THE REACTIONS OF HYDROGEN ATOMS WITH AMINES AND IMINES

by

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INTRODUCTION

The earliest successful attempt to isolate and study the properties of atomic hydrogen was the work of Langmuir in 1911 (1,2,3) in which he found that when a wire of tungsten, platinum or palladium, was heated above 1000°C. in an atmosphere of molecular hydrogen under low pressure, hydrogen atoms were produced and diffused away from the hot wire. The presence of hydrogen atoms was shown by their reduction of many metallic oxides and their reactivity with oxygen and phosphorous at room temperature. This method was later extended by Houtman et al (4) and has been used by LeRoy and co-workers (5,6,7,8) to study the reactions of hydrogen atoms with hydrocarbons. It is characterized by the production of low concentrations of hydrogen atoms and is very useful for investigating homogeneous reactions of hydrogen atoms in the gas phase.

Atomic hydrogen may also be produced by the mercury photosensitized decomposition of molecular hydrogen. The dissociation energy of the hydrogen molecule, i.e., D(H-H), is 103.5 kcal., corresponding to quanta of light of wave length 2750Å. If a sensitizer capable of absorbing light below 2750Å is mixed with molecular hydrogen and the mixture illuminated with a suitable ultra-violet lamp, energy transfer from the sensitizer to hydrogen can occur and lead to production of atomic hydrogen. Mercury vapour, which absorbs

strongly at the 2537Å resonance line, was first used by Taylor in 1925 (9) and is still generally used as the photosensitizer. The reaction may be represented by

$$Hg(^3P_1) + H_2 \rightarrow Hg(^1S_0) + 2\,H$$

The disadvantages of this method are that the atom concentration is low (of the order of 0.01 per cent) and that the reactant gas may itself undergo photolysis or photosensitized decomposition.

Darwent and Roberts (10,11) have used direct photolysis of H_2S to obtain atomic hydrogen in a static system according to the following reaction

$$H_2S + h\nu \rightarrow H + HS$$

It was first shown by Wood (12) in 1920, that molecular hydrogen could be dissociated into atoms by applying a suitable potential between the electrodes in a discharge tube at low pressures of hydrogen. Further, it was shown that the atoms could be pumped to considerable distances before recombination occurred. A number of reactions of atomic hydrogen with other reactants were studied in a rather cursory manner by Levi (13) using this method. He observed that atomic hydrogen acted as a comparatively mild reducing agent in most reactions. Using a Wood tube,

Bonhoeffer (14) investigated the reactions of atomic hydrogen with many substances, as a result of which the experimental approach has become known as the Wood-Bonhoeffer fast flow method. It should be noted that this method of producing atomic hydrogen is characterized by its low operating pressure and relatively high concentration of hydrogen atoms that may be produced. In fact, concentrations of hydrogen atoms as high as 50 per cent have been obtained at distances several centimetres from the discharge tube, when the inner surface of the apparatus is suitably poisoned and the pumping speed is sufficiently high.

There has been so much work done on hydrogen atom reactions that only a brief review is possible within the scope of this thesis. However, an excellent and detailed discussion of the subject is available in a treatise on "Atomic and Free-Radical Reactions" by Steacie (15) and it will suffice here to examine some of the more important reactions of atomic hydrogen that are related to the reactions of concern in the present study.

SOME IMPORTANT REACTIONS OF HYDROGEN ATOMS

Reactions with Saturated Hydrocarbons

The primary process is, in all cases, the abstraction of a hydrogen atom

$$RH + H \rightarrow R. + H_2$$

Reactions of this type have been investigated by many workers using hydrogen atoms and deuterium atoms produced in different ways.

Methane

When H-atoms from a discharge tube were introduced into methane, no reaction appeared to occur (16,17,18) even at temperatures up to 183°C. (19). The apparent inertness was confirmed by Geib and Steacie (20), who found no reaction with deuterium atoms up to 100°C.

From studies of the methane deuterium exchange reaction, using either the Wood-Bonhoeffer or the mercury-photosensitized methods to produce deuterium atoms (21,22 23,24), the activation energy for the exchange has been estimated to have various values in the range of about 11 to 15.6 kcal., with an assumed steric factor of 0.1 (20,21). When the methane-deuterium atom exchange reaction was studied by photolysis of D_2S mixed with methane (11), an activation energy >9 kcal. was obtained for the same assumed steric factor.

Recent work has indicated, however, that the activation energy for the reaction of methane with H or D atoms is probably much lower than the earlier studies

indicated, and that the apparent inertness of methane in such reactions is due to a much lower probability factor than had previously been assumed. Steacie, Darwent and Trost (25) suggested that the temperature co-efficients for the H-atom reactions seemed to be considerably lower than the values calculated for a steric factor 0.1, and LeRoy and co-workers have recently adduced both experimental and theoretical evidence to support an activation energy as low as 4.1 kcal. for the methane H-atom reaction, with a steric factor of about 10^{-5}. Steacie (15) is of the opinion that more likely values are 6.6 kcal. and 10^{-4} for the activation energy and steric factors respectively, these being the values derived by LeRoy from an objective consideration of all the data (26). At the present time, therefore, it does not seem possible to fix the kinetic constants for the reaction more closely than about 2 kcal. in the activation energy and a factor of 10 in the probability term.

Ethane

Wartenberg and Schultze (17) and Bonhoeffer and Harteck (27) found that the relatively slow reaction of H-atoms (discharge tube) with ethane was accompanied by luminescence (27,17). Considerable loss of gas (25 per cent) during the former experiments suggests that methane

might have been formed in the reaction and lost through the liquid air trap. They suggested the following reaction steps to explain the recovery of ethane

$$C_2H_6 + H \rightarrow C_2H_5 + H_2$$
$$C_2H_5 + H + M \rightarrow C_2H_6 + M$$

Chadwell and Titani (18), using a discharge tube as the source of H-atoms, obtained small quantities of methane and ethylene.

Steacie and Phillips (21) studied the reaction with D-atoms formed in a discharge tube and concluded that, at room temperature, the main reactions were

$$C_2H_6 + D \rightarrow C_2H_5 + HD \qquad ...1)$$
$$C_2H_5 + D \rightarrow C_2H_5D \qquad ...2)$$

The same reaction was further investigated by Trenner, Morikawa and Taylor (24), who found that the main product was methane, deuterated to the extent of 50 per cent. They postulated that it was formed by

$$D + C_2H_6 \rightarrow CH_3 + CH_3D \qquad ...3)$$
$$CH_3 + D \rightarrow CH_3D^{*} \rightarrow CH_2D + H$$

followed by subsequent hydrogenation and exchange of methyl radicals. However, ethane formed up to 100°C. was undeuterated

thereby ruling out reaction 2. They agree with Steacie's mechanism for ethane formation above 100°C. Steacie (28) later confirmed that methane was highly deuterated and ethane was slightly deuterated in the reaction. Reinvestigation of the reaction by Trost and Steacie (28) in a mercury photosensitized system yielded an activation energy of 9 kcal. with an assumed steric factor 0.1. It should be noted that in all experiments outlined above, the temperature coefficient of the reaction was not measured. Activation energies were calculated, from collision yields, with an assumed steric factor of 0.1.

Berlie and LeRoy (7) have reinvestigated the reaction of H-atoms with ethane, using the hot filament technique for producing hydrogen atoms. They obtained an activation energy of 6.8 kcal. and a steric factor of 4.8×10^{-3}. This activation energy is in excellent agreement with estimates of the activation energy for the back reaction and the bond dissociation energies. They suggest the following reactions

$$H + C_2H_6 \rightarrow H_2 + C_2H_5$$

$$H + C_2H_5 \rightarrow 2\ CH_3$$

$$H \rightarrow 1/2\ H_2$$

$$H + C_2H_5 \rightarrow C_2H_6$$

$$H + CH_3 \rightarrow CH_4$$

The reaction of ethane with H-atoms and D-atoms, obtained by the photolysis of H_2S and D_2S, has been studied by Darwent and Roberts (10). They obtained 9.8 kcal. and 0.6 for the activation energy and steric factor respectively.

The reaction of H-atoms and D-atoms with other saturated hydrocarbons follow the same type of reaction mechanism outlined above and need not be detailed here.

Reaction of H-atoms with Unsaturated Hydrocarbons

Studies of the mercury photosensitized reactions of ethylene with hydrogen or deuterium have shown that the reaction is quite complicated.

Taylor and Marshall (29) observed a high reaction rate and suspected á chain reaction. Ethane was the main product. Using a mass-spectrometer, Olson and Meyers (30, 31) found that among the reaction products were propane, butane and possibly methane in addition to ethane, while Klemenc and Patat (32) and Bates and Taylor (33) observed some polymerisation to accompany the hydrogen atom attack. A thorough investigation of this reaction by Taylor and Hill (34,35) revealed ethane as the only important product. With higher ethylene to hydrogen ratio, however, other hydrocarbon products were formed.

In contradiction to Taylor and Hill, Jungers and

Taylor (36) found that butane was the main product when hydrogen was in excess. They ascribe the discrepancy to the presence of polymer in Taylor and Hill's experiments.

The primary process in the reaction of ethylene (and unsaturated hydrocarbons generally) is, in all probability, addition of a hydrogen atom, rather than hydrogen atom abstraction as with saturated hydrocarbons,

$$H + C_2H_4 \rightarrow C_2H_5$$

Since very little ethane is formed, according to Jungers and Taylor, the reaction

$$H + C_2H_5 \rightarrow C_2H_6$$

did not occur to any appreciable extent. This is not surprising in view of the very low H-atom concentration present in the photosensitized system. The reaction

$$2\ C_2H_5 \rightarrow C_4H_{10}$$

would favour the formation of butane especially in the presence of excess ethylene to act as a third body. The formation of small quantities of ethane could result from

$$2\ C_2H_5 \rightarrow C_2H_6 + C_2H_4$$

which has been shown by LeRoy and Kahn (37) to have an activation energy $\leq$ 1.2 kcal.

The reaction of ethylene with H-atoms from a discharge tube was shown to be very fast, and to result mostly in ethane, together with a small quantity of acetylene (17).

The reaction of ethylene with H- and D-atoms has been studied recently by Toby and Schiff (38). The major products of the reaction were methanes, ethanes and ethylenes with minor amounts of propanes and butanes. The methanes were found to be highly deuterated while ethanes were only slightly deuterated. The following mechanism was proposed to explain the formation of various products

$$H + C_2H_4 \rightarrow C_2H_5 \quad ...1)$$

$$C_2H_5 \rightarrow C_2H_4 + H \quad ...2)$$

$$H + C_2H_5 \rightarrow C_2H_6^{*} \quad ...3)$$

$$C_2H_6^{*} \rightarrow C_2H_5 + H \quad ...4)$$

$$M + C_2H_6^{*} \rightarrow C_2H_6 + M \quad ...5)$$

$$C_2H_6^{*} \rightarrow C_2H_4 + H_2 \quad ...6)$$

$$C_2H_6^{*} \rightarrow 2\ CH_3 \quad ...7)$$

$$H + CH_3 \rightarrow CH_4^{*} \quad ...8)$$

$$CH_4^{*} + M \rightarrow CH_4 + M \quad ...9)$$

$$2\ CH_3 \rightarrow C_2H_6 \quad ..10)$$

Corresponding reactions with D-atoms and ethylene were presumed to occur.

Geib and Harteck (39) found that, even at liquid air temperatures, H-atoms reacted with ethylene to give ethane, which indicates a very low activation energy for hydrogenation under these conditions, when reaction was probably surface catalysed.

