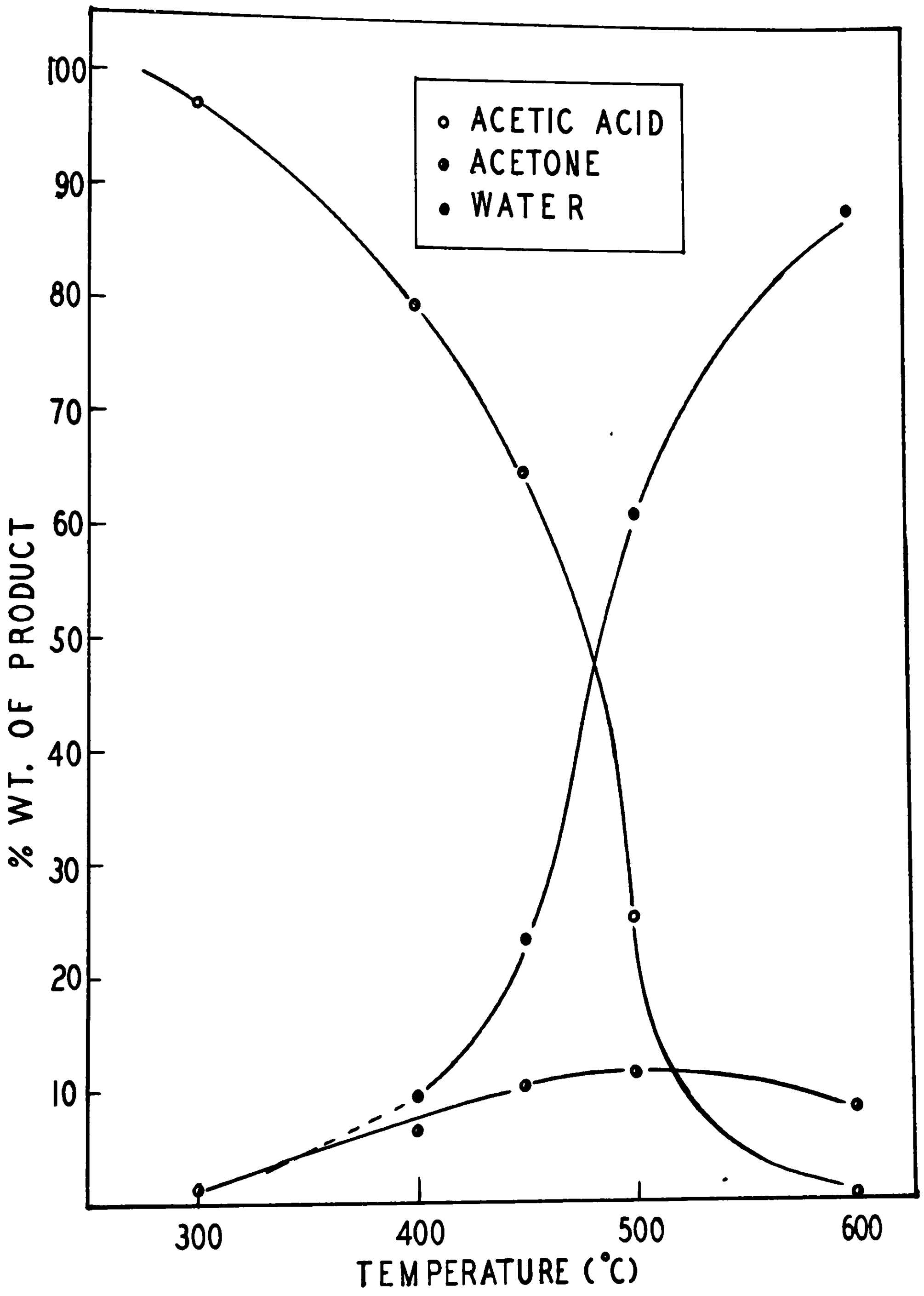


Figure 8

Pyrolysis of Acetic Acid
Temperature vs. Yield

Comparison of the two pyrolyses (Figures 7 and 8) shows that the formation of water and of acetone may be represented by graphs of similar characteristics. But whereas the percentage of water in the products from the pyrolysis of acetic acid is greater than that from the anhydride, the reverse is the case for acetone. This trend suggests that acetic acid is more effectively dehydrated than acetic anhydride, and that the formation of water is the reaction of greatest magnitude when acetic acid is pyrolyzed over Morden bentonite at temperatures exceeding 400°C.; a finding which is in disagreement with Wasson's result that decomposition of the acid to carbon dioxide and methane constitutes the chief reaction. Wasson distilled the liquid products and considered the first fraction of distillate as consisting of acetone and water, and the second fraction as consisting of acetic acid. No temperature ranges for the distillation are given and it would appear that his second fraction was still rich in water.

The formation of acetone from acetic acid may take place in accordance with the equations

$$\begin{tikzcd}
2\,CH_3COOH \arrow[r] \arrow[dd] & (CH_3CO)_2O + H_2O \arrow[d] \\
 & CH_3COCH_3 + CO_2 \\
CH_3COCH_3 + CO_2 + H_2O &
\end{tikzcd}$$

In either case condensation of two acetic acid molecules has to precede acetone formation and ketone yields must of necessity be smaller than those obtained when passing acetic anhydride directly over the catalyst.

Another important difference between the pyrolysis of acetic anhydride and acetic acid over Morden bentonite is the relative rate of disappearance of the reactant from the products. Thus the pyrolysis of acetic anhydride at 400°C. causes 97.1 per cent conversion whereas pyrolysis of acetic acid at this temperature leads to only 20.1 per cent conversion. Considering that Morden bentonite is an efficient dehydration catalyst (see Table VIII) the observed experimental results may be adequately explained. The rapid fall of acetic anhydride concentration in the products has been discussed already and was interpreted as resulting from a thermal hydrolysis of reactant molecules by the water formed during reaction. Hence, the acetic acid concentration increases, reaching a maximum value at 400°C. When pyrolyzing acetic acid the dehydrating action of the catalyst leading to the formation of acetic anhydride and water according to the equation

$$2\ CH_3COOH \longrightarrow (CH_3CO)_2O + H_2O$$

will also be reduced in magnitude as a result of the interaction of the products during their passage through the reactor. This interaction, which may even proceed non-catalytically, will lead to the re-formation of acetic acid, and hence the concentration of the acetic acid in the products must fall off slowly, as was found to be the case. In contrast to Wasson's results no acetic anhydride could be isolated at temperatures 100°C. below or above 400°C.

The general trends of the two vapor-phase reactions may therefore be summarized as follows. When passing acetic anhydride over Morden bentonite at temperatures up to 400°C. hydrolysis caused by the water formed during pyrolysis converts unchanged reactant to acetic acid and so decreases the concentration of reactant molecules in the system. When pyrolyzing acetic acid under similar conditions interaction of anhydride and water formed during pyrolysis, regenerates acetic acid and so increases the concentration of reactant molecules in the system. Furthermore, this increase in acetic acid concentration in the system may be enhanced in each case by the interaction of two of the reaction products - ketene and water.

$$\begin{tikzcd}
 & 2\ CH_3COOH \arrow[r, leftrightarrow] & (CH_3CO)_2O + H_2O \arrow[dr, leftrightarrow] & \\
2CH_2{=}C{=}O + 2H_2O \arrow[ur, leftrightarrow] & & & CH_3COOH + CH_2{=}C{=}O
\end{tikzcd}$$

Considerable experimental evidence for such interaction was found when benzaldehyde and ketene were pyrolyzed over Morden bentonite.

At temperatures higher than 400°C. the per cent decrease of acetic acid in the products obtained on pyrolysis both of acetic acid and of the anhydride may be represented by graphs resembling each other very closely. In each case the acetic acid, either as reactant or as primary reaction product, is progressively decomposed to give water, which may be collected and the intermediate ketene which is broken down further.

More direct evidence for these conclusions could be secured if one were to pyrolyze acetic acid in the presence of a substance which is unaffected by the catalyst but would react with the acetic anhydride formed during pyrolysis. One such substance is benzaldehyde and styrene formation during pyrolysis of acetic acid-benzaldehyde mixtures may be visualized as the interaction of the aldehyde with the anhydride formed by dehydration of the acid. It is interesting to note that styrene formation occurred when pyrolyzing an equimolar acetic acid-benzaldehyde mixture at 300°C. (Table XXVII), and the yield obtained could, theoretically, be increased by the amount of styrene-polymer remaining in the catalyst bed. Acetic acid itself is practically unchanged when passed over the catalyst at this temperature (Table XXX). Hence, the experimental results obtained when pyrolyzing it together with benzaldehyde would indicate that even at 300°C. the acid actually is partly converted to the anhydride but the anhydride quickly re-forms acetic acid by reaction with the water of dehydration. Many dehydration as well as condensation reactions studied by previous workers were most efficiently carried out at temperatures ranging from 250-350°C. (152, 154, 155).

Only at 400°C. could a small amount of acetic anhydride be isolated from the reaction products. At higher temperatures the acetic acid itself and any anhydride which may still be formed from it are effectively attacked and dehydrated to ketene and water, while passing through the catalyst bed.

Distinct evidence for this reaction trend was the formation of two product layers during pyrolysis of acetic acid or acetic anhydride-benzaldehyde mixtures carried out at more elevated temperatures. Formation of two product layers could even be observed at 400°C. during the initial stages of pyrolysis when the catalyst displayed highest activity. Further experimental evidence against direct condensation of acetic acid and benzaldehyde to form an intermediate addition compound will be given later.

Pyrolysis of Cinnamic Acid over Morden Bentonite

Since acetic anhydride and benzaldehyde are the reactants used in the Perkin synthesis of cinnamic acid, and since cinnamic acid by decarboxylation in the liquid phase (10, 32, 33) as well as in the vapor phase by non-catalytic thermal pyrolysis (237) forms styrene, the question of whether or not cinnamic acid was an intermediate reaction product of the pyrolysis of acetic anhydride-benzaldehyde mixtures had to be investigated. For this purpose a product aliquot from runs carried out at 200 and 300°C. was made alkaline with sodium carbonate and steam distilled to free it of volatile aromatics. The residual solution, when filtered hot by suction and acidified with hydrochloric acid, did in neither case show the slightest precipitate of cinnamic acid.

Some theoretical considerations based upon experimental data would also make cinnamic acid a doubtful intermediate in the pyrolysis of acetic anhydride-benzaldehyde mixtures over Morden bentonite. It is known that the Perkin synthesis can only be carried out in the presence of a basic catalyst (238) and after much controversy regarding the reaction mechanism it is now generally believed that the basic catalyst enolizes the anhydride. The enolate anion then condenses with the aldehyde to form an anion in which the negative charge is located on the oxygen atom. This anion takes up a proton from the medium forming the intermediate "aldol", which loses water to give cinnamic-acetic anhydride, and the mixed anhydride, by subsequent treatment, is converted to the unsaturated acid (239, 240). Morden bentonite, however, is not a basic catalyst and experiments to be described later show that the efficiency with which the vapor-phase pyrolysis of acetic anhydride-benzaldehyde mixtures can be carried out decreases when the catalyst is impregnated with basic reagents. Furthermore, the Perkin reaction does not proceed when acetic acid-benzaldehyde mixtures are used as reactants, whereas the vapor-phase pyrolysis of such a mixture over Morden bentonite does yield styrene (Table XXVII).

However, since both these considerations and experimental results do not by themselves disprove the possibility of a transient existence of cinnamic acid as a precursor of styrene, the catalytic effect of Morden bentonite on cinnamic acid itself was investigated.

The experimental conditions were adjusted so as to favor the decarboxylation reaction if it were to take place. A 6.5 per cent solution of cinnamic acid (Eimer & Amend, Reagent Grade, M.P. 133°C.) in benzene was prepared and 100 cc. were passed over the catalyst at a temperature of 200°C. and a feed rate of 2.0 cc. (0.00088 moles of cinnamic acid) per minute. Only 0.09 l. of gas were evolved, yet from 89.2 g. of feed only 80.9 g. of liquid products were obtained. Evaporation of a sample of the pyrolyzate on the steam bath left no residue. All the acid had apparently stayed in the catalyst bed. This fact became evident when a slow stream of air was passed through the system in order to activate the catalyst, for during the process crystals of cinnamic acid were swept out of the reactor and collected in the small suction flask attached to its exit. It was also noticed that activation of the catalyst was not accompanied by any sharp temperature rise and in consequence only negligible carbonization had occurred during pyrolysis. In order to evaluate quantitatively the amount of cinnamic acid which could be recovered the experiment was repeated. Although a slow stream of nitrogen was used as carrier gas, the same observations were made - no cinnamic acid nor styrene could be detected in the products - but the application for one hour of gentle suction to the system caused 3.1 g. of pure cinnamic acid (M.P. 133°C.) to collect in a dry-ice acetone trap. More cinnamic acid could probably have been recovered if the catalyst had been removed from the reactor at completion of the run and subjected to extraction. However these results were thought to prove sufficiently that cinnamic acid is not an intermediate reaction product of the pyrolysis of acetic anhydride-benzaldehyde mixtures over Morden bentonite and no further low temperature experiments were carried out.

Minute amounts of crystalline material could also be collected in similar fashion during activation of the catalyst with a stream of air after the pyrolysis of acetic anhydride-benzaldehyde mixtures at 200°C. Purification of this material, however, showed that it was benzoic acid formed by oxydation of the aldehyde which had remained adsorbed on the catalyst.

Since decarboxylation of cinnamic acid is a feasible method of styrene preparation, the suitability of Morden bentonite for this type of reaction was investigated.

Melted cinnamic acid could not be pyrolyzed by itself at 300°C. because the reactor clogged after about 40 cc. had passed through it. In order to prevent this disturbing feature the reaction was carried out at a more elevated temperature (525°C.) and steam was used as diluent (Table XXXI). The experimental setup devised for feeding the melted acid into the reactor at a constant rate has been described earlier. The products were collected in a flask which was attached directly to the reactor exit and provided with a reflux

TABLE XXXI

Pyrolysis of Cinnamic Acid over Morden Bentonite

Volume of Cinnamic Acid Pyrolyzed: 100 cc.
Feed Rate of Cinnamic Acid: 1.5 cc./min.
Feed Rate of Water: 1.5 cc./min.
Volume of Catalyst: 220 cc.
Temperature of Reactor: 525°C.
Temperature of Cinnamic Acid Fed: 145°C.

Weight of Aromatic Products	62.3 g.
Gas Evolved	16.8 l.

Composition of Aromatic Products	
Benzene	7.5 % by wt.
Toluene	2.9
Ethylbenzene	44.6
Styrene	36.7
High Boiling Material	8.3

Composition of Gaseous Products	
Carbon Dioxide	51.9 % by vol.
Alkenes	--
Carbon Monoxide	27.5
Hydrogen	14.7
Alkanes	5.9

condenser in order to prevent blocking of the system by any unchanged cinnamic acid. After separation from the aqueous layer the aromatics were dried and fractionated under reduced pressure in an atmosphere of nitrogen. Treatment of an aliquot in accordance with the procedure recommended for the isolation of cinnamic acid from the products of the Perkin reaction showed that all of the acid had been converted. Some was broken down to benzene and a small amount of toluene could also be identified. Since ethylbenzene constituted the main reaction product, most of the styrene formed by decarboxylation of the acid was apparently hydrogenated. This reaction has been discussed earlier but appeared to be of particularly great magnitude in this instance. Evidently, some of the water used as diluent interacts with the carbon deposited on the catalyst during pyrolysis, and in accordance with the equation

$$H_2O + C \longrightarrow CO + H_2$$

forms carbon monoxide and hydrogen which may attack the monomer side chain. The large proportion of carbon monoxide in the gaseous products is further support for the water-gas reaction which was also observed by Gleason (153).

The formation of toluene may be caused by a free radical type of dealkylation of the ethylbenzene as found by Wasson (152)

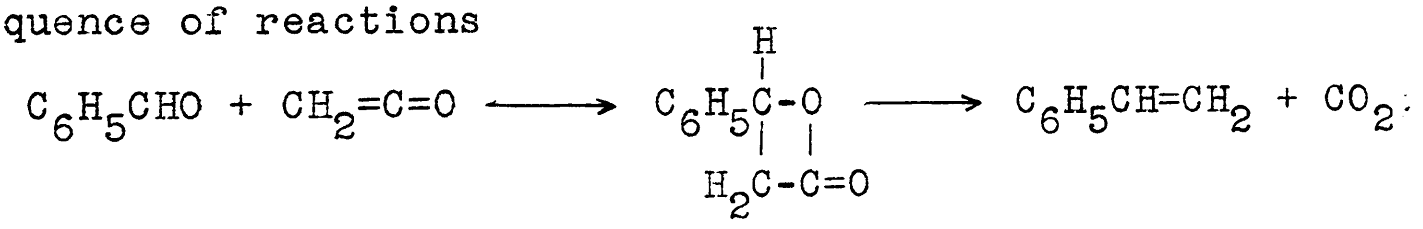
$$C_6H_5CH_2CH_3 \longrightarrow C_6H_5CH_2^{\bullet} + CH_3^{\bullet}$$

$$C_6H_5CH_2^{\bullet} + CH_3^{\bullet} + H_2 \longrightarrow C_6H_5CH_3 + CH_4$$

and the small amount of saturates in the gaseous products is further evidence that such over-all reaction may occur.

