POSSIBLE MECHANISMS FOR THE THERMAL DECOMPOSITION OF NITROCELLULOSE

A Thesis

by

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Ph.D. Chemistry

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POSSIBLE MECHANISMS FOR THE THERMAL DECOMPOSITION OF NITROCELLULOSE

Two specially synthesized cellulose nitrates are subjected to thermal decomposition, for the purpose of gaining information regarding the reaction mechanism. For these studies, an all-glass apparatus was constructed which recovered the reaction products quantitatively, and with which it was possible to work at fairly low pressures and at a variety of temperatures. This equipment was designed to accentuate the primary decomposition reaction.

Analytical methods are adapted for estimating the composition of the reaction products, both volatile and non-volatile. The analytical data are tabulated, and certain generalizations are apparent on the basis of this data. In conclusion, an attempt is made to explain the results of this investigation on theoretical grounds.

GENERAL INTRODUCTION

The object of this research has been to gain information regarding the mechanism of thermal decomposition of cellulose nitrate. It is believed that a thorough knowledge of the primary reactions involved in this decomposition would go far toward elucidation of the complicated burning mechanism of cordite and other propellants containing guncotton.

The reactions which occur during the thermal decomposition of the simplest nitrate ester are rather complex. This complexity is far more apparent with a material such as cellulose nitrate, which in the fully nitrated condition contains three ester groups per glucose residue. Recent work concerning reactivity of cellulose hydroxyls and of their derivatives gives good reason to believe that the two secondary nitrate groups and the primary nitrate group may all behave quite differently during decomposition.

All previous investigations in this field have been made using technical cellulose nitrates (12.6 - 13.4% N) which are fairly completely substituted, and in which the substitution is random in nature. Very recently it was found possible in these laboratories to synthesize nitrated celluloses by means which pre-determine structure(1). Thus there is now available a derivative which corresponds approximately to a partly acetylated cellulose-6-mononitrate. It has been demonstrated that a very large proportion of the nitrate groups in this compound actually do occupy the primary or sixth position. Furthermore, nitration of this "mononitrate" by methods which ordinarily yield a fully nitrated cellulose, has been found to yield what very nearly corresponds to a cellulose dinitrate containing a few acetyl groups.

Existence of these two compounds represents an immense simplification in the study of cellulose nitrate reactions, because of the nature of their substitution. It was hoped that controlled thermal decomposition of these derivatives would bring to light some of the inherent differences, if any, in the thermal behaviour of the primary and secondary nitrate ester groups of cellulose. The preparation of these substances has been discussed only briefly in this dissertation, since a more detailed account of the original syntheses is available (1).

The methods used for the study of this thermal decomposition differ in one significant respect from what seems to have been the ordinary approach. Initial products of the decomposition are removed continuously from the reaction zone, a procedure which in itself represents no innovation; however, in addition, these products are separated into two fractions as they form by means of condensation in dry-ice and liquid-air traps. This separation is believed to terminate all subsequent or secondary reactions, which in so many previous researches have confused the issue. Some very rapid secondary reactions may occur before the initial cleavage products are condensed and separated, but once fractionation has occurred no further interaction is possible even in the working up of the condensates.

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HISTORICAL INTRODUCTION

A review of the work which has been done on the thermal decomposition of cellulose nitrates must necessarily contain a summary of analogous experiments which involve simpler nitrate esters. The behaviour of alkyl mononitrates and of monomeric polynitrates when subjected to heat gives some indication of what may be expected from the heating of cellulose nitrates.

The following summary of previous work in this field cannot under any circumstances be considered comprehensive. Many of the publications are in obscure journals and available only in abstract form. Furthermore, it is certain that a large volume of the research on nitrate esters, especially those of significance as military explosives, has not appeared in technical journals, coming under the category of secret research. Reports of war-time research in this field in Great Britain and United States have been available and are included in this summary in abbreviated form.

1. Simple Alkyl Mononitrates:

The decomposition of methyl nitrate has been studied by Appin, Chariton and Todes (2). It was found that at temperatures of from 210°C to 240°C, and at 5mm. to 15mm. pressure, nitrogen dioxide occurred as one of the primary products of decomposition. The final reaction products contained formaldehyde and nitric oxide, and it was postulated that the nitrogen dioxide originally formed disappears as a result of secondary reactions, giving rise to nitric oxide. The primary reaction suggested is:

$$CH_3ONO_2 \longrightarrow 1/2(HCHO) + 1/2(CH_3OH) + NO_2.$$

Further work was done in the temperature range of 256-324°C (3), and it was observed that under these conditions decomposition was more complete than at temperatures below 240°C. The reactions were in reality explosions. On the basis of analyses of the products of these explosions, two possible primary high-temperature mechanisms were advanced:

$$CH_3ONO_2 \longrightarrow HCHO + 1/2(H_2O) + 1/2(NO_2) + 1/2(NO)$$

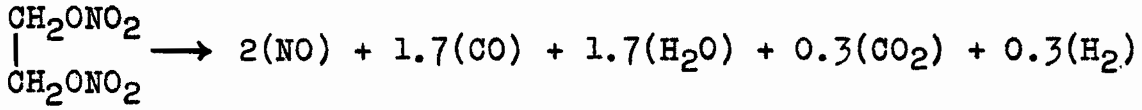
$$CH_3ONO_2 \longrightarrow 1/2(HCHO) + H_2O + 1/2(CO) + NO.$$

Recent work in Great Britain (4) has shown that ethyl nitrate decomposes in a manner quite similar to that of the methyl homologue. The reaction was studied in the temperature range of 180-215°C, and also at temperatures above 220°C, at pressures from 30 to 50mm. Above 220°C, the decomposition was spontaneous, resembling a mild explosion. For the lower temperature reaction, it was suggested that the primary step is the breaking of the $O-NO_2$ bond, giving nitrogen dioxide and the free-radical $CH_3CH_2O\bullet$, the latter then being oxidized to acetaldehyde and further to carbon monoxide and carbon dioxide by the nitrogen dioxide first formed.

Denigès (5) has examined the explosive decomposition of a series of nitric esters, and is of the opinion that primary esters tend to produce aldehydes, and secondary esters tend to produce ketones upon thermal cleavage of the O-NO_2 bond. Work was done on methyl and ethyl nitrate, which yielded formaldehyde and acetaldehyde respectively, and also on the nitrate esters of isopropyl alcohol and of α-phenyl ethyl alcohol, which were found to yield acetone and acetophenone, respectively.

2. Monomeric Polynitrates:

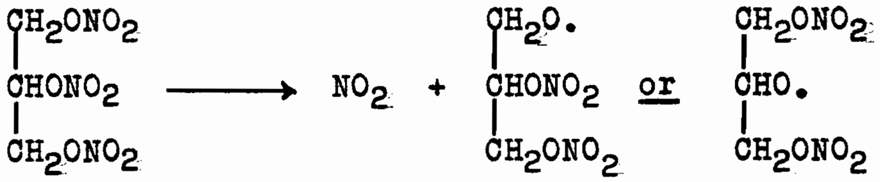
Inflammation of nitroglycol has been investigated by Andreew (6) and by Belajew (7). Analyses of the gases produced indicated that decomposition was very extensive. From analytical data, the break-down may be represented by:



$$\begin{matrix}CH_2ONO_2\\ |\\ CH_2ONO_2\end{matrix} \longrightarrow 2(NO) + 1.7(CO) + 1.7(H_2O) + 0.3(CO_2) + 0.3(H_2)$$

There seems to be no recorded study of decomposition of nitroglycol under milder conditions (i.e. at temperatures below the inflammation point), nitroglycerine having been investigated more fully than nitroglycol. Robertson (8), who followed the decomposition of nitroglycerine by continuous removal of the products, and by spectroscopic determination of the gases produced, found that nearly all the nitrogen was disengaged as nitrogen dioxide. Roginski (9) demonstrated the powerful catalytic nature of nitrogen dioxide in facilitating decomposition of nitroglycerine, and observed that in a closed system this initial product causes autocatalysis of the reaction.

Bawn (10) suggests the following picture for low temperature decomposition of nitroglycerine, assuming continuous removal of the reaction products:



$$\begin{matrix} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{matrix} \longrightarrow NO_2 + \begin{matrix} CH_2O\cdot \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{matrix} \ \underline{\text{or}} \ \begin{matrix} CH_2ONO_2 \\ | \\ CHO\cdot \\ | \\ CH_2ONO_2 \end{matrix}$$

Formaldehyde and other aldehydic residues may be expected from a break-down of the above free-radicals. Further, Bawn (10) anticipates that the aldehydic substances cleave in the presence of nitrogen dioxide to give carbon oxides, the nitrogen dioxide being reduced to nitric oxide or nitrogen. He points out that the latter reactions are known to be exothermic, and that they will result in pronounced self-heating which can ultimately lead to explosion. Audibert (11) found no nitric oxide or nitrogen dioxide in the gases resulting from explosive decomposition of nitroglycerine, which may indicate that a somewhat different mechanism is involved when the compound breaks up under detonating conditions. From analytical data he was able to establish the following equation for the so-called "explosive reaction":

$$C_3H_5(NO_3)_3 \rightarrow 2(CO) + CO_2 + 2.5(H_2) + 1.5(N_2O) + 1.75(O_2).$$

Thermal decomposition in the range of 130 to 140°C of pentaerythritol tetranitrate (P.E.T.N.) has been studied by Hay and Pollard (12). They found that nitrogen dioxide was first produced but subsequently diminished in amount, showing that it was consumed by a secondary reaction. This behaviour is paralleled in the case of methyl nitrate. The final gaseous products of the decomposition of P.E.T.N. were mainly nitric oxide, carbon monoxide and carbon dioxide, with smaller amounts of nitrogen dioxide, nitrogen and nitrous oxide. In addition, a deposit of formaldehyde polymer was found in the reaction chamber. The most probable primary stage was considered to be loss of NO_2 according to:

$$-CH_2ONO_2 \longrightarrow HCHO + NO_2$$

and the carbon monoxide, carbon dioxide and nitric oxide arise from the oxidation of formaldehyde:

$$HCHO + NO_2 \longrightarrow CO + NO + H_2O \qquad \underline{\text{or}}$$

$$HCHO + 2NO_2 \longrightarrow CO_2 + 2NO + 2H_2O.$$

3. Cellulose Nitrates:

From measurements of the gases evolved when nitrocellulose is heated at different temperatures and under various conditions, Will (13) came to the conclusion that when volatile products of decomposition are continuously removed from the system, the nitrogenous gases consist mostly of nitric oxide. Saposhnikov (14) arrived at a similar conclusion from the thermal decomposition of pyroxylin at 120 to 160°C, in which nitric oxide appeared to be the principal nitrogen gas evolved.

The predominance of nitric oxide as a reaction product of nitrocellulose decomposition has been noted in more recent investigations. Koehler and Marqueyrol (15), who examined the gases evolved by heating nitrocellulose in a vacuum, found that from 40 to 100°C, the gas composition did not vary much with temperature; nitric oxide was present to the extent of 60-65%, carbon dioxide was detected in appreciable amounts, and the balance of the gas mixture was found to be mainly carbon monoxide, nitrous oxide and nitrogen. Heating nitrocellulose for long periods at 110°C gave a gas which was nearly 50% nitric oxide, according to Landon (16). It is also reported by Hale (17) that much nitric oxide is given off in decompositions of nitrocellulose, and furthermore that nitrogen dioxide added to the system promotes the decomposition.

Vandoni (18) obtained a gas mixture from heating nitrocellulose at 108°C in the absence of air, which contained over 60% carbon dioxide, and in which the chief nitrogen gas was nitrous oxide, not nitric oxide. Another case in which carbon dioxide was found to be the predominant gas in nitrocellulose decomposition is referred to by Muraour (19) in quoting from the work of Saposhnikov. Saposhnikov obtained gas mixtures from decompositions in the range of 120 to 150°C, the composition of which varied considerably with temperature. At 120°C and 135°C, nitrogen was the chief nitrogen gas, whereas at 150°C nitric oxide was predominant. In his own work, Muraour (20) observed that nitrous oxide is produced during the low-temperature (110° C) thermal decomposition of nitrocellulose. He also found that burning of nitrocellulose in a confined space yielded appreciable amounts of hydrogen cyanide. It was assumed that nitroxyl formed as an intermediate in the decomposition, and that it could react with methane at high temperatures to produce hydrogen cyanide, and could break up into nitrous oxide and water at low temperatures.

The foregoing accumulation of data suggests rather strongly that the nitrogen present in the nitrocellulose reappears as nitric oxide in thermal decomposition and that, depending on conditions, the gases nitrous oxide and nitrogen may arise to some extent from the nitric oxide as a result of subsequent oxidations. There is no real evidence in the work so far reviewed that nitric oxide is a primary decomposition product. In other words, the possibility of the appearance of nitric oxide as a secondary effect, could not be denied.

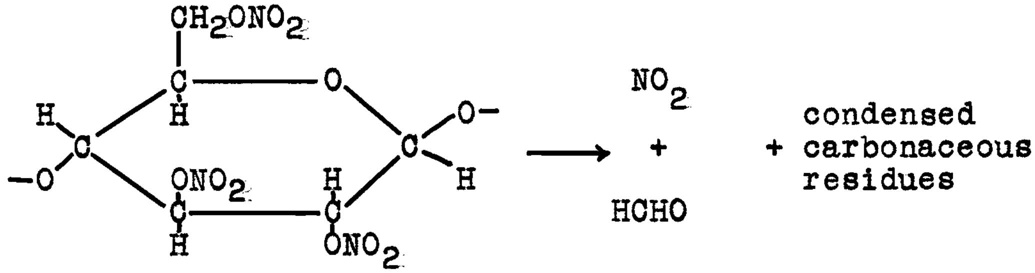
It seems to be generally accepted today that the initial product of the thermal decomposition of nitrocellulose is nitrogen dioxide and that nitric oxide is formed by an oxidative attack of the nitrogen dioxide on both the solid residue and the low molecular weight carbon-containing compounds which cleave from the residue. at an early stage of the decomposition. The development of this concept will be outlined briefly from a historical point of view.

In 1909, Robertson (8) conducted the first experiment which was designed to give information regarding the primary nature of the decomposition. He followed the reaction by spectroscopic determination of the nitrogen dioxide produced, nitroglycerine being examined in the same way. With nitrocellulose, he found that about 40% of the nitrogen was liberated as nitrogen dioxide. It will be recalled that an even higher proportion of this product was observed in nitroglycerine decomposition.

More recently, Goujon (21) carried out the Will stability test at 135°C on samples of nitrocellulose, the heating being continued for eight hours, and the system being continuously swept with dry nitrogen in order to minimize secondary reactions. The results showed that nearly all of the nitrogen of the nitrocellulose was disengaged as nitrogen dioxide.

It was on the basis of such information, plus data from careful experiments on the thermal decomposition of methyl nitrate (2) and ethyl nitrate (3), that Bawn (22) suggested a mechanism for the decomposition of nitrocellulose, which depends on the primary cleavage of nitrogen dioxide. Bawn actually extended the reasoning to explain the observed products of decomposition of cordite.

He assumed that cleavage of nitrogen dioxide was the primary reaction with nitroglycerine, as well as with nitrocellulose. The mechanism postulated for the latter case is as follows:



The nitrogen dioxide formed at first, disappears very quickly in secondary reactions unless removed from the system. Bawn considers that the chief reaction by which nitrogen dioxide is used up, is the oxidation of aldehydic materials. For example:

$$HCHO + NO_2 \longrightarrow CO + NO + H_2O \text{ -------------- } (1)$$

$$HCHO + 2NO_2 \longrightarrow CO_2 + 2NO + H_2O \text{ ------------ } (2)$$

$$(CHO)_2 + NO_2 \longrightarrow 2CO + NO + H_2O \text{ ------------- } (3).$$

Such reactions explain the high proportions of carbon monoxide and nitric oxide in products of the decomposition.

Bawn and co-workers (23) have investigated the reactions of nitrogen dioxide with formaldehyde, in order to substantiate such assumptions. With mixtures of nitrogen-dioxide and formaldehyde in the ratio of 2:1, subjected to temperatures from 116°C to 163°C, yields of nitric oxide, carbon monoxide and carbon dioxide were obtained which could be explained quantitatively by the occurrence of reactions

1 and 2. Thus, additional evidence has been provided for the suggested mechanism of decomposition of these esters.

In attempts to determine a possible mechanism for the thermal decomposition of nitrocellulose, Frazer and co-workers (24) observed that sheets of nitrocellulose yielded (a) a "white substance" (WS), and (b) a "red substance" (RS), when decomposed in air or in unreactive gases, at pressures of 2-10mm. The apparatus used for this investigation has been thoroughly described (25,27). In operation, the nitrocellulose is actually ignited, not slowly heated; the WS remains in the reaction chamber, while the RS passes over into a trap cooled by acetone and dry-ice mixture. Investigation of the chemical nature of these two products has formed the basis for a very extensive program of research. The principal worker in this field has been Wolfrom (26,27), although intermittantly Elderfield (28) and Frazer have been associated with the project.

It is worthwhile to consider yields of products which were obtained from this decomposition reaction, since the percent overall recovery is of great importance in assessing the significance of the results. Yields of WS were in the range of 40-55%, and RS in the range of 30-45%, giving overall recoveries of 70-100%, on the basis of the original nitrocellulose. The crude WS was purified by precipitation from methanol solution into water, and subsequent investigations were made only on this so-called purified "white substance" (PWS) which was obtained in 40% overall yield.

Prior to working up the RS, oxides of nitrogen were allowed to boil off from the liquid. Exactly what weight loss this represents has not been mentioned. Furthermore, the RS deposited a small amount of oxalic acid on standing, and these crystals were removed before proceeding with the analysis. Analyses of RS showed a typical composition in percentages approximately as follows (26):

Table I

Composition of the "Red Substance"

	From Nitrocellulose (12.6% N)	From Nitrocellulose (13.4% N)
Formaldehyde	4	8
Glyoxal	21	15
Formic Acid	24	19
Acetic Acid	5	7
Water	16	17
Ethyl Acetate	9	-
Nitric + Nitrous Acids	trace	-
Total:	79%	66%

The RS was actually collected and analyzed in two portions, which differed somewhat in composition. The above values have been calculated from the individual analyses reported, taking into account the relative weights of the two fractions. The ethyl acetate and acetic acid no doubt arise from retained solvent, since the nitrocellulose sheets used for these decompositions were cast from ethyl acetate solution. Analysis is by no means complete, but there is a fairly good picture of the general composition of the "red substance".

Most of the interest in this investigation has centered on the elucidation of the chemical nature of the purified "white substance". It was readily seen that this substance was a nitric acid ester of carbohydrate aldehydes and acids, containing about six hexose units per molecule. Obviously the nitrocellulose is not decomposed uniformly to such a substance; rather, PWS represents the least altered portion of the crude WS, and other portions of the original nitrocellulose are changed to a greater extent. Products of more advanced decomposition were presumed to be present in the water-soluble fraction from PWS preparation. This large fraction (50-60%) of the original solid residue (WS), which was soluble in methanol-water, was concluded to be a lower molecular weight material of the same general nature as PWS, which had been more drastically altered. Even yet, very little work has been done on this large fraction.

On the basis of methods for cellulose analysis which are available today, Wolfrom (29) was able to postulate an average picture for the group of substances composing PWS.

This cellohexaose derivative is reproduced in Fig. 1.