Propylene

In the reaction of propylene with hydrogen atoms produced in a discharge tube, Rabinovitch, Davis and Winkler (40) observed methane, ethane and propane among the reaction products, which consisted mainly of ethane. A C_4 hydrocarbon, possibly butane, was also produced. The reaction mechanism proposed included the formation of "hot" radicals, which, because of the excess energy inherent in them, were capable of reacting at room temperature in a way that would otherwise be possible only at elevated temperatures; e.g.,

$$H + C_3H_8 \rightarrow C_3H_7^{*}$$
$$C_3H_7^{*} + H_2 \rightarrow C_3H_8 + H$$
$$C_3H_7^{*} \rightarrow C_2H_4 + CH_3 \quad \text{etc.}$$

Melville and Robb (41,42) studied the propylene-H-atom reaction by comparing the rate at which yellow molybdenum oxide turned blue, in competition with the rate of

hydrogenation in the presence of H-atoms produced in a mercury photosensitized system. They found an activation energy of 2.5 kcal. for an assumed steric factor of 10^{-2} for the reaction. With D-atoms produced by photolysis of D_2S, Darwent and Roberts obtained a value, probably too high, of E = 5 kcal.

Reaction of Hydrogen Atoms with Alkyl Chlorides

Böhm and Bonhoeffer (43) found that rapid reaction occurred between methyl chloride and hydrogen atoms produced in a discharge tube. The reaction was reinvestigated by Chadwell and Titani (18) who identified hydrogen chloride, ethane and methane in the reaction products. They observed about 10 per cent reaction at 100°C. and the primary step was assumed to be

$$H + CH_3Cl \rightarrow HCl + CH_3.$$
$$CH_3. + H_2 \rightarrow CH_4 + H$$
$$CH_3. + H \rightarrow CH_4$$
$$2\ CH_3. \rightarrow C_2H_6$$

Cremer, Curry and Polanyi (44) observed that the activation energy for the reaction of H-atoms with methyl chloride was about 7 kcal. To account for the total observed loss of H-atoms, they suggested that in addition to HCl production, there also occurred the reaction

$$H + CH_3Cl \rightarrow H_2 + CH_2Cl$$

However, no products were obtained to substantiate this assumption. Steacie (15) has suggested that the loss of H-atoms might be due to the following reactions

$$H + HCl \rightarrow H_2 + Cl$$
$$H + CH_3 \rightarrow CH_4$$

The mercury photosensitized reaction of H-atoms with methyl chloride has been investigated by Lee and LeRoy (45), the main products at 25°C. being methane, ethane and dichloroethane. They postulated the mechanism

$$Hg\ (^3P_1) + H_2 \rightarrow Hg\ (^1S_0) + 2\ H$$
$$H + CH_3Cl \rightarrow HCl + CH_3$$
$$CH_3 + CH_3Cl \rightarrow CH_4 + CH_2Cl$$
$$2\ CH_2Cl \rightarrow C_2H_4Cl_2 + H_2$$

The reaction of ethyl chloride with H-atoms is important for the present study as it has been used in this laboratory to estimate the concentration of hydrogen atoms at room temperature. Chadwell and Titani (18) obtained results similar to those with methyl chloride, the main products being HCl, methane and ethane. They concluded that between 33 and 39 per cent reaction occurred at room temperature and that the primary process was

$$H + C_2H_5Cl \rightarrow HCl + C_2H_5$$

Reactions of Amines and Imines

Thermal decomposition of amines

Methylamine: The thermal decomposition of a number of amines has been studied by various authors and seemingly all conceivable mechanisms involving radicals have been postulated (46-62) to explain the formation of hydrogen, hydrogen cyanide, methane, ammonia etc. The complex reactions involved in these decompositions of amines have been discussed in detail by Schumacher (62).

Two mechanisms have been proposed by Emeléus and Jolley (56) for the thermal decomposition of methylamine. The decomposition reaction

$$CH_3NH_2 \rightarrow 2\ H_2 + HCN$$

was observed to be unimolecular and mostly homogeneous. This reaction has been investigated by Travers (61) who concluded that there is probably a process involving two molecules of methylamine, the overall change in which can be represented by the following equation

$$2\ CH_3NH_2 \rightarrow H_2 + CH_4 + HCN + NH_3$$

He postulated that H_2, CH_4 and HCN are formed by the decomposition of a compound which must have the formula C_2H_7N.

Carter and co-workers (63) have postulated that the decomposition involves three stages and that the reaction is initiated by a surface reaction

$$2\ CH_3NH_2 \rightarrow H_2 + \text{Product 1}$$
$$\text{Product 1} \rightarrow HCN + \text{Product 2}$$
$$\text{Product 2} \rightarrow HCN + ?$$

Ethylamine: The thermal decomposition of ethylamine has been investigated from 500-1000°C.(46). At 500°C., the products were ammonia and unsaturates, whereas at 700°C. the products were ammonia, HCN and ethane, with traces of unsaturates, hydrogen and nitrogen. Some evidence for the presence of acetonitrile was also obtained. Saturated hydrocarbons were formed at 1000°C. There was no ammonia or hydrogen cyanide, but free hydrogen and nitrogen were detected. Upson and Sands (46) suggest the following reaction mechanism

$$CH_3CH_2NH_2 \rightarrow CH_3CN + 4\ H$$
$$CH_3CN \rightarrow HCN + CH_2$$
$$2\ CH_2 \rightarrow C_2H_4$$

Taylor (47) found the thermal decomposition of ethylamine to be homogeneous and unimolecular, in a static system at 500-540°C., over a pressure range of 50-400 mm.

mercury. No mention of the products was made although it was assumed that the decomposition proceeded by

$$C_2H_5NH_2 \rightarrow C_2H_4 + NH_3$$

Schumacher and Wiig (50) suggested that the decomposition was heterogeneous and that the velocity of the reaction was influenced by foreign materials. Thermal decomposition of ethylamine at 600°C. and 900°C. gave CH_3CN and hydrogen, with smaller quantities of ammonia, ethylene, hydrogen cyanide and methane (48). The proposed mechanism considered the reaction to proceed through an aldimine

$$CH_3CH_2NH_2 \rightarrow \left[H_2 + CH_3.CH{:}NH\right] \begin{matrix} \nearrow CH_4 + HCN \\ \searrow CH_3CN + H_2 \end{matrix}$$

It was also postulated that the reaction of unreacted amine with hydrogen atoms yielded ammonia and ethane,

$$CH_3CH_2NH_2 + 2\,H \rightarrow C_2H_6 + NH_3$$

The above reaction has to be viewed with caution in the light of the reactions studied in this laboratory.

t-Butylamine: The thermal decomposition of tertiary-butyl amine has been investigated in a static system from 498-541°C. by Pritchard, Sowden and Trotman-Dickenson (65). The increase in pressure during the reaction has been

attributed to the following reactions

$$C(CH_3)_3NH_2 \rightarrow C(CH_3)_2{:}CH_2 + NH_3$$
$$C(CH_3)_3NH_2 \rightarrow C_3NH_7 + CH_4$$

They concluded from a measurement of ammonia and methane that the activation energies for the above reactions were not markedly different. No free radicals were involved in the reaction, as demonstrated by the addition of toluene.

Di- and trimethylamines: The thermal decomposition of dimethyl amine (52) in a static system at 480-500°C. was shown to be homogeneous and unimolecular with an activation energy of 44 kcal. Taylor concluded from his studies, "that the simplicity of the decomposition is illusory, due to mutual compensation of several concurrent reactions". and suggested that methyl hydrazine was formed at lower temperatures and complex products at elevated temperatures, the gaseous products of the reaction being hydrogen, methane and ethane. The reaction was represented by

$$2\ (CH_3)_2NH \rightarrow N(CH_3)_3 + CH_3.NH_2$$
$$N(CH_3)_3 \rightarrow CH_4 + CH_3.N{:}CH_2$$

The thermal decompositions of di- and trimethylamines, as well as methylamine, were studied by Carter et al (63) using chemical methods of analysis to follow the reaction.

They found the complexity of the reaction to increase on passing from trimethylamine to methylamine; however, marked similarity was observed in the thermal decomposition of dimethyl and trimethylamines. This is an interesting point to bear in mind in relation to the present problem.

Romeny (64) found that when trimethylamine was passed through a tube heated to dull redness, a liquid product having the formula $(C_2H_5N)_2$ was obtained, together with hydrocarbons, hydrogen cyanide and ammonia. He concluded that the main reaction could be represented by

$$(CH_3)_3N \rightarrow CH_4 + C_2H_5N$$

followed by the polymerisation of methyl methylene-imine (C_2H_5N).

Rice and Johnston (66) passed the vapours of trimethyl and dimethylamine through tubes heated to 1000°C. and measured the rate of removal of standard mirrors, thereby obtaining a measure of methyl radicals in the emerging gas streams. They obtained a value of 51-52 kcal. for $D(CH_3\text{-}N)$. Their results substantiated the work of Romeny. They also detected HCN in the reaction products at 480°C., but not below this temperature. The reaction mechanism suggested was

$$(CH_3)_3N \rightarrow CH_3. + (CH_3)_2N.$$

$$(CH_3)_3N + CH_3 \rightarrow CH_4 + (CH_3)_2N.CH_2.$$

$$(CH_3)_2N.CH_2. \rightarrow CH_3. + CH_3.CH_2.N:$$

The methyl radicals were the chain carriers. The chains appeared to originate in the gas phase and to be broken at the surface.

Photochemical decomposition of amines and imines

Photolysis: The photolysis of various amines has been investigated (33,67-75). The products of the photolysis of methylamine and ethylamine were hydrogen, ammonia, methane, nitrogen, ethane, ethylene and polymer (75). The primary process in the photolysis of primary and secondary amines appears to be

$$RNH_2 + h\nu \rightarrow RNH + H$$

followed by

$$H + RNH_2 \rightarrow RNH + H_2$$

It is suggested by Wetmore and Taylor (69) that the methyl amino radical, CH_3NH, produced during photolysis of methylamine could dissociate to give the methylenimine radical, i.e.,

$$CH_3NH \rightarrow CH_2NH + H$$

It may be pointed out that the HCN formed during the thermal

decomposition of methylamine (56) could be the result of decomposition of this radical, before it reacts with methylamine to yield ammonia, i.e.,

$$CH_2 = NH \rightarrow HCN + H_2$$

rather than

$$CH_2 = NH + CH_3NH_2 \rightarrow NH_3 + CH_2.N.CH_3$$

It is suggested by Bamford (73) that in the photolysis of primary and secondary amines, hydrogen atoms and alkylamino or dialkylamino radicals are produced. These radicals are assumed to undergo disproportionation reaction to yield the various products.

He suggests further that in the photolysis of trimethylamine, a methyl radical is liberated in the primary process; the products of photolysis were hydrogen, methane, ethane and polymer. The reaction mechanism suggested by Bamford (73) to account for the various products observed is the following

$$(CH_3)_3N + h\nu \rightarrow (CH_3)_2N. + CH_3.$$

$$2(CH_3)_2N. \rightarrow (CH_3)_2NH + CH_3.N:CH_2$$

$$(CH_3)_2NH + h\nu \rightarrow (CH_3)_2N. + H$$

$$(CH_3)_2NH + CH_3 \rightarrow (CH_3)_2N. + CH_4$$

$$H + CH_3 \rightarrow CH_4$$

$$2\ CH_3 \rightarrow C_2H_6$$

$$CH_3.N{:}CH_2 \rightarrow \text{Polymer}$$

The photolysis of trimethylamine has also been investigated recently by Gesser, Mullhaupt and Griffiths (76), over a temperature range from -78 to 175°C. The products were hydrogen, methane, ethane and a "liquid" which might be identical with the polymer from Bamford's studies. They suggested the following reaction mechanism for the photolysis,

$$(CH_3)_3N + h\nu \rightarrow (CH_3)_3N^{*}$$

$$(CH_3)_3N^{*} + M \rightarrow (CH_3)_3N + M$$

$$(CH_3)_3N^{*} \rightarrow (CH_3)_2N + CH_3$$

where M is a normal molecule or wall of the reaction vessel. They conclude that, at high temperatures, methane and ethane are formed by the abstraction and recombination reactions of methyl radicals, and hydrogen is produced by a molecular reaction. At low temperatures, both methane and hydrogen are produced by molecular elimination reactions. However, there is no general agreement about the composition of the polymer, nor about the reactions leading to its formation.