Pyrolysis of Acetone-Benzaldehyde Mixture over Morden Bentonite

Interpretation of the experimental results obtained when pyrolyzing acetic anhydride or acetic acid over Morden bentonite (Tables XXVI and XXX) made it imperative to assume the intermediate formation of ketene. Hence, styrene formation may also occur as a result of the interaction of ketene and the aldehyde, the intermediate lactone generated being subsequently decarboxylated in accordance with the following sequence of reactions



$$C_6H_5CHO + CH_2{=}C{=}O \longrightarrow \begin{array}{l} \quad\;\; H \\ \quad\;\; | \\ C_6H_5C{-}O \\ \quad\;\; | \quad | \\ \quad H_2C{-}C{=}O \end{array} \longrightarrow C_6H_5CH{=}CH_2 + CO_2;$$

In order to provide some experimental evidence for the assumption made, a mixture of acetone and benzaldehyde (mole ratio equal to 1.5) was passed through the reactor filled with copper wire spirals and quartz chips. These substances are known to be non-catalytic toward ketene (241) which is formed during pyrolysis in accordance with the equation

$$CH_3COCH_3 \longrightarrow CH_2{=}C{=}O + CH_4;$$

The reaction was carried out at 625°C. in order to prevent considerable breakdown of the aldehyde and at the same time obtain sufficient ketene to detect any styrene in the liquid products if it were to form according to the above equation. From 130 cc. of feed (per cent by weight composition: acetone 45.1, aldehyde 54.9) passed through the reactor at a rate of 1.0 cc. per min., 95.6 g. of liquid products were obtained. After being dried over calcium chloride, 40.0 g. on careful distillation at atmospheric pressure gave 15.7 g. acetone, 3.9 g. benzene, 14.1 g. benzaldehyde and 6.3 g. high boiling material. A 53.0 g. sample was fractionally distilled under reduced pressure and two fractions collected. One, totalling 28.3 g., consisted of acetone and benzene and the other, totalling 20.5 g., consisted of unchanged benzaldehyde. Distillation was discontinued when a faintly yellow solid crystallized at the condenser. After extraction of the column with ether and removal of the solvent, 1.8 g. was obtained which could be recrystallized from alcohol. A melting point of 60.1°C. suggested that the solid was benzoylacetone.

Using the values for acetone and benzene obtained by atmospheric pressure distillation, and those for benzaldehyde and benzoylacetone obtained by vacuum distillation, the overall per cent composition of the total liquid products may be given as follows:

Acetone	39.3
Benzene	9.8
Benzaldehyde	38.7
Benzoylacetone	3.4
High Boiling Material	8.8

The gaseous products, 20.8 l., leaving the flask in which the liquid products collected, passed through an aniline trap cooled in ice and 7.2 g. of acetanilide could be isolated according to the procedure outlined in Organic Syntheses, Vol.I, p.332. Hence, about 2 g. of ketene which were generated had passed through the system unreacted with the aldehyde.

The absence of styrene in the liquid products and the presence of ketene in the gaseous products was therefore a clear demonstration of the non-reactivity of ketene toward benzaldehyde. The experimental results are in line with Staudinger's observation that ketene fails to add to quinone and produce a β-lactone (242). Condensation of ketene and benzaldehyde has already been attempted as a liquid-phase process and various catalysts have been used as condensing agents. Hurd used potassium acetate as a catalyst and reported isolation of the β-lactone decarboxylation product, styrene, from this reaction (243). However, judging by the wording of his paper the yield obtained must have been exceedingly small. The styrene he isolated was contaminated with benzaldehyde and a derivative had to be prepared to insure its identification. Yet the melting point reported for the dibromide (61°C.) is 13°C. below that given in the literature (74-75°C.). It is puzzling also that he collected the unchanged benzaldehyde before taking off the styrene fraction.

Other experimental facts appear to indicate that intermediate lactone formation probably does not occur to any appreciable extent. Benzaldehyde itself is not attacked when passed over Morden bentonite at 200°C. Similarly, when acetic anhydride is pyrolyzed over Morden bentonite at this temperature only 0.4 l. of gas is evolved per mole of reactant, and no ketene can be identified in the gaseous products (Table XXVI). But when pyrolyzed together as an equimolar mixture (Table XI) 3.6 l. of gas are evolved per mole of feed or 7.2 l. per mole of acetic anhydride used. Again, no ketene can be identified as one of the gaseous products, and it is reasonable to assume a more direct condensation between the anhydride and the aldehyde.

Pyrolysis of Benzaldehyde and Ketene over Morden Bentonite

Although the non-reactivity of ketene toward benzaldehyde during thermal pyrolysis was demonstrated by the previous experiment, this non-reactivity need not necessarily exist when the reaction is carried out as a catalytic vapor-phase process. Accordingly, ketene and benzaldehyde were pyrolyzed together over Morden bentonite. The gas was generated by pyrolysis of acetone using a ketene lamp* and was passed through two water-cooled condensers and a trap kept at -20°C. in order to separate it from any acetone before entering the reactor.

---

*The lamp was obtained from the Physical Chemistry Laboratories through the courtesy of Prof. C.A. Winkler to whom grateful acknowledgement is expressed.

The actual amount of gas produced in unit time was determined prior to starting the main run by passing it for five minutes through 50 ml. of 2N potassium hydroxide solution and subsequently titrating the unused alkali. By this method of analysis the lamp was found to deliver 0.39 moles of ketene per hour.

The reaction was carried out at 400°C., the aldehyde was fed into the reactor at a rate of 1.0 cc. per minute, and a total volume of 70 cc. was pyrolyzed. The products (70.6 g.) showed an acid reaction toward litmus, and titration of an aliquot against standard alkali indicated the equivalent of 2.9 per cent of acetic acid in the pyrolyzate. Careful distillation at atmospheric pressure of a 20.0-g. sample permitted the isolation of 0.7 g. of material boiling from 56-60°C. and having a refractive index of 1.3590 at 20°C. Hence, unless it had persisted in the ketene stream, acetone was formed during pyrolysis. From 60-120°C., 0.9 g. of cloudy distillate was collected which had an acidic reaction toward litmus and the characteristic odor of acetic acid.

The remainder of the products was neutralized with sodium carbonate and extracted with ether. After removal of the solvent, washing with water and drying, fractional distillation showed that it had the following per cent by weight composition:

Styrene	2.7
Ethylbenzene	2.6
Benzaldehyde	83.4
High Boiling Material	11.3

Hence, styrene formation did occur, but since both acetone and acetic acid were also products of the reaction, acetic acid or acetic anhydride formation by interaction of the ketene with water present in the system, may possibly have preceded styrene formation. One potential source of water is the catalyst itself which was always activated with a stream of moist air. Strong experimental evidence for this assumption is the much higher percentage of acidity (8.7 per cent) shown by the products collected from 25 cc. of fore-run. The experiment did therefore not fulfill its real purpose. The desired information could possibly be obtained by using scrupulously dried reagents, pre-treating the catalyst for a long time with dried air and taking all possible precautions to exclude the ingress of moisture to the system.

The percentage of styrene formed, however, was relatively small and the strong decomposition of ketene over Morden bentonite was clearly seen by the evolution of 58 l. of gas in which no unchanged ketene could be detected. These observations strongly suggest that styrene formation by the pyrolysis of acetic anhydride- or acetic acid-benzaldehyde mixtures over Morden bentonite does not depend upon the formation of an intermediate lactone.

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixtures over Various Catalysts

Catalysts other than Morden bentonite were used for the pyrolysis of benzaldehyde-acetic anhydride mixtures not only in order to evaluate their efficiency, but also to obtain information regarding the mechanism of the reaction. The catalysts employed are given in Table XXXII.

In a number of cases these catalysts were heated before use for 5-6 hours at 500°C. while a slow stream of moist air was passed through the reactor. Such treatment has been reported to bring the efficiencies of freshly activated and regenerated catalyst to nearly the same level (155). A few experiments were also carried out in which Morden bentonite was used as a carrier. Impregnation was accomplished by covering regenerated catalyst with an aqueous solution of known concentration of either sodium hydroxide or sodium acetate. After standing for twenty-four hours the excess of solution was drained off and the water evaporated in order to compute the weight of reagent adsorbed by the catalyst.

Without exception the catalysts used gave the same type of compounds and hence the same procedure of analysis could always be followed. The investigation further showed that catalysts of nearly the same chemical composition differed greatly in their activity and catalysts of nearly the same catalytic activity differed greatly in chemical composition.

TABLE XXXII

Catalysts Used for Vapor-Phase Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixtures

Catalyst	Mesh Size	Source
Morden Bentonite, commercial product	200	Courtesy, Pembina Mountain Clays Limited
Morden Bentonite, freshly activated	4-8	Prepared by acid treatment of commercial product
Morden Bentonite, air-treated	4-8	Prepared by air treatment of freshly activated catalyst
Morden Bentonite, regenerated	4-8	Prepared by re-activation of used catalyst
Raw White Clay*	4-8	Courtesy, Pembina Mountain Clays Limited
Raw White Clay, regenerated	4-8	Prepared by re-activation of used clay
Synthetic Silica Alumina	3/16"	Courtesy, Davison Chemical Corporation
Silica Gel	3-8	Courtesy, Davison Chemical Corporation
Activated Alumina F-1	1/4"-8	Courtesy, Aluminum Ore Company
Activated Alumina F-10	1/4"-8	Courtesy, Aluminum Ore Company

*This unprocessed clay was received from the supplier in the form of large lumps which were broken up mechanically into pellets of 4-8 mesh.

The condition of the various catalysts prior to use for pyrolytic studies is shown in Table XXXIII and the composition of the products given in Table XXXIV.

As found by previous workers (155, 156, 157), freshly activated Morden bentonite was more efficient than the regenerated catalyst (Runs 1a and 16). The gas evolution was noted to be higher and product recovery was therefore less favorable. The difference with regard to catalytic behavior became still more marked when comparing the per cent by weight composition of the products. Superior performance of the freshly activated catalyst led to higher conversion of the aldehyde, yet the yield of styrene obtained was low because a large portion of it was hydrogenated to ethylbenzene.

When a 10 per cent aqueous solution of sodium hydroxide instead of sulfuric acid was used for activation the catalyst lost much of its efficiency (Runs 2a and 3a). Less gas was evolved and the aromatic products contained a large percentage of unchanged benzaldehyde. It was found, however, that the freshly activated catalyst was not as efficient as the reactivated one. Conversion was 5.4 per cent less and styrene formation reduced by 3.4 per cent. This behavior will be explained when experiments with impregnated catalysts are to be described.

Raw white clay was found to exhibit catalytic activity. Again, conversion efficiency of the crude material was higher and the styrene yield lower than that obtained when using reactivated clay (Runs 4a and 5a).

Synthetic silica-alumina was the most active of all catalysts tried. This catalyst is widely used in the petroleum industry for the production of high octane gasoline and its efficiency as a cracking catalyst may be evaluated from the composition of the products. Both the fresh as well as the reactivated compound yielded benzene, toluene and a large percentage of ethylbenzene (Runs 10a and 11a). It would appear, therefore, that this catalyst is not desirable for the preparation of styrene by pyrolysis of acetic anhydride-benzaldehyde mixtures but it would be valuable for the preparation of ethylbenzene and possibly substituted alkylbenzenes by this process.

Air-treated and regenerated silica gel showed very similar catalytic performance (Runs 6a and 7a). The regenerated material was found to be slightly less effective and this may have been due to a decrease in surface area and pore volume occurring during activation of the catalyst at 600-630°C. (244).

Activated Alumina F-1 was found to be slightly less effective than the silica gel, yet showed similar product distribution (Runs 8a and 9a).

Activated Alumina F-10 was found to be the most suitable catalyst for the styrene reaction (Runs 12 and 13a). The yield was 13.5 per cent higher than that obtained with reactivated Morden bentonite (Run 16) which was the second best catalyst used. No toluene and only a small amount of benzene was formed. Hence, cracking did not occur to a large extent. The 51.8 per cent yield of monomeric styrene represents 68.8 per cent of the theoretical yield obtainable at a conversion of 68.0 per cent.

TABLE XXXIII

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixtures over Various Catalysts

Composition of Feed:
Benzaldehyde 51.0 % by wt.
Acetic Anhydride 49.0
Volume Pyrolyzed: 100 cc.
Feed Rate: 2.0 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Run No.	Catalyst	Liquid Products g.	Gas Evolved l.	Aromatics g.
1a	Morden Bentonite, freshly activated, not air-treated	80.2	11.9	44.6
16	Morden Bentonite, regenerated	86.5	10.6	47.8
2a	Morden Bentonite, activated with 10% NaOH, not air-treated	90.5	9.2	46.8
3a	Morden Bentonite, from Run 2a, regenerated	90.1	9.1	47.2
4a	Raw White Clay, not air-treated	84.3	10.4	46.0
5a	Raw White Clay, from Run 4a, regenerated	85.7	10.1	47.1
10a	Synthetic Silica Alumina, fresh; air-treated	69.6	15.5	38.3
11a	Synthetic Silica Alumina, regenerated	75.5	14.7	40.1
6a	Silica Gel, fresh; air-treated	88.2	8.8	47.3
7a	Silica Gel, regenerated	90.2	8.4	48.5
8a	Activated Alumina F-1, fresh; air-treated	85.7	11.3	46.0
9a	Activated Alumina F-1, regenerated	88.8	10.6	46.3
12a	Activated Alumina F-10, fresh; air-treated	83.4	12.9	46.8
13a	Activated Alumina F-10, regenerated	85.0	12.6	48.0

TABLE XXXIV

Percent by Weight Composition of Aromatic Products from Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixtures over Various Catalysts

Run No.	Benzene	Toluene	Ethylbenzene	Styrene	Benzaldehyde	High Boiling Material
1a	4.3	1.9	28.1	29.8	30.8	5.1
16	1.6	--	16.0	38.3	40.3	3.8
2a	--	--	3.3	18.7	74.0	4.0
3a	--	--	4.6	22.1	68.6	4.7
4a	2.2	--	17.3	20.9	54.5	5.1
5a	--	--	9.0	27.1	59.8	4.1
10a	12.1	6.3	40.5	18.9	17.1	5.1
11a	9.2	5.1	38.0	22.5	20.5	4.7
6a	--	--	8.1	25.7	62.3	3.9
7a	--	--	5.6	23.5	67.6	3.3
8a	2.1	--	7.9	20.7	65.5	3.8
9a	--	--	7.3	19.7	69.1	3.9
12a	2.5	--	13.2	48.4	30.1	5.8
13a	1.2	--	10.1	51.8	32.0	4.9

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Synthetic Silica-Alumina

The results when using synthetic silica-alumina as catalyst for the pyrolysis of benzaldehyde-acetic anhydride mixtures (Tables XXXIII and XXXIV) showed that only low yields of styrene could be realized in spite of high conversions of the aldehyde. In an attempt to direct the activity of this catalyst toward styrene formation an experiment was carried out in which a larger volume (200 cc.) of feed was employed and the products corresponding to each 100 ml. of feed were collected and analyzed separately. It was found (Table XXXV) that the second 100 cc. fraction gave a much more satisfactory recovery than the first and that the aromatic portion contained a larger percentage of styrene, less benzene and no toluene. It also contained a larger percentage of benzaldehyde, which indicated the gradual deactivation of the catalyst with time.

These results show the existence of marked differences with regard to the catalytic behavior of synthetic silica-alumina and activated Morden bentonite. Whereas the effectiveness of the activated natural aluminum silicate for styrene formation was found to decrease with time (Table XXIII and Figure 6) the effectiveness of the synthetic catalyst for styrene formation was found to increase. Synthetic silica-alumina, an efficient cracking catalyst, apparently breaks down the reactants and reaction intermediates to a greater extent than Morden bentonite and hence ethylbenzene formation by hydrogenation of styrene molecules constitutes the chief reaction as long as the catalyst retains its activity at a high level. Carbonization accompanying pyrolysis gradually reduces the activity of the catalyst and as a result the hydrogenation reaction decreases also, but because it decreases at a faster rate than the reaction leading to the formation of styrene, the yield of the latter compound increases. It is evident however that there will be a maximum value because conversion of the aldehyde also is seen to fall off with time.

TABLE XXXV

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Synthetic Silica-Alumina

Composition of Feed:
  Benzaldehyde 51.0 % by wt.
  Acetic Anhydride 49.0
Volume Pyrolyzed: 200 cc.
Feed Rate: 2.0 cc./min.
Catalyst Volume: 220 cc.
Nitrogen: 10 l./hr.
Temperature: 400°C.