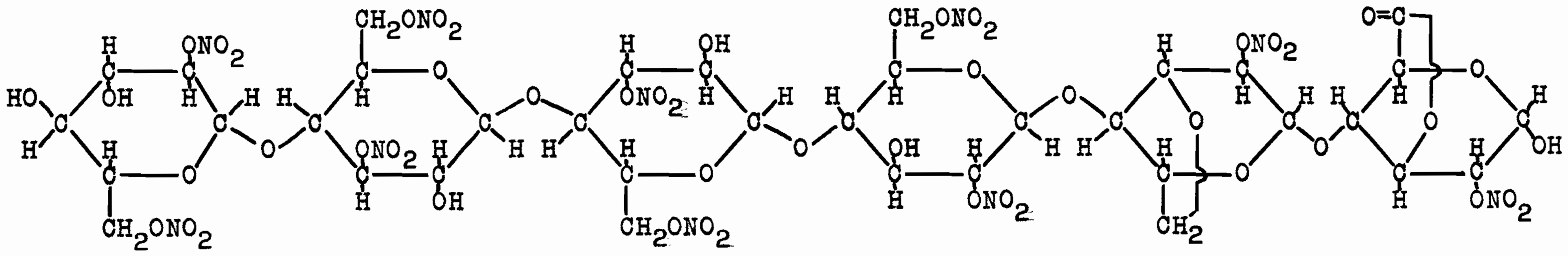
For some time, Wolfrom has been engaged in a study of PWS by methods which primarily involve de-nitration and chromatographic analysis of the saccharides formed (30). Certain evidence has come to light, but the problem of the chemical nature of this nitrated oxycellulose has not yet been completely solved.

By making use of data compiled on the chemical nature of WS and RS, Rice and Ginell (31) have recently put forward a free-radical mechanism for the thermal decomposition of nitrocellulose. They assume that the first attack is on the primary nitrate group, from which nitrogen dioxide splits off. This cleavage results in the establishment of a free-radical on the residue, the un-paired electron being resident on the oxygen atom of the former nitrate group. As a consequence of this condition, Rice and Ginell postulate that a chain of free-radical reactions occurs, which in step-wise fashion leads to cleavage of the glycosidic links.

A chart of the process has been drawn up, and is reproduced in detail in Fig. 2. The process begins with a hexose unit which has already been cleaved from one of the neighboring units. The residue is a free-radical, with the un-paired electron situated on the oxygen atom of the former glycosidic link. The authors say that there is justification for assuming the presence of such a free-radical in the steady-state burning of nitrocellulose. Two courses are possible for the subsequent degradation, depending on which of the bonds adjacent to the active center is ruptured first. From known data regarding the activation energies of analogous reactions, it has been concluded that these two processes are equally probable.

FIG. 1

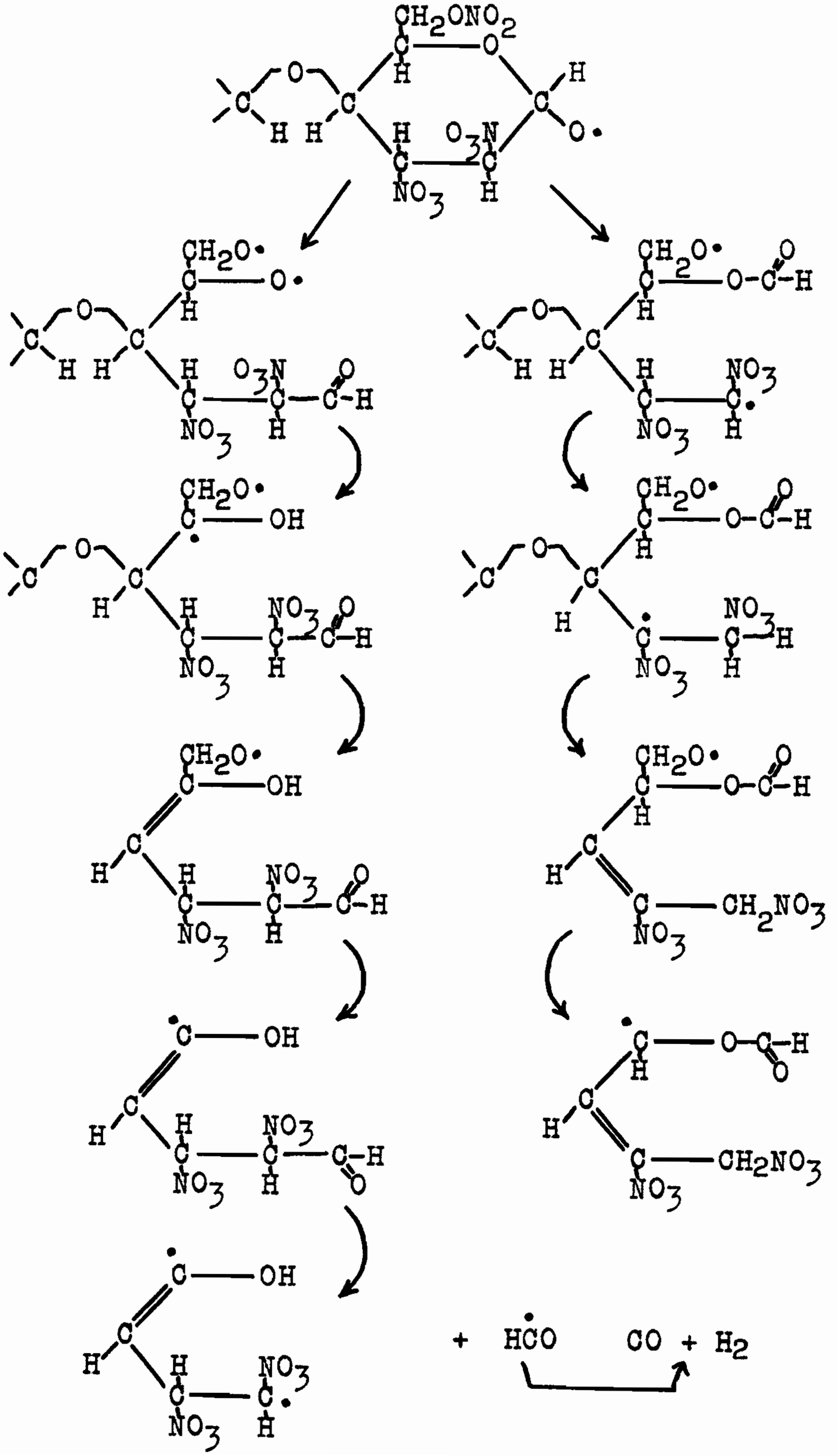
AVERAGE PICTURE FOR PWS (WOLFROM)



Empirical Formula: $C_{36}H_{46}O_{50}N_{10}$

FIG. 2

MECHANISM FOR NITROCELLULOSE DECOMPOSITION (RICE and GINELL)



Gases Evolved

1 mol NO_2

1 mol HCHO (polymerizes)

0.43 mol CO
0.27 mol H_2

EXPERIMENTAL PROCEDURES

A. SYNTHESIS OF A "CELLULOSE-6-MONONITRATE" AND OF A "CELLULOSE DINITRATE"

1. Cellulose from Technical Cellulose Acetate:

Technical cellulose acetate (116 g.; 38.6% acetyl; substitution 2.33) was heated under reflux with 3.2 liters of sodium methylate (0.0382 N) for three hours. The regenerated cellulose was recovered by filtration, and after thorough washing with distilled water, was pressed on the filter to remove as much water as possible. A moisture determination made on a portion of the water-wet cellulose permitted calculation of the dry-weight, which was 69 grams, representing a yield of 95%.

2. 6-Trityl Cellulose:

Regenerated cellulose (67 g.) was solvent-exchanged into anhydrous pyridine with one 800 ml. portion of pyridine-water azeotrope, and then with three 1000 ml. portions of anhydrous pyridine. The cellulose was treated with trityl chloride (270 g.) dissolved in anhydrous pyridine (1000 ml.). This etherification was allowed to proceed for forty-eight hours, with continuous stirring and heating on the steam bath (90-95°C). The completely homogeneous reaction mixture was poured with vigorous stirring into methanol (9 liters), and the product separated as light brown clots. This precipitate was filtered, washed in methanol (3 liters), and dried in air. The crude product was purified by precipitation from pyridine solution (1 liter) into methanol (3 liters) and was subsequently washed with hot water. Weight of dry product, 146 grams. Yield, 85% on the basis of trityl analysis.

Anal. $(C_6H_5)_3COH$: 61.1, 61.5%

All trityl determinations were by the method of Hearon, Hiatt and Fordyce (32).

3. 6-Trityl Cellulose Monoacetate:

Trityl cellulose (140 g.) was dissolved in dry pyridine (1.8 liters). Acetic anhydride (0.9 liters), cooled to -15°C, was added to the pyridine solution, also cooled to -15°C. The resulting mixture was maintained at this temperature for one hour, and then allowed to stand at room temperature for six days. The brown gel was broken up and added to ice-water (10 liters); a treatment which did not seem to decompose the pyridine-acetic anhydride-"trityl acetate" complex. Treatment with light petroleum ether (12 liters) succeeded in extracting the organic solvents, and left the "trityl acetate" in the form of brown horny chips. Purification was by solution in chloroform (1.2 liters) and subsequent precipitation in a fine stream into light petroleum ether (15 liters). The product separated as a continuous filament, yellow in colour. Weight, 168 grams.

Anal. Calculated for cellulose with 0.90 trityl and 0.91 acetyl groups: C,71.6; H,5.85; $(C_6H_5)_3COH$,52.3; CH_3CO,9.4. Found: C,71.8,72.5; H,6.00,6.16; $(C_6H_5)_3COH$,52.5,52.1; CH_3CO,9.60,9.16%.

All acetyl determinations were by the method of Cramer, Gardner and Purves (33).

4. Monoacetyl Cellulose-6-Nitrate:

Trityl cellulose monoacetate (134 g.) was dissolved in dry chloroform (2 liters), and the resulting solution treated with a nitrating mixture prepared by dissolving phosphoric anhydride (62 g.) in 99% nitric acid (835 ml.). The reaction mixture was kept at -15°C for twenty minutes, then brought to room temperature. After standing for one hour, the mixture was poured into ice-water (16 liters), and the large brown lumps which separated were broken up manually. The shredded product was washed with a saturated sodium bicarbonate solution, and finally washed with water and dried. The product was purified by solution in peroxide-free dioxane (1.6 liters) followed by precipitation into distilled water (15 liters). Weight of the dry product, 76.5 grams. To remove a slight yellow tinge, the material was subjected to further purification by precipitation from dioxane solution into water. A white, fluffy product was obtained, but the yield was reduced to 66 grams. Yield, 80% on the basis of analysis.

Anal. Calculated for cellulose with 1.20 nitrate and 0.91 acetyl groups: C,36.8; H,4.20; N,6.57. Found: C,37.1,37.2; H,4.45,4.35; N,6.50,6.55,6.55,6.68%

All nitrogen determinations were by a semi-micro Kjeldahl method (35).

5. Rate of De-acetylation of the 6-nitrate acetate:

A sample of the 6-nitrate acetate (1.270 g.) was dissolved in dry peroxide-free dioxane, and the solution made up with the pure solvent to a volume of 250 ml. in a graduated flask. Aliquots (10 ml.) were removed, standard sodium hydroxide (5 ml., 0.1945 N) was added to each, and the resulting solutions were titrated with standard sulfuric acid at different time intervals. It was possible in this way to determine the extent of saponification as a function of time. The results of this experiment are given in Table II; and the plot of time versus mols "acetyl" removed appears in Fig. 4.

Table II

Rate of De-Acetylation of the 6-Nitrate Acetate

Time (Minutes)	Grams NaOH per gram of Nitrate-Acetate	Mols acetyl removed (a)
0.5	0.074	0.44
1	0.125	0.74
1.5	0.157	0.93
2	0.169	1.00
3	0.189	1.12
4	0.203	1.20
6	0.208	1.23
17	0.236	1.40
30	0.242	1.43
60	0.250	1.48

(a; these values naturally incorporate the nitrate ester which has reacted with the alkali, and which is not necessarily removed on a mol per mol basis by the alkali).

6. Cellulose-6-Nitrate:

(a) Preliminary preparations:

The conditions used for the large scale de-acetylation of the cellulose nitrate monoacetate were arrived at from the data obtained in two preliminary experiments. These experiments are summarized in Table III.

Table III

Preliminary De-Acetylations

	A	B
Mols nitrate-acetate	0.0158(4.015g)	0.0129(3.274g)
Mols NaOH	0.0190	0.0122
Mols NaOH per mol nitrate-acetate	1.20	0.95
Yield (grams)	2.033	1.533
Percent nitrogen	7.06,7.17	7.45,7.25
Nitrate substitution	1.06	1.12

The yields were low in these de-acetylations, but fortunately this proved to be a characteristic only of the small scale on which they were carried out. It was possible to recover an additional 0.38 grams of product B from the colloidal mother liquor of the filtration, by first flocculating the colloidal solution , and then centrifuging. These colloids could be flocculated with inorganic salts such as sodium sulfate, or even with small amounts of mineral acids. The washings from such a separation as described above were colloidal, indicating that a further recovery was possible. In any case, the additional 0.38 grams of product B had identically the same analysis as the bulk of the yield, and was no doubt simply a lower molecular weight fraction. Product B was white in color, and appeared to be less degraded than product A, thus in the large scale de-acetylation, the conditions of the second experiment were closely duplicated, even at the risk of having a small amount of residual acetyl in the product.

(b) Large-scale Preparation:

Cellulose nitrate monoacetate (35 g., 0.216 mols) was dissolved in freshly purified dioxane (1.4 liters). For the de-acetylation, 422 ml. of 0.486 N sodium hydroxide (0.205 mols) was used. This amount of alkali was added drop by drop from a burette to the well-stirred dioxane solution over a period of ninety minutes. No water was added to the reaction mixture during the de-acetylation; dioxane was added instead when solids began to separate. This addition was to minimize the chance for any unreacted "acetate-nitrate" to precipitate from solution, since it was important to keep it fully exposed to the action of the alkali. Extra dioxane added amounted to 250 ml., giving an over-all ratio of dioxane to water of approximately 80:20 (by volumes). It is of interest here to point out that the de-acetylated product appeared to be completely soluble in a dioxane-water mixture of this composition, since the reaction mixture was completely homogeneous. This solvent differs considerably from the 60:40::dioxane:water ratio noted by Levi, Lemieux and Purves (1) as being the proportion necessary for solvation of their cellulose-6-nitrate.

After alkali addition, the solution was stirred until no longer alkaline to phenolphthalein (about forty-five minutes). The reaction mixture was precipitated from a dropping funnel into distilled water (8 liters), using mechanical stirring, and the product separated as small white fibrous clots. After collection on a large sintered glass filter, the product was washed very thoroughly with water. The grey paste was transferred to a shallow dish and dried over phosphoric anhydride and potassium hydroxide pellets in a vacuum desiccator for forty-eight hours. The partially dry lumps were ground to a powder and dried again *in vacuo* over phosphoric anhydride and potassium hydroxide. The product was almost pure white in color; weight, 43.5 grams. Yield, 95% on the basis on nitrogen analysis.

Anal. Calculated for cellulose with 1.16 nitrate groups: C,33.6; H,4.13; N,7.65. Found: C,33.7,34.0; H,4.54,4.32; N,7.60,7.51,7.48,7.65%.

7. Nitration of Cellulose-6-nitrate:

A nitrating mixture of 60:40::nitric acid:phosphoric acid composition was prepared as follows. Phosphoric anhydride (9.1 g.) was dissolved in 99% nitric acid (32.1 ml.)

and 85% phosphoric acid (13.7 ml.) was added to this solution. The nitrating mixture was cooled to -15°C, and cellulose-6-nitrate (1.981 g.) added. The mixture was allowed to stand at room temperature for thirty minutes with occasional shaking, then poured into an ethanol:water::1:1 mixture (400 ml.) cooled to -15°C. The nitrated product separated in a granular form, and was allowed to stand in the mother liquor for two hours at room temperature with frequent stirring, before being recovered by filtration and washed ten times with small portions of ethanol:water::1:1. Purification of the dried product was effected by dissolving the material in acetone (70 ml.) and pouring the solution into water (300 ml.). The white, finely fibrous product was recovered, washed with water, and dried in a vacuum desiccator over phosphoric anhydride and potassium hydroxide pellets. Weight, 2.138 grams. Yield, 89% on the basis of nitrogen analysis.

Anal. N, 11.58, 11.60, 11.60, 11.54%.

8. Iodination of Cellulose-6-nitrate:

A sample of the cellulose-6-nitrate (1.000 g.) was suspended in re-distilled acetone (30 ml.), and sodium iodide (8 g.) added. The cellulose-6-nitrate, insoluble in acetone, dissolved quite readily at room temperature upon addition of sodium iodide, giving a pale yellow solution. The completely homogeneous mixture was placed in a glass "liner" (capacity 75 ml.), which was inserted in a steel bomb (250 ml.) sealed by a lid carrying a lead gasket. The assembly was heated for eighteen hours at 100°C in a steam bath. After cooling slowly to room temperature, the bomb was opened and free iodine in the reaction mixture was eliminated by addition of aqueous sodium thiosulfate (0.1 N). Precipitation into distilled water yielded the 6-desoxy-6-iodocellulose as a grey powder. Weight, after drying in a vacuum desiccator over phosphoric anhydride, 1.065 grams. This amount represents a yield of 91% on the basis of analysis.

Anal. Calculated for cellulose with 0.76 iodine and 0.1 nitrate groups: N,0.56; I,38.6. Found: N,0.50,0.54; I,38.4,38.4%.