In one experiment, the polymer obtained from the photolysis of n-butylamine was carefully examined (73).

It was found that the polymer consisted of two fractions, one of which could be easily removed by pumping. The latter part of the polymer (odourless and inactive) is thought to be formed by the polymerisation of $CH_2.Pr.N:$ radicals produced by the following reactions,

$$2(Pr\ CH_2.NH) \rightarrow CH_2.Pr.NH_2 + CH_2.Pr.N:$$

$$CH_2.Pr.N: \rightarrow C_3H_8 + HCN$$

The above reaction accounts for the presence of propane and HCN among the reaction products.

Photosensitized decomposition: The mercury photosensitized decomposition of methylamine has been studied by Watson and Darwent (68). The primary process was considered to be

$$CH_3NH_2 + Hg\ (^3P_1) \rightarrow CH_3NH + Hg\ (^1S_0) + H$$

They consider it unlikely that the reaction

$$CH_3NH \rightarrow CH_2 = NH + H$$

should occur, as suggested by Wetmore and Taylor (69) since this would imply that unlike the similar radical CH_2OH, (70), the methylamine radical CH_3NH is very unstable. Reactions of the type

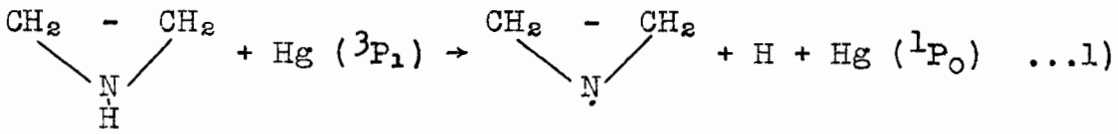
$$2\ CH_3\dot{N}H \rightarrow CH_3N = CH_2 + NH_3$$

and,

$$CH_2 = NH + CH_3NH_2 \rightarrow CH_2 = N.CH_3 + NH_3$$

were also considered to be unlikely owing to their complexity.

The mercury photosensitized decomposition of ethylenimine has been studied recently by Luner and Gesser (77). The non-condensable products were mainly hydrogen and nitrogen with smaller amounts of methane. The condensable fraction yielded mainly ethylene with small amounts of ammonia, hydrogen cyanide, ethane, propane, acetylene and butane. Since hydrogen and ethylene are obtained in relatively large quantities, it would appear that they are both obtained during the primary photodecomposition. It was suggested that the primary steps were:



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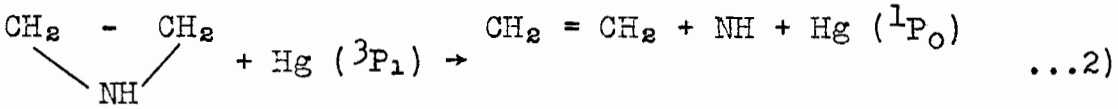

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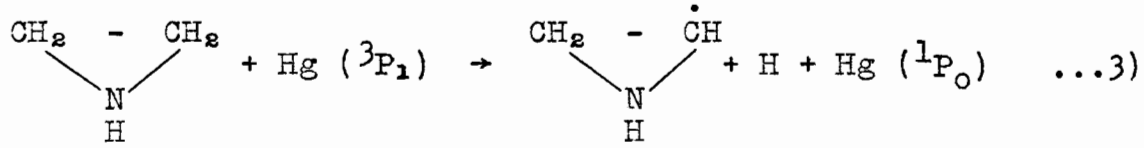

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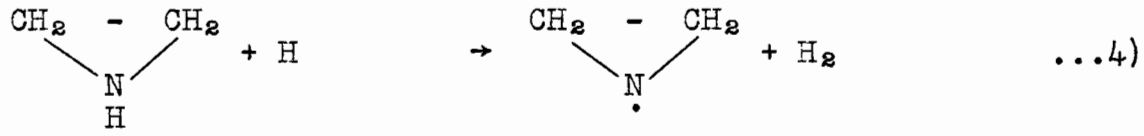
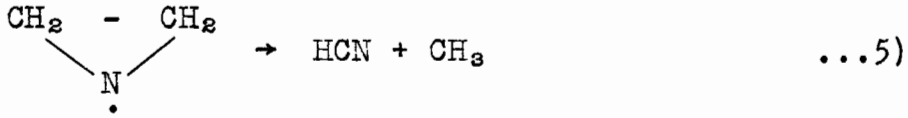


...4)

The presence of ammonia is explained by the successive H-atom abstraction by the NH radical, since NH radicals have been shown to react with ethylene to remove hydrogen (78). HCN may be formed by the decomposition reaction (79), i.e.,

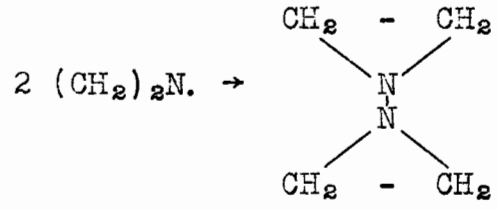


...5)

and methane by the reaction of CH_3 radicals with the imine, as shown by Brinton and Volman (80), i.e.,

$$CH_3 + (CH_2)_2NH \rightarrow CH_4 + (CH_2)_2N.$$

They did not detect any HCN although the radical $(CH_2)_2N$ could dissociate to give HCN by reaction 5. They assumed the radical to polymerise



or dissociate as follows

$$2\ (CH_2)_2N. \rightarrow N_2 + 2\ C_2H_4$$

Reactions of hydrogen atoms with ammonia, amines and imines

Ammonia: Böhm and Bonhoeffer (43) found that ammonia was inert to atomic hydrogen produced in a discharge tube and only slight reaction was reported by Dixon (81). Freeman and Winkler (82) investigated this reaction in some detail by the discharge tube method. They observed no reaction at room temperature, an increased amount of reaction with increase of temperature and a fast, irreproducible, fairly extensive reaction when the temperature was reduced to -67°C. It was suggested (83) that the high temperature reaction was due to

$$H + NH_3 \rightarrow NH_2 + H_2$$

and the low temperature reaction to a surface catalysed reaction. No hydrazine was detected.

Moore, Schuler, Silverman and Herman (84) studied the ammonia-atomic hydrogen reaction, using spectroscopic and chemical means to estimate the trapped products. They did not observe any reaction, but no mention was made of the temperature. However, they suspected an exchange reaction

between ammonia and hydrogen atoms, as proposed by Farkas and Melville (22). Geib and Harteck (39) found no reaction between ammonia and H-atoms at liquid air temperature.

The photodecomposition of ammonia has been found to be inhibited by molecular hydrogen at 400°C., but not at room temperature (39,85), while at room temperature, the reaction is inhibited by atomic hydrogen (86).

Amines: Very few reactions of atomic hydrogen with amines and imines have been studied in detail in spite of the fact that these reactions have been freely postulated as possible intermediates during the thermal and photo-decomposition of these compounds.

Wetmore and Taylor (69) examined the reaction of methyl amine with hydrogen atoms produced in a discharge tube. The major part of the reaction product was ammonia, which is in accordance with a more thorough investigation of the same reaction in this laboratory (87) as outlined later. No HCN was detected in the work of Wetmore and Taylor.

Trotman-Dickenson and Steacie (88) have studied the reaction of methyl radicals, produced by the photolysis of acetone, with ammonia and amines and the probable primary reactions with corresponding activation energies are given

below,

		E kcal.
$CH_3 + CH_3NH_2 \rightarrow CH_4 + CH_3\dot{N}H$		8.4
$CH_3 + (CH_3)_2NH \rightarrow CH_4 + (CH_3)_2N.$		7.2
$CH_3 + (CH_3)_3N \rightarrow CH_4 + (CH_3)_2.CH_2.N$		8.8
$CH_3 + NH_3 \rightarrow CH_4 + \dot{N}H_2$		10.0
$CH_3 + CH_2 - CH_2 \rightarrow CH_4 + CH_2 - CH_2$ (N, H) $\rightarrow$ (N·)		4.8 (80)

The only other studies of H-atom reactions with amines and imines appear to be two recent investigations made in this laboratory, details of which will be given later in outlining the basis for the present study.

ACTIVE NITROGEN

Although the present problem is concerned primarily with the reactions of hydrogen atoms, the study was undertaken originally because of its possible interest in relation to the mechanisms of certain reactions of active nitrogen. To understand the possible relation between the two types of reactions it is essential to review briefly the salient features of the reactions of active nitrogen, particularly its reaction with several types of organic molecules.

If nitrogen under low pressure be subjected to a

condensed discharge (89) or to a high frequency electrodeless discharge (90), a bright golden yellow colour is produced. The nitrogen afterglow may persist for some time after the discharge is turned off. The glowing "chamois-yellow mist" gas, which has rather remarkable physical and chemical properties is called active nitrogen. Bands in the afterglow has been associated with molecular nitrogen (89,90) and it is now established that the afterglow is due to transitions from 10th, 11th and 12th vibrational levels of $B^3\pi_g$ state to the metastable $A^3\Sigma_g^+$ state of molecular nitrogen.

In early studies of the chemistry of active nitrogen, Strutt found it to react rapidly with hydrocarbons to produce hydrogen cyanide and cyanogen (91) as principal products. On the basis of his experimental data, he assumed that atomic nitrogen was the main reactive constituent of active nitrogen. It is interesting to note that this was ten years before the work of Wood on the production of hydrogen atoms (12). After more than forty years of investigation into the physical and chemical properties of active nitrogen, the precise nature of active nitrogen is still uncertain. The chemical activity has been variously attributed to atomic nitrogen, excited nitrogen atoms, excited nitrogen moleculesand N_3, but there is considerable evidence

to show that atomic nitrogen is, as Strutt suggested, the main chemically reactive constituent of active nitrogen (85,93-98). Metastable molecules and vibrationally excited molecules in the ground state (92) might also contribute to its reactivity.

All the quantitative investigations of active nitrogen, except those with ammonia (82,99) and nitric oxide (100), can probably be explained on the basis of atomic nitrogen as the active species in active nitrogen. For these two reactions, however, it appears necessary to postulate a second species as suggested by Back (101) and Kelly (99).

REACTIONS OF ACTIVE NITROGEN

Several of the prominent features of active nitrogen reactions suggest strongly that reactant-nitrogen atom complexes play a rather well-defined and important part in the reactions. As will be seen later, the present problem developed from consideration of the probable nature of these complexes, and it is therefore desirable to outline briefly the main evidence for the presence of the complexes as significant chemical entities in these systems.

Review of the reactions of active nitrogen with

saturated and unsaturated hydrocarbons studied in this laboratory (102), shows that HCN is a major product of these reactions. To obtain HCN from a hydrocarbon molecule (other than methane) by its reaction with active nitrogen, it is evident that a C-C bond must be broken. The overall C-C bond strength increases from saturated to unsaturated hydrocarbons, i.e., C-C $<$C=C $<$C≡C. However, the relative rates of the active nitrogen reactions (to yield HCN) is in the reverse order of the bond strengths, i.e., C≡C$>$ C=C$>$ C-C.

This apparent contradiction can be understood if it is assumed that complex formation between a nitrogen atom and the reactant molecule is the rate governing (primary) step. Since it should be easier for the electronegative nitrogen atom to form complexes at centres of higher, than at centres of lower, electron density in the reactant molecules, complex formation should occur more readily at a double or triple, than at a single bond, and the relative rates of reaction should be as observed. In all cases, however, formation of HCN would be attributed to dissociation of the complex, and the overall process be represented

$$RH + N \rightarrow \left[RH.N\right] \rightarrow HCN + \text{other products}$$

At a given temperature, the yield of HCN from a hydrocarbon-active nitrogen reaction increases with the flow rate of reactant until, at sufficiently high flow rates, it attains a plateau value corresponding to complete consumption of active nitrogen. With chloromethane, methyl cyanide, ethylene and other reactants, it has been observed that increase of temperature increases the HCN plateau value until it eventually attains a maximum value and becomes independent of further temperature increase. This pronounced temperature effect has been investigated by Forst and Winkler (103) and they concluded that it may be explained by assuming that a reactant-nitrogen atom complex is formed and that this may react in two different ways:

(a) It may break up directly to give HCN.