Run No.	Feed Volume cc.	Liquid Products g.	Aromatics g.	Total Gas l.
15a	100 (0-100)	78.7	42.0	21.2
b	100 (100-200)	87.3	47.8	16.9

Run No.	Percent by Weight Composition of Aromatics					
	Benzene	Toluene	Ethylbenzene	Styrene	Benzaldehyde	High Boiling Material
15a	7.1	2.2	36.5	27.1	22.5	4.6
b	3.4	--	8.8	45.4	37.9	4.5

Relation between Catalyst Acidity and Catalyst Activity

As indicated in the historical part of this thesis, many heterogeneous vapor-phase reactions catalyzed by acid surfaces are, fundamentally, cases of general acid catalysis. This point of view has gained particular recognition by petroleum chemists because silica-alumina, silica-magnesia and acid-treated clays, all of which show strong surface acidity, are the most effective cracking catalysts.

Since a variety of catalysts were used in this investigation, an attempt was made to measure their relative acid strength and correlate it to catalytic activity (Table XXXVI). Two methods were used for this purpose.

Method I:- Ten grams of catalyst were shaken mechanically with 50.0 ml. of distilled water for eighteen hours at a temperature of 30°C. During this process all of the clay catalysts were extensively disintegrated. The silica-gel catalyst appeared to fracture when quenched with water and considerable heat of wetting was evolved. The alumina catalysts disintegrated only slightly and the synthetic silica-alumina catalyst remained almost completely intact. After settling for a further twelve hours 20 ml. aliquots were removed and titrated either with 0.1 N sodium hydroxide or 0.1 N sulfuric acid solution, using either phenolphthalein or methyl orange as indicator. Some samples which had not perfectly cleared were centrifuged prior to analysis.

TABLE XXXVI

Comparison of Acidity and Activity of Catalysts Used for Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixtures

Run No.	Catalyst	Percent Conversion(e)	mg.NaOH	mg.NaOH	mg.H_2SO_4
			Neutralized per g. of Catalyst		
			Method II	Method I	Method I
1a	Morden Bentonite(b)	69.2	38.5	0.48	--
16	Morden Bentonite(c), regenerated	59.7	32.6	0.03	--
2a	Morden Bentonite(b), 10% NaOH activated	26.0	3.0	--	12.5
3a	Morden Bentonite(c), 10% NaOH activated; regenerated	31.4	7.9	--	0.8
4a	Raw White Clay(d), unprocessed	45.5	28.6	0.12	--
5a	Raw White Clay(c), regenerated	40.2	25.5	0.02	--
10a	Synthetic Silica-Alumina(d)	82.9	40.5	0.31	--
11a	Synthetic Silica-Alumina(c), regenerated	79.5	36.5	0.09	--
6a	Silica Gel(d)	37.3	50.4	0.03	--
7a	Silica Gel(c), regenerated	32.4	----not determined----		
8a	Activated Alumina F-1(d)	34.5	4.6	--	1.4
9a	Activated Alumina F-1(c), regenerated	30.9	3.5	--	1.6
12a	Activated Alumina F-10(d)	69.9	10.2	0.02	--
13a	Activated Alumina F-10(c), regenerated	68.0	5.7	--	--

(b) Freshly activated catalyst titrated prior to use.
(c) Catalyst which had been used and reactivated.
(d) Catalyst as received from supplier.
(e) See Table XXXIV.

Results:- It was found that 1.0 g. of freshly activated Morden bentonite neutralized about 0.5 mg. of sodium hydroxide. This acidity cannot be regarded as an intrinsic property of the catalyst because it depends upon the thoroughness with which the acid-treated clay is washed. It is extremely difficult to remove the residual adsorbed mineral acid by washing. Thus, when 1200 g. of catalyst were prepared by the conventional procedure of activation and washed with 63 l. of distilled water, samples of the aqueous extract still showed a slight acidic reaction and precipitation with barium chloride.

Prior to its use for pyrolytic studies, 220 cc. of this catalyst when heated to 600°C., lost 10.0 g. of water which was strongly acidic and gave a heavy precipitate with barium chloride. These observations are in conformity with the results recorded in Table XXXVI which show that the titratable acidity of regenerated catalyst is considerably less than that of freshly activated catalyst.

Morden bentonite which had been activated with a 10 per cent aqueous sodium hydroxide solution neutralized 12.5 mg. of sulfuric acid per g. of clay. This large figure indicated strong retention of residual alkali which had not been removed by washing with distilled water.

"Activation" had been carried out by gently boiling 400 g. of the commercial bentonite powder with 600 cc. of a 10 per cent aqueous sodium hydroxide solution for four hours, keeping the suspension agitated and replacing from time to time the water lost by evaporation. The slurry was then diluted with 10 l. of water, most of which could be decanted after twenty-four hours. After filtration and washing with an additional 10 l. of water, the material was processed in the same manner as described for the acid activated clay.

Prior to use for pyrolytic studies, 220 cc. of this catalyst, when heated to 400°C., lost 10.3 g. of water which was neutral toward litmus, indicating that no sodium hydroxide had come off the surface, but still gave a very faint cloudiness with barium chloride.

After regeneration the titratable alkalinity of the catalyst was reduced to 0.8 mg. per g. of clay. This pattern of behavior was opposite to the general trend toward decrease in acidity of the catalyst once it had been used and reactivated.

Both silica gel and activated alumina F-10 showed very low acidity and activated alumina F-1 exhibited even titratable alkalinity. Yet in conformity with all other catalysts, except the sodium-hydroxide-activated bentonite, the activated aluminas, as received, were more acidic than the reactivated compounds.

Synthetic silica-alumina was found to exhibit distinct titratable acidity. Since this catalyst does not undergo any acid treatment during manufacture, its acidity is apparently real and an intrinsic property of the compound (244).

Method II:- The catalysts were heated at 550°C. for one hour in a muffle furnace and after they had cooled in a desiccator, exactly 2.0 g. were weighed out and shaken with 50.0 ml. of 0.1 N sodium hydroxide in an atmosphere of nitrogen for one hour at 30°C. It was noted that again the natural clays disintegrated to a greater extent than the synthetic catalysts and again the synthetic silica-alumina was least affected by this treatment. After standing for twelve hours 10.0 ml. aliquots were titrated with 0.1 N sulfuric acid using phenolphthalein as indicator. Samples which had not sufficiently settled were centrifuged in well-stoppered centrifuge tubes prior to analysis.

Results:- According to this method of analysis none of the catalysts showed alkalinity. Even Morden bentonite which had been activated with a 10 per cent sodium hydroxide solution became now an acidic catalyst, neutralizing 3 mg. of sodium hydroxide per g. of clay. This result showed that activation with a 10 per cent solution of sodium hydroxide had not entirely destroyed the acidity of the bentonite catalyst. After regeneration its acidity was more than doubled.

Activated Alumina F-1 now also had acidic properties and in conformity with the direct titration procedure, as well as with the behavior of all other catalysts - except the sodium-hydroxide-activated bentonite - the acidity of the fresh catalyst exceeded that of the reactivated compound.

Further study of the experimental data recorded in Table XXXVI showed that without exception a particular catalyst exhibited greater catalytic activity if it displayed a greater degree of acidity and this relationship applied not only to one particular catalyst but to a number of catalysts provided they belonged to the same class. Thus, comparing the acidity and catalytic activity of the silica-alumina catalysts used, it can be seen (Table XXXVII) that the catalyst which is least acidic is also the one showing least catalytic activity. In this table synthetic silica-alumina, which gave the highest conversion, was used as the reference catalyst (100 per cent catalytic activity). The acidity-activity relationship did not show up as clearly with regard to the activated aluminas because these catalysts were subjected to air treatment prior to pyrolysis (Table XXXIII) whereas their acidities (Table XXXVI) refer to the state in which they were received.

Observations of similar nature were made by Thomas (147) who activated samples of montmorillonite clay with hydrochloric acid solutions of different concentrations and then determined the catalytic activities of the preparations in accordance with a standardized test (245). He found that the activity of the catalyst increased with its acidity but fell

TABLE XXXVII

Comparison of Acidity and Activity of Aluminum Silicate Catalysts Used for Pyrolysis of Benzaldehyde-Acetic Anhydride Mixtures

Run No.	Catalyst	Percent Acidity g. NaOH Neutralized by 100 g. of Catalyst	Percent Activity
10a	Synthetic Silica-Alumina	4.1	100.0
11a	Synthetic Silica-Alumina	3.7	95.9
1a	Morden Bentonite	3.9	83.5
16	Morden Bentonite	3.3	72.0
4a	Raw White Clay	2.9	54.9
5a	Raw White Clay	2.6	48.5
3a	Morden Bentonite	0.8	37.9
2a	Morden Bentonite	0.3	31.4

off after it had reached a maximum. The present investigation has extended this observation to a number of catalysts and the results should serve to strengthen the novel concepts regarding the mechanism by which clays and clay-like catalysts are believed to act.

It is to be noted that silica gel, which had shown a very low acidity when titrated directly, was found to be the most acidic of all catalysts when tested in accordance with Method II. Yet in spite of this high acidity it displayed only little catalytic activity. Thomas, on the basis of an idealized atomic structure of montmorillonite, proposes the existence of both strongly acidic and weakly acidic hydrogen ions and suggests that only the strongly acidic type reflect the observed catalytic activity (147). Alkali treatment would not differentiate between strongly and weakly acidic hydrogen ions and titration would therefore show the sum of the two. On this basis, silica gel would contain a large percentage of weakly acidic hydrogen ions.

Activated Alumina F-10 showed both greater activity and acidity than the F-1 grade. The chemical composition of these two activated aluminas is very nearly the same (246) and would offer no clue regarding their differing catalytic activities, yet it is important to note that during the process of manufacture the F-1 grade does not undergo acid activation, whereas the F-10 grade material is subjected to a treatment with hydrochloric acid (247).

Comparison of the two methods of analysis shows that determination of catalyst acidity by Method II made the relationships detected by Method I more evident. It is to be understood, however, that these relationships are only semi-quantitative in nature, because the acidities determined are but relative values, depending on the experimental procedure chosen (temperature, concentration of the alkali, time of shaking, solvent etc.), and catalysts in turn will display different degrees of activity depending upon the type of reaction for which they are used. Deans, for instance, found that Morden bentonite catalyzed the conversion of p-cymene to toluene (72 per cent) while activated alumina and silica gel were both inactive (156).

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Sodium Hydroxide-Impregnated Morden Bentonite

Previous experiments (Tables XXXIII and XXXIV) had shown that activation of Morden bentonite with a 10 per cent aqueous sodium hydroxide solution had produced a catalyst which was much less efficient than the normal activated clay. In addition, certain anomalies were observed regarding the activity of the freshly activated catalyst when compared with that of the regenerated catalyst. In order to explain the discrepancies encountered experiments on sodium-hydroxide-impregnated catalyst were carried out.

The products were analyzed for styrene only and it was found that with increasing sodium-hydroxide concentration at the catalyst surface the yields of styrene fell off (Table XXXVIII).

TABLE XXXVIII

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Sodium-Hydroxide-Impregnated Morden Bentonite

Composition of Feed:
Benzaldehyde 51.0 % by wt.
Acetic Anhydride 49.0
Volume Pyrolyzed: 100 cc.
Feed Rate: 2 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Run No.	% wt. by vol. of NaOH on Catalyst	Total Liquid Products g.	Aromatics g.	Styrene % by wt. in Aromatics	Acidity* % by wt. in Total Liquid Products	Gas Evolved l.
16	0	86.5	47.8	38.3	32.2	10.4
19a	4	89.4	47.3	33.9	27.6	7.9
20a	7	96.0	46.7	19.9	28.9	6.2
21a	13	95.7	49.1	16.2	26.3	5.7

*Determined by titration of 1.0 g. of total liquid products with 0.5 normal alkali.

The initial decrease in styrene yield when using a 4 per cent sodium-hydroxide-impregnated Morden bentonite amounted to only 4.4 per cent. It became more marked (14 per cent) following the second impregnation of the catalyst and again decreased only slightly when the sodium hydroxide concentration was increased from 7 to 13 per cent.

The explanation was found when 1.0-g. samples of the total liquid products were titrated with 0.5 N alkali, for these analyses showed that in spite of the decreased catalytic activity, as indicated by the steadily falling rate of gas evolution, the acidity of the total liquid products did not change materially. Apparently some of the sodium hydroxide was removed from the catalytic surface during pyrolysis, probably by reaction with acetic acid to form sodium acetate and water. The experimental data would indicate that this reaction occurred particularly during the first run when the alkali was not yet strongly incorporated into the crystal lattices of the catalyst.

This phenomenon must also have occurred during pyrolysis when the alkali activated Morden bentonite was used (Tables XXXIII and XXXIV) and it would explain why the regenerated catalyst displayed a stronger acidity, and also greater catalytic activity, than the freshly activated catalyst.

The same catalyst was used for all three runs carried out with sodium-hydroxide-impregnated Morden bentonite. The alkali concentration at its surface was calculated without taking into account any losses that occurred during pyrolysis. For this reason the values for the alkali concentration are given to the nearest per cent only.

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Sodium-Acetate-Impregnated Morden Bentonite

Impregnation of Morden bentonite with sodium acetate, the classical catalyst for the Perkin reaction, did not enhance the quality of the clay for producing styrene by pyrolysis of benzaldehyde-acetic anhydride mixtures (Table XXXIX).

The reaction was carried out at 300°C. in order to suppress decarboxylation of any cinnamic acid if it were to form during pyrolysis.

It was found that in spite of the higher gas evolution, as compared to a similar run carried out with acid-activated Morden bentonite (Tables XI and XII; Run 15), conversion of the aldehyde was practically the same. Apparently the sodium-acetate-impregnated clay favored decomposition of the anhydride. When removed from the reactor after the normal process of regeneration the clay was still black and carbonized. There was also a relatively large percentage of high boiling material. No cinnamic acid, however, could be isolated from 30.0 g. of liquid products which were treated in accordance with the procedure applied when isolating the unsaturated acid from the products of the Perkin reaction.

TABLE XXXIX

Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture over Sodium-Acetate-Impregnated Bentonite

Composition of Feed

Benzaldehyde	51.0 % by wt.
Acetic Anhydride	49.0

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.0 cc./min.
Catalyst: 220 cc. Morden Bentonite containing 17.8% $\frac{w}{v}$ CH_3COONa
Temperature: 300°C.

Weight of Liquid Products	88.0 g.
Gas Evolved	7.1 l.
Aromatics	47.7 g.

Composition of Aromatics

Ethylbenzene	7.0 % by wt.
Styrene	22.8
Benzaldehyde	60.3
High Boiling Material	9.9

Pyrolysis of Substituted Aromatic and Heterocyclic Aldehyde-Acetic Anhydride Mixtures over Morden Bentonite

In an attempt to determine the scope of the vapor-phase reaction described above and also to accumulate additional experimental evidence regarding the reaction mechanism, the pyrolysis of seven substituted aromatic aldehydes and two heterocyclic aldehydes in presence of acetic anhydride was investigated. In all cases, except m-nitrobenzaldehyde, equimolar mixtures of reactants were used, and the pyrolyses all carried out under standardized conditions.

When chlorobenzaldehydes and toluic aldehydes were used the liquid products were treated in accordance with the general procedure of analysis, and these pyrolyses have therefore been omitted from a detailed discussion. Many of the runs were repeated in order to obtain sufficient material for determining the main physical constants of the various products. In some cases the vinyl compounds were further characterized by carbon-hydrogen analyses and the preparation of derivatives (Table LVII).

All liquid aldehydes were purified by distillation under reduced pressure and in an atmosphere of nitrogen through the Stedman column prior to use. Sources of supply and the physical constants of the purified compounds are given in Table XL, and the results of the various pyrolyses listed in Tables XLI-LVI.

TABLE XL

Physical Constants of Aldehydes Used for Pyrolyses

Aldehyde	Boiling Point °C.	Refractive Index n_D^{20}	Density d_4^{20}	Supplier
o-Chlorobenzaldehyde	84/11 mm.	1.5660	1.252	Eastman Kodak Co.
m-Chlorobenzaldehyde	85/10 mm.	1.5651	1.241	Unknown
p-Chlorobenzaldehyde*	----	----	---	Gift of Heyden Chemical Corp.
m-Methylbenzaldehyde	67/2 mm.	1.5410	1.019	Gift of Heyden Chemical Corp.
p-Methylbenzaldehyde	85/11 mm.	1.5454	1.020	City Chemical Corporation
p-Methoxybenzaldehyde	128/14 mm.	1.5730	1.122	Eastman Kodak Co.
m-Nitrobenzaldehyde**	----	----	---	Eastman Kodak Co.
2-Furfuraldehyde	54/16 mm.	1.5260	1.160	Eastman Kodak Co.
2-Thiophenealdehyde	66/5 mm.	1.5890	1.219	Arapahoe Chemicals Inc.

*Used as received. M.P. °C. given 47.5; found 46.3
**Used as received. M.P. °C. given 58.0; found 57.0

TABLE XLI

Pyrolysis of Equimolar o-Chlorobenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed:
o-Chlorobenzaldehyde 57.9 % by wt.
Acetic Anhydride 42.1
Volume Pyrolyzed: 100 cc.
Feed Rate: 2.1 cc./min.
Catalyst Volume: 220 cc.