FIG. 3

SUMMARY OF THE SYNTHESES

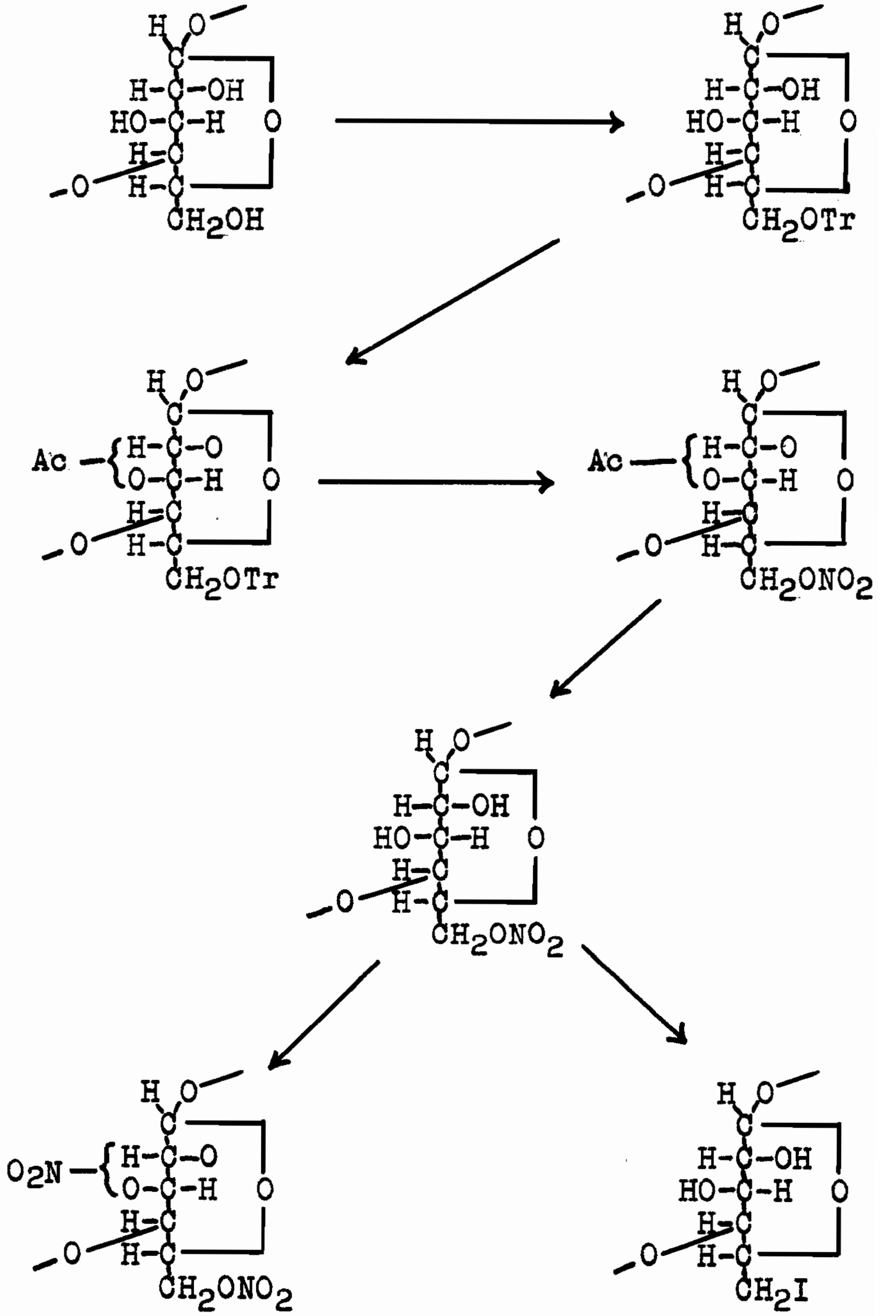
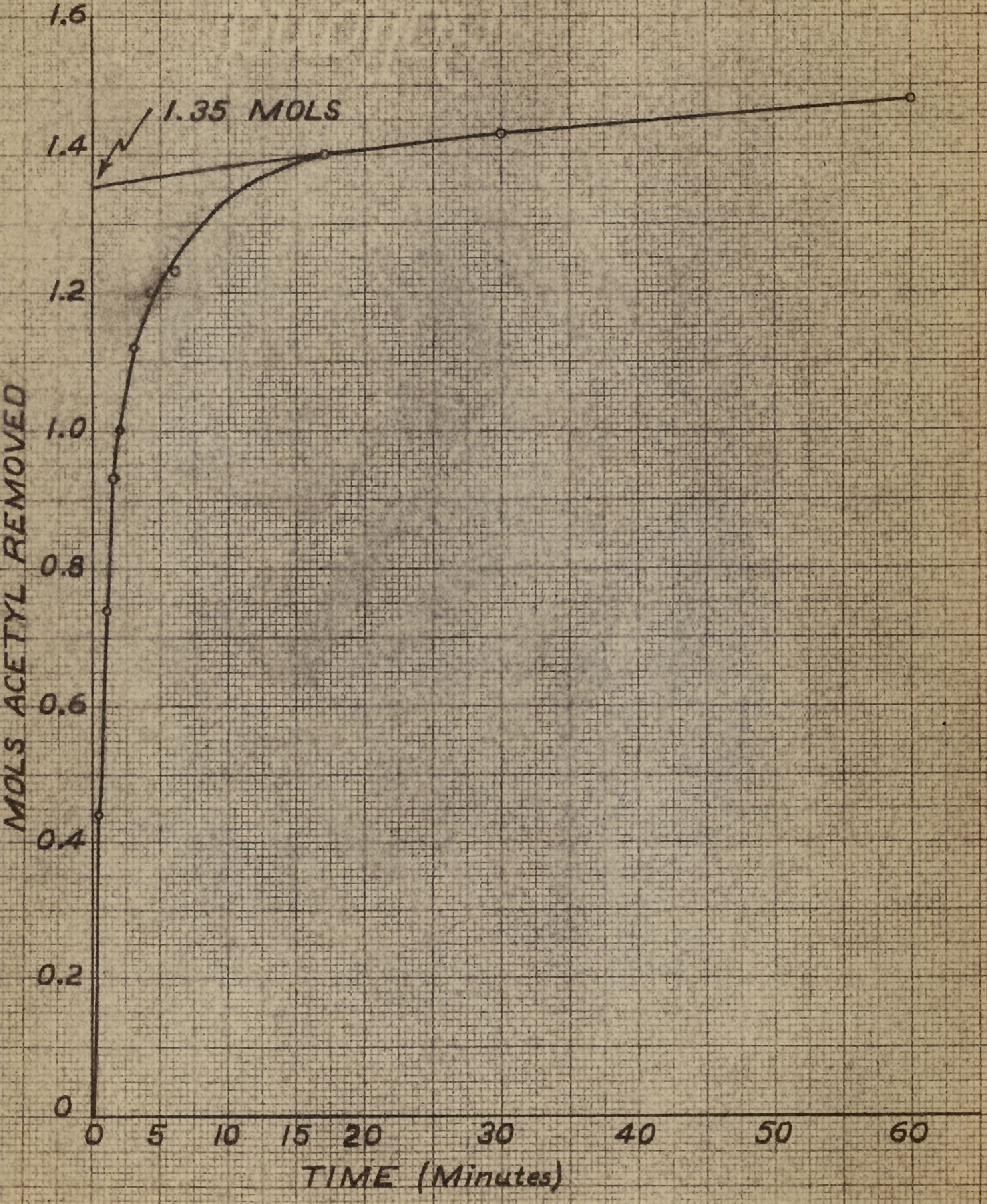


FIG. 4

RATE OF DE-ACETYLATION OF CELLULOSE-6-NITRATE MONOACETATE



B. DESCRIPTION OF THE THERMAL DECOMPOSITION APPARATUS

The thermal decomposition of nitrate esters is known to give rise to corrosive gases (oxides of nitrogen), thus any apparatus used for such studies must be of all-glass construction. The attack of these gases on rubber connections would only lead to further sources of error in a decomposition which is already an extremely complicated one, and which presents numerous analytical difficulties.

The equipment used in this work was constructed entirely of Pyrex glass, and is illustrated in Fig. 5. The reaction flask (A), the two receivers (B) and (C), and the collecting bulb (D) are detachable, being connected together by means of standard-taper ground-glass joints. An adapted Claisen flask of 250 ml. capacity forms the reaction chamber, and the two receivers are essentially of the coil type. The collecting bulb (D) was designed from a 125 ml. round-bottomed flask, and is connected to the system by a stop-cock arrangement which permits sampling of the gases condensed in receiver C.

These four units, which form the main part of the decomposition assembly, are of such a size that they can be weighed on an analytical balance to an accuracy of about one milligram. With judicious use of stop-cock grease for lubrication of these joints, it was found possible to obtain duplicate weighings which checked to within one milligram. Use of too much lubricant resulted in a transfer of grease of unpredictable amount from one joint to another during the procedure of assembling and disassembling, and the accuracy of reproduction of weighings was lowered.

All stop-cocks used were of Corning ₮ 2 variety (2 mm. bore), and capable of holding a high vacuum indefinitely. The connecting ground-glass joints were of Corning ₮ 10/30 size, carrying hooks for the attachment of springs or rubber bands. These joints provided the main leak in the vacuum system, as indicated by testing the evacuated assembly with a high-frequency discharge in the usual way. It is to be recommended in future work of this nature that size ₮ 3, or stop-cocks of some even larger bore be used, since one of the destructive explosions which occurred in the course of this investigation was directly caused by partial stoppage of the 2 mm. bore of one of the stop-cocks. A further recommendation is that Corning ₮ 10/30 standard joints be specially ground with a fine abrasive before installation, in order to eliminate their slight tendency to leak.

The system was connected to a Cenco Hyvac pump capable of producing a vacuum of 0.1 millimeters of mercury. A ten-liter expansion bottle was installed between the apparatus and pump to provide the capacity necessary to handle sudden increases in pressure in the system. Such increases were caused by sudden gas evolution during heating. The decomposition assembly was provided with a mercury manometer and a McLeod gauge; and also with a constant-volume manometer for determining the volumes of the various units. Beyond the second receiver was an auxiliary trap (E), which was used only in special cases as will be mentioned later.

In normal operation, the reaction flask (A) was surrounded by a heating bath of clear mineral oil; the trap B by an acetone-dry ice mixture, and the trap C by liquid air.

With this equipment it was possible to carry out thermal decomposition of cellulose nitrates at pressures in the range of 0.3 to about 1.0 millimeters, and at a wide range of temperatures. Furthermore, a fractionation of the products of decomposition took place during operation; water and all carbon-containing compounds (except carbon dioxide) were retained in B, while nitrogen gases and carbon dioxide were retained in C. This initial fractionation represented a great simplification of the analytical problem and, what was equally important, prevented secondary reactions from taking place. In normal operation recoveries were excellent, and retention of the products of decomposition was close to 100%.

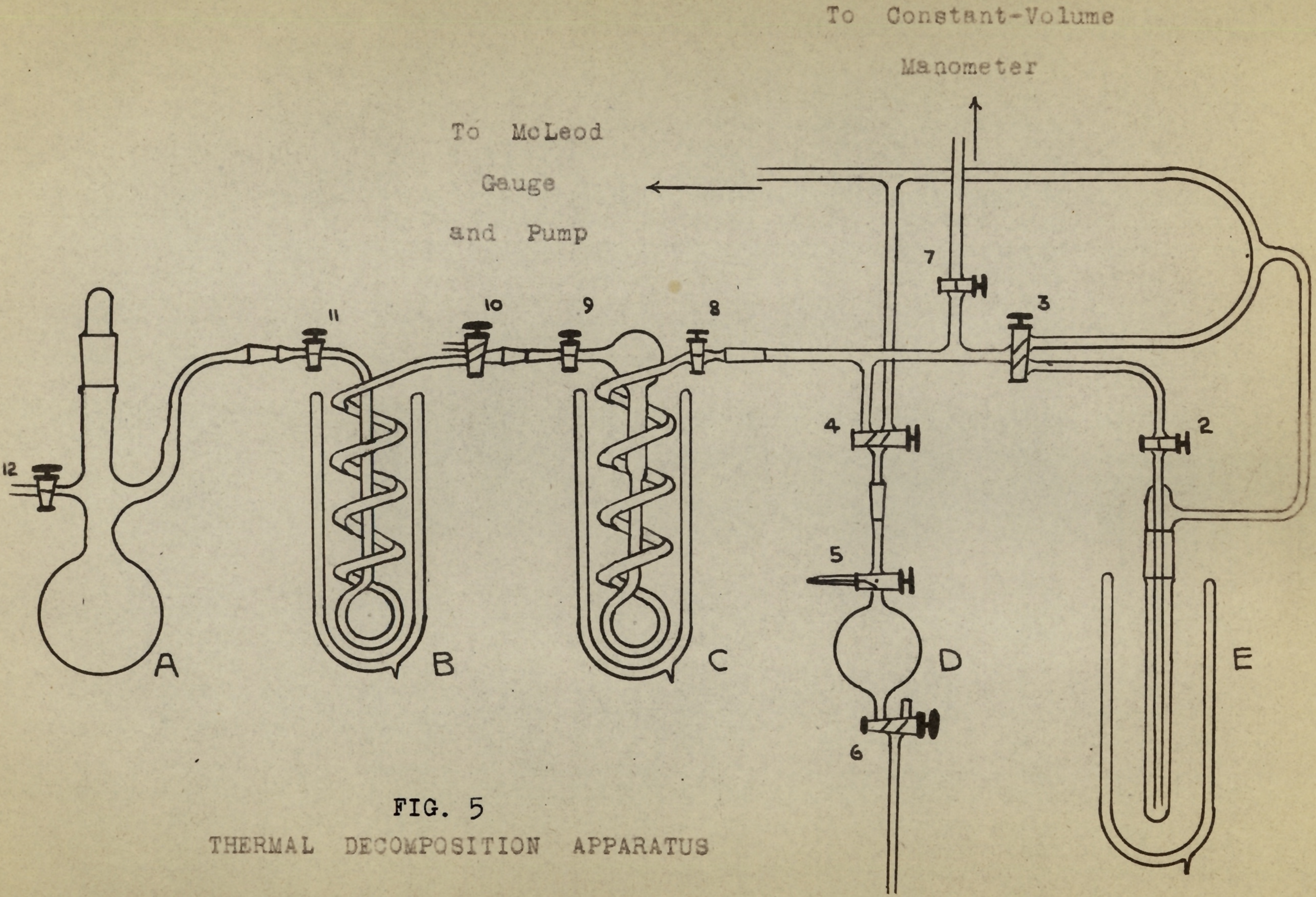


FIG. 5
THERMAL DECOMPOSITION APPARATUS

C. OPERATION OF THE APPARATUS

Prior to starting a run, the reaction flask and the two receivers (thoroughly cleaned) were connected, and the system evacuated for about two hours. Then stop-cock No. 11 was closed, No. 12 opened and the reaction flask detached and weighed. The sample to be studied (previously weighed) was placed in the reaction flask with the aid of a long funnel made from paper. The reaction flask was weighed with its contents and the sample weight checked by difference. It was not considered advisable to make runs on much more than 1 gram of either the cellulose "mono" or "di" nitrate, since very extensive damage was caused by an accidental explosion of 1 gram of the latter.

Stop-cock No. 9 was then closed, and the two-way stop-cock No. 10 rotated so as to admit air to the space between No. 9 and No. 10. Thus it was possible to detach receiver B while still evacuated. Similarly, by closing stop-cock No. 3, then No. 8, and admitting air to the space between No. 3 and No. 8 through No. 4 (collecting bulb not attached at this stage), it was possible to detach receiver C while still evacuated. The two receivers were weighed, and then replaced. Finally, the reaction flask was replaced and its contents dried for two hours under vacuum at a temperature of about 70°C, obtained by surrounding the flask with a hot-water bath. After this drying period, the reaction flask was detached, weighed quickly, and then replaced. This last operation gave the weight of "dried" material which was to be subjected to the thermal decomposition.

When liquid air and acetone-dry ice coolers had been placed in position, and the reaction flask surrounded by a mineral-oil bath with a thermometer immersed, the run was started. The oil bath was heated with a gas flame, and the temperature raised rather slowly, thirty to forty-five minutes being required to reach a temperature of 165°C. Pressure and temperature readings were taken at regular intervals during the run.

Runs were ordinarily terminated after four hours of heating. Although this period was arbitrary, it was sufficiently long for the decomposition at the temperatures used, to give distillates in analyzable amounts, and not long enough to decompose the non-volatile residue unnecessarily.

The decomposition was arrested by removal of the heating bath. After the reaction flask had cooled somewhat, it was freed from adhering oil by thorough washing with benzene. At the conclusion of a run, the various units of the assembly were detached and weighed in the same manner as already outlined. As before, the two receivers were weighed while evacuated, thus it was possible to obtain weights of the volatile fractions without permitting air to come in contact with the substances. This precaution was important in the case of the liquid air condensate which contained easily oxidized nitrogen gases.

In one run it was desired to test the completeness of separation of the volatile material into the two fractions; acetone-dry ice condensate and liquid air condensate. The method of operation in this particular case was slightly changed. Receivers B and C were both surrounded by acetone-dry ice mixtures, and the remainder of the volatile material collected in receiver E, using liquid air. The results showed that the usual separation was very sharp and efficient, as receiver C contained negligible traces of condensate.

The first fraction of the distillate (B) was prepared for analysis in the following way. Distilled water was admitted to the evacuated receiver to wash out the contents. The aqueous solution was made up to 100 ml. volume in a calibrated flask, and aliquots were taken for analysis. In one instance, where it was desired to determine the water content of the first condensate, absolute methanol was used to rinse out the receiver. Methanol solutions, however, could not be analyzed satisfactorily for constituents other than water.

Preparing the liquid air condensate for analysis was a much more complex operation. Rather than weigh the condensate directly, it was found to be more satisfactory to expand the gases contained in the second receiver into the calibrated bulb, or gas collector (D), which had previously been evacuated and weighed. Knowing the weight of gas expanded, and the volumes of the bulb and of the receiver, it was possible to calculate the total yield of liquid air condensate. This procedure also permitted a second sampling of the condensate, and furthermore the total yield could be checked by weighing the receiver with its contents after expansion. When gases were collected in the auxiliary trap (E), this method of obtaining the yield (i.e. expansion into a standard volume vessel) had no alternative, since the auxiliary trap was not designed to be detached and weighed with volatile contents.

After the gases were collected in receiver C, the manipulation in expanding them into D involved attaching the bulb (D) to the system as shown in Fig. 5. Bulb D was then evacuated through two-way stop-cock No. 4, detached, weighed, replaced on the assembly, and connected to the pump again to ensure re-evacuation. Then the two-way stop-cock No. 3 was closed, No. 8 was opened, and the liquid air bath removed from the receiver. After temperature equilibrium was reached, stop-cock No. 4 was rotated so that the evacuated bulb drew in the volatilized gases. Stop-cock No. 4 was closed, then the two-way stop-cock No. 5, so that air was admitted to the space between the two stop-cocks. The bulb (D) was detached and weighed again to get the weight of its contents, and the liquid air bath was replaced around the receiver (C) to "freeze out" the remaining gas in preparation for further sampling. The procedure for expanding gas from the auxiliary receiver (C) into the collecting bulb is obvious from an examination of Fig. 5, and will not be described in detail.

The examination of the gas mixture in bulb D can be more appropriately described in the following sub-section, "Analytical Methods".

D. ANALYTICAL METHODS

Limitations imposed on the size of cellulose nitrate samples used for the thermal decompositions resulted in small yields of distilled fractions. Since these fractions from different runs could not very satisfactorily be combined, and furthermore since it was required to carry out many different determinations on each, careful analytical manipulation was necessary. Most of the analyses were definitely on a micro scale, and during the course of the work certain micro techniques had to be adapted from well-known macro methods.

In the tabulations of results, it will at once be noted that there are many blanks where the amount recovered of one constituent or another is omitted. The omissions arose from the fact that the easiest way to get material for analytical experiments was to obtain it from nitrocellulose decompositions, rather than to prepare similar mixtures synthetically. In the course of the investigation many individual determinations were in consequence failures, until satisfactory routine methods had been developed.

It seemed justifiable to combine the non-volatile still residues from different runs into a composite sample. Whether justifiable or not, the step was necessary in that the carbonyl and carboxyl assays could probably not be adapted to a micro scale.

I Reaction Flask Residue

1. Nitrogen:

Unless specifically stated otherwise, all nitrogen determinations reported in connection with analysis of the reaction flask residues were by a standard semi-micro adaptation of the Gunning method, modified for nitrate nitrogen (34). Boric acid was used as the absorbent for the ammoniacal distillates (35).

Nitrometer determinations were attempted using the DuPont semi-micro nitrometer described by Elving and McElroy (36). It was found that these residues, particularly that from the cellulose mononitrate, tended to decompose very rapidly, and to dissolve very slowly in the concentrated sulfuric acid. Oxides of nitrogen were evolved during the long process of dissolving, and could easily be detected. The results obtained were extremely low. It was concluded that the nitrometer reaction is not applicable to these thermally altered cellulose nitrates. This rapid decomposition in sulfuric acid was, of course, not of any consequence in the Kjeldahl method of nitrogen analysis, since nitration of the aromatic nuclei present (salicylic acid added) prevented the escape of the nitrogen oxides.

2. Carbonyl and Carboxyl Determinations:

The combined carbonyl and carboxyl content of the residues was determined by the general procedure of

Bryant and Smith (37), as modified by Gladding and Purves (38). Essentially, this method consisted of treating the sample of oxycellulose with an excess of aqueous hydroxylamine hydrochloride buffered to a pH of about 5. Since both oximation and salt formation occurred, the hydroxylamine consumption as determined potentiometrically by titration with standard acid to the inflection point at pH 3.2, was a measure of the carbonyl plus carboxyl content.

A value for the carboxyl content alone was obtained by treating samples of the residue with 0.5 normal calcium acetate (39), twenty-four hours being allowed for completion of the cationic exchange. After filtration, filtrates were titrated potentiometrically for acetic acid to a pH of 9.0, using 0.01 normal alkali; and blanks were always run simultaneously. The carbonyl contents were found by difference.

In an attempt to ascertain the reason for the partial water-solubility of the oxycellulose residues, the latter were extracted with water. Carbonyl and carboxyl determinations, as well as nitrogen estimations, were made on both the extracted substance and the extract. The extracts were titrated directly with standard alkali, using a potentiometer, and carboxyl values were calculated from this data. Otherwise the carboxyl and carbonyl analyses were done in the same manner as described above.