(b) It may collide with another nitrogen atom or a second complex, with the result that recombination of nitrogen atoms occurs (catalytic-recombination).

To account for the behaviour of the HCN plateau with increase of temperature, it is then necessary only to assume that temperature increase favours the direct dissociation of the complex to form HCN at the expense of the catalytic recombination process. The maximum plateau value for HCN at a sufficiently high temperature may then

be reasonably interpreted to measure the concentration of nitrogen atoms in the active-nitrogen stream. The effectiveness of complex molecules such as CH_3CN, for catalysing the recombination of nitrogen atoms is probably due to their ability to absorb the energy of recombination of nitrogen atoms (225 kcal.) into their many degrees of freedom.

Further circumstantial evidence for the formation of a reactant-nitrogen atom complex is available from the reaction of active nitrogen with HCl (104). Here, direct reaction does not seem possible since the reaction

$$HCl + N \rightarrow NH + Cl$$

is quite endothermic. However, the decomposition of HCl by active nitrogen does occur and can be explained by the following mechanism

$$HCl + N \rightarrow [HCl.N]$$
$$[HCl.N] + N \rightarrow N_2 + H + Cl$$
$$2\,[HCl.N] \rightarrow H_2 + Cl_2 + N_2$$

Still further evidence that reactant-nitrogen atom complexes probably play an important part in active nitrogen reactions may be adduced from the reaction with acetylene (105).

In this, the production of HCN at low flow rates of acetylene has been observed to be second order in acetylene and this may be explained by assuming the interaction of nitrogen atom-acetylene complexes,

$$2\ C_2H_2N \rightarrow HCN + CH \equiv C.CN + H_2$$
(cyanoacetylene)

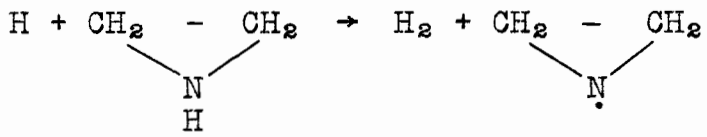
The composition and amount of polymer is well explained by assuming cyanoacetylene to be responsible for polymer formation.

Since evidence of the type outlined above strongly suggested that nitrogen atom complexes probably play an important part in the mechanisms of active nitrogen reactions, it became of obvious interest to obtain any information that might be possible about the nature of the probable complexes. The complex for the active nitrogen-ethylene reaction was assumed by Greenblatt (106) to have a probable cyclic structure.

$$CH_2 = CH_2 + N \rightarrow CH_2 \overset{N}{=\!=\!=} CH_2 \rightarrow HCN$$

In the course of other studies, Dr. C. Luner noted that this structure would presumably resemble the residue from the attack of ethylenimine by H-atom reaction, if the

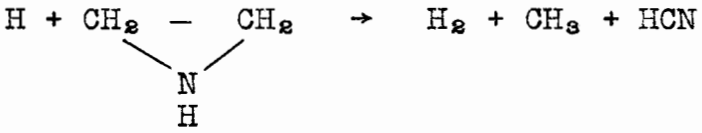
imino hydrogen is abstracted, i.e.,



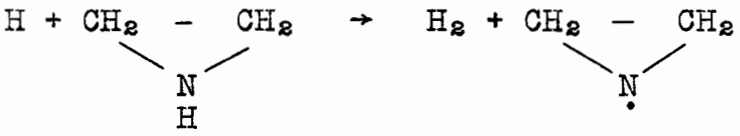
If this residue resembles the ethylene - nitrogen atom complex, which was known to dissociate to give HCN, it might be expected that the H-atom attack on ethylenimine should also produce HCN. Conversely, the production of HCN from the reaction of H-atoms with ethylenimine might be regarded as <u>indicative</u> (not proof) that the structure of the complex in the ethylene - active nitrogen reaction might be similar to the intermediate from the reaction of the imine with H-atoms.

To investigate Dr. Luner's suggestion, Jamieson studied the reactions of ethylenimine and N-methyl ethylenimine with hydrogen atoms in this laboratory (79), using a Wood-Bonhoeffer fast flow system. As suggested by Luner, the reactions produced mainly HCN, together with methane and C_2 hydrocarbons in the temperature range of 55°-300°C.

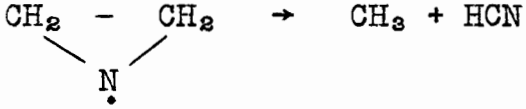
With ethylenimine, the imine consumption and HCN yield were linear with imine flow rates at low imine flow rates, and independent of temperature. About 90 per cent of the imine that reacted was converted to hydrogen cyanide. The reaction mechanism suggested was



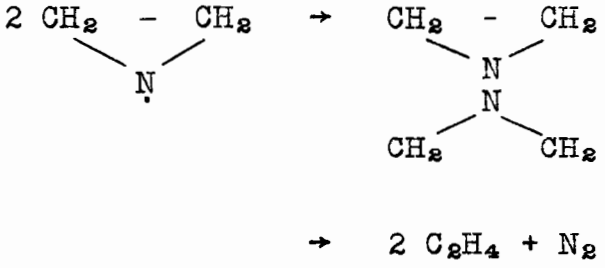
The primary process was assumed to be



followed by

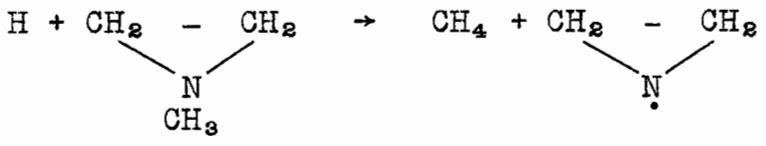


A difference was observed between the imine consumption and HCN yield at high flow rates and this was assumed to be due to



However, the dimer of ethylenimine radical was not detected. It was suggested that methane was formed by

The reaction of H-atoms with N-methyl ethylenimine was slower than with the unsubstituted imine. The main products of the reaction were HCN and methane, with smaller quantities of C_2 hydrocarbons (ethylene and ethane), which increased with temperature. The reaction



$$\rightarrow \quad CH_4 + HCN + CH_3$$

did not account for all the HCN produced. Hence, the reaction

$$H + C_3H_7N \rightarrow H_2 + C_3H_6N$$
$$C_3H_6N \rightarrow HCN + C_2H_5$$

was postulated, where C_2H_5 radicals were assumed to undergo "atomic cracking". The results indicated that primary reactions other than the abstraction of the methyl group probably occurred.

Since the H-atom reactions with ethylenimine appeared to be so successful in reproducing the behaviour postulated for the N-atom complex with ethylene, it was of obvious interest to attempt the production of complexes of

the type that might be expected in the reactions of active nitrogen with saturated hydrocarbons. No directly comparable system could be obtained, but something analogous to the ethane-active nitrogen system was studied by Wright when he investigated the reactions of H-atoms with ethyl amine (87).

The reaction was characterized by low yield of HCN and ethane, and high yields of methane and ammonia. The mechanism proposed was the following

$$CH_3.CH_2.NH_2 + H \rightarrow CH_3.CH_2.NH + H_2$$

$$CH_3.CH_2.NH + H \rightarrow CH_3.CH_2.NH_2^{*}$$

$$CH_3.CH_2.NH_2^{*} \rightarrow CH_3.CH_2.N + H_2$$

$$CH_3.CH_2.N + H \rightarrow HCN + H_2 + CH_3$$

Again, the approximate counterpart of a possible $C_2H_6.N$ complex, viz. $CH_3.CH_2.NH$, may be reasonably considered as the precursor to HCN formation. The decrease in methane and HCN yield at high flow rates was ascribed, at least in part, to the interaction of the radicals, viz.

$$2\ CH_3.CH_2.NH \rightarrow CH_3.CH_2.NH_2 + CH_3.CH_2{:}N$$

$$2\ C_2H_5NH \rightarrow 2\ C_2H_6 + N_2.$$

The reactions of methyl and dimethyl amines with H-atoms were also investigated by Wright (87,107) to see if

amines in general yield HCN as one of the products of their reactions with H-atoms. Both reactions were characterized by maxima in HCN and methane yields as the flow rates were increased. In both cases a fraction known as "No titre" was separated at -80°C; this gave titration for neither base nor cyanide. The yield of "No titre" was about 20-30 per cent of HCN yield. The production of ethane and ammonia appeared to level out at higher flow rates of amines, as did also the amount of amine reacted. The mechanisms postulated for these reactions were

I. $CH_3NH_2 + H \rightarrow CH_3NH + H_2$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!NH + H \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\dot{N} + H_2$$

The radicals produced in the above reactions could react further with hydrogen atoms, to yield the corresponding excited amines,

II. $CH_3\dot{N}H + H \rightarrow CH_3NH_2^{*}$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\dot{N} + H \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!NH^{*}$$

These highly energetic amine molecules could dissociate as follows

III. $CH_3NH_2^* \rightarrow CH_3N + H_2$

$CH_3N \rightarrow HCN + H_2$

$CH_3NH_2^* \rightarrow CH_3 + NH_2$

$NH_2 + H_2 \rightarrow NH_3 + H$

$2\ NH_2 \rightarrow N_2 + 2\ H_2$

$CH_3 + CH_3NH_2 \rightarrow CH_4 + CH_3NH$

IV. $(CH_3)_2NH^* \rightarrow CH_3 + CH_3NH$

$\rightarrow CH_3N + CH_4$

These reactions, in turn, might be followed by the same type of secondary reactions as with methyl amine. The decrease in HCN production in both cases was explained as due to increased recombination of CH_3N radicals

$$2\ CH_3N \rightarrow C_2H_6 + N_2$$

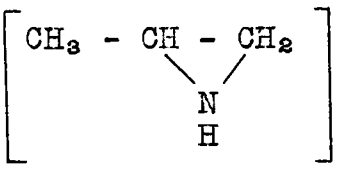
PRESENT PROBLEM

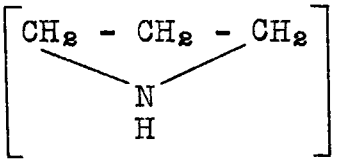
The present problem stemmed directly from the preceding considerations and had two main aspects.

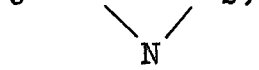
(i) To investigate if trimethylamine $(CH_3)_3N$ like methyl and dimethylamine, could react with hydrogen atoms to yield HCN as one of the products. This was of

interest since the tertiary amine has no abstractable (labile) hydrogen on the nitrogen atom.

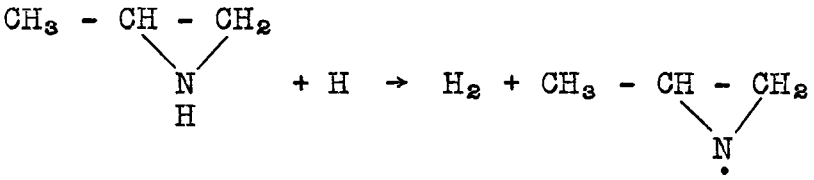
(ii) The reactions of H-atoms with

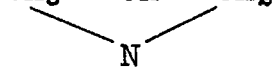
2-methyl ethylenimine 

and 1-3 propylenimine 

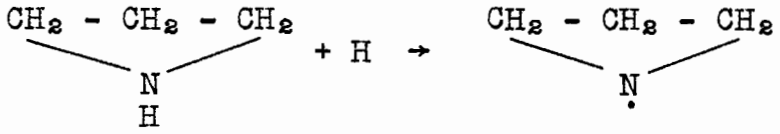
appeared to be of interest in relation to the possible structure of the complex formed by the reaction of propylene and active nitrogen. If the structure of the propylene-active nitrogen complex were  ,

then reaction of 2-methyl ethylenimine with H-atoms might simulate the complex. Thus,



On the other hand, if the structure of propylene-active nitrogen complex were 

then the corresponding reaction of hydrogen atoms with 1-3 propylenimine might yield a residue of similar structure, viz.