Run No.	Temp. °C.	Liquid Products g.	Gas Evolved l.	Aromatics g.	Distillate from Aromatics % by wt.	High Boiling Material % by wt.
102	300	90.9	8.1	58.2	94.7	5.3
100	400	91.4	12.9	61.8	94.1	5.9
101	500	75.6	26.2	55.9	92.9	7.1

Run No.	Percent by Weight Composition of Distillate					o-Chlorostyrene
	Chloro-benzene	o-Chloro-toluene	o-Chloro-ethylbenzene	o-Chloro-styrene	o-Chloro-benzaldehyde	% by wt. in Aromatics
102	--	--	9.9	45.8	44.3	43.4
100	2.0	--	17.7	65.2	15.1	61.3
101	4.2	2.4	25.8	60.6	7.0	56.3

TABLE XLII

Physical Constants of Products from Pyrolysis of Equimolar o-Chlorobenzaldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index n_D^{20}	
	Given	Found	Given	Found	Given	Found
Chlorobenzene	132.1	132	1.1066	1.107	1.5251	1.5245
o-Chlorotoluene	159	158	1.0817	1.083	1.5238	1.5243
o-Chloroethylbenzene	179.2	178.5	$1.055\frac{25}{25}$	1.065	----	1.5217
o-Chlorostyrene	60-61/4 mm.	67/8.5 mm.	1.100	1.101	1.5648	1.5640
o-Chlorobenzaldehyde	208/748 mm.	213	1.252	1.252	1.567	1.5660

*d_4^{20}, unless otherwise specified

TABLE XLIII

Pyrolysis of Equimolar m-Chlorobenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

m-Chlorobenzaldehyde	57.9 % by wt.
Acetic Anhydride	42.1

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.1 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Weight of Liquid Products	89.9 g.
Gas Evolved	11.9 l.
Weight of Aromatics	62.2 g.

Distillate	93.5 % by wt.
High Boiling Material	6.5

Composition of Distillate

m-Chloroethylbenzene	10.9 % by wt.
m-Chlorostyrene	56.2
m-Chlorobenzaldehyde	32.9

Percent m-Chlorostyrene in Aromatic Products 52.5

TABLE XLIV

Physical Constants of Products from Pyrolysis of Equimolar m-Chlorobenzaldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index n_D^{20}	
	Given	Found	Given	Found	Given	Found
m-Chloroethylbenzene	183	184	$1.045\frac{20}{20}$	1.058	---	1.5189
m-Chlorostyrene	62-63/6 mm.	59/10 mm.	1.090	1.092	1.5630	1.5620
m-Chlorobenzaldehyde	214	213	1.241	1.241	1.5650	1.5641

*d_4^{20}, unless otherwise specified.

TABLE XLV

Pyrolysis of Equimolar p-Chlorobenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

p-Chlorobenzaldehyde	57.9 % by wt.
Acetic Anhydride	42.1

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.2 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Weight of Liquid Products	90.3 g.
Gas Evolved	11.1 l.
Weight of Aromatics	59.8 g.

Distillate	93.9 % by wt.
High Boiling Material	6.1

Composition of Distillate

p-Chloroethylbenzene	10.1 % by wt.
p-Chlorostyrene	47.8
p-Chlorobenzaldehyde	42.1

Percent p-Chlorostyrene in Aromatic Products	44.9

TABLE XLVI

Physical Constants of Products from Pyrolysis of Equimolar p-Chlorobenzaldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index**	
	Given	Found	Given	Found	Given	Found
p-Chloroethylbenzene	184.6	183	$1.044\frac{25}{25}$	1.057	1.5223^{18}	1.5188
p-Chlorostyrene	53-54/3 mm.	65/4 mm.	1.090	1.091	1.5658	1.5645
p-Chlorobenzaldehyde***	214	212	---	---	----	----

*d_4^{20}, unless otherwise specified.

**n_D^{20}, unless otherwise specified.

***M.P. °C. given 47.5; found 47.3

TABLE XLVII

Pyrolysis of Equimolar m-Methylbenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

m-Methylbenzaldehyde	54.0 % by wt.
Acetic Anhydride	46.0

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.2 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Weight of Liquid Products	85.5 g.
Gas Evolved	8.8 l.
Weight of Aromatics	50.8 g.

Distillate	95.9 % by wt.
High Boiling Material	4.1

Composition of Distillate

Toluene	2.3 % by wt.
m-Methylethylbenzene	14.4
m-Methylstyrene	29.7
m-Methylbenzaldehyde	53.6

Percent m-Methylstyrene in Aromatic Products	28.5

TABLE XLVIII

Physical Constants of Products from Pyrolysis of Equimolar m-Methylbenzaldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index**	
	Given	Found	Given	Found	Given	Found
Toluene	110.8	110	0.866	0.867	1.4957	1.4951
m-Methylethylbenzene	162	162.7	0.867	0.866	1.4975	1.4966
m-Methylstyrene	50-51/3 mm.	169.5 62.5/17 mm.	0.906^{16}	0.901	1.5410	1.5402
m-Methylbenzaldehyde	199	198	$1.02^{21.4}_{4}$	1.019	$1.5407^{21.4}$	1.5412

*d^{20}_{4}, unless otherwise specified.

**n^{20}_{D}, unless otherwise specified.

TABLE XLIX

Pyrolysis of Equimolar p-Methylbenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

p-Methylbenzaldehyde	54.0 % by wt.
Acetic Anhydride	46.0

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.2 cc./min.
Catalyst Volume: 220 cc.
Temperature: 400°C.

Weight of Liquid Products	86.8 g.
Gas Evolved	9.3 l.
Weight of Aromatics	51.3 g.

Distillate	97.2 % by wt.
High Boiling Material	2.8

Composition of Distillate

Toluene	2.8 % by wt.
p-Methylethylbenzene	15.1
p-Methylstyrene	35.0
p-Methylbenzaldehyde	47.1

Percent p-Methylstyrene in Aromatic Products	34.0

TABLE L

Physical Constants of Products from Pyrolysis of Equimolar p-Methylbenzaldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index**	
	Given	Found	Given	Found	Given	Found
Toluene	110.8	110	0.866	---	1.4957	1.4961
p-Methylethylbenzene	161-162	162	0.862	0.861	1.4943	1.4952
p-Methylstyrene	65-66/18 mm.	171.8/760 mm. 58-59/13 mm.	$0.9003^{16.4}_{4}$	0.897	$1.5447^{16.4}$	1.5419
p-Methylbenzaldehyde	204	202.5	$1.019^{16.6}_{4}$	1.020	1.5469	1.5459

*d^{20}_{4}, unless otherwise specified.

**n^{20}_{D}, unless otherwise specified.

TABLE LI

Pyrolysis of Equimolar p-Methoxybenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

p-Methoxybenzaldehyde	57.1 % by wt.
Acetic Anhydride	42.9

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.2 cc./min.
Catalyst Volume: 220 cc.
Nitrogen: 10 l./hr.
Temperature: 400°C.

Weight of Liquid Products	93.2 g.
Total Gas	15.8 l.
Weight of Aromatics	52.3 g.

Composition of Aromatics
(by distillation under reduced pressure)

p-Methoxybenzene	7.6 % by wt.
p-Methoxyethylbenzene	8.0
p-Methoxystyrene	16.3
p-Methoxybenzaldehyde	59.8
High Boiling Material	8.3

TABLE LII

Physical Constants of Products from Pyrolysis of Equimolar p-Methoxybenzaldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index**	
	Given	Found	Given	Found	Given	Found
Methoxybenzene	155	154	0.9954	0.994	1.5179	1.5173
p-Methoxyethylbenzene	196	195	$0.9624\frac{15}{4}$	0.960	1.5094	1.5086
p-Methoxystyrene	53-54/2 mm.	45-46/1 mm.	$1.0029\frac{15}{4}$	1.001	1.5612	1.5597
p-Methoxybenzaldehyde	247	247	$1.13^{12.7}$	1.122	$1.5764^{12.7}$	1.5729

*d_{4}^{20}, unless otherwise specified.

**n_{D}^{20}, unless otherwise specified.

Pyrolysis of m-Nitrobenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

The results when pyrolyzing a mixture of m-nitrobenzaldehyde and acetic anhydride over Morden bentonite are given in Table LIII. A molar ratio of aldehyde to acetic anhydride equal to 2:3 had to be used in order to dissolve the aldehyde.

The products were neutralized with sodium carbonate, extracted with ether and after washing and drying subjected to fractional distillation under reduced pressure. From 48.2 g. of aromatics there was obtained 1.4 g. of nitrobenzene, 1.7 g. of m-nitroethylbenzene and 5.4 g. of m-nitrostyrene, the remainder consisting of unchanged m-nitrobenzaldehyde and high boiling material.

The main purpose of the experiment was to detect any m-nitrocinnamic acid in the products of the pyrolysis since it has been reported that this acid resists conventional decarboxylation methods (10). However, when the products obtained from an identical run were treated in accordance with the usual procedure for isolation of α,β-unsaturated aromatic acids prepared by the Perkin reaction, no m-nitrocinnamic acid could be detected. Hence, this experiment, like those already performed, would also indicate that a β-arylacrylic acid is not likely as an intermediate reaction product during the pyrolysis. No precedent for the synthesis of m-nitrostyrene by a continuous vapor-phase process could be found in the literature.

TABLE LIII

Pyrolysis of m-Nitrobenzaldehyde-Acetic Anhydride Mixture over Morden Bentonite

Composition of Feed

m-Nitrobenzaldehyde	49.7 % by wt.
Acetic Anhydride	50.3

Volume Pyrolyzed: 100 cc.
Feed Rate: 2.1 cc./min.
Catalyst Volume: 220 cc.
Nitrogen: 10 l./hr.
Temperature: 400°C.

Weight of Liquid Products	89.0 g.
Total Gas	18.7 l.
Weight of Aromatics	48.2 g.

Composition of Aromatics (by distillation under reduced pressure)

Nitrobenzene	2.9 % by wt.
m-Nitroethylbenzene	3.5
m-Nitrostyrene	11.3
m-Nitrobenzaldehyde and High Boiling Material	82.3

TABLE LIV

Physical Constants of Products from Pyrolysis of m-Nitrobenzaldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index n_D^{20}	
	Given	Found	Given	Found	Given	Found
Nitrobenzene	210.9	210	1.205_{4}^{18}	1.206	1.5524	1.5512
m-Nitroethylbenzene	242	241	1.135	1.136	----	1.5427
m-Nitrostyrene	96-100/3 mm.	101/3 mm.	---	1.171	1.5830	1.5810
m-Nitrobenzaldehyde**	---	110/3 mm.	---	---	----	----

*d_4^{20}, unless otherwise specified.

**M.P. °C. given 58.0; found 57.8

Pyrolysis of Equimolar Furfuraldehyde-Acetic Anhydride Mixture over Morden Bentonite

A volume of 100 cc. of the equimolar mixture (48.5 g. furfuraldehyde, 51.5 g. acetic anhydride) was passed over the catalyst at 400°C. and at a rate of 1.8 cc. per minute. A slow stream of nitrogen (10 l. per hour) was used as carrier gas.

The liquid products were neutralized in the cold with sodium carbonate and extracted with ether. The extract after washing with a small quantity of water was dried over calcium chloride and then carefully fractionated at atmospheric pressure. Hydroquinone was used as polymerization inhibitor. The distillation, conducted up to a temperature of 110°C., gave 6.3 g. of distillate which consisted of 0.9 g. of 2-methylfuran, 3.7 g. of 2-ethylfuran and 1.7 g. of 2-vinylfuran.

When the aromatics (45.4 g.), obtained from a run carried out under similar conditions, were distilled under reduced pressure (600 mm.), their per cent by weight composition was found to be as follows:

2-Methylfuran	3.5
2-Ethylfuran	6.2
2-Vinylfuran	14.4
2-Furfuraldehyde	63.7
High Boiling Material	12.2

No attempt was made to characterize the high boiling tar. It consisted probably to a large extent of polymerized vinylfuran because the distillation had to be carried out at high reflux ratio and at not too low a pressure in order to obtain satisfactory separation of 2-ethylfuran from the vinyl compound.

TABLE LV

Physical Constants of Products from Pyrolysis of Equimolar 2-Furfuraldehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index**	
	Given	Found	Given	Found	Given	Found
2-Methylfuran	65	64	0.913	0.915	1.4344	1.4351
2-Ethylfuran	92-93/768 mm.	92	0.912_{13}^{13}	0.912	1.4466^{13}	1.4418
2-Vinylfuran	99	99.8	$0.9445_{4}^{18.5}$	0.945	$1.4992^{18.5}$	1.5000
2-Furfuraldehyde	161.7	161.0	1.1598	1.160	1.5261	1.5258

*d_4^{20}, unless otherwise specified.

**n_D^{20}, unless otherwise specified.

Pyrolysis of Equimolar Thiophenealdehyde-Acetic Anhydride Mixture over Morden Bentonite

A volume of 100 cc. of the equimolar mixture (52.3 g. thiophenealdehyde, 47.7 g. acetic anhydride) was passed over the catalyst at 400°C. and at a rate of 1.9 cc. per minute. A slow stream of nitrogen (10 l. per hour) was used as carrier gas.

From 90.1 g. of total liquid products, 49.5 g. of aromatics were obtained. Fractional distillation at atmospheric pressure up to 150°C. gave 7.5 g. of distillate consisting of 2.0 g. of thiophene, 1.7 g. of 2-methylthiophene, 2.5 g. of 2-ethylthiophene, and 1.3 g. of 2-vinylthiophene.

Using hydroquinone as polymerization inhibitor, the aromatics, isolated from a run carried out under identical conditions, were distilled under reduced pressure and found to have the following per cent by weight composition:

Thiophene	2.5
2-Methylthiophene	4.1
2-Ethylthiophene	6.1
2-Vinylthiophene	12.0
2-Thiophenealdehyde	66.5
High Boiling Material	8.8

It was noticed that the gas evolved during these runs had a strong odor of hydrogen sulfide and when passing it through a silver nitrate solution (10 g. in 25 cc.) 2.1 g.

of silver sulfide was obtained. Hence, ring rupture had occurred during pyrolysis. This phenomenon was also noticed by Hartough (202) during the vapor-phase pyrolysis of acetic anhydride-thiophene mixtures over aluminum silicate catalysts. He obtained only low yields of acetylated products. In addition to this tendency of thiophene to undergo ring rupture, it is known to be a catalyst poison because the free-electron pairs of the sulfur atom take part in the formation of strong covalent bonds by which the molecules are held at the surface (248).

TABLE LVI

Physical Constants of Products from Pyrolysis of Equimolar 2-Thiophenealdehyde-Acetic Anhydride Mixture

Compound	Boiling Point °C.		Density*		Refractive Index**	
	Given	Found	Given	Found	Given	Found
Thiophene	84	84	$1.07\frac{15}{4}$	1.064	1.5285	1.5280
2-Methylthiophene	113	112	$1.02\frac{15.3}{4}$	1.019	$1.524^{15.3}$	1.5205
2-Ethylthiophene	132	133	$0.990\frac{24}{24}$	0.992	1.513	1.5139
2-Vinylthiophene	145	141 63.5/50 mm.	1.044	1.043	$1.5612^{23.4}$	1.5679
2-Thiophenealdehyde	198	197	$1.215\frac{21}{21}$	1.219	----	1.5893

*d^{20}_{4}, unless otherwise specified.

**n^{20}_{D}, unless otherwise specified.

TABLE LVII

Characterization of Vinyl Compounds Obtained by Pyrolyses of Acetic Anhydride-Aromatic Aldehyde Mixtures over Morden Bentonite

Vinyl Compound	Chemical Characterization							
	Carbon-Hydrogen Analyses*				Dibromide M.P. °C.		Halogen Content of Dibromide	
	Carbon		Hydrogen					
	Found	Calc.	Found	Calc.	Found	Given	Found	Calc.
m-Methylstyrene	91.38	91.47	8.43	8.53	47.3	45-47		
p-Methylstyrene	91.40	91.47	8.50	8.53	45.0	45.0		
m-Nitrostyrene	64.46	64.45	4.92	4.73	80.1	78-79		
p-Methoxystyrene					80.9-81.2	78-81	54.27	54.36
p-Chlorostyrene					43.7	44.0		
2-Vinylfuran	Maleic Anhydride Adduct M.P. 150°C., Literature Value 149-150°C.							

*These were carried out by Y. Perron, Dept. of Chemistry, University of Montreal.

Pyrolysis of Equimolar Benzaldehyde-Propionic Anhydride Mixture over Morden Bentonite

The propionic anhydride used was supplied by Brickman & Company, Montreal. It had the following physical constants:

B.P., (°C. corr.) 165; n_D^{20} 1.4033; d_4^{20} 1.013

and was used without further purification.

A volume of 100 cc. of the equimolar mixture (44.9 g. benzaldehyde, 55.1 g. propionic anhydride) was passed over the catalyst at 400°C. and at a rate of 2.3 cc. per minute.

The pyrolyzate (85.5 g.) after treatment in accordance with the adopted procedure yielded 54.3 g. of products which on fractional distillation under reduced pressure and in an atmosphere of nitrogen gave four fractions.

Fraction 1 (5.3 g.; B.P. 100-105°C.) consisted of diethylketone.