3. Staudinger Viscosities:

Since the residue from the cellulose mononitrate was insoluble in organic solvents, it was not possible to carry out viscosity determinations directly on this substance. It was nitrated by Berl's method (40), and the intrinsic viscosity of the product determined in butyl acetate solvent using Kraemer and Lansing's modification (41) of Staudinger's procedure. There is good evidence in the work of Davidson (42) that nitration under such conditions does not bring about degradation of oxycelluloses, and for this reason the intrinsic viscosity of the nitrated material may be regarded as a measure of that of the mononitrate residue.

The residue from the decomposition of the cellulose dinitrate had substantially the same solubility characteristics as the original dinitrate, and its intrinsic viscosity was measured directly in butyl acetate.

II Acetone-Dry Ice Condensate:

All analyses of this condensate were made on aliquots of the aqueous solution.

1. Nitrogen:

Portions of the condensate were tested for nitrate and nitrite using diphenylamine, and also by the Devarda method. Except in cases where an explosion or spontaneous decomposition occurred, these tests were all negative.

2. Formaldehyde:

The aqueous solutions of the condensates were analyzed for formaldehyde by a modification of Vorländer's original dimedon method (43). The precipitation was carried out in a sodium acetate-hydrochloric acid buffer solution at a pH of 4.6, as recommended by Yoe and Reid (44). Although it was conceivable that other carbonyl compounds (e.g. glyoxal) could give a precipitate with the dimedon reagent, such precipitation apparently did not occur. The formaldehyde condensation product was isolated in a pure condition, as indicated by melting-point and mixed melting-point using an authentic sample of the substance. Precipitates obtained melted in the range of 186-189°C, whereas the accepted melting-point is 189°C (45). Mixed melting-points were consistently in the range of 186-190°C. The dimedon reagent used for this work was the Eastman Kodak Co. preparation (dimethyl dihydro resorcinol, E.K. No. 1259).

3. Total Acidity:

The total acidity was obtained by titrating the solutions quickly with 0.01 normal sodium hydroxide to a phenolphthalein end-point. This is the same procedure as used by Wolfrom in the investigation of the distillable liquids from ignition of technical nitrocellulose (26). A rapid titration was necessary, since the alkaline rearrangement of glyoxal begins at a pH of between 8 and 9, and this rearrangement gave rise to additional acidity in the form of glycolic acid (46).

4. Volatile Acidity:

Since negative tests were obtained for nitrate and nitrite, it was at once apparent that the acidity observed in the acetone-dry ice condensate was entirely caused by organic acids. Formic and acetic acids, which were the only volatile fatty acids likely to be present, were estimated by a modification of Dyer's steam-distillation method (47). The apparatus used is illustrated in Fig. 6, and represents a small-scale model of Dyer's apparatus, designed for micro analyses. Glass tubes were used in the steam-generator to ensure a steady flow of steam. Samples placed in the distillation flask were diluted to a volume of about 50 ml. and acidified with 1 ml. of 1:10 phosphoric acid, before commencing the actual steam-distillation. The volume of liquid in the distillation flask was kept fairly constant by heating the flask with a small flame. In practise, no attempt was made to have the apparatus function as a constant-volume distillation device, since chemical analysis of the distillates was the method chosen for this work, rather than graphical analysis of the distillation characteristics (47).

Successive volumes of each distillate were collected in graduated cylinders, and were titrated separately with 0.01 normal alkali to phenolphthalein end-points. These titrations were carried out on composites of the distillate already titrated. In other words, the fraction to be analyzed was always transferred to the same flask for titration, so that it was mixed with fractions already neutralized. This interval-titration procedure was adopted to reduce any error in the final end-point.

The weight of fatty acids present in any actual analysis of the aliquots never exceeded 6 milligrams. Consequently it was of interest to standardize the steam-distillation apparatus for small amounts of acid. Known amounts of formic acid were used in order to obtain some indication of what volume of distillate should be collected for a recovery approaching 100 percent. In this standardization work, the necessity became apparent of neutralizing the distilled water used in the steam-generator to a pH of above 8, prior to making a determination. The laboratory distilled water had a pH of less than 7, and at least a portion of this acidity was volatile with steam. High results were inevitably obtained when the neutralization procedure was omitted.

To conserve the aqueous solution of the acetone-dry ice condensate, samples were taken for the volatile acidity determination which had already been titrated for total acidity. To liberate the fatty acids, it was necessary to acidify these aliquots with some non-volatile inorganic acid. It was found that phosphoric and sulfuric acids were suitable for this purpose, the former being selected for most of the work. The distillates gave negative tests for phosphate ion and sulfate ion, respectively. It was not of any great advantage to make the solutions strongly acidic prior to distillation (see Fig. 7), and in the final standardized procedure 1 ml. of 1:10 phosphoric acid was added to a 50 ml. volume of sample. With control solutions of formic acid containing no foreign acidity (phosphoric or sulfuric acids), the distillation proceeded at a noticeably slower rate (Fig. 7).

Recoveries of at least 95% were obtained in 400 ml. of distillate from 11.6 milligrams of formic acid dissolved in 50 ml. of water, containing 1 ml. of 1:10 phosphoric acid. (See Fig. 7). Distillations of unknowns were arrested after about 400 ml. of distillate had been collected. Assuming 5 milligrams of formic acid to be present, its behaviour can be predicted graphically from Fig. 7. In such a case, the first 300 ml. of distillate represented a recovery of over 90%, from plot 2. Such a recovery was considered sufficiently quantitative for this work. Collecting larger volumes of distillate merely served to complicate chemical analyses, which in themselves could not possibly be of any higher degree of accuracy than ±10%, when dealing with such small amounts.

5. Formic Acid:

Formic acid was determined in the distillate from the volatile acidity procedure, using Fincke's method (48), which involved reduction of mercuric chloride to mercurous chloride. Formic acid is the only member of the fatty acid series capable of bringing about this reduction. The mercuric chloride reagent used was prepared according to the directions of Shaffer and Friedemann (46). Distillates of about 400 ml. volume, to which 2 ml. of 1:10 acetic acid and an excess of the mercuric chloride reagent had been added, were heated under reflux at steam-bath temperature for eight hours in all-glass apparatus. The solutions were allowed to cool completely to room temperature before recovering the precipitated mercurous chloride by filtration through a sintered-glass filter. The procedure gave fairly satisfactory results when applied to known amounts of formic acid (see Table IV), and some of the error may be due to loss occasioned by a slight solubility of mercurous chloride in the large volume of solution.

Table IV

Estimation of Formic Acid

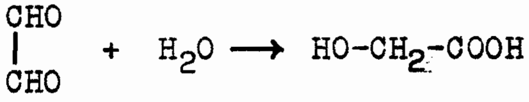
Anal.	Weight of HgCl (g.)	Equiv. as HCOOH	HCOOH Present	Percent Recovery
1	0.1980	0.0194	0.0232	84
2	0.1150	0.0112	0.0116	97
3	0.0290	0.0028	0.0029	98

6. Glyoxal:

Several methods were used to estimate the amount of glyoxal present. None of these methods were entirely satisfactory, and checks between methods were not good in some cases. However, it is felt that the average glyoxal values obtained were of reasonable accuracy.

Method A: Aliquots of the unknown solutions were treated with acidified aqueous 2,4-dinitrophenyl-hydrazine, following the directions of Grangaard and Purves (49). Formaldehyde was observed to give a precipitate with the reagent, but it was possible to separate this from the highly insoluble glyoxal precipitate, since the 2,4-dinitrophenyl-hydrazone of formaldehyde is quite soluble in hot water. Accordingly, after digesting on the steam-bath to complete the precipitation of the glyoxal derivative, the solutions were filtered while hot, and the precipitates washed with hot water. The 2,4-dinitrophenyl-hydrazone of glyoxal was never obtained in sufficient amount to permit purification by recrystallizing. The unpurified material melted over a range of 10°C, and between 280 to 310°C, whereas the accepted melting-point of glyoxal bis-2,4-dinitrophenyl-hydrazone is 330°C (50). Although some impurities were accordingly present, the melting-points were sufficiently high to justify the presence of glyoxal. This inference was apparent after consulting recently recorded data for melting-points of various 2,4-dinitrophenyl-hydrazones (50,51).

Method B: Glyoxal is known to undergo a Cannizzaro reaction in alkaline media, giving one mol of glycolic acid per mol of glyoxal:



$$\begin{array}{c} CHO \\ | \\ CHO \end{array} + H_2O \longrightarrow HO\text{-}CH_2\text{-}COOH$$

This reaction has been investigated as a means of determining glyoxal quantitatively, and some of the reaction conditions have been reported (46,52). The procedure of Shaffer and Friedemann (46) was followed in this work. Samples which had been used for total acidity titration, were treated with about 20 ml. of 0.01 N sodium hydroxide, and the alkaline solutions allowed to stand for five hours. They were then back-titrated with 0.01 N hydrochloric acid (phenolphthalein indicator), and the amount of sodium hydroxide consumed as a result of the alkaline rearrangement, calculated to its equivalent of glyoxal.

Method C: This method depends on the oxidation of one mol of glyoxal to two mols of formic acid, by means of alkaline hydrogen peroxide.

$$\begin{array}{c} H\text{-}C{=}O \\ | \\ H\text{-}C{=}O \end{array} \longrightarrow \begin{array}{c} H\text{-}COOH \\ \\ H\text{-}COOH \end{array}$$

This mode of oxidative attack has been observed also in the case of methyl glyoxal, from which one mol of formic acid and one mol of acetic acid arise (52).

Alkaline peroxide oxidizes formaldehyde in high yield to formic acid, and this reaction forms the basis of Blank and Finkenbeiner's method for formaldehyde analysis (53). Known amounts of formaldehyde were treated with alkaline peroxide under the conditions for glyoxal determination, as described by Hatcher, Holden and Toole (54). After oxidation had proceeded for four hours, the reaction mixtures were acidified with phosphoric acid, and steam-distilled. The distillates were analyzed for formic acid with mercuric chloride reagent as described on page 48. The results shown in Table V are typical of these oxidations.

Table V

Peroxide Estimation of Formaldehyde

Anal.	HCHO Present	HgCl	HCOOH Equiv.	HCHO Equiv.	Percent Recovery
1	0.0021	0.0376	0.0037	0.0024	114
2	0.0042	0.0537	0.0053	0.0035	83
3	0.0085	0.0939	0.0092	0.0060	71

It would appear that amounts of formaldehyde such as would be present in an actual glyoxal determination were more or less completely converted to formic acid, and the correction for formaldehyde was made on the basis that the oxidation was quantitative. Higher concentrations of formaldehyde gave lower recoveries, possibly because some further oxidation to carbon dioxide occurred, as was postulated by Fry and Payne (55).

Method C consisted of direct alkali titration of the formic acid in the reaction mixture, as it was produced. Such titrations using phenolphthalein indicator (54) were very difficult with these solutions containing hydrogen peroxide. End-points were poor, and in time the oxidizing media caused deterioration of the indicator. Potentiometric titration would no doubt have given more reliable results. Two mols of alkali correspond to one mol of glyoxal, in the calculations.

<u>Method D</u>: This method was really a modification of Method C, and also depends on the oxidation of glyoxal to formic acid. The formic acid produced was steam-distilled, and the distillate titrated with 0.01 N alkali to a phenolphthalein end-point. The total volatile acidity determined in this way, was corrected for the volatile acidity known to be present originally, and for that produced by the oxidation of any formaldehyde present.

<u>Method E</u>: This procedure involved a direct formic acid determination on the steam-distillate from a peroxide oxidation. Mercuric chloride reagent was used. As before, corrections were made for the formic acid known to be present originally, and for the formaldehyde oxidation.

Since none of these methods has been checked using known amounts of glyoxal contained in synthetic mixtures resembling the acetone-dry ice condensate, it is difficult to say which of the procedures is best.

7. <u>Acetic</u> <u>Acid</u>:

Samples (25 ml.) of the original solutions of the acetone-dry ice condensate were heated under reflux with mercuric oxide (0.1 g.) for ninety minutes in all-glass apparatus. This procedure eliminated formic acid by oxidation to carbon dioxide (56). The excess mercuric oxide was then destroyed with 10% sulfuric acid (3 ml.). The solutions were filtered, and the filtrates quantitatively transferred to the steam-distillation apparatus. The steam-distillate was titrated potentiometrically with 0.01 N sodium hydroxide, since introduction of foreign organic matter in the form of acid-base indicator would complicate the final identification of acetic acid. The neutralized distillate was evaporated to dryness at reduced pressure in all-glass distilling apparatus, and the minute residue of sodium salt was dissolved in a few drops of water. This solution was boiled under reflux with a large excess of 2% alcoholic p-bromophenacyl-bromide (57). After not more than two days standing at 5°C, the mixture deposited needle-crystals of the ester, which melted at 87°C. The accepted melting-point for α-acetoxy-p-bromoacetophenone is 86°C (58).

Precipitation of the ester was by no means quantitative, and no attempt was made to adapt this reaction for quantitative work. It was assumed that the volatile acidity not destroyed by mercuric oxide was entirely acetic acid, since it is most unlikely that higher fatty acids than acetic could arise from the thermal decomposition of cellulose nitrates.

8. Oxalic Acid:

Small samples of the original solutions were tested for oxalic acid by a standard method involving calcium oxalate precipitation (59). The results were negative in all cases.

9. Water:

For this purpose, the acetone-dry ice condensate arising from a run was taken up in anhydrous methanol rather than in water, and water was determined using the Karl Fischer reagent (60). The method used gave small titrations in blank determinations, and these corrections were applied. It was found that the methanol solutions could not be analyzed satisfactorily for all the constituents other than water, interference being noted especially in the case of dimedon and 2,4-dinitrophenylhydrazine precipitations.

The acetone-dry ice condensate was never large enough to be usefully divided into two parts; one diluted with methanol, and the other with water. Consequently, the results do not contain a complete analysis of any one condensate. Control analyses of the moisture content on the nitrocellulose samples were also carried out with the Karl Fischer reagent (61).

III Liquid Air Condensate:

Examination of the liquid air condensate involved working with compounds which were gases at normal temperature and pressure. The analytical procedures developed were partly chemical and partly gasometric, and all depended on selective absorption of the gaseous constituents in appropriate solvents. After a gas sample had been obtained in the collecting bulb in the manner described in the section "Operation of the Apparatus" (pages 35-39), analysis proceeded by one or other of the two general methods:

1. Absorption in 40% aqueous potassium hydroxide: (nitrogen trioxide, nitrogen dioxide and carbon dioxide dissolved; nitric oxide, nitrous oxide did not).
2. Absorption in concentrated sulfuric acid: (nitrogen trioxide, nitrogen dioxide dissolved; nitric oxide, nitrous oxide and carbon dioxide did not).

The second method was used in only one instance; for the purpose of obtaining a value for the carbon dioxide content by a gas analysis procedure.

In both methods the same device was applied for transferring unabsorbed gases to a gas burette to be stored over mercury for subsequent analysis. This apparatus is shown in Fig. 8, which is self-explanatory. The two-way stop-cocks No. 5 and No. 6 are typical of gas-collecting bulbs of this type (62), and permit introduction of an absorbent or displacing liquid without entry of air. The stop-cock system also facilitates transfer of gases from the bulb to other vessels.

1. Absorption in 40% aqueous potassium hydroxide:

A small volume (3-5 ml.) of 40% aqueous potassium hydroxide was admitted to the bulb through stop-cock No. 6, and after absorption was complete as indicated by the disappearance of the brown gas (five minutes), freshly boiled-out water was drawn into the bulb from the reservoir shown in Fig. 8. It was found advisable to use freshly boiled-out water in this work in order to avoid introduction into the system of dissolved gases. The gaseous constituents were transferred under slight pressure from the bulb to a small gas burette, and stored over mercury. The alkaline solution filling the bulb was drained out and made up to volume in a calibrated flask (usually 250 ml. capacity).

(a) Analysis of the Potassium Hydroxide Absorbate:

The following reactions of nitrogen trioxide and nitrogen dioxide are well-known:

$$N_2O_3 + 2KOH \longrightarrow 2KNO_2 + H_2O$$

$$N_2O_4 + 2KOH \longrightarrow KNO_2 + KNO_3 + H_2O.$$

Actually, the gases first dissolve giving nitrous and nitric acids, and salt formation occurs later. If water is present, the nitrogen trioxide is supposed to form some nitrate owing to decomposition of part of the nitrous acid produced at the moment of solution (63,64,65).

$$3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$$

It has been suggested (64) that this slight decomposition can be avoided by absorbing the gases over dry caustic potash. This method was tried, and was found to be very slow and incomplete.

Although the decomposition of nitrous acid to nitric acid might have occurred to some extent in absorbing these gases in 40% potassium hydroxide solution, the absorption was extremely rapid under the conditions used, and this source of error was probably insignificant. It may be inferred, however, that there was a tendency toward low nitrite values in the determination of these two nitrogen gases by analysis of their aqueous alkali absorbates. The analyses for nitrogen trioxide (or nitric oxide) reported are therefore probably minimum values, and those for nitrogen dioxide are probably maximum values.

Nitrite was determined in the aqueous potassium hydroxide solution by a standard method involving the use of chloramine-T reagent (sodium p-toluene-sulfochloramide) as an oxidizing agent (66).

Nitrate plus nitrite was determined using a micro adaptation of the standard Devarda method (67). A special all-glass apparatus was constructed for this analysis, and is shown in Fig. 9. Results using a solution of pure potassium nitrate as a standard were as follows:

Table VI

Micro-Devarda Estimation for Nitrate

Anal.	NO_2 in KNO_3 (mg)	HCl 0.00946N	NO_2 found (mg)	Recovery Percent
1	1.23	2.76	1.20	97.5
2	1.23	2.82	1.23	100.0
3	2.46	5.61	2.44	99.4
4	2.46	5.72	2.48	101.0
5	6.15	13.89	6.05	98.5
6	6.15	14.32	6.24	101.6
7	12.30	28.17	12.25	99.5
8	12.30	28.72	12.56	102.0

The sample, contained in a 100 ml. volume, was placed in the reaction flask (Fig. 9), and 0.8 grams of Devarda alloy was added. The flask, with its contents, was then attached to the apparatus, and a 125 ml. Erlenmeyer flask containing 10 ml. of 2% boric acid was placed at the outlet of the vertical condenser, with the tip of the condenser dipping into the boric acid solution. From the dropping funnel, 10 ml. of 20% sodium hydroxide was added, and the reduction allowed to proceed for about one hour before applying heat (micro gas-burner) to the reaction flask. Distillation was continued until 70-80 ml. of distillate had been collected. The distillate was titrated with 0.01 N hydrochloric acid using the mixed indicator (methyl red and bromcresol green) recommended by Ma and Zuazaga (35). Blank determinations were always run, and these gave titrations of about 0.5 ml. of 0.01 N hydrochloric acid. This small blank presumably arose from nitrates or nitrites present in the alkali used.

From nitrate plus nitrite values as obtained by the Devarda method, and from nitrite values obtained by the chloramine-T procedure, it was possible to calculate the amounts of nitrogen trioxide and nitrogen dioxide present in the absorbed gases.

(b) Analysis of the Unabsorbed Gases:

This analysis was carried out in the simplest and most obvious way; namely by using the appropriate gas-absorbents in small Hempel pipettes (50 ml. capacity). These pipettes were moderately satisfactory, but they were somewhat too large for the work. Regulation micro gas-analysis equipment is to be recommended for investigations of such small volumes of gas. The absorbents used were the customary ones: acidified ferrous sulfate for nitric oxide; 30% potassium hydroxide for carbon dioxide; potassium pyrogallate solution for oxygen; and cuprous chloride solution for carbon monoxide.