The present investigation attempts to resolve these two possibilities.

EXPERIMENTAL

MATERIALS

Reagent grade anhydrous trimethylamine b.p.3.5°C. was obtained from Matheson Company, Inc., U.S.A., and subjected to repeated bulb to bulb distillation under reduced pressure, the first and last fractions being discarded each time. The first bulb had a few KOH pellets to remove possible traces of moisture.

Anhydrous 2-methyl ethylenimine was obtained from Brickman and Company, Montreal, and was treated in the same way as trimethylamine.

1-3 propylenimine (azetidine) was not available in the market and it was prepared in the laboratory according to the method suggested by W. Marckwald (108) with certain modifications as outlined in Appendix A.

Ethyl chloride of reagent grade was obtained from Ingram and Bell Ltd., and subjected to the repeated bulb to bulb distillation mentioned previously.

In most of the experiments, hydrogen from Dominion Oxygen Company was used directly after it had been passed through a trap immersed in liquid nitrogen to remove traces

of moisture. A few experiments were made with hydrogen from which traces of oxygen were first removed by passing it through a furnace filled with copper gauze at 400°C. However, the results did not differ significantly with hydrogen treated in the two ways, and the furnace was therefore generally omitted.

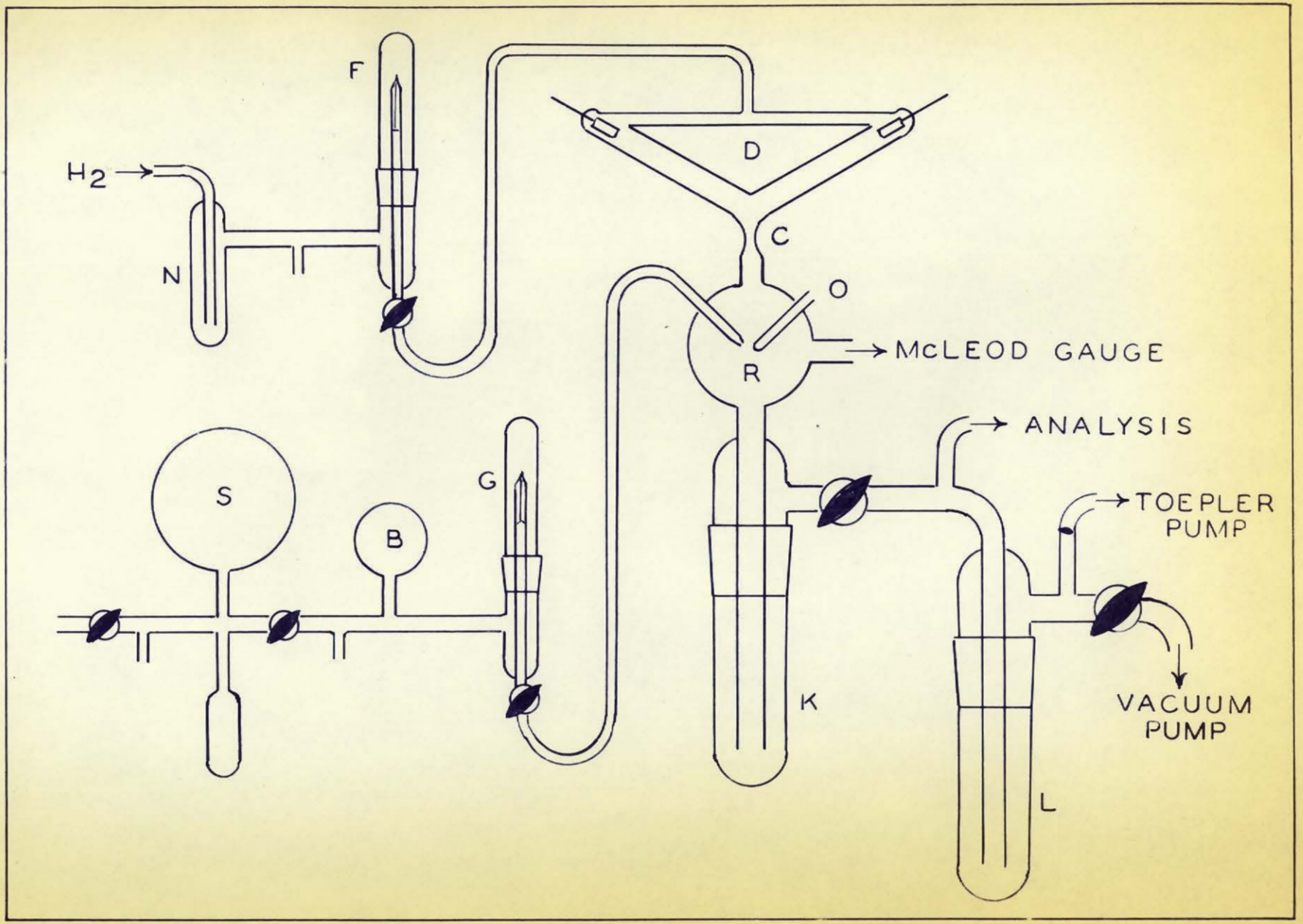
APPARATUS

The apparatus was a fast flow system of the conventional Wood-Bonhoeffer type, similar to those used previously in this laboratory to study the reactions of atomic hydrogen and active nitrogen. The apparatus was made from pyrex glass and is shown diagramatically in figure 1.

Hydrogen from a cylinder was admitted through a bubbler that could be adjusted to give a constant pressure head regardless of the atmospheric pressure. Dibutylphthalate was chosen as the liquid in the manostat, since it has very low vapour pressure at room temperature and is relatively stable. The hydrogen was dried by leading it slowly through the liquid nitrogen trap, N, after which it was fed through the capillary flow-meter, F, and finally into both ends of the discharge tube, D. The discharge tube was made from a 28 mm. O.D. pyrex tube, 76 cm. in length, which was bent in the middle in the shape of 'V'

Figure 1

DIAGRAM OF THE APPARATUS


F
H2
N
D
C
O
McLEOD GAUGE
R
ANALYSIS
S
B
G
TOEPLER
PUMP
K
VACUUM
PUMP
L

to allow the "poison" to be drawn up into the discharge tube without touching the electrodes. The electrodes were made from aluminium rod from which cylinders were turned on the lathe and were attached to tungsten leads sheathed in nonex glass and sealed into both ends of the discharge tube.

Molecular hydrogen, together with atomic hydrogen produced in the discharge flowed through a constriction, C, at the outlet of the discharge tube, through a connecting tube 10 cm. long and 10 mm. in diameter and into the spherical reaction vessel, R, of about 300 ml. volume. The dimensions of the connecting tube were so chosen that back diffusion into the discharge tube did not occur. The constriction, C, was very effective in preventing such back diffusion. The flow rate of molecular hydrogen was determined by measuring the rate of its removal from a previously calibrated volume through the capillary flow meter, F.

Trimethylamine and ethyl chloride were stored as gases in the reservoir, S, of known volume, while 2 methyl ethylenimine and 1-3 propylenimine were stored as liquids in the bulb, N, which was in turn connected to the reservoir, S, through 8 mm. tubing. The liquids were kept at 0°C.

when not in use. When required, the appropriate liquid was warmed to such a temperature that its vapour pressure in the reservoir, S, was sufficient to provide a constant pressure head in the ballast volume, B, during an experiment by adjusting a scratched stop-cock.

The reactant was allowed to pass through the capillary flow meter, G, then enter the reaction vessel through a jet. By altering the ballast pressure on the flow meter, a wide range of reactant flow rates was obtained. With trimethylamine and ethyl chloride, the pressure in the reservoir, S, was observed both before and after an experiment and, knowing the temperature, the flow rate of the reactant was calculated, using the ideal gas equation. However, the low vapour pressure of 2-methyl ethylenimine and 1-3, propylenimine, did not allow their flow rates to be determined from such P-V-T data. In all cases, the vapour was expanded into a large volume, and the flow rate determined by collecting the amount of amine or imine that flowed in a given time and titrating it against standard H_2SO_4 to methyl red end point.

An approximate idea of the exothermicity of the reaction was obtained with a chromel-alumel thermocouple inserted in the well, O, near the centre of the reaction

vessel. Temperatures from above room temperature up to 450°C. in the reaction vessel were obtained with an electrically heated asbestos furnace moulded around the reaction vessel. The furnace was made in two hemispheres that could be removed when necessary. Temperatures registered by the thermocouple were probably somewhat higher than they would have been in the absence of recombination of hydrogen atoms on the surface of the thermocouple well, but reasonably good estimates of the reaction temperatures were probably obtained.

A McLeod gauge connected to the reaction vessel enabled the pressure inside the main part of the apparatus to be measured at will.

The condensable products of reaction could be collected in traps K, and L, which were about 30 cm. long and of much wider diameter than the rest of the flow system to decrease the linear flow across the cold surface. The inner tube of the traps was sufficiently large (1.8 cm. O.D.) to permit condensation of products without impeding the flow of gas and this arrangement increased the trapping efficiency. In practice, it was observed that quantitative condensation was obtained with one trap, L, and only one trap was employed for collecting the condensable products

of reaction.

Samples of non-condensable products of reaction, which consisted mainly of excess of hydrogen, methane and traces of free nitrogen, were removed from the gas stream with a Töepler pump located after the second trap. These samples were compressed into a special cell for analysis by gas-chromatography in the study with trimethylamine and 2-methyl ethylenimine, and by mass-spectrometry in the study of 1-3 propylenimine.

The walls of the reaction vessel and discharge tube were "poisoned" by drawing a 2 per cent solution of phosphoric acid into these parts and draining it out slowly so as to leave a thin film of phosphoric acid on the surface. Later, it was found that a 20 per cent solution of disodium phosphate (Na_2HPO_4) was a more reproducible and efficient poison. The system was evacuated for 4 hours, during which time the reaction vessel was "baked" at 300°C. The hydrogen atom flow-rate was checked from time to time and whenever it had decreased significantly the reaction vessel and discharge tube were cleaned with hot cleaning solution, rinsed several times with distilled water, and re-poisoned.

The flow system was kept under vacuum at all times

except when it was necessary to clean and re-poison the reaction vessel or grease the stop cocks.