Fraction 2 (10.4 g.; B.P. 150-167°C.) was not definitely identified, but judging by the boiling points, refractive indices and behavior toward bromine shown by the individual subfractions, it appeared to be a mixture of n-propylbenzene and allylbenzene, the latter being formed as a result of the isomerization of β-methylstyrene which was isolated and identified. Such isomerization is known to occur in the vapor phase over clay catalysts (249, 250).

Fraction 3 (26.5 g.; B.P. 167-176°C.) represented a mixture of isomeric β-methylstyrenes.

Fraction 4 (6.7 g.; B.P. 176-185°C.) was unchanged benzaldehyde and high boiling material.

The refractive indices of the individual fractions making up Fraction 3 increased gradually from 1.5431-1.5500.

A fraction of 3.3 g. collected at 61.5°C. (10 mm. pressure) had the following physical constants:

B.P. (°C. corr.) 174; n_D^{20} 1.5492; d_4^{20} 0.911

These values closely approximated those given in the literature for the high boiling isomer of β-methylstyrene.

An aliquot of this sample was titrated for unsaturation according to the method outlined by d'Alelio (231) and found to be 99.8 per cent pure.

The dibromide was prepared in accordance with the procedure given by Rügheimer (251) and after four recrystallizations from ethanol and drying under vacuum over phosphorus pentoxide its melting point was 68.0-68.3°C. The melting points recorded in the literature range from 64-68°C. (252) but none of the authors elaborates on the purification of the compound prior to the melting point determination.

A Carius analysis gave 57.31 per cent bromine (Theoretical 57.50 per cent).

Further characterization of the vinyl compound was carried out by determining its ultraviolet absorption spectrum using a Beckmann quartz photoelectric spectrophotometer. (see Figure 9). Maximum absorption, ϵ=16310, occurred at 250 mu., that is, in the region where conjugated alkyl substituted benzene derivatives absorb with an extremely high intensity. T.W. Campbell et al. (253) reported the extinction coefficient of the trans-compound at 249 mu. as equal to 14710. Their sample, obtained by rearrangement of allylbenzene with potassium hydroxide in butanol, was however contaminated with some cis-isomer. By treating the mixture on a chromatographic column and subjecting the product to careful fractionation, they believe they obtained the pure trans-isomer for which they give the following constants (254):

B.P. 177-178°C.; n_D^{25} 1.5468; $\epsilon_{249\text{ mu.}}$ 17850

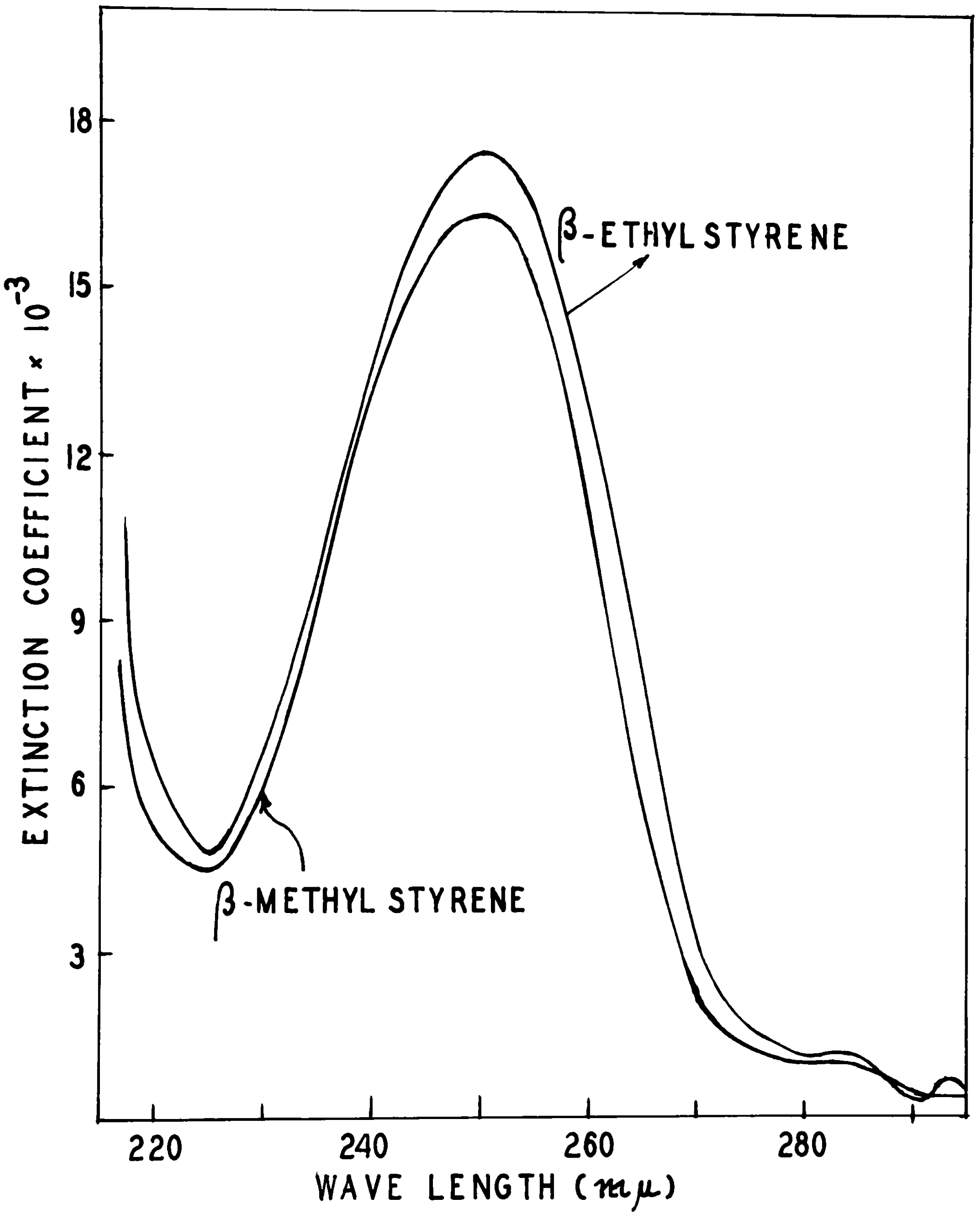


Figure 9

Absorption Spectrum of β-Methylstyrene and β-Ethylstyrene

Solvent: 95% Ethyl Alcohol
Styrene Concentration: 0.004 g./l.

Pyrolysis of Equimolar Benzaldehyde-Butyric Anhydride Mixture over Morden Bentonite

The anhydride used was supplied by Eastman Kodak & Co. It had the following physical constants:

B.P. (°C. corr.) 191; n_D^{20} 1.4168; d_4^{20} 0.992

and was used without further purification.

A volume of 100 cc. of the equimolar mixture (40.1 g. benzaldehyde, 59.9 g. butyric anhydride) was passed over the catalyst at 400°C. and at a rate of 2.7 cc. per minute.

The pyrolyzate (84.7 g.) after neutralization with sodium carbonate solution and extraction with ether yielded 51.3 g. of products, which were washed until neutral and dried over calcium chloride. Distillation under reduced pressure and in an atmosphere of nitrogen gave four fractions.

Fraction 1	(4.9 g.; B.P. 140-150°C.) consisted of heptanone-4.
Fraction 2	(18.1 g.; B.P. 170-185°C.) was not subjected to further analysis, but judging by the boiling points, refractive indices, and behavior toward bromine shown by the individual subfractions it probably contained a large percentage of buten-2-ylbenzene and buten-3-ylbenzene.
Fraction 3	(20.4 g.; B.P. 185-199°C.) represented a mixture of isomeric buten-1-ylbenzenes (β-ethylstyrenes).
Fraction 4	(2.1 g.; B.P. 199-210°C.) was high boiling material and not identified.

The refractive indices of the individual fractions making up Fraction 3 increased gradually from 1.5290-1.5428. A fraction of 3.9 g. collected at 66.4°C. (5 mm. pressure) had the following physical constants:

B.P. (°C. corr.) 197; n_D^{20} 1.5418; d_4^{20} 0.910

These values closely approximated those given in the literature for the high boiling isomer of β-ethylstyrene.

The dibromide was prepared according to the procedure given by Radiszewski (255) and after four recrystallizations from ethanol and drying over phosphorus pentoxide its melting point was 71.5-71.8°C. The melting points recorded in the literature range from 67-71°C. (17, 107, 255).

A Carius analysis gave 54.59 per cent bromine (Theoretical 54.73).

The ultraviolet absorption spectrum of the vinyl compound was also determined and it was found that maximum absorption (ϵ=17520) occurred at exactly the same wave length at which β-methylstyrene absorbed with greatest intensity (see Figure 9).

The absorption curve itself was very nearly the same as that of the lower homologue with regard to shape and spectral intensity, which observation is in agreement with Ramart-Lucas' finding (250), that lengthening the side chain of β-methylstyrene modifies but slightly the ultraviolet absorption. This author prepared β-ethylstyrene by dehydration of 4-phenyl-1-butanol at 500°C. over infusorial earth and obtained a mixture of all three butenylbenzenes, the buten-1-ylbenzene (β-ethylstyrene) making up the largest fraction.

The Mechanism of the Reaction

The direct analogy which may so often be drawn between acid-catalyzed homogeneous liquid-phase reactions and heterogeneous processes occurring in the vapor phase at acidic surfaces cannot be extended to include the interaction of benzaldehyde and acetic anhydride. The liquid-phase reaction, which has been studied by Man, Sanderson and Hauser (256), yields benzylidene diacetate. It is carried out at 0-5°C. and only minute amounts of boron trifluoride (etherate) are required to effect condensation.

The reaction has not yet been applied to substituted aromatic aldehydes and a detailed mechanism remains still to be proposed. It is reasonable, however, to assume that the condensation proceeds by the same mechanism as similar aliphatic aldehyde-acid anhydride condensations which are assumed to involve ionic intermediates (257).

Valuable information regarding the mechanism of the vapor-phase process may be gained by comparing it with another liquid-phase reaction, the Perkin synthesis of α,β-unsaturated acids (Table LVIII).

TABLE LVIII

Comparison of Vapor-Phase Process and Perkin Reaction

Vinyl Compound Obtained by Vapor-Phase Process	% Yield	See Page No.	Acrylic Acid Obtained by Perkin Synthesis	% Yield	Reference
m-Methylstyrene	28.5	167	m-Methylcinnamic Acid	23	258
p-Methylstyrene	34.0	169	p-Methylcinnamic Acid	33	258
Styrene	38.3	70	Cinnamic Acid	45-50	258
p-Chlorostyrene	44.9	165	p-Chlorocinnamic Acid	52	258
m-Chlorostyrene	52.5	163	m-Chlorocinnamic Acid	63	258
o-Chlorostyrene	61.3	161	o-Chlorocinnamic Acid	71	258
p-Methoxystyrene	16.3	171	p-Methoxycinnamic Acid	30	259
m-Nitrostyrene	11.3	174	m-Nitrocinnamic Acid	75	258
2-Vinylfuran	14.4	176	2-Furylacrylic Acid	65	260
2-Vinylthiophene	12.0	179	2-Thienylacrylic Acid	Not Given	261
				Low	262

It is seen that the yields of styrene, methylstyrenes and chlorostyrenes, vary in the same manner as those of the corresponding cinnamic acids obtained by the Perkin synthesis. These results would indicate that the activity of substituted benzaldehydes in the vapor-phase process reflects similar trends observed in other reactions involving the carbonyl group. A methyl group in either the meta- or para-position decreases the yield and a halogen in any position increases the yield, the effect being strongest for the ortho, less for the meta and weakest for the para isomer.

Since it was shown in the experimental portion of this thesis, however, that cinnamic acid is not an intermediate in the vapor-phase process, another common characteristic must be found in order to account for the experimental results. It is fairly well established that the Perkin synthesis of acrylic acids is an ionic reaction, and the historical part of this thesis has enumerated many examples of, and data on, contact catalytic reactions which can be interpreted on the basis of intermediate ionic states, similar to those occurring in homogeneous catalytic reactions.

Unfortunately, in spite of the considerable support which may be drawn from the literature, this view has not yet received the general attention it deserves. The pyrolytic process which has now been studied strengthens this view because with its aid the process can be extensively correlated with a classical liquid-phase reaction that has been the subject of much research for nearly 100 years and whose mechanism is generally considered ionic in nature.

It was shown that the vapor-phase reaction does not take place in the absence of a catalyst nor in the presence of an inert contact substance, such as pure silica. It proceeds readily however at acid surfaces, and since a correlation between catalyst acidity and catalyst activity was found to exist one is encouraged to conclude that the hydrogen ions associated with the catalytic surface are most likely the sites where reaction is initiated.

It was also found that silica gel (SiO_2=99.7 per cent) as well as activated alumina (Al_2O_3=99.0 per cent) catalyzed the vapor-phase process. Hence, neither silicon nor aluminum atoms are to be regarded as fundamental requirements for the reaction to take place. The only common feature of all positive catalysts used was their acidity.

Another possibility regarding the catalytic action of aluminum silicates remains to be considered. It has been postulated (264) that their adsorptive power and catalytic activity are associated with the oxygen atoms whose distance (2.50 Å) within the crystal lattice is close to the distance between alternate carbon atoms in a zigzag hydrocarbon-chain (2.54 Å). This postulate cannot explain, however, why other similar structures, such as the micas or talc, which contain the same type of silica-oxygen bonds, are catalytically inactive; nor does it account for the increase in catalytic activity caused by acid treatments.

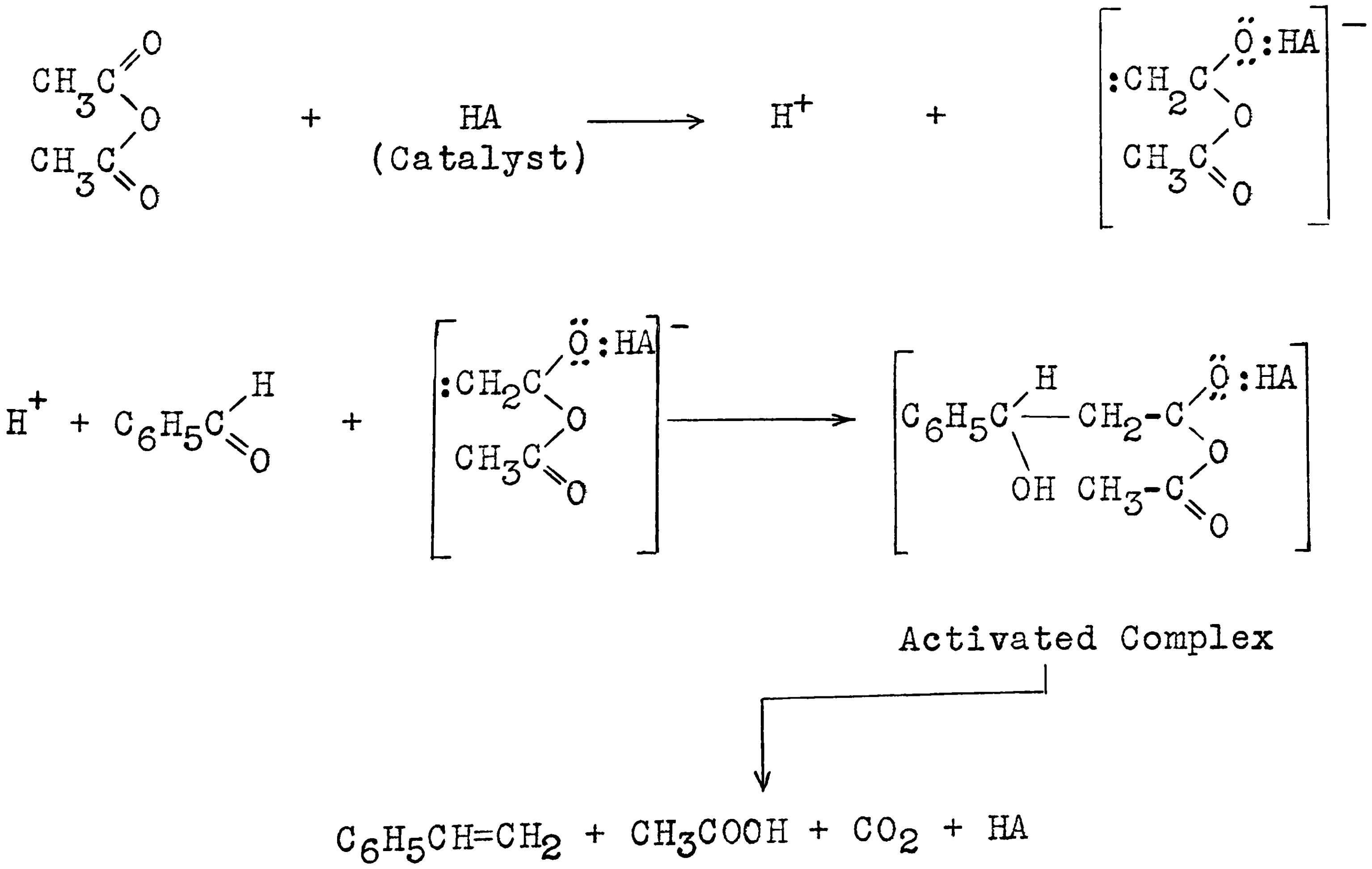
Of the two aluminas investigated, the one which had been acid-treated gave considerably higher conversion. This greater activity may be interpreted on the basis of experimental work carried out by Graham and Thomas (263). These workers believe that hydrous alumina is a co-ordinated structure made up of Al-O-Al and $\mathrm{Al}\text{-}\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}\text{-}\mathrm{Al}$ linkages. Anions may form complexes with the aluminum ion in acid solution by approaching the $\mathrm{Al}\text{-}\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}\text{-}\mathrm{Al}$ link at the surface, breaking the aluminum-oxygen bond

$$A^{-} \longrightarrow \mathrm{Al}\ .....\ \underset{\mathrm{H}}{\mathrm{O}}\text{-}\mathrm{Al}$$

and thereby converting the "ol" group $\mathrm{Al}\text{-}\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}\text{-}\mathrm{Al}$ into a "hydroxo" group which reacts readily with a proton from the medium. It follows that alumina which has undergone this type of acid activation will contain a higher concentration of hydrogen ions at its surface than the unprocessed material. This inference has been confirmed, since the titratable acidity of the freshly activated as well as of the regenerated acid activated alumina was considerably higher than that of the unprocessed sample under identical test conditions (Table XXXVI).