Gases not absorbed in 40% aqueous potassium hydroxide in the bulb, were also unabsorbed in any of the above reagents. This observation left only nitrous oxide and nitrogen for consideration in speculations as to the identity of these unabsorbed gases. The presence of nitrogen was unlikely since it would not have been condensed in a liquid air trap, especially at the pressure used (less than 1 mm.). This unabsorbed gas residue was therefore reported as nitrous oxide.

2. Absorption in Concentrated Sulfuric Acid:

The following reactions are familiar:

$$N_2O_3 + 2H_2SO_4 \longrightarrow 2HO.SO_2.ONO + H_2O$$

$$N_2O_4 + H_2SO_4 \longrightarrow HO.SO_2.ONO + HNO_3.$$

Absorption of these oxides in concentrated sulfuric acid is the basis for a standard method for their analysis (68), which is not subject to the error discussed regarding alkali absorption. The nitrosyl sulfuric acid can be estimated with certain precautions, by titration with potassium permanganate; and the total nitrogen by utilizing the nitrometer reaction.

It was found that this analytical procedure was not applicable in this investigation. Amounts of nitrosyl sulfuric acid were too small to be determined precisely by permanganate titration. Furthermore, concentrated sulfuric acid in reaction with the stop-cock lubricant yielded materials which were also oxidizable by permanganate. Results were unreasonably high, and end-points were extremely indefinite. The use of syrupy phosphoric acid instead of grease as a stop-cock lubricant, did not provide a sufficiently good seal.

The sulfuric acid absorption technique was of value only in obtaining an estimate of the carbon dioxide content of the liquid air condensate. The unabsorbed gases were transferred to the gas burette by displacement with concentrated sulfuric acid, and carbon dioxide was determined in proper sequence by absorption in 30% caustic potash.

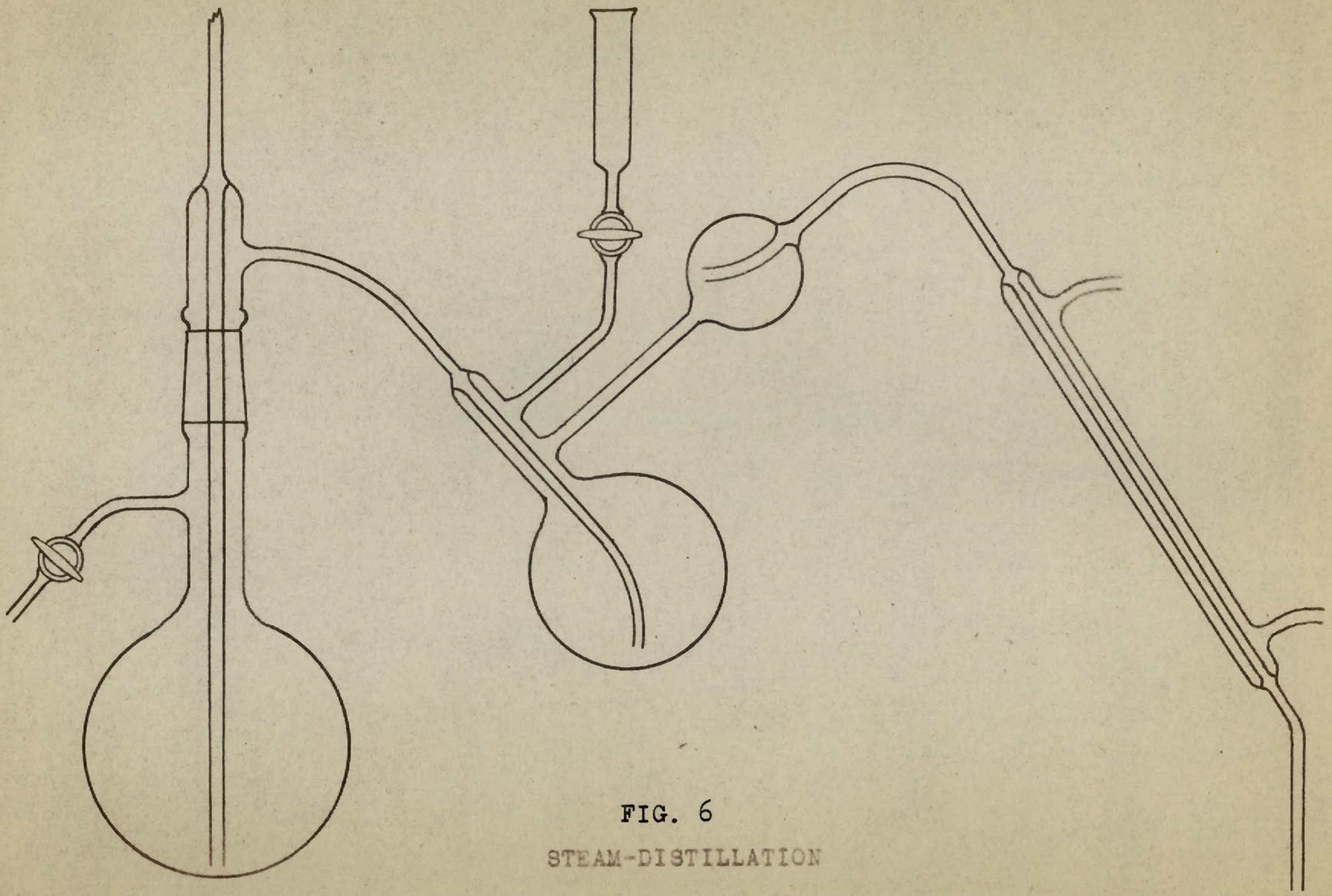


FIG. 6

STEAM-DISTILLATION

APPARATUS

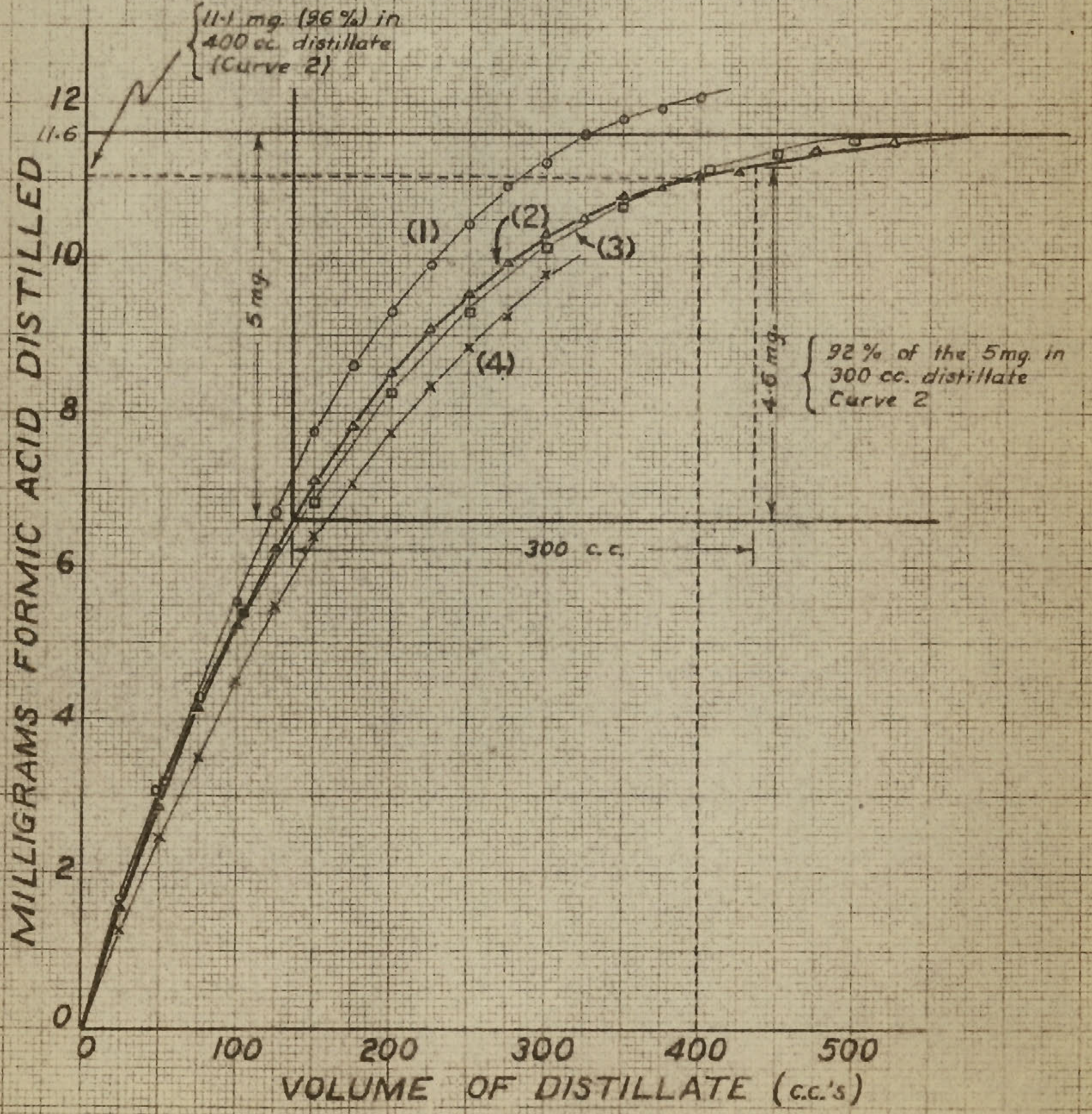
FIG. 7

STEAM-DISTILLATION OF FORMIC ACID

KEY

1. 1 ml. H_3PO_4 (85%); generator water not neut.
2. 1 ml. H_3PO_4 (1:10); generator water neut.
3. 3 ml. H_3PO_4 (85%); generator water neut.
4. No foreign acidity; generator water not neut.

Note: All Curves are for distillation of 11.6 milligrams of formic acid, contained in a volume of 50 ml.



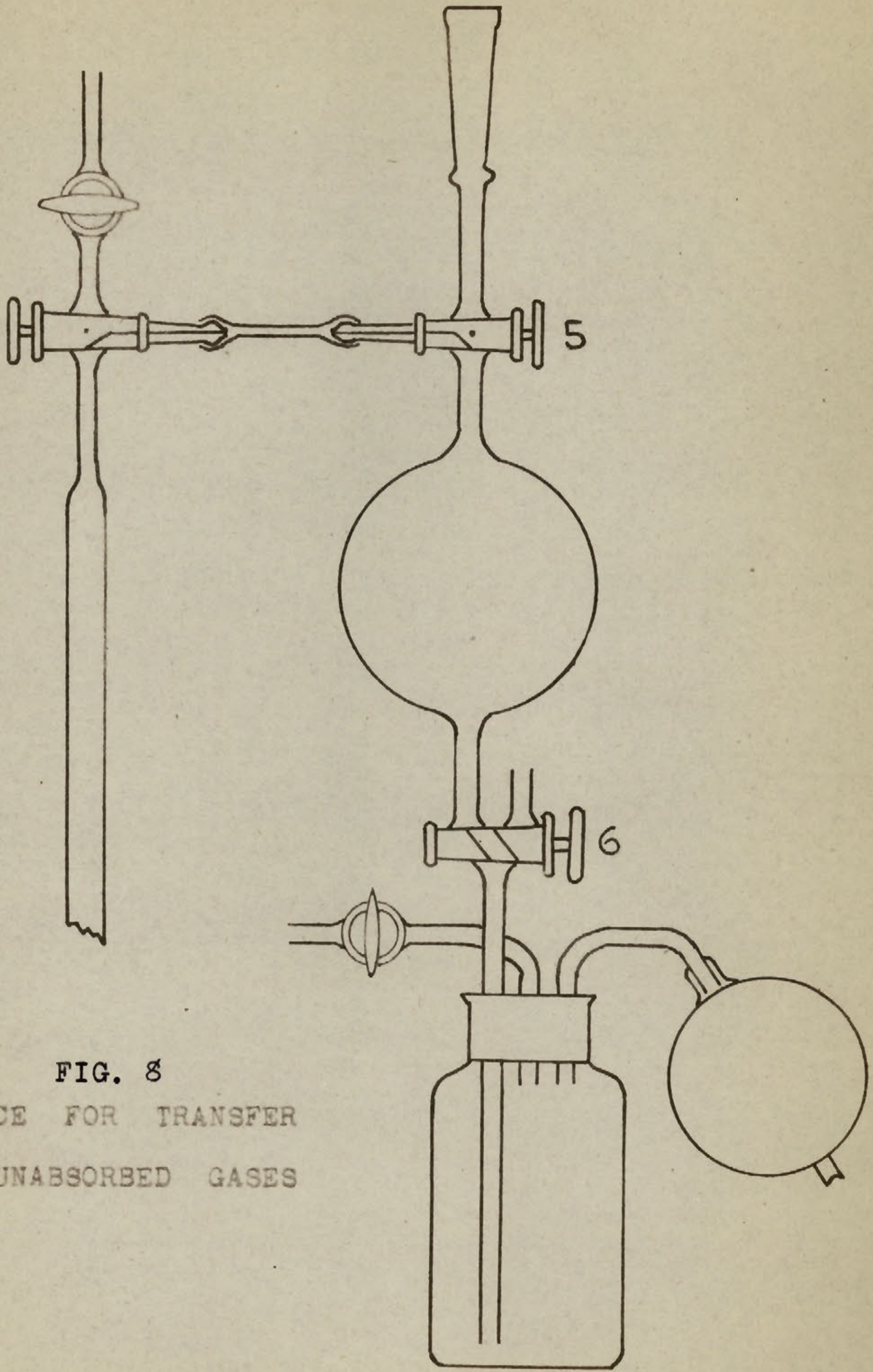
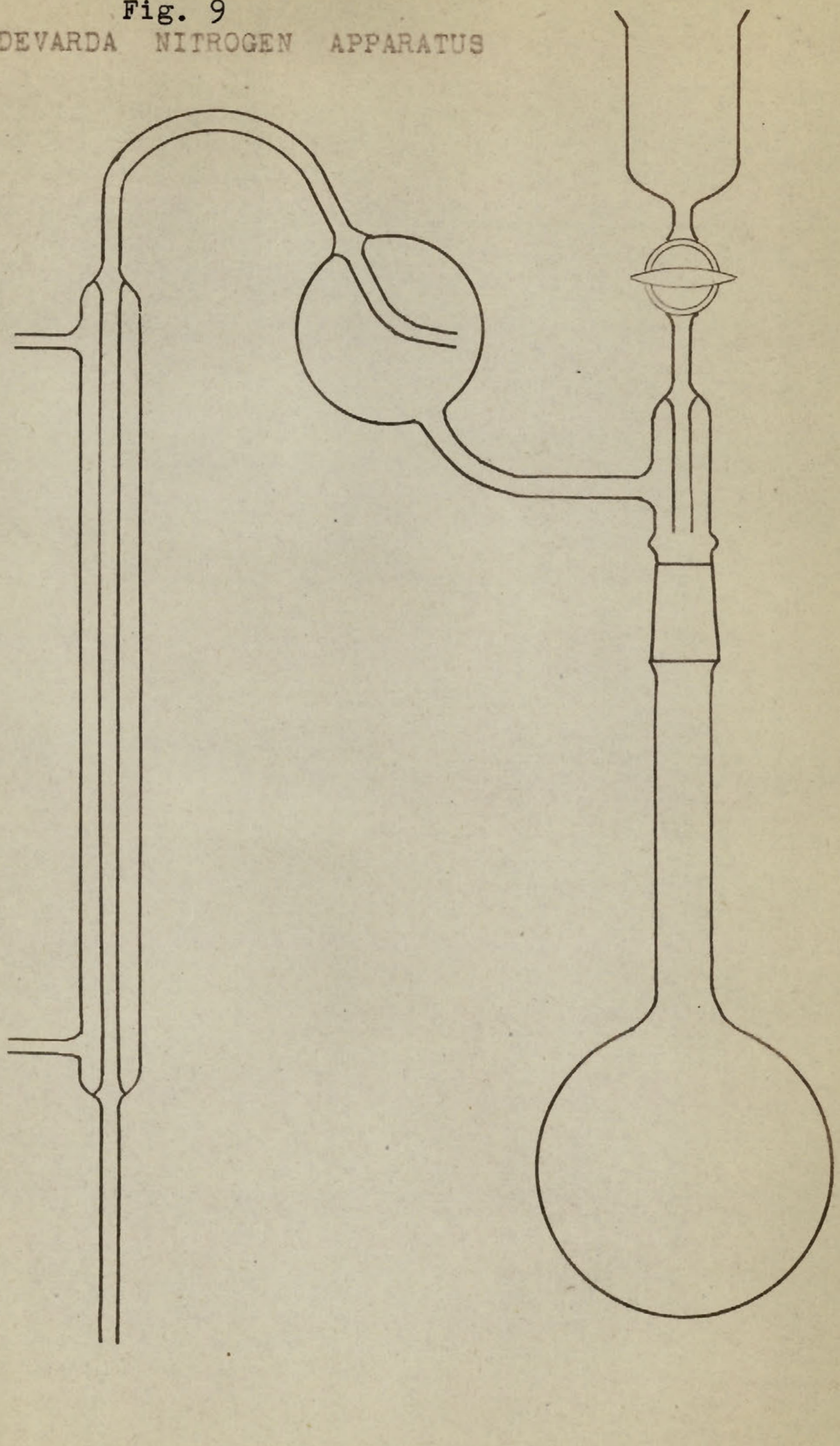


FIG. 8
DEVICE FOR TRANSFER
OF UNABSORBED GASES

Fig. 9
MICRO-DEVARDA NITROGEN APPARATUS



RESULTS

A. QUALITATIVE OBSERVATIONS

1. Controlled Decompositions:

As far as outward manifestations are concerned, the mononitrate and the dinitrate behaved in exactly the same way during controlled decomposition. The snow-white samples of nitrocellulose placed in the reaction flask slowly darkened in color, and were a very pale brown at the conclusion of a four-hour run. The intensity of this color varied depending on the temperature, and seemed to be a direct measure of the extent of decomposition.

In physical form, the nitrocellulose was not altered during decomposition; the mononitrate remained a powder and the dinitrate remained fibrous.

The mononitrate residues resembled the starting material in being generally insoluble in organic solvents. However, the material was partially soluble in water, giving bright yellow solutions, and differed from the original mononitrate in this respect. The residues also swelled somewhat in dioxane and in acetic anhydride, and swelled and slowly decomposed in pyridine. Nitration by Berl's method (34) yielded a pale yellow product which had all the solubility properties of the cellulose dinitrate.

The dinitrate residues were soluble in acetone, ethyl acetate, butyl acetate, glacial acetic acid, nitromethane, acetic anhydride, dioxane and pyridine; decomposition being apparent in the latter case. This behaviour paralleled that of the original dinitrate. A point of difference was that the thermally decomposed residues were found to have a slight water-solubility.

A faint fogginess appeared on the cool upper parts of the reaction flask during the experiments, and this material, although it was not identified, did not give positive tests for glyoxal or formaldehyde. The material represented a very small fraction of the residue. As well as could be determined, all low molecular weight aldehydes (such as glyoxal and formaldehyde) and acids were drawn out of the reaction flask into the receiver assembly.

The acetone-dry ice condensate was a white crystalline material at the temperature of the cooling bath (-55 to -60°C), which melted with no outgassing, upon warming, to give a clear colorless liquid with approximately the mobility of water. The material seemed to be very readily condensed at -55°C, since it was always completely concentrated within the first few inches of the coil receiver. The condensates gave no test with diphenylamine.

Within twenty minutes of heating at temperatures of 155-165°C, a beautiful blue crystalline material was in evidence in the liquid air receiver. This "blue substance" increased steadily in amount during the decomposition. It was observed to have the physical properties of nitrogen trioxide, and analysis showed that this nitrogen oxide actually made up a large proportion of the liquid air condensate. The "blue substance" melted to give a blue liquid when warmed slightly, and this liquid did not recrystallize at acetone-dry ice temperature. Upon warming to room temperature, the liquid volatilized, filling the receiver with a reddish-brown gas. Re-cooling in acetone-dry ice regenerated the blue liquid, which crystallized at liquid air temperature.