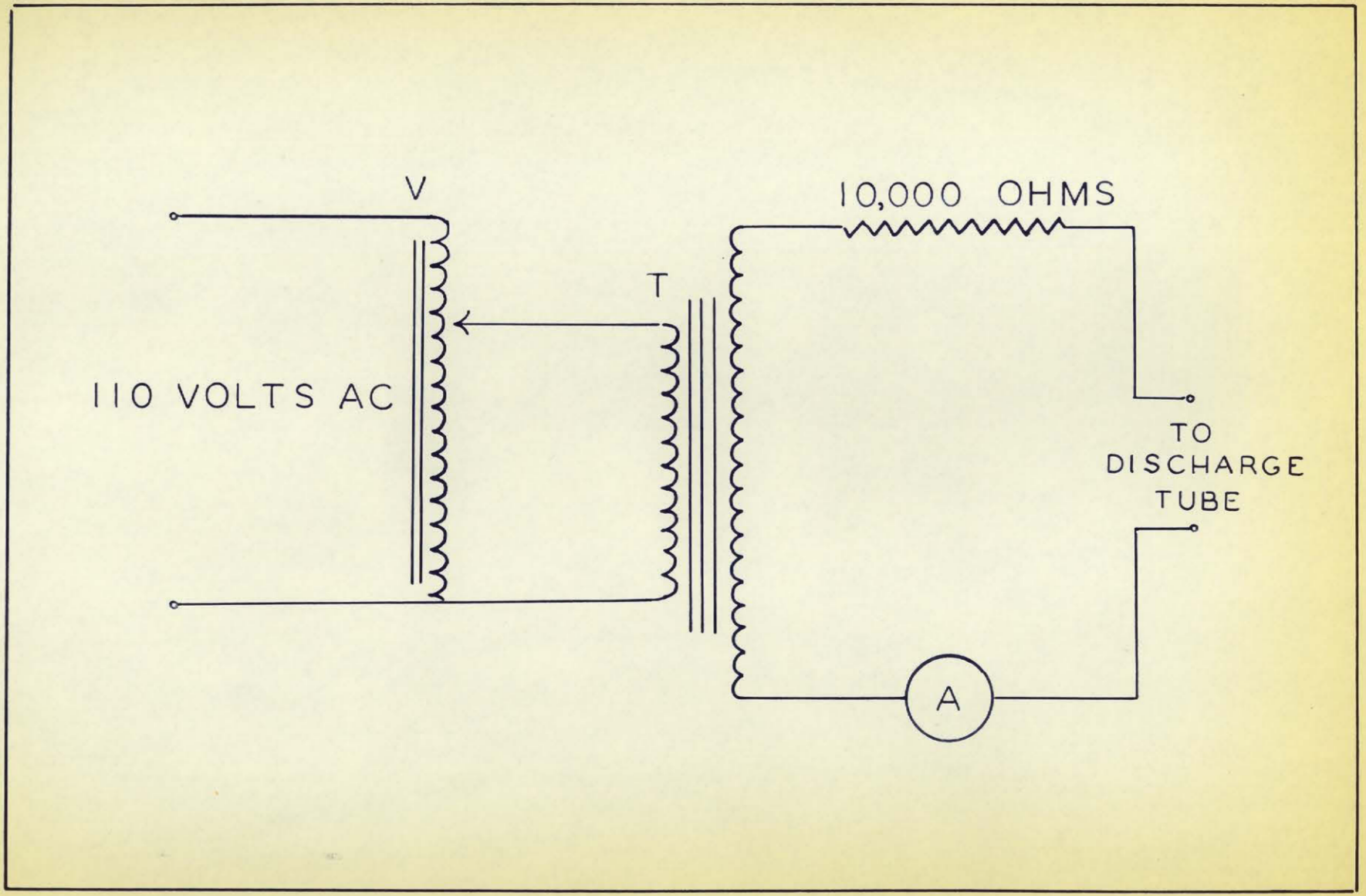
Before starting a new series of experiments, it was customary to allow reaction of H-atoms with the reactant to proceed for several minutes to condition the walls of the reaction vessel.

The pumping system consisted of a Hypervac No.23 rotary oil pump which gave an ultimate vacuum of 1×10^{-3} mm. mercury, as measured with a McLeod gauge. The pumping capacity at 1 mm. mercury was rated at 5 litres per second. A molecular hydrogen flow rate of 7.6×10^{-5} mole per second corresponding to 0.73 mm. mercury in the reaction vessel, was used in the reaction of trimethylamine and 2-methyl ethylenimine. After this, the flow system had to be modified, after which the molecular hydrogen flow rate was 15×10^{-5} mole per second, corresponding to a pressure of 1.55 mm. mercury in the reaction vessel.

The electrical circuit used to generate the continuous hydrogen discharge is shown schematically in figure 2. The 110 volt A.C. line was connected to the primary of a variac, V, rated at 18 amperes, the output of which passed to the primary of a 6000 volt transformer, T. The output from this transformer was directly connected to

Figure 2

ELECTRICAL DISCHARGE CIRCUIT


V
10,000 OHMS
T
110 VOLTS AC
TO
DISCHARGE
TUBE
A

the discharge tube through a 10,000 ohm resistor and an ammeter in series. In all experiments the variac was adjusted to give a steady current of 0.40 ampere in the discharge tube circuit. The potential drop across the discharge tube was about 2000 volts.

PROCEDURE FOR A TYPICAL EXPERIMENT

The absorber containing about 10 ml. of distilled water and a drop of methyl red indicator was attached to the tube marked "analysis" by a ground glass joint and evacuated slowly to remove dissolved air from the solution. It was then immersed in a dewar flask containing liquid nitrogen to freeze the contents, after which the entire system, including the removable absorber, was evacuated to about 1×10^{-3} mm. The trap, L, was immersed in liquid nitrogen, and the hydrostatic head of the dibutyl phthalate manostat was adjusted and the cold junction of the thermocouple immersed in crushed ice.

Before the experiment started, it was customary to do a blank experiment to avoid changes in surface conditions inside the reaction vessel that might have resulted from overnight shut-down of the flow system.

The hydrogen flow was started, the pressure being recorded with a McLeod gauge, and the discharge was turned

on after setting the variac to the desired position. The discharge was allowed to operate for about 100 seconds before a reaction started, since it was observed that the temperature rose from room temperature to about 40°C. during the first two minutes that the discharge was passed. The brightness of the hydrogen discharge and the rise in temperature after the discharge was turned on, gave a rough idea of H-atom concentration.

To initiate the reaction, the stop-cock between the reactant flow meter, G, and the reaction vessel was opened, and the pressure head across the flow meter held constant by careful manipulation of the scratched stop-cock connected to the reservoir, S, as described previously. The pressure and temperature inside the reaction vessel were measured during each experiment. Generally, the duration of an experiment, accurately timed with a stop-watch, was of the order of 100 seconds. However, when the reactant flow-rate was very small, it was necessary to allow the experiment to continue for 200 seconds to collect sufficient products for analysis.

The reaction was stopped by turning off the reactant flow, the discharge and the hydrogen flow in the order mentioned. The system was then evacuated to 1×10^{-3} mm.

mercury, and the trap, L, isolated from the pump and the flow system by turning off the appropriate stop-cocks. The liquid nitrogen surrounding the trap was removed and the products distilled under vacuum into the absorber. If hydrogen cyanide was a product of the reaction, the trap was immersed in carbon tetrachloride for about 10 seconds as soon as the liquid nitrogen was removed. The layer of carbon tetrachloride that froze on the outside of the trap prevented the hydrogen cyanide from warming rapidly and undergoing polymerisation during distillation. It was found that 30 to 45 minutes were required for a complete distillation to a vacuum of 1×10^{-3} mm. mercury.

The absorber, closed with a stop-cock,was disconnected from the system after it had been removed from the liquid nitrogen trap. The bottom of the absorber was then carefully immersed in hot water. This melted some of the frozen absorbing solution without causing liquefaction of the rest of the frozen material. The absorber was then rotated, tilted and immersed periodically in hot water, so that the liquid dissolved the reaction products without causing any detectable polymerisation of hydrogen cyanide. The stop-cock was then opened and the contents analysed by appropriate means.

For detailed analysis of the products, the absorber

was not used. Instead, the reaction products collected in trap, L, were distilled directly into an evacuated LeRoy still kept at liquid nitrogen temperature.

ANALYTICAL PROCEDURES

Reaction with ethyl chloride

Hydrogen chloride produced during the reaction of ethyl chloride with atomic hydrogen was absorbed in distilled water containing a drop of methyl red indicator and titrated against standard sodium hydroxide.

Reaction with hydrogen bromide

The hydrogen bromide destroyed by atomic hydrogen was also determined by titration of the recovered reagent with standard alkali.

Reaction with trimethylamine, 2-methyl ethylenimine and 1-3 propylenimine

These amines were estimated by titration against standard sulphuric acid to the methyl red end point. Knowing the amount of ammonia present as impurity and the amount of it produced during the reaction, the amount of material recovered and the amount of material reacted were calculated.

After titration of the base, the amount of HCN produced in the reaction was estimated by the method of Liebig-Déniges (109) as follows. The solution was rendered

basic by the addition of about 5 cc. of 6 Normal ammonium hydroxide followed by 0.2 gm. of potassium iodide (indicator) and the solution was titrated against standard silver nitrate

$$Ag^{+} + 2\ CN^{-} \rightleftarrows Ag(CN)_2^{-}$$

$$Ag(CN)_2^{-} + Ag^{+} \rightleftarrows Ag\ .\ Ag(CN)_2$$

$$Ag\ .\ Ag(CN)_2 + 2\ NH_3 \rightleftarrows Ag(NH_3)_2^{+} + Ag(CN)_2^{-}$$

$$Ag(NH_3)_2^{+} + I^{-} \rightleftarrows Ag\ I + 2\ NH_3$$

This end point was reached when the first permanent turbidity was reached. The turbidity was best seen by viewing the solution against a black background.

RESULTS

When the discharge tube was turned on and before the reactant was allowed to enter the reaction vessel, the temperature registered by the thermocouple increased by an amount which depended on the initial temperature of the reaction vessel, and was about 40°C. in the unheated vessel. Reproducible results were obtained by making the experiments of relatively short duration (100 seconds) after the temperature had attained a constant value. When the reactant was introduced, a further increase in temperature was observed, the extent of which also depended on the initial temperature as well as the exothermicity of the reaction. The increase in temperature, whether in the presence or absence of reactant, was less the higher the initial temperature of the reaction vessel.

DETERMINATION OF H-ATOM CONCENTRATION

As in the previous studies, the H-atom flow-rate at lower temperatures was estimated from the maximum destruction of HBr in an unheated reaction vessel, under which conditions the reaction appears to consume all the available H-atoms at sufficiently high flow-rate of HBr. The data recorded in Table I and figure 3, which are applicable to the studies subsequently made with

TABLE I

REACTION OF HBr WITH HYDROGEN ATOMS

Temp. °C.	HBr Flow Rate*	HBr Destroyed
	11.0×10^{-6}	5.85×10^{-6}
65 ± 3	16.0	5.75
	22.80	5.60
	24.80	5.70