Accepting then the conclusion that the hydrogen ions at the catalytic surface are the ultimate sources of activity, the reaction mechanism becomes a case of general acid catalysis and may be visualized as an acid catalyzed "aldol" condensation.

The first step toward reaction of an aromatic aldehyde-aliphatic anhydride mixture would be co-ordination of the anhydride with the catalyst, whose acidity facilitates the loss of a proton and enolizes the reactant. The proton adds to the negatively charged oxygen of the aldehyde, whose positively charged carbon atom subsequently becomes attached to the "carbanion" held at the solid surface by covalent bonds. The complex thus formed is of transient existence only, breaking up into its most stable components, i.e. styrene, acetic acid and carbon dioxide:



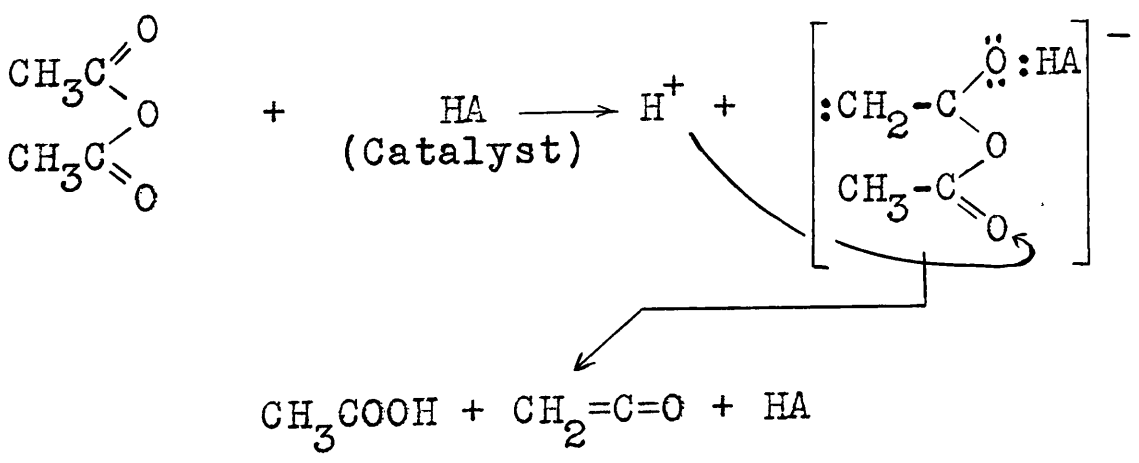
Considerable evidence that the reaction investigated has the most characteristic feature of an acid-catalyzed aldol condensation (condensation of the aldehyde with the alpha methylene group of the anhydride) is afforded by the isolation of the β-substituted vinyl compounds, β-methylstyrene or β-ethylstyrene, when pyrolyzing propionic anhydride or butyric anhydride-benzaldehyde mixtures over Morden bentonite.

Very little is known regarding the intimate mechanisms of aldol-condensations (265, 266, 267) and the various intermediate steps assumed are always only suggestive of the course these reactions may follow in order to give the products they actually yield. In none of these reactions do the experimental facts prove by themselves the intermediate stages visualized; yet it is equally important that they also do not offer any contradictions to the existence of such stages.

A great deal of valuable information regarding the mechanism of the reactions studied may be gained from the results obtained when the pyrolysis was carried out under such mild conditions that potential side reactions were reduced in both number and magnitude. Thus, at 200°C. styrene was the only aromatic product formed during pyrolysis of the equimolar benzaldehyde-acetic anhydride mixture (Table XII), and acetic acid together with unchanged acetic anhydride, were the only non-aromatic components (see pages 62 and 63). However, if the acetic acid had been formed solely in accordance with the equation

$$(CH_3CO)_2O + C_6H_5CHO \longrightarrow C_6H_5CH{=}CH_2 + CH_3COOH + CO_2$$

only 2.1 g. would have been obtained, instead of the 11.7 g., actually found in the aqueous phase. The "excess" of 9.6 g. would have to be reduced by the amount of acetic acid corresponding to the weight of styrene retained by the catalyst, since it was found that the monomer was less efficiently removed from the reactor than either acetic acid or anhydride at a temperature of 200°C. (Table XI). Taking the data when nitrogen was used as carrier gas (Table XVI), the "excess" acetic acid would amount to 7.7 g. Even this value indicates that acetic acid formation must take place by other reactions as well. Very likely it arises by a mechanism analogous to the one leading to styrene formation. Some protons, formed by co-ordination of one carbonyl group of the anhydride with the catalyzing surface, may become attached to the oxygen of the other carbonyl group which has not co-ordinated with the surface:



The intermediate ketene is decomposed further, or it reacts with adsorbed water from the catalyst to form acetic acid.

The last named in the presence of benzaldehyde may enter the reaction cycle leading to styrene formation.

Furthermore, acetic acid formation may occur as a result of direct hydrolysis of some acetic anhydride molecules by both structural and retained water from the catalyst but the amount obtained cannot be due to such interaction exclusively (see Table XXVI; Run 56).

Strong experimental support for formation of the postulated intermediate complex comes from the composition of the gas evolved during pyrolysis (Table XIII). When the catalysis of the equimolar benzaldehyde-acetic anhydride mixture was carried out at low temperature, carbon dioxide made up the largest portion of the gas. Since not even a trace of acetone was detected in the liquid products, decarboxylation could not possibly have affected the anhydride but only the intermediate condensation product. The presence of carbon monoxide and unsaturates in the gaseous products showed that the side reaction leading to the formation of acetic acid and ketene did occur, and the small quantity of hydrogen found indicated that even at 200°C. the total breakdown of some reactant molecules also took place.

Another interesting observation in accord with the proposed mechanism relates to the gas volumes generated during pyrolysis (Table XI; Figure 10). It was found that at both 200 and 300°C. the volume generated per mole of feed was

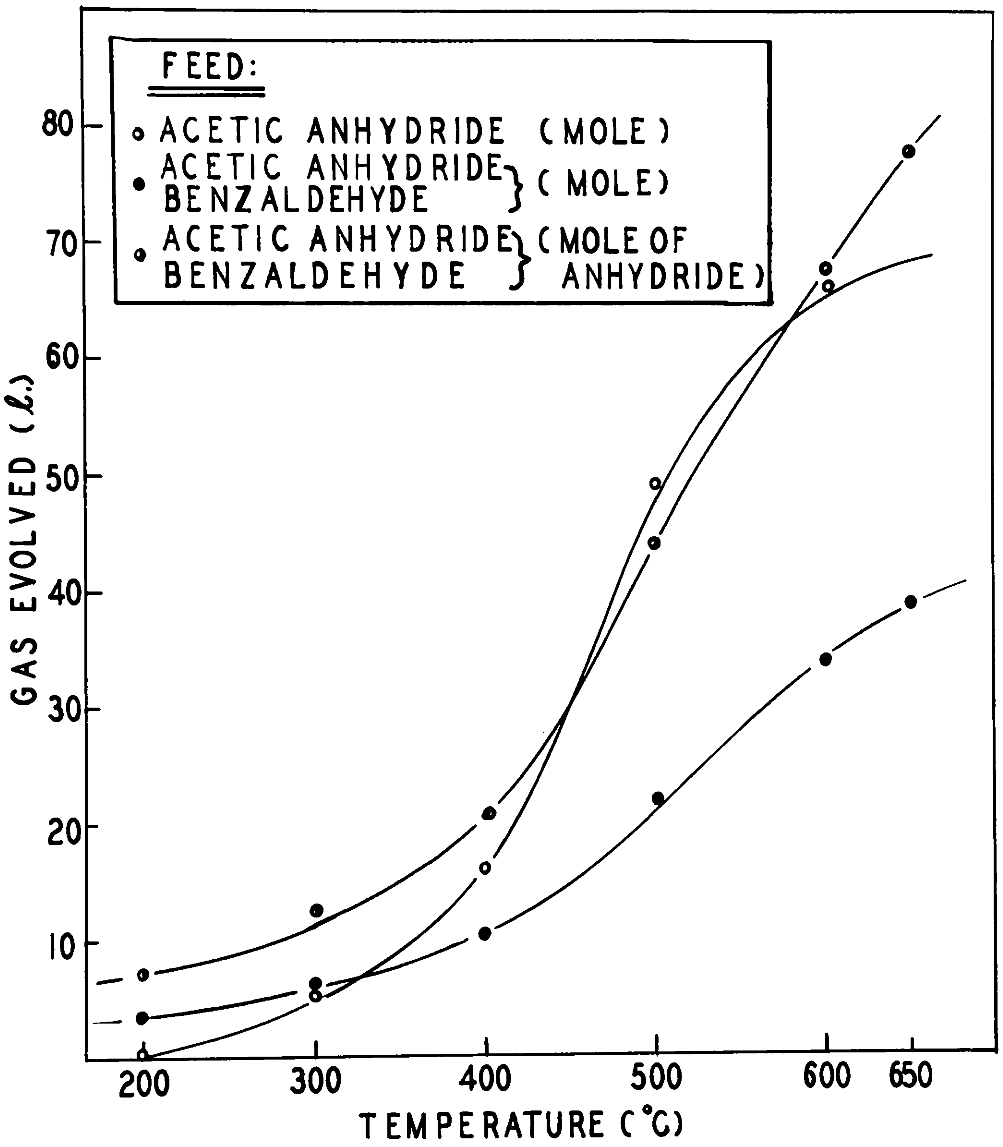


Figure 10

Pyrolyses of Acetic Anhydride and Equimolar Benzaldehyde-Acetic Anhydride Mixtures Temperature vs. Gas Evolved greater during pyrolysis of equimolar benzaldehyde-acetic anhydride mixtures than that generated during pyrolysis of acetic anhydride alone (Table XXVI). The difference was particularly marked at 200°C. and became less at 300°C. At higher temperatures this trend reversed. This result is important because at any given temperature acetic anhydride alone was found to be more effectively attacked than the aromatic aldehyde (Tables XV and XXVI). Apparently, in the presence of the aldehyde reaction occurs with greater ease, the polarized carbonyl group enhancing the reactivity of the catalyzing surface concerned with the removal of a proton from the anhydride. Hence, under mild conditions both formation and decarboxylation of the intermediate complex constitute the chief reactions which may be recognized by the nature of the liquid as well as gaseous products.

At higher temperatures the reaction becomes increasingly complex because the reactants and primary products are attacked further in accordance with the data reported earlier. However, the aromatic aldehyde as well as the aromatic products of the pyrolysis are not attacked as efficiently by the catalyst as are the acetic anhydride and its reaction products. It is for this reason that at a temperature slightly above 300°C. the rate of gas evolution during pyrolysis of the benzaldehyde-acetic anhydride system starts to increase more slowly than that occurring during pyrolysis of the anhydride at comparable temperatures (Figure 10).

The effect of the aldehyde on the pyrolysis is still more strikingly demonstrated by comparing the gas volume generated from the anhydride with that from the anhydride-benzaldehyde mixture, based in each case upon 1 mole of acetic anhydride. Such comparison also graphically represented in Figure 10, is justifiable because only negligible amounts of gas may be expected to be evolved during pyrolysis of benzaldehyde over Morden bentonite at temperatures up to 400°C. (Table XV).

Further evidence supporting the proposed reaction mechanism comes from the pyrolysis of acetic anhydride-benzaldehyde mixtures of molar ratio greater than 1 (Table XVIII). It was found that the volume of gas generated, when feeding 100 ml. of reactants, increased from 10.8 l. for the equimolar mixture to 12.2 l. for the mixture of mole ratio equal to 2.5. The volume fell slightly below this value for pyrolysis of a mixture of molar ratio equal to 3.0. Such direct comparison is not really justified because of the varied composition of the feeds. When basing the comparison, however, on the volume of gas which would be generated if enough of the reactants were pyrolyzed in order to yield 1 mole of styrene in each case - assuming that this could be done without altering in any way the reaction conditions which existed when pyrolyzing 100 ml. of feed - the gas evolution is seen to increase steadily with increased acetic anhydride concentration in the feed over the entire concentration range investigated. Considering the fact that no interaction of the reactants occurs in the absence of the catalyst, it can be suggested with considerable experimental backing that co-ordination of the acetic anhydride with the surface constitutes the rate-controlling step for the pyrolytic reaction.

Comparison of the composition of the gaseous products reveals that more carbon dioxide is evolved during pyrolysis of the benzaldehyde-acetic anhydride mixture made up of 1 mole of aldehyde and 3 moles of anhydride than during pyrolysis of the equimolar mixture (Tables XIII and XIX). This again indicates that, with increasing acetic anhydride concentration in the feed, formation of the intermediate complex is enhanced and constitutes the main reaction. The percentages of alkenes and carbon monoxide, on the other hand, are less than those found in the gaseous products obtained by pyrolysis of the equimolar mixture. Evidently the side reaction leading to the formation of acetic acid and ketene has been reduced in magnitude. Since a higher percentage of hydrogen was also found to be evolved, it would appear that even at the faster feed rate (3.8 cc./min.) complete breakdown of some reactant molecules and reaction intermediates occurs but that the hydrogen formed does not attack the monomer as efficiently because of the shorter contact time.

This consideration also explains the decrease of ethylbenzene formation noted with increase in acetic anhydride concentration (Table XIX; Figure 5).

It has already been pointed out that the aldehyde by virtue of its high proton affinity may also co-ordinate with the surface. Such co-ordination decreases the rate of the reaction and increases in magnitude whenever the concentration of the aldehyde is increased or its contact time prolonged. Both these phenomena have been observed (Table XXII). But the aldehyde will also be favored in its competition for space on the catalyzing surface if it contains substituents such as a methoxy or nitro group, or atoms, such as sulfur or oxygen, which are capable of similar co-ordination. This phenomenon, too, was confirmed experimentally. p-Methoxybenzaldehyde, 2-thiophenealdehyde, 2-furfuraldehyde and m-nitrobenzaldehyde gave only low yields of the corresponding vinyl compounds.

These results strongly suggest that formation of a co-ordinated complex of the acetic anhydride with the catalyzing surface constitutes the rate-controlling step, which assumption is supported further by the observation that optimum styrene yields are obtained at the same temperature, namely 400°C., when using different aldehydes for pyrolyses under otherwise similar conditions (Tables XII and XLI). At this optimum temperature for styrene formation acetic anhydride itself gave maximum yields of acetic acid (Table XXVI) whose formation may be explained in terms of an ionic mechanism also.

Finally, the postulated mechanism is in accord with the experimentally observed fact that the acidity of the catalyst determines the efficiency with which the reaction may be carried out. It was found that pre-treatment of the catalyst with a mineral acid increased its activity, whereas pre-treatment with a base decreased its activity. Hence the characteristic effect of the catalyst appears to be the increase in concentration of the acidic group necessary for reaction, i.e. to function as a potential proton reservoir.

SUMMARY

1. The synthesis of twelve vinyl aromatic compounds was accomplished by the pyrolysis of binary mixtures of an aromatic aldehyde and the anhydride of an aliphatic acid over a variety of catalysts. These compounds were:

    Styrene
    o-Chlorostyrene
    m-Chlorostyrene
    p-Chlorostyrene
    m-Methylstyrene
    p-Methylstyrene
    p-Methoxystyrene
    m-Nitrostyrene
    2-Vinylfuran
    2-Vinylthiophene
    β-Methylstyrene
    β-Ethylstyrene

    m-Nitrostyrene has been obtained for the first time by a continuous vapor-phase process.

2. Optimum conditions for the pyrolysis, studied on benzaldehyde-acetic anhydride mixtures, required high ratios of the anhydride, a temperature of about 400°C., the use of nitrogen as carrier gas, and rapid feed rates. Activated Morden bentonite was used as catalyst in this investigation.

    When pyrolyzing an equimolar mixture at 400°C. and at a feed rate of 2 cc. per minute per 220 cc. of catalyst, 38.3 per cent of the aromatic products consisted of styrene. This yield could be increased by 4.3 per cent when using nitrogen as carrier gas and be further improved by

increasing the acetic anhydride ratio in the feed. With pyrolysis at the same temperature, but with a benzaldehyde-acetic anhydride mixture of molar ratio equal to 0.33 and a feed rate of 3.8 cc. per minute, the aromatics contained 53.7 per cent of styrene. This recovery represents 80.9 per cent of the theoretical yield obtainable at a conversion of 61.3 per cent.