2. Spontaneous Decompositions:

Both starting materials produced brown fumes, in those experiments in which spontaneous decomposition occurred, which filled the reaction flask momentarily before being drawn off through the vacuum line to the receivers. Small amounts of solid material were blown into the acetone-dry ice receiver by the force of the decomposition.

The mononitrate left an appreciable amount of dark brown residue in the reaction flask, which could be removed and examined. It was found to be very largely water-soluble. Spontaneous decompositions of the dinitrate were obviously far more complete than those of the mononitrate; reaction flask residues being practically non-existant. The cellulose dinitrate seemed to decompose very quickly and completely to low molecular weight materials which were not retained in the reaction flask.

The acetone-dry ice condensates differed from those arising from controlled decomposition experiments, in that they outgassed noticeably on warming, and gave positive diphenylamine tests. Liquid air condensates from spontaneous decompositions consisted of small amounts of white crystalline material at liquid air temperature, which seemed to sublime on warming and gave a very faint brown color throughout the receiver.

When conditions were substantially the same, the dinitrate tended to decompose spontaneously at a somewhat lower temperature than the mononitrate. Two explosions may be appropriately mentioned in this section; one involving the mononitrate and the other involving the dinitrate. Certain comparisons are possible, since the conditions (sample weight, pressure, temperature, etc.) were practically the same in both cases. Both explosions occurred at 165°C, which may mean that if other conditions happen to be favorable, the mononitrate is just as capable of detonating as the dinitrate. There was a great difference in the intensity of these explosions, however. The mononitrate blew the ground-glass stopper out of the reaction flask, with no serious damage resulting; the dinitrate shattered the 250 ml. reaction flask and the neighboring apparatus almost completely, in a very violent detonation.

B. RECORD OF ANALYTICAL DATA

In this section, analytical results have been arranged in tabular form. This device was considered to be the most satisfactory method of presenting such a varied accumulation of data. Care has been taken to organize the material as logically as possible in the interests of clarity.

The compounds studied, a cellulose mononitrate and a cellulose dinitrate, had the following compositions.

Mononitrate: 7.56% nitrogen. Substitution 1.16 mols nitrate ester per glucose residue. Base weight, 214.

Dinitrate: 11.64% nitrogen. Substitution 2.15 mols nitrate ester per glucose residue. Base weight, 259.

The substitutions and base weights were calculated from the nitrogen analyses, no account being taken of the presence of a few acetyl groups.

In the tables, runs 1-12 inclusive are mononitrate decompositions; runs involving the dinitrate are marked with the letter "D", thus 13D, etc.

Table VII

General Data Regarding Decompositions

Run	Press. mm.	Temp. C°	Time hrs.	Starting Wt. (g.)	Residue Wt.	Acetone-Dry Ice Condens.	Liquid Air Condens.	Total Condens.	Total Recov.	Weight Gain or Loss
1	0.3-1.0	165±3	2	0.692	0.628	0.029	(c)	0.029	0.657	-0.035
2	0.3	165±3	4	0.784	0.663	(b)	0.130	0.130	0.793	+0.009
3	0.3	165±3	4	1.003	0.845	0.061	0.107	0.168	1.013	+0.010
4	0.5-0.6	165±3	4	1.008	0.866	0.055	0.092	0.147	1.013	+0.005
5	0.9-1.3	165±3	4	1.016	0.832	0.077	0.119	0.196	1.028	+0.012
6	0.5-0.8	165±3	4	1.049	0.913	0.067	0.070	0.137	1.050	+0.001
7	0.9-1.0	165±3	4	1.193	0.920	0.092	0.190	0.282	1.202	+0.009
8	0.6-0.9	165±3	4	1.189	0.991	0.106	0.111	0.217	1.208	+0.019
9	0.3-0.8	155±3	4	1.184	1.087	0.037	0.066	0.103	1.190	+0.006
10	0.3-0.8	150-190(a)	0.3	0.539	0.374	0.128	(c)	0.128	0.502	-0.037
11	0.3-0.8	150-180(a)	1	0.488	0.265	0.122	(c)	0.122	0.387	-0.101
12	0.6	150-184(a)	0.2	0.566	0.231	0.176	0.086	0.262	0.493	-0.073
13D	0.8-0.9	150-176(a)	0.5	0.334	0.011	0.041	(c)	0.041	0.052	-0.282
14D	0.9	155±3	4	1.215	1.064	0.046	0.109	0.155	1.219	+0.004
15D	0.6	155±3	4	1.018	0.897	0.037	0.076	0.113	1.010	-0.008

(a) Decomposed spontaneously at highest temperature in the range given.

(b) No acetone-dry ice trap used.

(c) No liquid air trap used.

Table VIII

Yields of Fractions as Percentages of Starting Material

Run	Residue	Acetone-Dry Ice Condens.	Liquid Air Condens.	Total Condens.	Total Recovery
1	90.8	4.2	-	4.2	95.0
2	84.6	-	16.6	16.6	101.2
3	84.5	6.1	10.7	16.8	101.3
4	86.5	5.5	9.1	14.6	101.1
5	82.0	7.6	11.7	19.3	101.3
6	87.0	6.4	6.8	13.2	100.2
7	77.0	7.7	15.9	23.6	100.6
8	83.5	8.9	9.3	18.2	101.7
9	91.7	3.1	5.6	8.7	100.4
10	69.5	23.8	-	23.8	93.3
11	54.3	25.0	-	25.0	79.3
12	40.8	31.0	15.2	46.2	87.0
13D	3.3	12.3	-	12.3	15.6
14D	87.5	3.8	9.0	12.8	100.3
15D	88.2	3.6	7.6	11.2	99.4

Table IX

Nitrogen Balance (A)

Run	Starting Weight	Nitrogen Weight	% N in Res.	%N Loss	Loss as % of Original	Res. Wt.	Wt. N in Residue	Wt. N Volatilized	% of orig. N volat.	m-mols ester cleaved/g. orig. NC (b)
1	0.692	0.0524	5.99	1.57	20.7	0.628	0.0376	0.0148	28.2	1.53
2	0.784	0.0593	5.33	2.23	29.4	0.663	0.0354	0.0239	40.3	2.18
3	1.003	0.0760	5.30	2.26	29.9	0.845	0.0448	0.0312	41.0	2.22
4	1.008	0.0762	5.52	2.04	27.0	0.866	0.0479	0.0283	37.2	2.00
5	1.016	0.0768	4.95	2.61	34.5	0.832	0.0412	0.0356	46.3	2.50
6	1.049	0.0792	5.68	1.88	24.8	0.913	0.0519	0.0273	34.5	1.87
7	1.193	0.0904	4.42	3.14	41.5	0.920	0.0407	0.0497	55.0	2.97
8	1.189	0.0899	5.23	2.33	30.8	0.991	0.0519	0.0380	42.3	2.29
9	1.184	0.0895	6.29	1.27	16.8	1.087	0.0683	0.0212	23.7	1.28
10	0.539	0.0407	4.13	3.43	45.4	0.374	0.0155	0.0252	61.9	3.34
11	0.488	0.0370	5.44	2.12	28.0	0.265	0.0144	0.0226	61.1	3.31
12	0.566	0.0429	4.65	2.91	38.4	0.231	0.0108	0.0321	74.9	4.05
13D	0.334	0.0389	(a)	(a)	(a)	0.011	(a)	(a)	ca 100	ca 8.3
14D	1.215	0.1415	9.93	1.71	14.7	1.064	0.1058	0.0357	25.2	2.10
15D	1.018	0.1185	10.10	1.54	13.2	0.897	0.0906	0.0279	23.6	1.96

(a) Residue too small to permit removal and analysis; in any case there must be nearly 100% volatilization of the original nitrogen.

(b) Calculated from weight of nitrogen volatilized. Example, Run 1:

$$\frac{0.0148}{14} \times \frac{1000}{0.692} = 1.53 \text{ millimols/g.}$$

Table X

Nitrogen Balance (B)

Run	Wt. N in Sample	Wt. N in Residue	Wt. N in Acetone-Dry Ice Condens.	% of Volatile Nitrogen	Wt. N in Liquid Air Condens. (absorbable)	% of Volatile Nitrogen	Wt. N in unabsorbed gases of Liquid Air Condens. (N_2O)	Total N accounted for	% vol. N accounted for
7	0.0904	0.0407	0	0	0.0390	79	0.0140	0.0937	107
8	0.0899	0.0519	0	0	0.0274	72	0.0098	0.0891	98
9	0.0895	0.0683	0	0	0.0158	75	0.0020	0.0861	84
10	0.0407	0.0155	0.0017	6.7	-	-	-	0.0172	6.7
11	0.0370	0.0144	0.0021	9.3	-	-	-	0.0165	9.3
12	0.0429	0.0108	0.0031	9.7	0.0025	7.8	0.0078	0.0242	42
13D	0.0389	-	0.0004	1.0	-	-	-	0.0004	1.0
14D	0.1415	0.1058	0	0	0.0303	85	0.0081	0.1442	107
15D	0.1185	0.0906	0	0	0.0200	72	0.0110	0.1216	110

Table XI

Composition of Liquid Air Condensate (By Weights)

Run	Wt. of Liq. Air Condens.	N as N_2O_3 (Devarda)	N as N_2O_3 Det'd as Nitrite	N_2O_3	N_2O_4	NO in the N_2O_3	Total N_2O_4	CO_2	N_2O
6	0.070	(a)	(a)	(a)	(a)	(a)	(a)	0.0095	0.0070
7	0.190	0.1060	0.0890	0.0719	0.0414	0.0284	0.0849	-	0.0220
8	0.111	0.0742	0.0636	0.0529	0.0258	0.0209	0.0578	-	0.0155
9	0.066	0.0429	0.0370	0.0311	0.0144	0.0123	0.0332	-	0.0031
12	0.086	0.0067	0.0066	0.0065	0.0003	0.0026	0.0042	-	0.0123
14D	0.109	0.0821	0.0691	0.0561	0.0314	0.0221	0.0654	-	0.0127
15D	0.076	0.0542	0.0504	0.0466	0.0092	0.0184	0.0374	-	0.0173

(a) Condensate absorbed in conc. sulfuric acid; not possible to analyze solution for nitrogen trioxide and nitrogen dioxide.

Table XII

Composition of Liquid Air Condensate (By Percentages)

Run	N_2O_3 %	N_2O_4 %	Total N_2O_3+ N_2O_4	NO %	Total N_2O_4	Total NO+ N_2O_4	Nitrite N_2O_3 as percent of Devarda N_2O_3	CO_2 %	N_2O %	Mol Ratio N_2O_3/N_2O_4	Mol Ratio NO/N_2O_4
6	-	-	-	-	-	-	-	14	10	-	-
7	37.8	21.8	59.6	14.9	44.7	59.6	84	-	12	2.10	1.02
8	47.6	23.2	70.8	18.8	52.0	70.8	86	-	14	2.48	1.11
9	47.1	21.8	68.9	18.7	50.2	68.9	86	-	5	2.62	1.14
12	7.6	0.4	8.0	3.1	4.9	8.0	99	-	14	26.2	1.88
14D	51.5	28.8	80.3	20.3	60.0	80.3	84	-	12	2.16	1.04
15D	61.4	12.1	73.5	24.2	49.3	73.5	93	-	23	6.14	1.51

Table XIII

Nature of the Acidity of Acetone-Dry Ice Condensate

Run	Wt. of Condens.	Acidity ml. 0.01N Alkali	Volatile Acidity (appx.)	Percent Volatile Acidity (appx.)	ml. 0.01N Alkali due to HCOOH	ml. 0.01N Alkali due to CH_3COOH	Total from HCOOH and CH_3COOH	Percent of Total	Percent of Volatile
3	0.061	32.4	32	100	9.8	-	-	-	-
4	0.055	32.4	28	85	11.1	-	-	-	-
5	0.077	48.3	38	80	-	19.7	-	-	-
7	0.092	38.9	39.5	100	13.0	18.0	31.0	79.5	78.5
8	0.106	44.8	43.5	100	17.8	19.1	36.9	82.5	85.0
9	0.037	15.4	15	100	5.3	8.2	13.5	87.5	90.0
10	0.128	70.5	-	-	-	-	-	-	-
11	0.122	69.5	-	-	-	-	-	-	-
12	0.176	93.0	97	100	61.0	38.2	99.2	107	102
14D	0.046	27.4	26	100	-	7.5	-	-	-
15D	0.037	24.7	21	85	11.5	10.2	21.7	88.0	103

Table XIV

General Composition of Acetone-Dry Ice Condensate (Weights)

Run	Wt. of Condens.	Water($\bar{a}$) (Karl Fischer)	HCHO	Glyoxal Determinations (a)					Glyoxal Ave.	HCOOH	CH_3COOH	Total Carbon-contng. Compds.	Diff. as Water
				A	B	C	D	E					
3	0.061	-	0.0031	0.0055	0.0059	-	-	-	0.0057	0.0045	-	-	-
4	0.055	-	0.0027	0.0033	0.0047	-	-	-	0.0040	0.0051	-	-	-
5	0.077	-	0.0035	-	0.0057	0.0059	0.0119	0.0067	0.0075	-	0.0118	-	-
6	0.067	0.053	-	-	-	-	-	-	-	-	-	-	-
7	0.092	-	0.0044	0.0064	0.0115	-	0.0082	0.0041	0.0075	0.0060	0.0108	0.0287	0.0633
8	0.106	-	0.0038	0.0079	0.0071	-	0.0076	-	0.0075	0.0082	0.0115	0.0310	0.0750
9	0.037	-	0.0011	0.0017	0.0037	-	-	-	0.0027	0.0016	0.0049	0.0103	0.0267
10	0.128	-	0.0106	-	-	-	-	-	-	-	-	-	-
11	0.122	-	0.0104	-	-	-	-	-	-	-	-	-	-
12	0.176	-	0.0181	0.0292	0.0256	-	-	-	0.0274	0.0280	0.0229	0.0964	0.0796
13D	0.041	-	0.0010	0.0002	-	-	-	-	0.0002	-	-	-	-
14D	0.046	-	0.0007	0.0026	0.0061	-	-	0.0045	0.0044	0	0.0045	0.0096	0.0364
15D	0.037	-	trace	0.0024	0.0064	-	0.0033	-	0.0040	0.0053	0.0061	0.0154	0.0216

(a) Analytical methods A, B, C, D and E have been described.

($\bar{a}$) Water determination made on starting material for Run 6; Value found, 0.036 g. H_2O in 1.049 g. of the cellulose mononitrate.

Table XV

General Composition of Acetone-Dry Ice Condensate (Percentages)

Run	Water (Karl Fischer)	HCHO	CHO CHO	HCOOH	CH_3COOH	Total Carbon-contng. Compds.	Water (by Diff.)
3	-	5.1	9.3	7.4	-	-	-
4	-	4.9	7.3	9.3	-	-	-
5	-	4.6	9.7	-	15.3	-	-
6	79	-	-	-	-	-	-
7	-	4.8	8.2	6.5	11.7	31.2	68.8
8	-	3.6	7.1	7.7	10.8	29.2	70.8
9	-	3.0	7.3	4.3	13.2	27.8	72.2
10	-	8.3	-	-	-	-	-
11	-	8.5	-	-	-	-	-
12	-	10.3	15.6	15.9	13.0	54.8	45.2
13D	-	2.4	0.5	-	-	-	-
14D	-	1.5	9.6	0	9.8	20.9	79.1
15D	-	trace	10.8	14.3	16.5	41.6	58.4

Table XVI

Carboxyl and Carbonyl Content of Residues

A: Composite of Mononitrate Residues 3-8, inclusive

B: Mononitrate Residue 9

C: Composite of Dinitrate Residues 14D and 15D

Material	COOH as % CO_2	C=O as % CO	millimols per g. of residue			mols per base weight of original material (a)		
			COOH	C=O	Total	COOH	C=O	Total
A	2.58	2.34	0.59	0.84	1.43	0.13	0.18	0.31
B	-	-	-	-	0.88	-	-	0.19
C	0.18	2.13	0.04	0.76	0.80	0.01	0.20	0.21

(a) Base weights: Mononitrate (7.56% N): 214
Dinitrate (11.64% N): 259

Table XVII

Water Extraction of Residues

(70 ml. water per g. of material;
four days at room temperature)

(a) Solubilities and Nitrogen Analyses:

Material	Portion	First Extraction Weight	%	N%	Second Extraction Weight	%	N%
		1.511 g. at 5.17% N			1.132 g.		
A	Soluble	0.156	10.3	4.01	0.062	5.5	2.8
	Insoluble	1.355	89.7	-	1.070	94.5	5.36
		0.722 g. at 6.29% N			0.527 g.		
B	Soluble	0.029	4.0	5.38	0.015	2.8	2.7
	Insoluble	0.693	96.0	-	0.512	97.2	6.36
		0.311 g. at 10.01% N					
C	Soluble	0.003	1.0	-			
	Insoluble	0.308	99.0	-			
		0.520 g. at 4.95% N			0.339 g. at 5.07% N		
D	Soluble	0.089	17.2	3.72	0.017	5.0	6.63
	Insoluble	0.431	82.8	5.07	0.322	95.0	5.14

(b) Carbonyl and Carboxyl Analyses:

		First Extraction				
Material	Portion	COOH as % CO_2	C=O as % CO	COOH m-mols/g.	C=O m-mols/g	COOH+C=O mm/g.
A	Soluble	12.6	0.09	2.86	0.03	2.89
	Insoluble	1.59	2.15	0.36	0.77	1.13
B	Soluble	-	-	-	-	3.62
	Insoluble	-	-	-	-	0.74

Note: In tables above, materials assigned as A, B, C are the same as in Table XVI.

Material D is mononitrate residue 5

Table XVIII

Molar Yields of Nitrogen Gases

(Expressed as their equivalent in millimols
nitrate ester per gram of starting material)

Run	Starting Weight	N_2O_3 (76/2=38)	N_2O_4 (92/2=46)	N_2O (44/2=22)	Total
6	1.049	-	-	0.30	-
7	1.193	1.58	0.76	0.88	3.22
8	1.189	1.17	0.47	0.59	2.23
9	1.184	0.69	0.26	0.10	1.05
14D	1.215	1.22	0.56	0.47	2.25
15D	1.018	1.21	0.20	0.77	2.18

Table XIX

Molar Yields of Volatile Carbonyl Compounds

(Expressed as their equivalent in millimols
of carbonyl per gram of starting material)

Run	Starting Weight	HCHO (30/1=30)	HCOOH (46/1=46)	$(CHO)_2$ (58/2=29)	CO_2 (44/1=44)	$(CHO)_2$+ HCOOH+ HCHO Total
3	1.003	0.10	0.10	0.20	-	0.40
4	1.008	0.09	0.11	0.14	-	0.34
5	1.016	0.12	-	0.26	-	-
6	1.049	-	-	-	0.21	-
7	1.193	0.12	0.11	0.22	-	0.45
8	1.189	0.11	0.15	0.22	-	0.48
9	1.184	0.03	0.03	0.08	-	0.14
10	0.539	0.66	-	-	-	-
11	0.488	0.71	-	-	-	-
12	0.566	1.06	1.07	1.67	-	3.80
13D	0.334	0.10	-	0.02	-	-
14D	1.215	0.02	0	0.13	-	0.15
15D	1.018	0	0.11	0.14	-	0.25

Table XX

Yields of Carbon Dioxide (By Difference)

Run	Wt. of Liq. Air Condens.	$N_2O_3+N_2O+N_2O_4$ (Table XI)	Diff. as CO_2 (grams)	m-mols CO_2 per g. of original NC	$HCHO+(CHO)_2+HCOOH$ (Table XIX)	Total m-mols per gram
7	0.190	0.135	0.055	1.05	0.45	1.50
8	0.111	0.094	0.017	0.33	0.48	0.81
9	0.066	0.049	0.017	0.33	0.14	0.47
12	0.086	0.019	0.067	2.69	3.80	6.49
14D	0.109	0.100	0.009	0.17	0.15	0.32
15D	0.076	0.073	0.003	0.07	0.25	0.32

Table XXI

Staudinger Viscosities

Material	% N	Solvent	Intrinsic Viscosity(a)	D.P.(b)
Cellulose-Dinitrate	11.64	Butyl Acetate	0.77	208
Composite Dinitrate Residue	10.01	Butyl Acetate	0.17	46
Nitrated Composite Mononitrate Residue	9.94	Butyl Acetate	0.12	32

(Viscosities measured at 25°C)

(a) Intrinsic Viscosity= $[\eta] = \left|\frac{\eta_{sp}}{c}\right._{c \to 0}$

(b) Assuming Kraemer's formula for cellulose nitrates in acetone solvent: D.P.= $270[\eta]$

DISCUSSION OF RESULTS

A. SYNTHESIS OF A "CELLULOSE-6-MONONITRATE" AND OF A "CELLULOSE DINITRATE"

As a preliminary to studies on the thermal decomposition of the cellulose mononitrate and the cellulose dinitrate, it was necessary to synthesize a fairly large amount of the materials. The synthesis of these cellulose derivatives has already been described in detail by Levi, Lemieux and Purves (1). However, it was considered worthwhile here to report the relatively large-scale preparation, if only briefly, because of the value of confirming yields and reaction conditions.