*Units of flow-rate are mole/sec. $\times 10^{-6}$

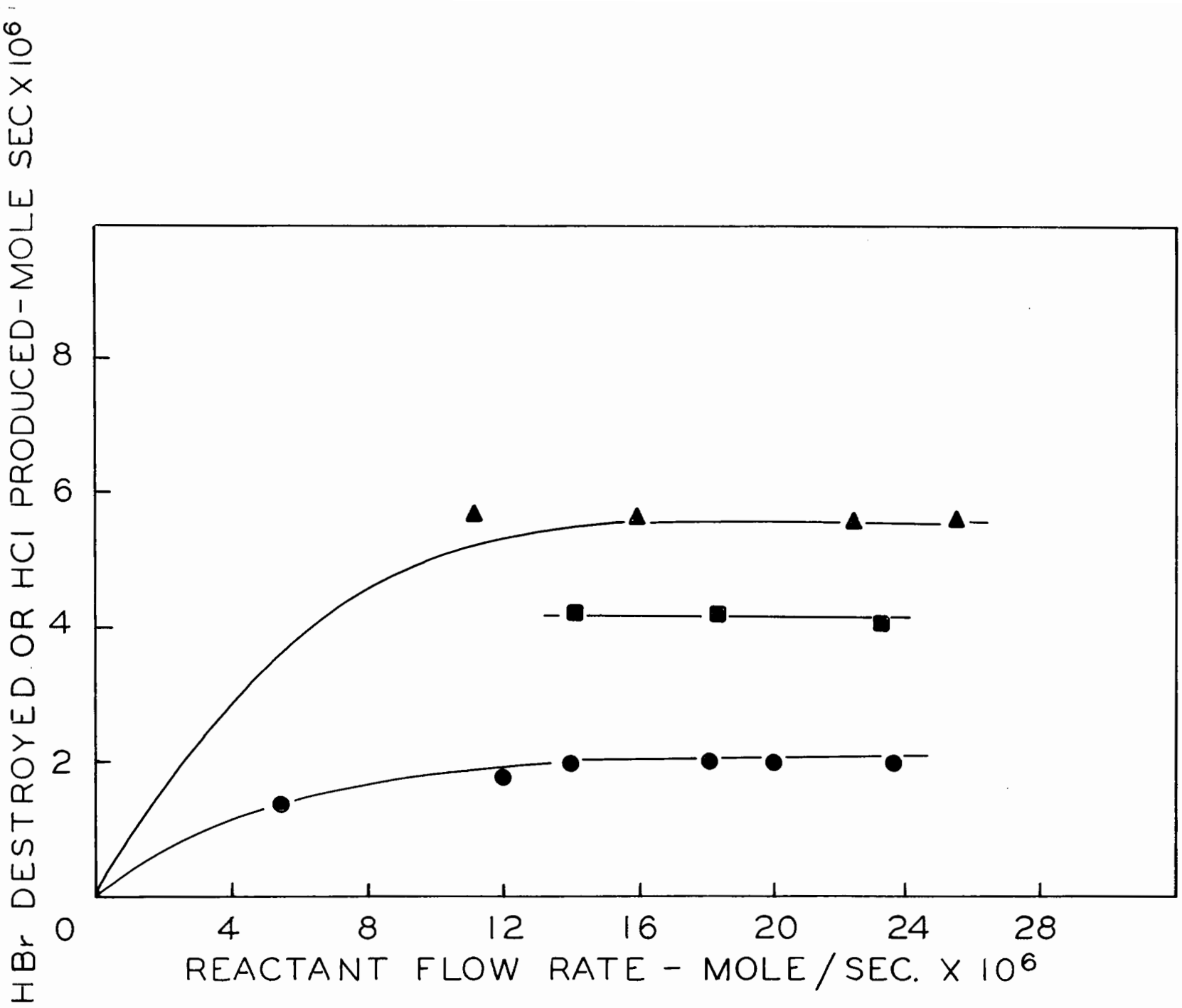
Figure 3

REACTION OF H-ATOMS WITH HBr AND C_2H_5Cl

● HCl Produced from C_2H_5Cl at Room Temperature.

■ HCl Produced from C_2H_5Cl at 275°C.

▲ HBr Destroyed at Room Temperature.


HBr DESTROYED OR HCl PRODUCED-MOLE SEC X 10⁶
0
2
4
6
8
4
8
12
16
20
24
28
REACTANT FLOW RATE - MOLE/SEC. X 10⁶

trimethylamine, give a flow-rate of H-atoms in the unheated vessel of about 5.7×10^{-6} mole/sec. Similar data were obtained during the later studies with 2-methyl ethylenimine and 1-3 propylenimine to indicate that the H-atom flow-rate during these studies were 5.7 and 10.8×10^{-6} mole/sec. respectively at the lower temperature used.

Unfortunately the reaction of H-atoms cannot be used to obtain the H-atom flow-rate at high temperatures, owing to the reaction of Br atoms with H_2 under such conditions. Accordingly, the H-atom flow-rate at higher temperatures was obtained by measuring the production of HCl in the high temperature reaction of H-atoms with excess ethyl chloride. From earlier studies there is little doubt that the maximum HCl production from this reaction at higher temperatures gives a reliable measure of H-atom concentration, although in an unheated reaction vessel the HCl yield corresponds to only about one-third the H-atom flow-rate. The data from the present experiments recorded in Tables I and II and figure 3, and applicable to the subsequent study with trimethylamine, correspond to a high temperature (285°C.) atom flow-rate of about 4.2×10^{-6} mole/sec. and to about 35 per cent reaction of alkyl halide in the unheated reaction vessel. For the later studies

TABLE II

REACTION OF ETHYL CHLORIDE WITH HYDROGEN ATOMS

Temp. °C.	C_2H_5Cl Flow-rate*	HCl Produced
	5.0×10^{-6}	1.35×10^{-6}
60±3	12.0	1.80
	15.0	2.0
	17.5	2.0
	20.0	1.90
	23.6	2.10
	13.0×10^{-6}	4.30×10^{-6}
285±5	18.30	4.20
	23.80	4.10

* Units of flow-rate are mole/sec. $\times 10^{-6}$

with 2-methyl ethylenimine and 1-3 propylenimine, the H-atom flow-rates for the higher temperatures used were similarly determined to be 4.2 and 9.7 x 10^{-6} mole/sec. respectively.

CALIBRATION OF FLOW RATES

The flow meter was calibrated separately for each reactant. The appropriate reactant was passed for measured times, with different pressure differentials (flow-heads) across the flow meter, into the molecular hydrogen stream (i.e., no discharge in operation) and trapped at liquid air temperatures. The amount trapped for each flow-head was then determined by titration with standard H_2SO_4. The resulting calibration lines are shown in Tables III, IV and V and plotted in figure 4. However, with trimethylamine, because of its high vapour pressure, it was also possible to measure the pressure decrease in the calibrated volume and to calculate the loss of amine on the assumption that it behaved as an ideal gas. This calculated line is shown in figure 4 and in Table III, from which it is evident that trimethylamine vapour is significantly non-ideal even at pressures of 1 atmosphere or less.

TABLE III

RELATION BETWEEN TRIMETHYLAMINE FLOW RATE AND FLOW HEAD

Flow Head cm.	Flow Rate Calculated (mole/sec. x 10-6)	Flow Rate by Titration (mole/sec. x 10-6)
2.40	1.0	1.0
3.60	1.60	1.75
7.0	3.50	3.90
10.0	5.0	5.90
14.70	7.60	8.90

TABLE IV

RELATION BETWEEN 2-METHYL ETHYLENIMINE FLOW RATE AND FLOW HEAD

Flow Head cm.	Flow Rate by Titration (mole/sec. x 10^{-6})
2.0	4.0
3.40	7.80
4.0	9.10
5.0	13.0
6.0	16.0

TABLE V

RELATION BETWEEN 1-3 PROPYLENIMINE FLOW HEAD AND FLOW RATE

Flow Head cm.	Flow Rate by Titration (mole/sec. x 10^{-6})
1.75	2.80
3.75	9.50
5.0	14.0
6.0	17.5

Figure 4

RELATION BETWEEN TRIMETHYLAMINE, 2-METHYL ETHYLENIMINE AND 1-3 PROPYLENIMINE FLOW RATES (Mole/Sec. x 10^{-6}) AND THE CORRESPONDING FLOW HEADS (cm.)

A. Trimethylamine

● Flow Rate (Titrated).

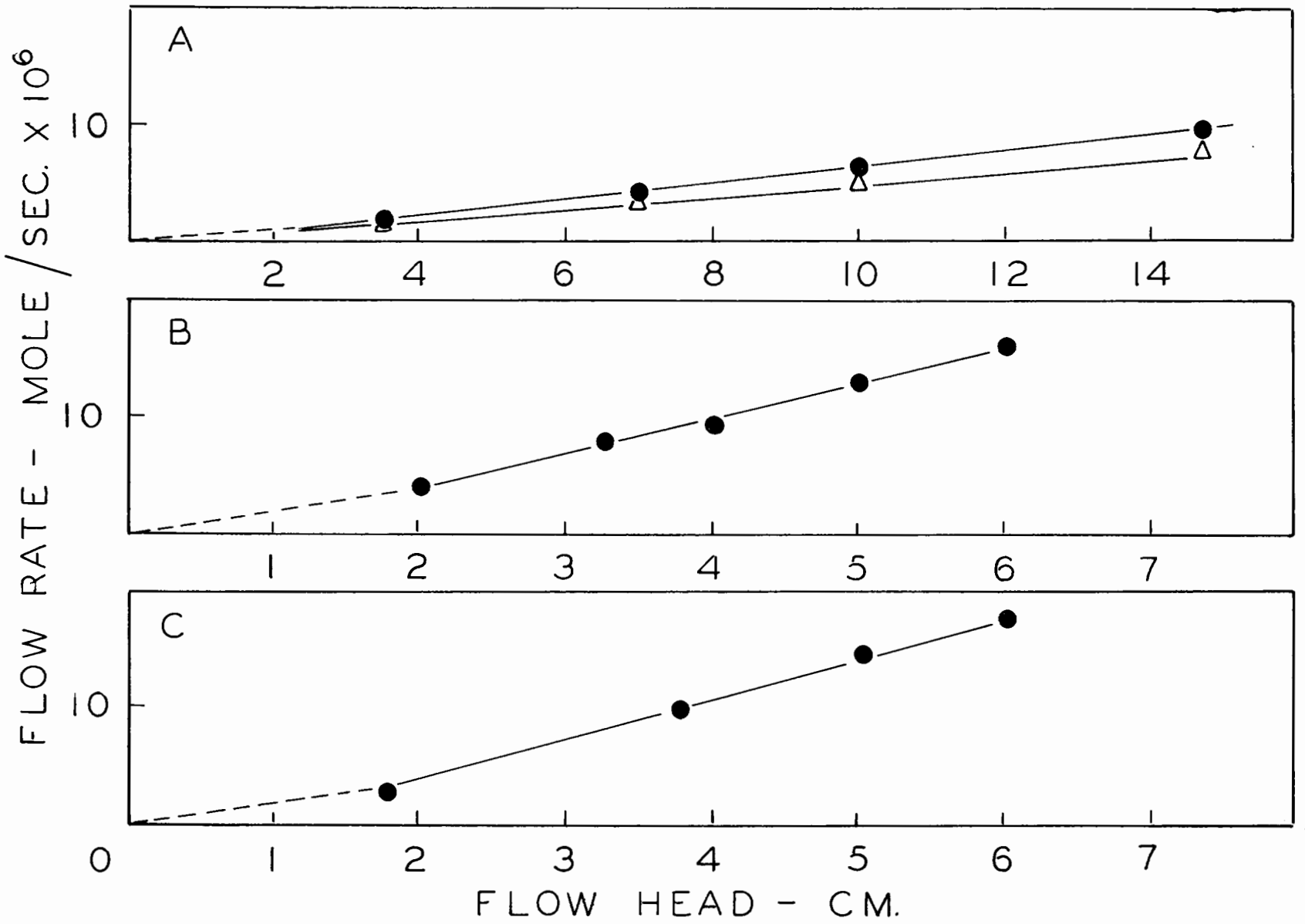
Δ Calculated.

B. 2-Methyl ethylenimine

● Flow Rate (Titrated).

C. 1-3 Propylenimine

● Flow Rate (Titrated).


A
B
C
10
10
10
2
4
6
8
10
12
14
1
2
3
4
5
6
7
0
1
2
3
4
5
6
7
FLOW RATE - MOLE / SEC. X 10^6
FLOW HEAD - CM.

PRODUCTS OF THE REACTIONS

A. Trimethylamine

Then trimethylamine was admitted to a molecular hydrogen stream, (no discharge in operation) the pressure inside the reaction vessel increased from 0.73 mm. to 0.80 mm. No further increase in pressure was detected during the reaction. Two series of experiments were made, the one at room temperature, the other at 275°C. The results are summarized in Table VI and represented graphically in figure 5 for average reaction temperatures of 56°C. and 275°C.

HCN was indeed recovered as one of the products of reaction of trimethylamine with hydrogen atoms. The difference between the number of micromoles per second of trimethylamine passed into the reaction vessel and the number of micromoles per second recovered obviously gave the number of micromoles per second of amine that suffered reaction. The relation of these values, and of the corresponding HCN yields, to the flow rates of amine are shown in Table VI and figure 5. It is apparent that the yield of HCN increases linearly with flow rate of amine at relatively low flow rates, and that HCN production increased somewhat with temperature. For the reactions at both temperatures, HCN yields went through a maximum

TABLE VI

REACTION OF TRIMETHYLAMINE WITH HYDROGEN ATOMS

Flow Rates - micromoles per sec.