Ethylbenzene could be isolated as a hydrogenation product at all temperatures in excess of 200°C. Its formation from styrene was favored by low space velocities, highly active catalysts, and elevated temperatures. These variables also favored the decomposition of the aldehyde to benzene and toluene.

With Morden bentonite as catalyst styrene yields were dependent on the process period. They fell off with time, particularly during the initial stages of pyrolysis and at more elevated temperatures. When synthetic silica-alumina was used as catalyst, styrene yields were found to increase with time over a certain interval in spite of a steady, gradual decrease in the conversion.

3. Benzaldehyde-acetic acid mixtures on pyrolysis over Morden bentonite yielded the same types of compounds as benzaldehyde-acetic anhydride mixtures. On passing equimolar quantities over the activated clay at 400°C., using a feed rate of 1.6 cc. per minute per 220 cc. of catalyst, the

styrene obtained comprised 20.3 per cent of the total aromatics. A four-fold increase in acid concentration in the feed brought the yield up to 35.5 per cent, which is only slightly below that obtained by pyrolysis of an equimolar acetic anhydride-benzaldehyde mixture.

4. Acetic anhydride yielded mainly acetic acid, when pyrolyzed over Morden bentonite, the maximum yield of 72.2 per cent being obtained at 400°C. At higher temperatures dehydration was the chief reaction. Ketene, which was probably formed, decomposed to ethylene and carbon monoxide, and further to hydrogen and carbon. Acetone was also identified as a reaction product.

5. Acetic acid, when passed over Morden bentonite, was only slightly attacked at 300°C., but efficiently dehydrated at higher temperatures. The same products as those obtained by pyrolysis of acetic anhydride were formed. Only at 400°C. could a small amount of acetic anhydride be isolated.

6. Cinnamic acid was unaffected by Morden bentonite at 200°C., but when pyrolyzed at 525°C. in the presence of water vapor it was converted to ethylbenzene (44.6 per cent), styrene (36.7 per cent), benzene and toluene.

7. Ketene, which can be generated by passing acetone over copper turnings and silica chips at 625°C., was found to

be unreactive toward benzaldehyde when an acetone-benzaldehyde mixture was pyrolyzed under similar conditions.

8. Ketene and benzaldehyde, when passed together over Morden bentonite at 400°C., yielded a small quantity of styrene as well as ethylbenzene. Direct condensation of the reactants was doubtful, however, because acetic acid and acetone were also products of the pyrolysis, and interaction of the unsaturated gas with water adsorbed by the catalyst probably preceded styrene formation.

9. In addition to Morden bentonite silica gel, synthetic silica-alumina and activated alumina catalysts were investigated. It was found that the activity of the various catalysts was related to their acidity. Within a given class (aluminum silicates, or activated aluminas) the more strongly acidic catalysts showed stronger catalytic activity. Only silica gel, in spite of its marked titratable acidity, did not display high catalytic activity. Hydrochloric acid activated alumina was found to be the most suitable catalyst for the pyrolysis. It gave 51.8 per cent of styrene, representing 68.8 per cent of the theoretical yield obtainable at a conversion of 68.0 per cent.

10. The activity of methyl- and chloro-substituted benzaldehydes during pyrolyses with acetic anhydride was found to be similar to the trends observed in familiar liquid-phase condensations involving the carbonyl group. A methyl group

decreased and a chloro group increased the yield of the corresponding styrene from the reaction, the effect being strongest for the ortho-, less for the meta-, and weakest for the para-position.

11. Pyrolysis of benzaldehyde together with anhydrides of acetic acid homologues yielded β-substituted styrenes, thereby providing additional evidence for an ionic mechanism for the reaction in accordance with the general theory of acid catalysis.

CLAIMS TO ORIGINAL RESEARCH

1. The first preparation of vinyl aromatic compounds by the pyrolysis of binary mixtures of an aromatic aldehyde and the anhydride of an aliphatic acid over a variety of catalysts.

2. The first preparation of styrene by pyrolysis of benzaldehyde-acetic acid mixtures over activated Morden bentonite.

3. The first preparation of m-nitrostyrene by a continuous vapor-phase process.

4. The first reported study of the pyrolysis of benzaldehyde over activated Morden bentonite.

5. The first reported study of the pyrolysis of acetic anhydride over an aluminum hydrosilicate catalyst.

6. The first catalytic vapor-phase pyrolysis of cinnamic acid.

7. The first observation that ketene and benzaldehyde do <u>not</u> condense in the vapor phase over copper and silica.

8. The first preparation of ethylbenzene by pyrolysis of an equimolar benzaldehyde-acetic anhydride mixture over synthetic silica-alumina.

9. The first determination of a semi-quantitative relationship between the activity and acidity of bentonitic clays and the first observation that such relationship exists with regard to activated aluminas.

10. The first mechanism suggested for the catalytic vapor-phase condensation of aromatic aldehydes and aliphatic anhydrides.

BIBLIOGRAPHY

1. Ostwald, W., Zeitschr. f. Electrochem. 1, p. 1004 (1901)
2. Dow, W., Ind. Eng. Chem. 34, 1267 (1942)
3. Schroeder, C.H., C.R. Report # 455, Sept. 1944
4. Perkin, W.H., J. Chem. Soc. 31, 388 (1877)
5. Knoevenagel, E., Ber. 31, 2596 (1898)
6. Doebner, O., Ber. 33, 2140 (1900)
   35, 1137 (1902)
7. Creamer, G.B., M.Sc. Thesis, Syracuse University, Syracuse, N.Y., 1943
8. Overberger, C.G., Luhrs, E.J., and Chien, P.K., J. Am. Chem. Soc. 72, 1200 (1950)
9. Bernthsen, A., and Bender, F., Ber. 15, 1982 (1882)
10. Walling, Ch., and Wolfstirn, K.B., J. Am. Chem. Soc. 69, 852 (1947)
11. Marvel, C.S., and Hein, D.W., J. Am. Chem. Soc. 70, 1895 (1948)
12. Wiley, R.H., and Smith, N.R., J. Am. Chem. Soc. 70, 1560 (1948)
13. Kunz-Krause, H., Ber. 30, 1617 (1897)
14. Tiedcke, C., Zeitschr. f. Unters. Lebensm. 71, 393 (1936) Chem. Zentr. II., 2038 (1936)
15. Ley, H., Ber. 51, 1808 (1918)
16. Claisen, L., Ber. 29, 1005 (1896)
17. Perkin, W.H., J. Chem. Soc. 32, Vol.II, 660 (1877)
    Ber. 11, 515 (1878)
18. Wiley, R.H., and Hobson, P.H., J. Am. Chem. Soc. 71, 2429 (1949)

19. Carr, E., CR. Report # 1661, Nov. 4, 1947

20. Fries, K., and Fickewirth, G., Ber. 41, 367-373 (1908)

21. Kunz-Krause, H., and Manicke, P., Arch. Pharm. 267, 555 (1929) Chem. Zentr. II., 3004 (1929)

22. Ruhemann, S., J. Chem. Soc. 79, 918 (1901)

23. Grischkewitsch-Trochimowski, J. Russ. Phys.-Chem. Soc. 42, 1543 Chem. Zentr. 1, 1511 (1911)

24. Hudson, B.J.F., and Robinson, R., J. Chem. Soc., 715 (1941)

25. Moureu, Ch., Bull. Soc. Chim. (3) 31, 493 (1904) Chem. Zentr. I., 1602 (1904)

26. Riegel, B., and Wittcoff, H., J. Am. Chem. Soc. 68, 1913 (1946)

27. Reichstein, T., Helv. Chim. Acta 15, 1450 (1932)

28. Phillips, M., and Goss, M.J., Ind. Eng. Chem. 24, 1436 (1932)

29. Ruhemann, S., and Beddow, F., J. Chem. Soc. 77, 984 (1900)

30. Ruhemann, S., and Wragg, E., J. Chem. Soc. 79, 1185 (1901)

31. Ruhemann, S., and Stapleton, H.E., J. Chem. Soc. 77, 1179 (1900)

32. Abbott, T.W., and Johnson, J.R., "Org. Synth.", Coll. Vol. I John Wiley & Sons, New York, N.Y. 1941 p. 440

33. Kraemer, G., and Spilker, A., Ber. 23, 3269 (1890)

34. Perkin, W.H., J. Chem. Soc. 33, 211 (1878)

35. Wiley, R.H., and Smith, N.R., J. Am. Chem. Soc. 70, 2295 (1948) J. Polymer Sci. 3, 444 (1948)

36. Von Braun, J., and Nelles, J., Ber. 66, 1464 (1933)

37. Von Auwers, K., Ann. 413, 253 (1917)

38. Mueller, W., Ber. 20, 1212 (1887)

39. Von Auwers, K., Ber. 45, 2764 (1912)

40. Einhorn, A., Ber. 16, 2208 (1883)

41. Prausnitz, G., Ber. 17, 595 (1884)

42. Basler, A., Ber. 16, 3001 (1883)

43. Fittig, R., and Binder, F., Ann. 195, 131 (1879)

44. Perkin, W.H., Bull. Soc. Chim. (2), 30, 309 (1878)

45. Perkin, W.H., Chemical News, Vol. 36, 211 (1878)

46. Bachman, G.B., and Hellman, H.M., J. Am. Chem. Soc. 70, 1772 (1948)

47. Dreisbach, R.R., and Day, J., U.S. Pat. 2,295,077 to The Dow Chem. Co., Chem. Abstr. 37, 888 (1943)

48. Dourough, G.L., U.S. Pat. 1,892,386 Dec. 27, 1932 to E.I. DuPont de Nemours & Co. Chem. Zentr. I., 2872 (1933)

49. Emerson, W.S., and Lucas, V.E., J. Am. Chem. Soc. 70, 1180 (1948)

50. Woodcock, D.J., J. Chem. Soc. 203 (1949)

51. Ross, S.D., Markarian, M., and Nazzewski, M., J. Am. Chem. Soc. 69, 1914 (1947)

52. Levine, A.A., and Cass, O.W., U.S. Pat. 2,193,823 to E.I.duPont de Nemours & Co. Chem. Abstr. 34, 4746 (1940)

53. Wingfoot Corp., Br. Pat. 571,829 (1947) Chem. Abstr. 41, 3323 (1947)

54. Frank, R.L., Adams, C.E., Allen, R.E., Gander, R., and Smith, P.V., J. Am. Chem. Soc. 68, 1365 (1946)

55. Klages, A., and Keil, R., Ber. 36, 1632 (1903)

56. Inskeep, G.E., and Deanin, R., J. Am. Chem. Soc. 69, 2237 (1947)

57. Klages, A., and Eppelsheim, A., Ber. 36, 3584 (1903)

58. Klages, A., Ber. 37, 2301 (1904)

59. Fosdick, L.S., Fancher, O., and Urbach, K.F., J. Am. Chem. Soc. 68, 840 (1946)

60. Quelet, R., Bull. Soc. Chim. (5), 1, 905 (1934)

61. Quelet, R., and Galse, R., Compt. Rend. 223, 159 (1946)

62. Quelet, R., Compt. Rend., 202, 956 (1936)

63. Sommelet, M., and Marszak, I., Fr. Pat. 787,655; Chem. Zentr. 1., 3217 (1936)

64. Quelet, R., Bull. Soc. Chim. (5), 7, 196 (1940)

65. Quelet, R., and Ducasse, J., Compt. Rend. 208, 1317 (1939)

66. Barger, G., and Jowett, H.A.D., J. Chem. Soc. 87, 967 (1905)

67. Klages, A., Ber. 36, 2574 (1903)
35, 2251 (1902)

68. I.G. Farbenindustrie A.G., Fr. Pat. 729,730; Chem. Zentr. 2, 3015 (1932)

69. Mannich, C., Neumann, P., and Jacobsohn, W., Arch. Pharm. 248, 127 (1910)

70. Schramm, J., Ber. 24, 1332 (1891)

71. Strassburg, R.W., Gregg, R.A., and Walling, Ch., J. Am. Chem. Soc. 69, 2141 (1947)

72. Zal'kind, Yu.S., Berkovich, I.P., and Amusin, M.K., Plast. Mass. I, 14-20 (1934)

73. Smith, O.H., U.S. Pat. 1,687,903 to Naugatuck Chem. Co., Oct. 16, 1929. Chem. Abstr. 23, 156 (1929)

74. Quattlebaum, W.M., and Young, D.M., U.S. Pat. 2,265,312 to Carbide and Carbon Chemicals Corp., Nov. 14, 1940

75. Deluchat, M., Compt. Rend. 192, 1387 (1931)

76. Lespieau, D., and Deluchat, R., Compt. Rend. 190, 683 (1930)

77. Ingle, H., Ber. 27, 2528 (1894)

78. Klages, A., and Allendorff, P., Ber. 31, 998 (1898)

79. Quelet, R., Compt. Rend. 199, 150 (1934)

80. Quelet, R., Bull. Soc. Chim (5), 7, 205 (1940)

81. Perrier, G., Ber. 33, 815 (1900)

82. Mowry, D.T., Renoll, M., and Huber, F., J. Am. Chem. Soc. 68, 1105 (1946)

83. Hunter, W., and Groombridge, W.H., Brit. Pat. 589,015; Chem. Abstr. 41, 6897 (1947)

84. Marvel, C.S., and Overberger, C.G., J. Am. Chem. Soc. 68, 185 (1946)

85. Emerson, W.S., Heyd, J.W., Lucas, V.E., Owens, G.R., and Shortridge, R.W., J. Am. Chem. Soc.
68, 1665 (1946)
69, 1905 (1947)

86. Shorygin, P.P., and Shorygina, N.V., J. Gen. Chem. U.S.S.R. 9, 845 (1939)
Chem. Abstracts 34, 389 (1940)

87. Brown, J.H., and Marvel, C.S., J. Am. Chem. Soc. 59, 1176 (1937)

88. Ziegler, K., and Tieman, P., Ber. 55, 3414 (1922)

89. Quelet, R., Bull. Soc. Chim. (4), 45, 75 (1929)

90. Bachman, G.B., and Lewis, L.L., J. Am. Chem. Soc. 69, 2022 (1947)

91. Marvel, C.S., and Overberger, C.G., J. Am. Chem. Soc. 66, 475 (1944)

92. Marvel, C.S., Allen, R.E., and Overberger, C.G., J. Am. Chem. Soc. 68, 1088 (1946)

93. Sulzbacher, M., and Bergmann, E., J. Org. Chem. 13, 303 (1948)

94. Emerson, W.S., Heyd, J.W., Lucas, V.E., Chapin, E.C., Owens, G.R., and Shortridge, R.W., J. Am. Chem. Soc. 68, 674 (1946)

95. Ushakov, S.N., and Matuzov, P.A., J. Gen. Chem. U.S.S.R. 14, 120 (1944); Chem. Abstr. 39, 916 (1945)

96. Brooks, L.A., J. Am. Chem. Soc. 66, 1295 (1944)

97. Marvel, C.S., and Schertz, G.L., J. Am. Chem. Soc. 65, 2054 (1943)

98. Staudinger, H., and Suter, E., Ber. 53, 1099 (1920)

99. Mowry, D.T., Huber, W.F., and Ringwald, E.L., J. Am. Chem. Soc. 69, 851 (1947)

100. Marvel, C.S., and Overberger, C.G., J. Am. Chem. Soc. 67, 2250 (1945)

101. Marvel, C.S., Overberger, C.G., Allen, R.E., Johnston, H.W., Saunders, J.H., and Young, J.D., J. Am. Chem. Soc. 68, 861 (1946)