Appreciable deviation from the course of the previous synthesis (1) occurred in the acetylation of the trityl cellulose. Trityl cellulose of substitution 1.05, yielded a "trityl-acetate" of the following composition: trityl substitution 0.90, acetyl substitution 0.91. Although this compound has as high a trityl substitution as the one reported by Levi, Lemieux and Purves (1), the acetyl value is about 10% lower. This would account for the higher nitrate substitution observed in the product obtained by nitration of the "trityl-acetate", which in turn explains the higher nitrate substitution of the cellulose mononitrate. The relative proportion of primary and secondary nitrate groups in the mononitrate (substitution, 1.16) was estimated by the iodination technique adapted for cellulose nitrates by Murray and Purves (69). The procedure actually used was similar to that employed by Oldham and Rutherford (70) in iodination of nitrated methyl glucosides. Results indicate that 66% of the nitrate ester groups of the cellulose mononitrate are in the primary position. In other words, the substitution value of 1.16 mols of nitrate ester per glucose residue, is made up as follows: 0.76 mols of primary ester, and 0.40 mols of secondary ester.

Nitration of the cellulose-6-nitrate using a mixture of nitric and phosphoric acids as described by Berl (40), yielded the "dinitrate", which was also subjected to thermal decomposition studies.

The following is a summary of the synthesis. Values given are mols of substituent per glucose anhydride unit. Values in brackets are those reported by Levi, Lemieux and Purves in the original synthesis.

Table XXII

Summary of the Synthesis

	Trityl	Acetyl	Nitrate
Trityl-Cellulose	1.05(0.97)	-	-
Trityl-Acetate	0.90(0.87)	0.91(1.04)	-
Acetate-Nitrate	-	0.91(1.04)a.	1.20(1.05)
Nitrate	-	nil a.	1.16(0.97)
Dinitrate	-	nil a.	2.15(2.05)

(a. these values are assumed)

The justification of assuming the absence of acetyl in the cellulose mononitrate and dinitrate is somewhat in doubt, in view of recent work (71). These substances probably contain quite a scattering of acetyl groups, and the substitution values quoted are therefore subject to some alteration.

B. GENERAL OBSERVATIONS AND CONCLUSIONS REGARDING THE THERMAL DECOMPOSITIONS

In this section, the discussion concerns the analytical results appearing in Tables VII to XXI; and in addition, use is made of certain average data incorporated in Tables XXIII to XXIX. These "run-averages" pertain to the following three conditions:

A: Cellulose mononitrate, heated at ca. 1 mm. and 165±3°C for four hours.

B: Cellulose mononitrate, heated at ca. 1 mm. and 155±3°C for four hours.

C: Cellulose dinitrate, heated at ca. 1 mm. and 155±3°C for four hours.

Comparisons are possible between series A and B, and between B and C; the first comparison showing the effect of temperature; the second showing the effect of the nature of the starting material.

1. Tables VII, VIII and XXIII show the quantitative recovery of products of controlled decomposition when liquid air is used to condense the volatile compounds.

Table XXIII

Yields of Fractions as Percentages of Starting Material

Condition	Runs Averaged	Residue	Acetone-Dry Ice Condens.	Liquid Air Condens.	Total Condens.	Total Recov.
A	2-8	83.5	7.0	11.4	18.4	101.9
B	9	91.7	3.1	5.6	8.7	100.4
C	14D-15D	87.9	3.7	8.3	12.0	99.9

The recoveries signify that nothing escapes from the system, and therefore that theoretical conclusions are possible on the basis of analytical data. There is no justification in attaching importance to the fact that the recoveries were rather consistently above 100%, by a very small margin, since such deviations were well within the experimental error.

In runs where only acetone-dry ice cooling was employed, there is an appreciable weight-loss, since nitrogen gases cannot be condensed by acetone-dry ice at pressures of less than 1 mm. Similar weight-losses are evident when the nitrocelluloses decomposed spontaneously, even with liquid air cooling. It is probable that the very sudden production of gas in spontaneous decompositions caused volatile products to pass through the receiver assembly too quickly to be condensed quantitatively, even at liquid air temperature. Nevertheless, the cooling surface of the receivers was extensive, and weight losses were so substantial, that some major reaction product is believed to escape in these cases. This reaction product is in all probability nitric oxide, since consultation of vapor pressure data shows clearly that this gas cannot be retained in a liquid air trap at pressures below 1 mm. If nitrogen dioxide is also present then compound formation is possible, giving the much less volatile trioxide. Therefore no nitric oxide escapes when the molar amount of the dioxide is at least as great as that of the former.

2. Tables VII and VIII also give some indication of the reproducibility of the decompositions, when conditions are kept the same. Such variations are to be expected since there was no control over other factors, including the extent of the surface of the decomposing nitrate, and photochemical effects.

Other Tables also illustrate these variations, but with a given set of conditions (temperature, pressure and duration of heating), the runs seem to differ only in extent, not in nature of the decomposition. For example, from Tables VII and VIII it is seen that in runs 5, 7 and 8, the reaction has proceeded farther than the mean of runs 2-8, which were all carried out under the same conditions. These runs, 5, 7 and 8, underwent more extensive decomposition as judged by the values for percent of nitrogen in the residue, and for relative nitrate ester cleavage, given in Table IX.

3. The fact that the cellulose dinitrate tends to decompose spontaneously at a somewhat lower temperature than the mononitrate is evident in Table VII. If the temperatures (165°C) for the two explosions, which have already been described, are included, the average spontaneous decomposition temperature for the mononitrate is 180°C, whereas that for the dinitrate is 170°C.

4. Under the same set of controlled conditions (Table XXIV), the extents of ester cleavage and of nitrogen gas formation in dinitrate decomposition are about double those observed in the case of the mononitrate.

Table XXIV

Molar Yields of Nitrogen Gases

Condition	Runs Averaged	N_2O_3 (76/2=38)	N_2O_4 (92/2=46)	N_2O (44/2=22)	Total	m-mols ester cleaved/g. orig. NC
A	7-8	1.38	0.61	0.74	2.73	2.63
B	9	0.69	0.26	0.10	1.05	1.28
C	14D-15D	1.22	0.38	0.62	2.22	2.03

(Note: The values for nitrogen gases are in millimols of nitrate ester per gram of starting material, and thus are comparable with values given in the right-hand column).

Such comparisons, of course, can only be made in a semi-quantitative way, because surface conditions of the two nitrates are entirely different; one being a powder and the other a fine fiber. The study of this problem from the point of view of chemical kinetics would require much greater precision, much more elaborate equipment, and probably an entirely different technique.

5. Tables IX and XXV (Series A) show that controlled decomposition of four hours duration at 165±3°C brings about the removal of nearly half of the nitrogen from the original mononitrate.

Table XXV

Nitrogen Balance

Condition	Runs Averaged	% N in Residue	% N Loss	% of original nitrogen Volatilized	m-mols ester cleaved/g. orig. NC
A	2-8	5.20	2.36	42.3	2.29
B	9	6.29	1.27	23.7	1.28
C	14D-15D	10.01	1.63	24.4	2.03

Although this is a very profound chemical change, even visual examination of the residues suggests that degradation of the cellulose has been slight. It would seem that 40-50% of the nitrogen has been removed from the mononitrate by ester cleavages which may demolish the alcoholic nature of the group concerned, but which do not in general, lead to demolition of the main glucose structure. This observation definitely accentuates the primary nature of the decompositions studied. Even in runs 10, 11 and 12, where spontaneous decomposition of the mononitrate occurred, the amount of nitrogen volatilized was not much greater than that observed in controlled decompositions.

Dinitrate decompositions 14D and 15D have volatilized nitrogen values of only 20-25%, but there is almost twice as much nitrogen originally present in the case of the dinitrate. Spontaneous decomposition results in nearly 100% volatilization of the nitrogen originally in the dinitrate, which in this respect departs from the behaviour of the mononitrate.

Four hours' treatment of the mononitrate at 155±3°C, rather than at 165±3°C, gives about half the volatilized nitrogen value; the reaction rate being doubled for an increment of about ten degrees. Although decompositions were not carried out at temperatures lower than 155°C, it is probable that the temperature influence is exponential in nature, as in most chemical reactions.

6. In Table X, an attempt has been made to account for the volatilized nitrogen on the basis of analysis of the condensates. In runs 7, 8, 9, 14D and 15D, which are controlled decompositions, the volatilized nitrogen can be fairly well accounted for by the amounts of nitrogen dioxide, nitrogen trioxide and nitrous oxide detected. The discrepancies are certainly within the range of experimental error. Similar data can be found in

Table XXIV, which indicates that the number of millimols of nitrate ester cleaved checks with the total molar amount of nitrogen gases.

Spontaneous decompositions show very large discrepancies, the greater part of the volatilized nitrogen being lost. In run 13D, a dinitrate decomposition, only 1% could be explained on the grounds of distillate analysis.

7. There is evidence regarding the nature of the primary decomposition process in the data of Tables XI, XII, and XXIV. The three compounds, nitrogen dioxide, nitrogen trioxide and nitrous oxide, form the bulk of the liquid air condensate. Furthermore, the oxide with nitrogen in the higher valence form, NO_2, is present in large proportion when the amount condensed with nitric oxide as nitrogen trioxide, is included. The presence of N_2O_3 should not be assigned any great significance, since nitrogen dioxide and nitric oxide always produce this compound, which normally decomposes into its two constituent gases upon volatilizing.

The large amount of nitrogen dioxide observed could not very well be formed from nitric or nitrous oxides as a secondary effect, since atmospheric oxygen is the only agent which might, under the experimental circumstances, cause the conversion. Nitrous oxide is inert to such oxidation, and can be eliminated as a possible precursor of nitrogen dioxide. As for nitric oxide, it is known that atmospheric oxygen does convert it to nitrogen trioxide, the reaction proceeding quite readily at liquid air temperature (72). However, calculation showed that there could not be sufficient residual oxygen present in the highly-evacuated system at a given instant to cause appreciable re-oxidation. If this oxidation were an accumulative effect over the period of four hours, the nitric oxide molecule would have to be retained in the liquid air receiver for a finite length of time pending reaction with an oxygen molecule, and this retention is known to be impossible because of the volatility of nitric oxide.

The only logical conclusion is that nitrogen dioxide is the primary decomposition product of the nitrocellulose. Other workers have also produced evidence for this inference (8,21,22). The lower oxides of nitrogen most certainly arise from the nitrogen dioxide as the result of secondary reactions, which are almost inevitable in view of the powerful oxidizing character of nitrogen dioxide, and the abundance of easily oxidizable organic material in the system.

It would seem reasonable that if pentavalent nitrogen had any significance as a primary decomposition product, then nitrogen pentoxide would occur in admixture with the lower nitrogen oxides, just as nitrogen dioxide occurs in their presence. No nitrogen pentoxide was detected among the products from these decompositions, and its formation is not to be expected on theoretical grounds.

8. The mol ratios of nitrogen trioxide to nitrogen dioxide, and nitric oxide to nitrogen dioxide, listed in Table XII, shall be left without extensive comment. There is not enough evidence to make any generalizations about differences in these ratios from one run to another, or from one set of conditions to another. Apart from run 15D, all the controlled decompositions seem to have fairly constant ratio values. The very high value for run 12 may confirm what is suspected about spontaneous decompositions; namely that secondary reactions come into prominence, giving nitrogen oxides which are generally lower in state of oxidation.

9. Tables XIV, XV, XXVI and XXVII give quantitative data concerning the relatively small amounts of carbonyl compounds which must cleave from the main body of the nitrocellulose at some stage of the decomposition.

Table XXVI

General Composition of Acetone-Dry Ice Condensate

Condition	Runs Averaged	HCHO %	$(CHO)_2$ %	HCOOH %	CH_3COOH %	H_2O % (by diff.)
A	3-8	4.6	8.3	7.7	12.6	66.8
B	9	3.0	7.3	4.3	13.2	72.2
C	14D-15D	0.8	10.2	7.2	13.2	68.6

Table XXVII

Molar Yields of Volatile Carbonyl Compounds

Condition	Runs Averaged	HCHO (30/1=30)	$(CHO)_2$ (58/2=29)	HCOOH (46/1=46)	CO_2 (44/1=44)	Total
A	3-8	0.11	0.21	0.12	0.69	1.13
B	9	0.03	0.08	0.03	0.33	0.47
C	14D-15D	0.01	0.14	0.06	0.12	0.33

In the above Table, yields are expressed as their equivalent in millimols of carbonyl (C=O) per gram of starting material. The values for carbon dioxide, which have actually been obtained from analytical data for the liquid air condensate by a difference method, have been included, because carbon dioxide is considered to have arisen from carbonyl groups in a process of oxidation and decarboxylation. Acetic acid is not included in Table XXVII, since it was assumed to originate in residual acetyl groups present in the starting material. The carbonyl which it contains was also present originally, and was not formed in the decomposition.

Values for water, obtained by difference, are also included in Tables XIV, XV and XXVI. Only one actual water analysis is reported, but it was of the same order of magnitude as calculated water values in controlled decompositions.

In run 6, in which water was analyzed directly, the water content of the starting material was also estimated using a representative sample. It will be seen (Table XIV) that there is not nearly enough water present in the original material to account for that found in the distillate. This is therefore definite evidence that water is formed in the decomposition.

10. Carbon dioxide occurs in the liquid air condensate in appreciable amounts (see Tables XI, XII, XX, and XXVIII), and could be produced in the reaction in one of two ways: (a) by thermal decarboxylation of carboxyl groups known to be formed in the decomposition (Tables XVI and XVII) or, (b) by secondary oxidative attack of nitrogen dioxide on low molecular weight aldehydes (glyoxal and formaldehyde) cleaved from the nitrocellulose residue.

Table XXVIII

Composition of Liquid Air Condensate

Condition	Runs Averaged	N_2O_3 Percent	N_2O_4 Percent	N_2O Percent	CO_2 % (by diff.)
A	7-8	43.7	22.5	13.0	20.8
B	9	47.1	21.8	5.0	26.1
C	14D-15D	56.5	20.5	17.5	5.5

There is a strong possibility that the carbon dioxide found arises mostly by method (a). It is known that uronic acids decarboxylate readily upon treatment with hot 12% hydrochloric acid, and pyrolytic treatment may be equally effective in causing this reaction. Evidence for this concept lies in the fact that the dinitrate gives a residue with a much lower carboxyl content than that from the mononitrate (Table XVI), and at the same time has much less carbon dioxide in the liquid air condensate (Tables XX and XXVIII).

11. The formic acid which is produced in the decomposition reaction (Tables XIV, XV, XIX, XXVI and XXVII) presumably is an oxidation product of formaldehyde, although there is no direct evidence on this point. Steacie and co-workers (73) have shown that oxidation of gaseous glyoxal does not yield oxalic acid, and none was detected among the decomposition products. Kistiakowsky (74) postulated the formation of formaldehyde and formic acid in the oxidation of gaseous glyoxal, and Lenher (75) has demonstrated that nitrogen dioxide probably catalyzes the reaction.

It is very probable that any glyoxal oxidation under these conditions (presence of nitrogen oxides) proceeds by the course which is characteristic of 1,2-dicarbonyls, namely by carbon from carbon cleavage. This cleavage would, in the present case, give more formaldehyde and formic acid, thus making difficult the comparison of volatile carbonyl data with the nature of nitrate substitution in the starting material.

12. Comparison of Series B and C in Tables XXVI and XXVII shows that under similar conditions, the dinitrate tends to produce relatively more glyoxal and less formaldehyde

than the mononitrate. The importance of the formaldehyde difference is diminished when we compare relative formic acid yields; the dinitrate seemingly producing more formic acid than the mononitrate. The glyoxal values, although not differing greatly, are considered to be of significance. It would appear that secondary nitrate substitution tends to encourage glyoxal formation, a 2,3-diester grouping perhaps being the requisite. The cellulose dinitrate no doubt carries its secondary nitrate groups predominantly in one of the two possible positions. Even so, the probability of 2,3-diester groupings would be much greater in the dinitrate than in the mononitrate from which it was derived, and which must possess a small scattering of these secondary nitrate ester configurations.

13. Table XVI clearly shows the difference in carboxyl to carbonyl distribution in residues from mononitrate and dinitrate decomposition. This difference is reflected in the water-solubility (Tables XVII(a) and XVII(b)), where it is evident that the mononitrate residues are much more soluble than those from the dinitrate. Water-solubility, of course, could not in itself be taken as a measure of carboxyl content, since the degree of substitution and other factors are of importance.

14. Extraction of the residues with water removes the most changed or most decomposed portion, as indicated by nitrogen analyses (Table XVII(a)) and total carbonyl analyses

(Table XVII(b)), and also removes the portion of high carboxyl content (Table XVII(b)). The evidence for this inference is very striking. It is to be expected, then, that water-solubility should increase with extent of decomposition. This expectation is strongly supported by a comparison of the solubility data for composite residue A, and residues B and D in Table XVII(a). (D represents a mononitrate decomposition which proceeded farther than the mean depicted in A). Although numerical data have not been incorporated, it was observed that residues from the spontaneous decomposition of the mononitrate were even more soluble than residue D.

When the residues from the thermal decompositions were extracted by water (Tables XVII(a) and XVII(b)), 0.0033 g. of nitrogen were present in the extract and 0.0219 g. remained in the residue, in case D. The sum of 0.0252 g. agreed well with that, 0.0257 g., in the original residue. A re-extraction of the extracted residue (D), containing 0.0172 g. of nitrogen, accounted for a total of 0.0178 g. in the soluble and insoluble portions. In the same way, in an extraction of material A, the original carbonyl plus carboxyl content of 2.16 millimols was recovered to the extent of 1.98 millimols in residue plus extract. Such nitrogen and carbonyl balances afford convincing evidence as to the analytical accuracy of the various estimations.

15. Values for Series A, B and C in Tables XXIII to XXVIII can be related to data concerning A, B, and C which were obtained using composite samples in the case of A and C. Such data appear in Tables XVI, XVII and XXI. The most important of these relations is probably the following, which compares total carbonyl formation with total nitrogen-gas evolution.

Table XXIX

Balance Between Carbonyl Formation and Nitrogen Gas Evolution

Condition	Total Molar Yield of Carbonyls (mm/g.)	C=O+COOH in resid. (mm/g.)	Total Carbonyl Residue+ Volatile	Nitrogen *Gases mm. nitrate ester/g.)
A	1.13	1.19	2.32	2.73
B	0.47	0.74	1.21	1.05
C	0.33	0.67	1.00	2.22

Values in the above Table are expressed in millimols per gram of starting material. For column 3, this necessitated a re-calculation of the data in Table XVI, which was on the basis of millimols per gram of residue. In the re-calculation, residue percentages as shown in Table XXIII were used. Calculation for A: (1.43 x 83.5)/100=1.19 millimols per gram of starting material.

There is a strong indication in Table XXIX that in mononitrate decompositions (A and B) one carbonyl group is established for every nitrate ester group cleaved, on the average. The carbonyl group may be aldehydic, ketonic or carboxylic, and may cleave from the nitrocellulose residue, but regardless of its nature or location (distillate or residue) it must, in general, be established as the result of a single ester cleavage.

If subsequent oxidation by the primary nitrogen oxide decomposition product had the function of establishing additional carbonyls, then there would be a great discrepancy between the values shown in the last two columns of Table XXIX, particularly since the conversion of nitrogen dioxide to the substantial amounts of nitric oxide and nitrous oxide detected, represents an extensive oxidation.

It is believed, therefore, that subsequent oxidations by the initial decomposition product, nitrogen dioxide, are fairly well limited to:

(a) completion of the carbonyl formation,

(b) oxidation of aldehydic carbonyls to carboxyl groups both on the solid residue and in the gas phase, into which formaldehyde and glyoxal molecules are continually being ejected.

The corresponding data for condition C is not as satisfying. Here the data might suggest that nitrate ester cleavages produce carbonyls only 50% of the time. There may well be some special mechanism operative in secondary ester cleavage which manifests itself in the case of the dinitrate, and this possibility should not be overlooked. However, there is not enough evidence in hand to support any speculations on such a difference in behaviour. One explanation for the low carbonyl results would be that secondary ester cleavages produce ketonic groups on the more sterically hindered No. 2 and No. 3 positions, which are not completely estimated by the hydroxylamine reagent in the heterogeneous oximation. The actual synthesis of the cellulose mono- and dinitrates studied depends on steric hindrance in one of the secondary positions (1), and it is therefore to be expected that a similar hindrance would be in effect concerning the reactions of a secondary carbonyl group.

In fact, the anomalous behaviour shown in condition C, Table XXIX, may well be taken as more evidence for this postulated effect, rather than for any difference in the thermal decomposition mechanism.

16. The elimination of alcoholic groups in thermal decomposition is revealed by a re-nitration of the mononitrate residues (Series A). A product of nitrogen content 9.94% is obtained from this treatment, whereas nitration of the original mononitrate yields a product which analyzes for 11.64% nitrogen (Table XXI). Assuming the glucose anhydride base weight of 162 in both cases, these nitrogen analyses signify nitrate ester substitutions of 1.69 and 2.15, the decrease being 0.46 groups. For the mononitrate (base weight, 214) this decrease indicating loss of alcoholic hydroxyls, can be expressed as 2.15 millimols

per gram. From Table XXIX, it will be seen that this value agrees fairly well with the value for total carbonyl formation (2.32 millimols per gram) and that for the total nitrogen gas evolution (2.73 millimols per gram), in Series A.

17. The viscosities recorded in Table XXI refer to the re-nitrated cellulose mononitrate and its decomposition product. Since the method used in the re-nitrations is known to cause no appreciable degradation of cellulose, the viscosities refer to the mononitrate and its decomposition product, as well as to those of the re-nitrated derivatives. Moreover, since the degree of nitration of the products is similar, it seems legitimate to assume that the intrinsic viscosities of 0.77, 0.17 and 0.12 are proportional to the weight-average molecular weight of the substance.

The values for degrees of polymerization as calculated from intrinsic viscosities in Table XXI are not absolute, because the constant of proportionality had to be assumed. Nevertheless, they are certainly correct as regards relative order of magnitude.

It is apparent that in these controlled decompositions the average D.P. or molecular weight has been reduced to one-fifth or one-sixth of its original value. However this decrease does not represent very extensive cleavage of glycosidic bonds, as will be shown in the treatment to follow.

Kuhn (76) derived the following relationship for the degradation of polymer molecules of infinite length:

$$\alpha = 2/(n + 1)$$

where α is the optimum degree of hydrolytic cleavage for production of n-membered fragments. Substituting the data for the dinitrate residue, we have:

$$\alpha = 2/(46 + 1) = 0.0425$$

In other words, fission of about 4% of the glycosidic links should be the most favorable condition for formation of 46-membered fragments. The value for the mononitrate decomposition is roughly of the same order. This is really a maximum value, since the original chain is not infinite, but only about 200 units in length. The α-value obtained above indicates cleavage of 8 out of 200 bonds.

If every nitrate ester group split in thermal decomposition leads to breaking of the cellulose chain in one place, then 0.04 mols of nitrate ester cleaved from each glucose residue should be sufficient to cause the observed degradation. In the case of the mononitrate (base mol. wt. 214), this represents $(0.04 \times 1000)/214 = 0.19$ millimols per gram, and in the case of the dinitrate (base mol. wt. 259), $(0.04 \times 1000)/259 = 0.15$ millimols per gram.

The corresponding values in Table XXV indicate that the actual cleavages were 2.29 and 2.03 millimols per gram, respectively.

The conclusion from this calculation is that more than 90% of the time, the nitrate ester cleavage does not set off a chain of reactions which lead to cleavage of glycosidic links. Rather, the normal behaviour seems to be a change which is localized at the ester group concerned. A carbonyl may form and stay attached to the nitrocellulose residue, or may cleave from the residue during its formation, giving the low molecular weight aldehydic substances observed. If in this latter case, a stable state is not reached with one carbon from carbon fission, further bond cleavages can conceivably occur, and such a chain of reactions would ultimately demolish the glycosidic link.

Consultation of Table XXVII shows that the values for the total formaldehyde plus formic acid plus glyoxal are: 0.44 millimols per gram in A, and 0.21 millimols per gram in C; A and C being the conditions for which there is comparable viscosity data. Comparison of these values with the 0.19 and 0.15 millimols per gram calculated for cleavage, suggests that when there is a partial decomposition of the carbon structure of the glucose units, as evidenced by formation of volatile carbonyl compounds, a large number of the carbon from carbon fissions set off a chain of reactions which lead to cleavage of the glycosidic bonds.

C. THEORETICAL CONSIDERATIONS

1. The Primary Reaction:

Fission of the nitrate ester groups is considered to proceed by a free radical mechanism. For a primary nitrate group, this cleavage may be depicted as follows:

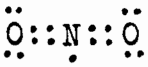
$$-CH_2O:NO_2 \longrightarrow -CH_2O\cdot + \cdot NO_2$$

and for a secondary nitrate group as:

$$\rangle CHO:NO_2 \longrightarrow \rangle CHO\cdot + \cdot NO_2$$

the two processes being entirely analogous.

One of the fragments produced, $\cdot NO_2$, does not need to undergo any further disintegration to reach a stable state. It is well known that the compound nitrogen dioxide is slightly paramagnetic, and modern electronic theory formulates it as an odd-electron molecule:

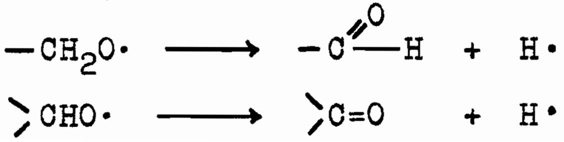


$$\underset{\cdot\cdot}{\ddot{O}}::\underset{\cdot}{N}::\underset{\cdot\cdot}{\ddot{O}}$$

The free radical shown above as resulting from the ester cleavage is identical with nitrogen dioxide.

The $\cdot NO_2$ free radical can proceed in one of two ways:
(a) leave the system as gaseous nitrogen dioxide, or
(b) react with other free radicals and compounds in processes which are primarily oxidative in nature.

The other product of symmetrical bond fission is not a stable free radical, but can readily stabilize itself by loss of atomic hydrogen, as follows:



$$-CH_2O\cdot \longrightarrow -C(=O)-H + H\cdot$$

$$\rangle CHO\cdot \longrightarrow \rangle C=O + H\cdot$$

with establishment of carbonyl groups. It is evident from the results of this work, that the carbonyl formation depicted forms part of the primary decomposition reaction.

The expulsion of atomic hydrogen may be encouraged by the proximity of $\cdot NO_2$ free radicals, and may even depend on it, but whether or not this is the case, $\cdot H$ will readily react as follows:

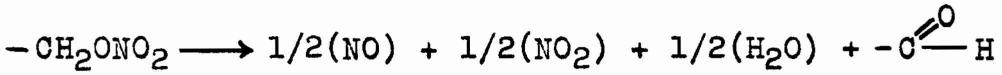
$$H\cdot \quad + \quad \cdot NO_2 \longrightarrow HNO_2$$

The nitrous acid produced would not be stable under these conditions, and would dissociate:

$$2HNO_2 \longrightarrow H_2O \quad + \quad (N_2O_3) \longrightarrow NO_2 \quad + \quad NO$$

This dissociation probably accounts for the water which is produced in the thermal decomposition, and for the large proportion of nitrogen trioxide (NO_2 + NO) found in the liquid air condensate. In this condensate, controlled decompositions always yielded more nitrogen dioxide than required for the trioxide formation, and therefore some $\cdot NO_2$ free radicals must escape from the system without taking part in the reaction with atomic hydrogen. This occurrence, and the possible consequences of it, are discussed in the section, "Secondary Reactions".

The overall primary process shall be considered as cleavage of $\cdot NO_2$, with subsequent establishment of aldehydic carbonyls on the No. 6 position, and of ketonic carbonyls on the No. 2 and No. 3 positions, the reactions being:



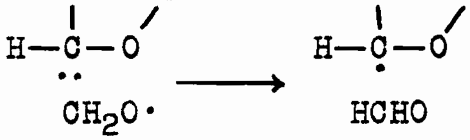
$$-CH_2ONO_2 \longrightarrow 1/2(NO) + 1/2(NO_2) + 1/2(H_2O) + -C\overset{O}{\diagup\!\!\!\diagup}\!\!-H$$

$$>CHONO_2 \longrightarrow 1/2(NO) + 1/2(NO_2) + 1/2(H_2O) + >C=O$$

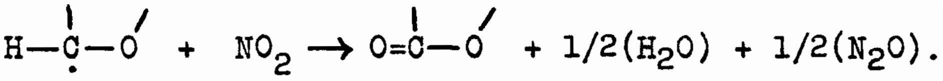
2. Secondary Reactions:

(a) Volatile Carbonyl Cleavage:

It is held to be likely that when $\cdot NO_2$ moves away from the decomposing nitrocellulose without having reacted with atomic hydrogen, the other free radical may choose in some cases to rearrange in a manner which involves carbon from carbon cleavage:



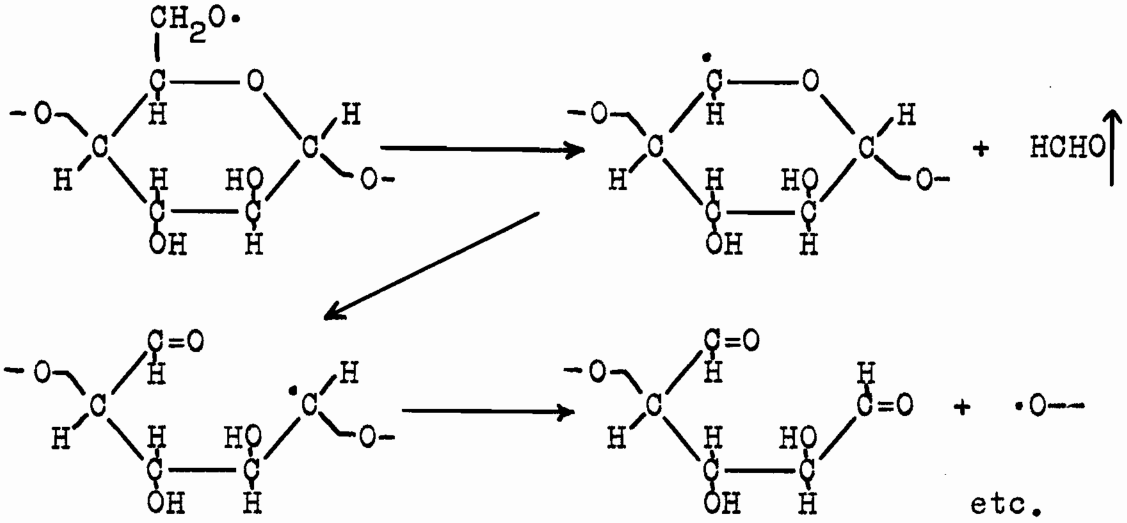
As a result, the carbon-containing fragment formaldehyde is released. The process could be terminated at this point by an oxidative attack on the No. 5 position of the cellulose, perhaps resulting in lactone formation:



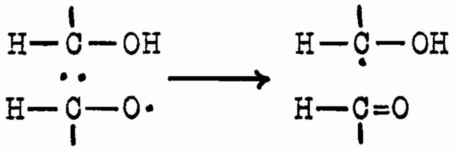
$$H-\overset{|}{\underset{\bullet}{C}}-O\diagup + NO_2 \rightarrow O=\overset{|}{C}-O\diagup + 1/2(H_2O) + 1/2(N_2O).$$

The occurrence of nitrous oxide can be explained on such grounds. However, it is postulated that to some extent a chain of free radical reactions is initiated when formaldehyde is cleaved; a chain which could be, and no doubt is, terminated in different stages by oxidation.

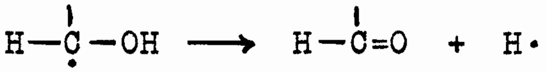
The following is an illustration of this scheme in the case of the cellulose-6-nitrate. It is quite evident that fission of the glycosidic links would occur in this process.



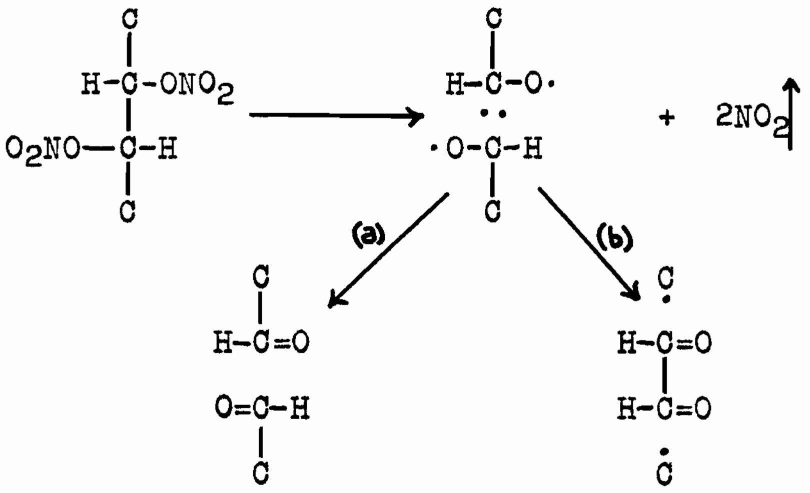
A single secondary ester cleavage may produce the same sort of chain effect:



or stabilization may be quickly attained by expulsion of atomic hydrogen:

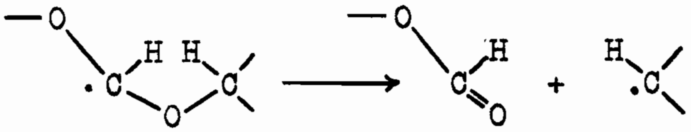


The 2,3-diester grouping can have the following reactions:



Route (a) leads to stabilization in one step; route (b) yields glyoxal, and two active centers which can set up chain reactions. It is believed that the glyoxal found present as a decomposition product arises to a large extent from 2,3-diester groupings, and hence route (b) must be followed part of the time.

Active center establishment on the No. 1 carbon atom such as results from glyoxal formation, can cause fission of the glycosidic bond in one step:



Therefore it is to be expected that No. 2 nitrate ester cleavages should, in general, be very effective in causing degradation.

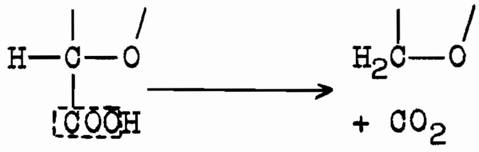
A natural conclusion from this discussion is that secondary nitrate substitution in cellulose gives products which are more apt to disintegrate profoundly on heating, than cellulose nitrates substituted in only the primary position.

(b) <u>Carboxyl-Group Formation and Subsequent Behaviour</u>:

Carbonyl groups established on the No. 6 position would be very readily oxidized, perhaps as follows:

$$\text{H}-\overset{|}{\text{C}}=\text{O} + \text{NO}_2 \longrightarrow \overset{|}{\text{C}}\text{OOH} + \text{NO}$$

Thermal decarboxylation of these structures would account for the sizeable amounts of carbon dioxide found in the liquid air condensate:



(c) Vapor-phase Reactions:

Vapor-phase reactions would be chiefly concerned with the oxidation of volatile carbonyl compounds. In this work, the formic acid detected is postulated to have its origin in such a secondary reaction, namely the partial oxidation of formaldehyde. Formic acid and formaldehyde may occur to some extent as products of partial oxidation of glyoxal, as was discussed in the section "General Observations and Conclusions".

These vapor-phase reactions involving nitrogen dioxide and aldehydic substances, carried to completion, probably assume great importance in the explosive decomposition of nitrocellulose, in which the concentrations of the reactants are much higher than in slow controlled decomposition *in vacuo*. A large increase in gas volume is to be expected from such reactions, as the result of formation of carbon monoxide, carbon dioxide, water vapor and lower nitrogen oxides, and this sudden production of gases may well account for some of the explosive power. What is more important, these exothermic oxidations, occurring most readily in the high-concentration area near the surface of the decomposing nitrate, would lead to intense surface heating, which would in turn accelerate the decomposition of the nitrate. The explosion of cellulose nitrate is probably dependent on such a sequence of rapidly developing, self-propagating effects.

CLAIMS TO ORIGINAL RESEARCH

1. A "cellulose-6-mononitrate" and its re-nitrated product were synthesized by slight modifications of published methods, and slight deviations in properties from published data were noted.

2. The controlled thermal decomposition *in vacuo*, of the above cellulose nitrates was extensively studied with the aid of a specially constructed all-glass apparatus. This apparatus made it possible to collect the volatile products of the decomposition as fractions retained in a dry-ice trap and in a liquid-air trap. It was possible to control many of the variable factors during the decomposition, and to recover the volatile and non-volatile products almost quantitatively.

3. Micro-scale adaptations of standard methods were developed for the estimation of the individual substances found mixed with each other in the volatile fractions. The mixture in the dry-ice trap consisted of water, formic acid, formaldehyde, glyoxal and acetic acid. That in the liquid-air trap included nitrogen dioxide, nitric oxide, nitrous oxide and carbon dioxide.

4. It was demonstrated that the thermal cleavage of one ester group in the mononitrate was accompanied by the formation of approximately one carbonyl group from the cellulose moiety. This carbonyl group largely remained

with the non-volatile residue but to some extent cleavage of the latter occurred with the liberation of volatile formaldehyde and glyoxal. The other primary product of the thermal decomposition was nitrogen dioxide. Results with the cellulose dinitrate were not inconsistent with the above interpretation, but were not so decisive, and certain differences in behaviour were noted.

5. The cellulose chain was degraded to an extent roughly corresponding with one glycosidic cleavage for each mol of volatile carbonyl compound. Non-volatile carbonyl units were apparently formed without involving degradation of the cellulose.

6. Rice and Ginell's free radical mechanism for the thermal decomposition of cellulose nitrates was modified to bring it into accord with the results of this investigation.

7. The experimental data, together with the modified theory, suggested that the secondary thermal decompositions in the gas phase concerned the reduction of the primary product, nitrogen dioxide, by atomic hydrogen, and also by lesser amounts of glyoxal and formaldehyde liberated from the cellulose residue. Thermal cracking of carboxyl groups in the latter might be the source of some of the carbon dioxide recovered among the volatile products.

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