102. Michalek, J.C., and Clark, C.C., Chem. Eng. News 22, 1559 (1944)

103. Shamshurin, A.A., J. Gen. Chem. U.S.S.R. 1, 99 (1946)

104. Sachs, F., and Sachs, L., Ber. 38 511 (1905)

105. Marvel, C.S., Overberger, C.G., Allen, R.E., and Saunders, J.H., J. Am. Chem. Soc. 68, 736 (1946)

106. Marvel, C.S., Saunders, J.H., and Overberger, C.G., J. Am. Chem. Soc. 68, 1085 (1946)

107. Gauthier, D., and Gauthier, P., Bull. Soc. Chim (4), 53, 323 (1933)

108. Levy, J., and Dvoleitzka-Gombinska, Bull. Soc. Chim. 49, 1765 (1931)

109. Achalme, P., Compt. Rend. Acad. des Sci. 154, 353 (1912)

110. Renoll, M.W., J. Am. Chem. Soc. 68, 1159 (1946)

111. Mannich, C., and Jacobsohn, W., Ber. 43, 189 (1910)

112. Tiffeneau, M., Ann. Chim. (8) 10, 322 (1907)

113. Pauly, H., and Neukam, N., Ber. 41, 4151 (1908)

114. Eisenlohr, F., and Schulz, L., Ber. 57, 1808 (1924)

115. Bradsher, C.K. and Wert, R.W., J. Am. Chem. Soc. 62, 2806 (1940)

116. Huber, W.F., Renoll, M., Rossow, A.G., and Mowry, D.T., J. Am. Chem. Soc. 68, 1109 (1946)

117. Laage, E., German Patent 533,827 to I.G. Farbenindustrie A.G.

118. Hochwalt, C.A., U.S. Pat. 2,390,368 to Monsanto Chem. Co. Dec. 4, 1945; Chem. Abstr. 40, 1878 (1946)

119. Palfray, L., Sabetay, S., and Sontag, D., Compt. Rend. 195, 1392 (1932)

120. Palfray, L., Sabetay, S., and Sontag, D., Compt. Rend. 196, 622 (1933)

121. Harispe, J.V., Ann. Chim. (11) 6, 249 (1936) Chem. Zentr. 1, 581 (1937)

122. Matui, E., J. Soc. Chem. Ind. Japan, Suppl. Binding, 44, 107 (1941); Chem. Abstr. 38, 3748 (1944)

123. Shorygin, P.P., and Shorygina, N.V., J.Gen. Chem. U.S.S.R. 5, 555 (1935); Chem. Abstr. 29, 6885 (1935)

124. Matui, E., J. Soc. Chem. Ind. Japan 44, 38 (1941)

125. Sabetay, S., Bull. Soc. Chim. (4), 45, 69 (1929)

126. Peytral, E., Compt. Rend. 193, 1199 (1931) Bull. Soc. Chim. 35, 969 (1924)

127. Sabetay, S., Compt. Rend. 192, 1109 (1931)

128. Pfisterer, H.A., and Eastham, A.M., CR Report # 1671, Nov. 4, 1947

129. Ostromislensky, I., and Shepard, M.G., U.S. Pat. 1,552,874 Sept. 8, 1925; Chem. Abstr. 19, 3492 (1925)

130. Stanley, H.M., Brit. Pat. 541, 587 Nov. 13, 1939 to Distillers Co.Ltd.

131. Nickels, J.E., Webb, G.A., Heintzelman, W., and Corson, B.B., Ind. Eng. Chem. 41, 563 (1949)

132. Imperial Chem. Industries Ltd., Brit. Pat. 351,310 (1929) Chem. Abstr. 26, 2990 (1932)

133. Ostromislensky, I., and Shepard, M.G., U.S. Pat. 1,541,175 to Naugatuck Chem. Co., 1925 Chem. Abstr. 20, 424; 3461 (1926)

134. Mark, H., and Wulff, K., Germ. Pat. 550,055 to I.G. Farbenindustrie A.G. (1929)

135. Dow Chemical Co., U.S. Pat. 2,240,764 (1941)

136. Gallay, W.A., Can. J. Research, B16, 6-34 (1938)

137. Hofmann, U., Endell, K., and Humbert, R.P., Z. Krist. 86, 238, 340 (1933)

138. Pauling, L., Proc. Nat. Acad. Sci., U.S.A. 16, 578 (1930)

139. Stinton, A.W., M.Sc. Thesis, McGill University (1945)

140. Wilson, J.N., Sands, Clays and Minerals 2, 45 (1934)

141. Davis, C.W., and Messer, L.R., Amer. Inst. Min. Eng. Tech. Pub. No. 207, 18pp. (1929)

142. Ribet, G., Industria Meccanica 8, 215-217; 280-284 (1936)

143. Ladoo, R.B., The Non-Metallic Minerals, McGraw-Hill Book Co., New York, N.Y. 91-97 (1925)

144. Berg, B.B., and Donitriev, N.W., Liteinoe Delo 9, No. 8-9, 30-35 (1938)

145. Ross, C.B., and Shannon, E.V., J. Am. Ceram. Soc. 9, 77 (1926)

146. Oulten, T.D., U.S. Pat. 2,440,756 to Filtrol Corp. May 4, 1948

147. Thomas, C.L., Hickey, J., and Stecker, G., Ind. & Eng. Chem. 42, 866 (1950)

148. Universal Oil Prod. Co., Ital. Pat. 351,078, May 15, 1937

149. Duffey, H.R., and Snow, R.D., Ind. Eng. Chem. 44, 180 (1934)

150. Schulze, W.A., U.S. Pat. 2,151,721, March 28, 1939

151. Broughton, G., J. Phys. Chem. 44, 180-184 (1940)

152. Wasson, B.K.M., Ph.D. Dissertation, McGill University, 1942

153. Gleason, C.H., Ph.D. Dissertation, McGill University, 1947

154. Bourns, A.N., Ph.D. Dissertation, McGill University, 1944
Can. J. Research, 25B, 80 (1947)
26B, 81 (1948)

155. Tonks, D.B., Ph.D. Dissertation, McGill University, 1949

156. Deans, S., Ph. D. Dissertation, McGill University, 1942

157. Morton, M., Ph.D. Dissertation, McGill University, 1945 J. Can. Research 26B, 581 (1948)

158. Lewis, G.N., "Valence and the Structure of Atoms and Molecules", Chemical Catalog Company, New York, 1923

159. Price, C.C., Chem. Reviews 29, 37 (1941)

160. Bodendorf, K., and Bohme, H., Ann. 516, 1 (1935)

161. Wertyporoch, E., and Firla, T., Ann. 500, 287 (1933)

162. Fairbrother, F., J. Chem. Soc. 503 (1945)

163. Henne, A.L., and Matuszak, A.H., J. Am. Chem. Soc. 66, 1649 (1944)

164. Child, W.C., and Adkins, H., J. Am. Chem. Soc. 45, 3013 (1923)

165. Tischtschenko, W., Chem. Zentr. 77, 1309, 1552 (1906)

166. Conant, J.B., and Bartlett, P.D., J. Am. Chem. Soc. 54, 2881 (1932)

167. Westheimer, F.H., J. Am. Chem. Soc. 56, 1962 (1934)

168. Price, C.C., J. Am. Chem. Soc. 58, 2101 (1936)

169. Pfeifer, P., and Schneider, P., J. prakt. Chem. 129, 129 (1931)

170. Wizinger, R., Zeitschr. angew. Chem. 46, 756 (1933)

171. Lucas, H.J., J. Am. Chem. Soc., 52, 803 (1930)

172. Bowden, E., J. Am. Chem. Soc. 60, 645 (1938)

173. Brown, H.C., J. Am. Chem. Soc. 61, 1483 (1939)

174. Whitmore, F.C., and Bernstein, H., J. Am. Chem. Soc. 60, 2626 (1938)

175. Cox, E.H., J. Am. Chem. Soc. 52, 352 (1930)

176. Kane, H.L., and Lowy, A., J. Am. Chem. Soc. 58, 2605 (1936)

177. Turkevich, J., and Smith, R.K., Div. of Physical and Inorganic Chemistry, 109th meeting of the A.C.S., Atlantic City, N.J., p. 29P (1946)

Turkevich, J., and Smith, R.K., J. Chem. Phys. 16, 466 (1948)

178. Ciapetta, F.G., Ind. Eng. Chem. 37, 1210 (1945)

179. Hansford, R.C., Ind. Eng. Chem. 39, 849 (1947)

180. Norton, F.H., and Hodgdon, F.B., J. Am. Ceram. Soc. 15, 191 (1932)

181. Quattlebaum, W.M., Toussaint, W.J., and Dunn, J.T., J. Am. Chem. Soc. 69, 596 (1947)

182. Grenall, A., Ind. Eng. Chem. 41, 1485 (1949)

183. Thomas, Ch.L., Ind. Eng. Chem. 41, 2564 (1949)

184. Greensfelder, B.S., Voge, H.H., and Good, G.M., Ind. Eng. Chem. 41, 2573 (1949)

185. Whitmore, F.C., Chem. Eng. News 26, 668 (1948)

186. Whitmore, F.C., Ind. Eng. Chem. 26, 94 (1934)

187. Whitmore, F.C., J. Am. Chem. Soc. 54, 3274 (1932)

188. Whitmore, F.C., and Stahly, E.E., J. Am. Chem. Soc. 55, 4153 (1933)

189. O'Kelly, A.A., Kellett, J., and Plucker, J., Ind. Eng. Chem. 39, 154 (1947)

190. Rheinische Kampfer Fabrik, Fr. Pat. 681,049 (1930) Chem. Abstr. 24, 4051 (1930)

191. Sachanen, A.N., and Caesar, P.D., Ind. Eng. Chem. 38, 43 (1946)

192. Schöllkopf, K., U.S. Pat. 1,747,604 (1930)

193. Ipatieff, V.N., Corson, B.B., and Pines, H., J. Am. Chem. Soc. 58, 919 (1936)

194. Wunderley, H.L., Sowa, F.J., and Niewland, B., J. Am. Chem. Soc. 58, 1007 (1936)

195. Simon, J.H., and Archer, S., J. Am. Chem. Soc. 60, 986, 2952 (1938)

196. Francis, A.W., and Reid, E.E., Ind. Eng. Chem. 38, 1194 (1946)

197. Grosse, A.V., and Ipatieff, V.N., J. Org. Chem. 1, 559 (1936)

198. Schorger, A.W., J. Am. Chem. Soc. 39, 2671 (1917)

199. Boedtker, E., and Halse, O.M., Bull. Soc. Chim. (4) 19, 444 (1916)

200. McKee, R.H., Can. Pat. 181,426, Jan. 1, 1918

201. Ipatieff, V.N., Pines, H., and Komarewski, V.I., Ind. Eng. Chem. 28, 222 (1936)

202. Hartough, H.D., Kosak, A.I., and Sardella, J.J., J. Am. Chem. Soc. 69, 1014 (1947)

203. Weinmayr, V., J. Am. Chem. Soc. 72, 918 (1950)

204. Egloff, G.; see Gillman "Organic Chemistry", 2nd edition, John Wiley & Sons, Inc., New York, 1943, Chapter 1

205. Gayer, L., Ind. Eng. Chem. 25, 1122 (1933)

206. Burk, R.E., Twelfth Catalysis Report, Natl. Res. Counsil, John Wiley & Sons, Inc., New York, N.Y. 1940 p. 192

207. Hay, R.G., Montgomery, C.W., and Coull, J., Ind. Eng. Chem. 37, 335 (1945)

208. Ciapetta, F.G., Macuga, S.J., and Leum, L.N., Ind. Eng. Chem. 40, 2091 (1948)

209. Moldowski, B.L., and Bezedel, L.S., J. Gen. Chem. U.S.S.R. 16, 1633 (1946)

210. Gomberg, M., J. Am. Chem. Soc. 22, 757 (1900) Ber. 33, 3150 (1900)

211. Paneth, F., and Hofeditz, W., Ber. 62, 1335 (1929)

212. Rice, F.O., and Herzfeld, K.F., J. Am. Chem. Soc. 56, 284 (1934)

213. Kossiakoff, A., and Rice, F.O., J. Am. Chem. Soc. 65, 590 (1943)

214. Voge, J.H., and Good, G.M., J. Am. Chem. Soc. 71, 593 (1949)
Greensfelder, B.S., Voge, H.H., and Good, G.M., Ind. Eng. Chem. 41, 2573 (1949)

215. Staveley, L.E.K., and Hinshelwood, C.N., Proc. Roy. Soc. A154, 335 (1936); ibid. A159, 192 (1937)

216. Rice, F.O., and Rodowskas, E.L., J. Am. Chem. Soc. 57, 350 (1935)

Steacy, E.W.R., and Shaw, G.T., J. Chem. Phys. 2, 345 (1934)

217. Eley, D., and Rideal, E.K., Proc. Roy. Soc. A178, 429 (1941)

218. Melville, H.W., Ann. Rpts of the Chem. Soc. 35, 71 (1939)

219. Parravano, G., Hammel, E.F., and Taylor, H.S., J. Am. Chem. Soc. 70, 2269 (1948)

220. Morikawa, K., Benedict, W.S., and Taylor, H.S., J. Am. Chem. Soc. 58, 1445, 1795 (1936)

221. Farkas, A., Farkas, L., and Rideal, E.K., Proc. Roy. Soc. A146, 630 (1934)

222. Bremner, G.M., and Keys, R.K.F., J. Chem. Soc. 1068 (1947)

223. Ipatieff, V.N., and Komarewsky, V.I., J. Am. Chem. Soc. 59, 720 (1937)

224. Vesterberg, A., Ber. 36, 4200 (1903)

225. Diels, O., and Karsten, A., Ber. 60, 2323 (1927)

226. Wood, W.H., and Capell, R.G., Ind. Eng. Chem. 37, 1148 (1945)

227. Marshall, C.E., Zeitschr. Krist. (A) 91, 433 (1935)

228. Adam, N.K., "The Physics and Chemistry of Surfaces", The Clarendon Press, Oxford 1930, chapt. VIII

229. Daniels, F., Paper presented at Meeting of Society of the Sigma Xi McGill Chapter, Nov. 3, 1949

230. Williams, G., J. Chem. Soc. pp. 246-53 (1938)

231. D'Alelio, G.F., "Experimental Plastics & Synthetic Resins", John Wiley & Sons, Inc., New York, N.Y., 1946, p. 177

232. Seyewetz, A., and Bardin, Bull. Soc. Chim. (3) 33, 1000 (1905); J. Soc. Chem. Ind. 25, 202 (1906)

233. Marvel, C.S., and Overberger, C.G., J. Am. Chem. Soc. 68, 185 (1946)

234. Han-Ying Li, J. Chem. Soc. Japan 62, 562 (1941)

235. Hinshelwood, C.N., and Hutchison, W.K., Proc. Roy. Soc. (London) A111, 245 (1926)

236. Dowden, D.A., J. Chem. Soc. p. 264 (1950)

237. Ostromislensky, I., Can. Pat. 261,326, June 1, 1926 Chem. Abstr. 20, 3461 (1926)

238. Dippy, J.F.J., and Evans, R.M., J. Org. Chem. 15, 451 (1950)

239. Hammett, L.P., "Physical Org. Chemistry", McGraw Hill Book Co., New York, N.Y., 1940, p. 343

240. Hauser, C.R., and Breslow, D.S., J. Am. Chem. Soc. 61, 786 (1939)

241. Clarke, H.T., and Waring, C.E., U.S. Pat. 1,723,724, Aug. 6, 1929 to Eastman Kodak Co.

242. Staudinger, H., and Klever, H.W., Ber. 41, 594 (1908)

243. Hurd, C.D., and Thomas, C.L., J. Am. Chem. Soc. 55, 275 (1933)

244. Davison Chemical Corporation, Private Communication

245. Shankland, R.V., and Schmitkons, G.E., Proc. Am. Petr. Inst. 27, III, 57 (1947)

246. Descriptive Literature on "Activated Aluminas" published by Aluminum Company of America, Jan. 12, 1950

247. Aluminum Company of America, Private Communication

248. Maxted, E.B., J. Soc. Chem. Ind. 67, 93 (1948)

249. Levina, R.Ya., J. Gen. Chem. U.S.S.R. 9, 2287 (1939)

250. Mme. Ramart-Lucas, and Mlle. P. Amagat, Bull. Soc. Chim. 51, 108 (1932)

251. Rügheimer, L., Ann. 172, 131 (1874)

252. Kharasch, M.S., Lambert, F.L., and Urry, W.H., J. Org. Chem. 10, 298 (1945)

Magnani, A., and McElvain, S.M., J. Am. Chem. Soc. 60, 813 (1938)

253. Campbell, T.W., Linden, S., Godshalk, S., and Young, W.G., J. Am. Chem. Soc. 69, 880 (1947)

254. Young, W.G., Professor of Chemistry, University of California, Los Angeles, Cal., Private Communication

255. Radiszewski, Br., Ber. 9, 261 (1876)

256. Man, H.E., Sanderson, J.J., and Hauser, C.R., J. Am. Chem. Soc. 72, 847 (1950)

257. Hauser, C.R., and Adams, J.T., J. Am. Chem. Soc. 66, 345 (1944)

Adams, J.T., and Hauser, C.R., J. Am. Chem. Soc. 67, 284 (1945)

258. Böck, F., Lock, G., and Schmidt, K., Monatshefte 64, 401 (1934)

259. Posner, T., J. prakt. Chem. (2) 82, 425 (1910)

260. Johnson, J.R., "Organic Syntheses" Vol. 20, 55 (1940)

261. Biedermann, A., Ber. 19, 1853 (1886)

262. King, W.J., and Nord, F.F., J. Org. Chem. 14, 407 (1949)

263. Graham, R.P., and Thomas, A.W., J. Am. Chem. Soc. 69, 816 (1947)

Thomas, A.W., and Clay, J.P., J. Am. Chem. Soc. 60, 2384 (1938)

264. Davidson, R.C., Ewing, F.J., and Shute, R.S., Natl. Petroleum News 35, No. 27R, 318 (1943)

265. Dewar, M.J.S., "The Electronic Theory of Organic Chemistry", The Clarendon Press, Oxford, 1949 p. 126

266. Branch, G.E.K., and Calvin, M., "The Theory of Organic Chemistry", Prentice-Hall, Inc., New York, N.Y., 1941, p. 464

267. Remick, A.E., "Electronic Interpretations of Organic Chemistry", John Wiley & Sons, Inc., New York, N.Y., 1949, p. 470