Temp. °C.	Amine Introduced	Amine Recovered	Amine Reacted	HCN Produced
	0.60	0	0.60	0.50
56±3	1.0	0	1.0	0.75
	1.80	0.50×10^{-6}	1.30	0.85
	2.20	0.90	1.30	0.92
	3.50	2.35	1.15	0.70
	4.20	3.20	1.0	0.35
	5.10	4.20	0.90	0.05
	6.0	5.25	0.75	
	0.60	0	0.60	0.60
275±5	1.0	0	1.0	1.0
	1.80	0.45	1.35	1.15
	2.20	0.65	1.55	1.30
	3.50	1.90	1.60	1.20
	4.20	2.50	1.70	0.85
	5.10	3.60	1.50	0.45
	6.0	4.40	1.60	0.05

Figure 5

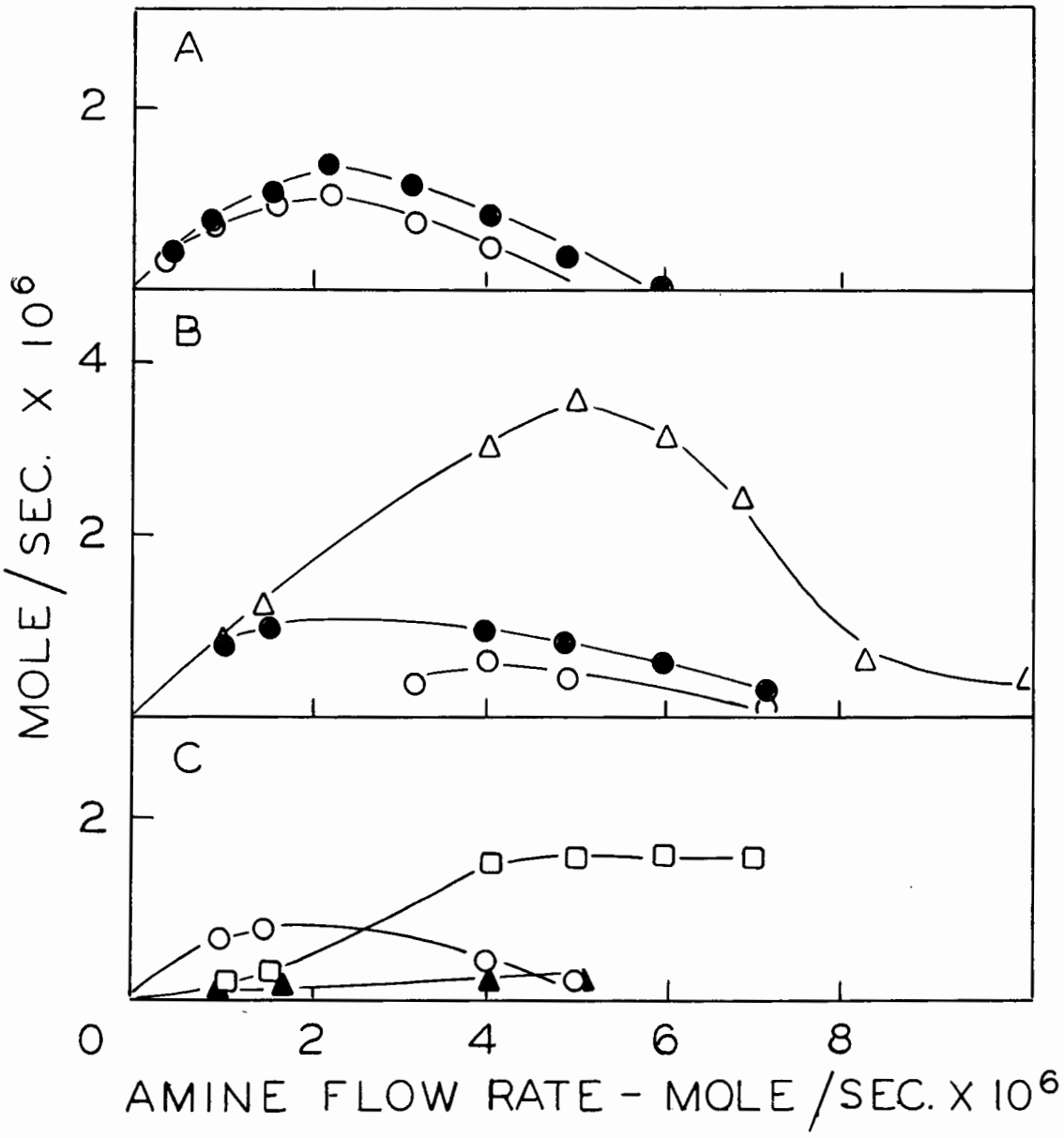
REACTION OF TRIMETHYLAMINE WITH HYDROGEN ATOMS

A
- ○ HCN at 65°C.
- ● HCN at 285°C.

B
- ● Amine Reacted at 65°C.
- ○ Free Nitrogen at 65°C.
- △ Methane Formed at 65°C.

C
- ○ HCN at 65°C.
- □ Ethane at 65°C.
- ▲ NH_3 at 65°C.

(Flow Rates of H-Atoms: 5.7×10^{-6} at 65°C., 4.2×10^{-6} at 285°C.)


A
B
C
2
4
2
2
0
2
4
6
8
MOLE / SEC. X 10⁶
AMINE FLOW RATE - MOLE / SEC. X 10⁶

beyond which they eventually decreased to zero. The initial slopes for amine consumption and HCN production were essentially the same at both temperatures. The number of micromoles per second of amine that reacted was less than the flow rate of H-atoms into the reaction vessel.

A small amount (1.5 per cent) of ammonia present in the amine as an impurity was taken into account in determining the amount of ammonia produced during the reaction. Trimethylamine was not purified from this ammonia, since no reaction has been observed between ammonia and atomic hydrogen at room temperature (82,84).

A complete analysis for the condensable products, for reactions at room temperature, was made with a low temperature LeRoy still (110). The results are summarized in Table VII and figure 5 (B and C). The duration and flow-rates for these experiments were so chosen as to give sufficient products for analysis without "flooding" the still.

The only condensable product of the reaction (liquid nitrogen) that did not give either a base or cyanide titration value was ethane, which was separated at -150°C. No free ethylene was detected. Ammonia was

TABLE VII

QUANTITATIVE ANALYSIS OF THE PRODUCTS OF TRIMETHYLAMINE H-ATOM REACTION AT ROOM TEMPERATURE FOR 100 SECONDS

Flow Rate - micromoles per second

Temp. °C.	Amine Introduced	C_2H_6	NH_3 Free	NH_3 Bound	Amine Free	Amine Bound	HCN Free	CH_4	Nitrogen
	100	20	-	10	-	-	80	100	-
56±3	150	25	-	15	-	50	35	135	-
	400	175	-	20	100	30	-	300	80
	600	175	25	-	300	-	-	350	30

identified and separated at -130°C. where it had a vapour pressure of 0.03 mm. Its volume was measured in a gas burette and confirmed by titration against standard H_2SO_4. Trimethylamine or HCN was removed at -105°C. No free HCN was detected if the basic material (ammonia and amine) in the reaction products exceeded the amount of HCN and, conversely, no free base could be detected when the amount of HCN exceeded the total amount of basic substances in the effluent from the reaction vessel. Ammonia and amine formed the corresponding cyanide complexes with HCN and these were characterized by their vapour pressures, by the equal amount of base and cyanide obtained by titration, and by infra-red spectroscopy. These materials had much lower vapour pressures than the corresponding free bases.

Samples of the non-condensables (methane and nitrogen) were removed from the gas stream by a Töepler pump and analysed by gas chromatography on a Fisher-Gulf Partitioner, using a molecular sieve column (type 5A, mesh size 30-70, temperature 50°C.) 20 feet long. The system was calibrated with known samples (pure methane and nitrogen and mixtures of the two). The gases were identified by their corresponding retention times on the column. By knowing the flow-rate of the hydrogen stream, the percentage of methane and nitrogen in the samples of known

size could be changed to the corresponding flow-rates in the reaction mixture. Estimates of the non-condensables are represented in figure 5 (B and C).

Mass spectrometry was not used in the determination of methane in the present study, since there is good evidence that molecular hydrogen may react with the carbon filament in the McGill instrument to yield methane.

The amount of trimethylamine that apparently suffered reaction, passed through a maximum. It seems reasonable to assume that this behaviour reflects the production of some basic material during the reaction, e.g., methyl- or dimethylamine, which would behave in titration as an equivalent amount of unreacted trimethylamine, but which could not be identified by fractional distillation or infra-red spectroscopy, since the vapour pressures and spectra of these amines are all quite similar. A sample of the trimethylamine used in the experiments was tested by benzene sulphonyl chloride ("Hinsberg's reagent"), $C_6H_5SO_2Cl$, without obtaining any indication of methyl or dimethyl amine in the sample. In a few experiments at high flow-rate of amine (where no HCN was produced), the products of the reaction indicated the presence of a secondary amine (probably dimethylamine) when they were tested in the same way.

The quantitative estimation of this secondary amine was difficult. It was found (after many unsuccessful trials with different columns) that trimethylamine could be separated from mixtures of dimethyl and trimethylamines by gas chromatography over a silica gel column at room temperature. Hydrogen was used as the carrier gas in all the gas chromatographic separations that were made.

In one experiment at high flow-rate, the ethane and ammonia were removed from the products of the reaction and the fraction (300 micromoles) containing dimethyl and trimethylamine was separated (-130 to -110°C.). Comparison of subsequent chromatographic separations with the results from synthetic mixtures of dimethyl and trimethylamines, made it possible to estimate that the product contained about 100 micromoles (about 33 per cent) of dimethylamine.

Finally, it should be noted that, unlike the production of HCN and methane, and the consumption of amine, all of which passed through maxima, the yields of ethane and ammonia attained limiting values as the reactant flow-rate was increased.

B. 2-Methyl ethylenimine

Production of HCN from this reaction was investigated at two different temperatures (as with trimethylamine).

Again, no visible reaction occurred between the imine and hydrogen atoms. The average temperature for reaction in the unheated vessel was 70°C. and that in the heated vessel was 284°C. As with trimethylamine, the pressure inside the reaction vessel, measured with a McLeod gauge, increased from 0.73 mm. (with molecular hydrogen flowing) to 0.80 mm. with the discharge turned on and the imine flowing.

At both temperatures, the HCN production increased linearly with imine flow-rate at relatively low flow-rates of imine, but passed through a maximum (at about 6 to 7 micromoles per second) as the flow-rate was increased. On the other hand, the amount of imine reacted attained limiting values at higher imine flow-rates. Increase of temperature appeared to have no significant influence on either the amount of imine reacted or the amount of HCN produced at low flow-rates of imine below about 2 to 3 micromoles per second, and to cause only little increase in these quantities at higher flow-rates. The data are summarized in Table VIII and figures 6 and 7.

The maximum amount of imine consumed at room temperature was less than the available H-atom flow-rate while that consumed at 275°C. approximated to the H-atom flow-rate at that temperature.

TABLE VIII

REACTION OF 2-METHYL ETHYLENIMINE WITH H-ATOMS

Flow-Rate - micromoles per second

Temp. °C.	Imine Introduced	Imine Recovered	Imine Reacted	HCN Produced
	1.0	0	1.0	1.0
70±3	4.40	1.60	2.80	2.75
	6.30	3.30	3.0	3.0
	8.25	5.20	3.05	2.70
	10.0	6.90	3.10	2.50
	12.0	8.80	3.20	2.0
285±4	1.80	0	1.80	1.85
	4.40	1.0	3.40	3.10
	6.30	2.80	3.50	3.30
	8.25	4.55	3.70	3.20
	11.40	2.0	3.40	2.90
	12.0	8.55	3.45	2.70

Figure 6

REACTION OF 2-METHYL ETHYLENIMINE WITH H-ATOMS

○ Amount reacted at 70°C.

● Amount reacted at 284°C.

(Flow Rates of H-Atoms: 5.7×10^{-6} at 70°C. / 4.2×10^{-6} at 284°C.)

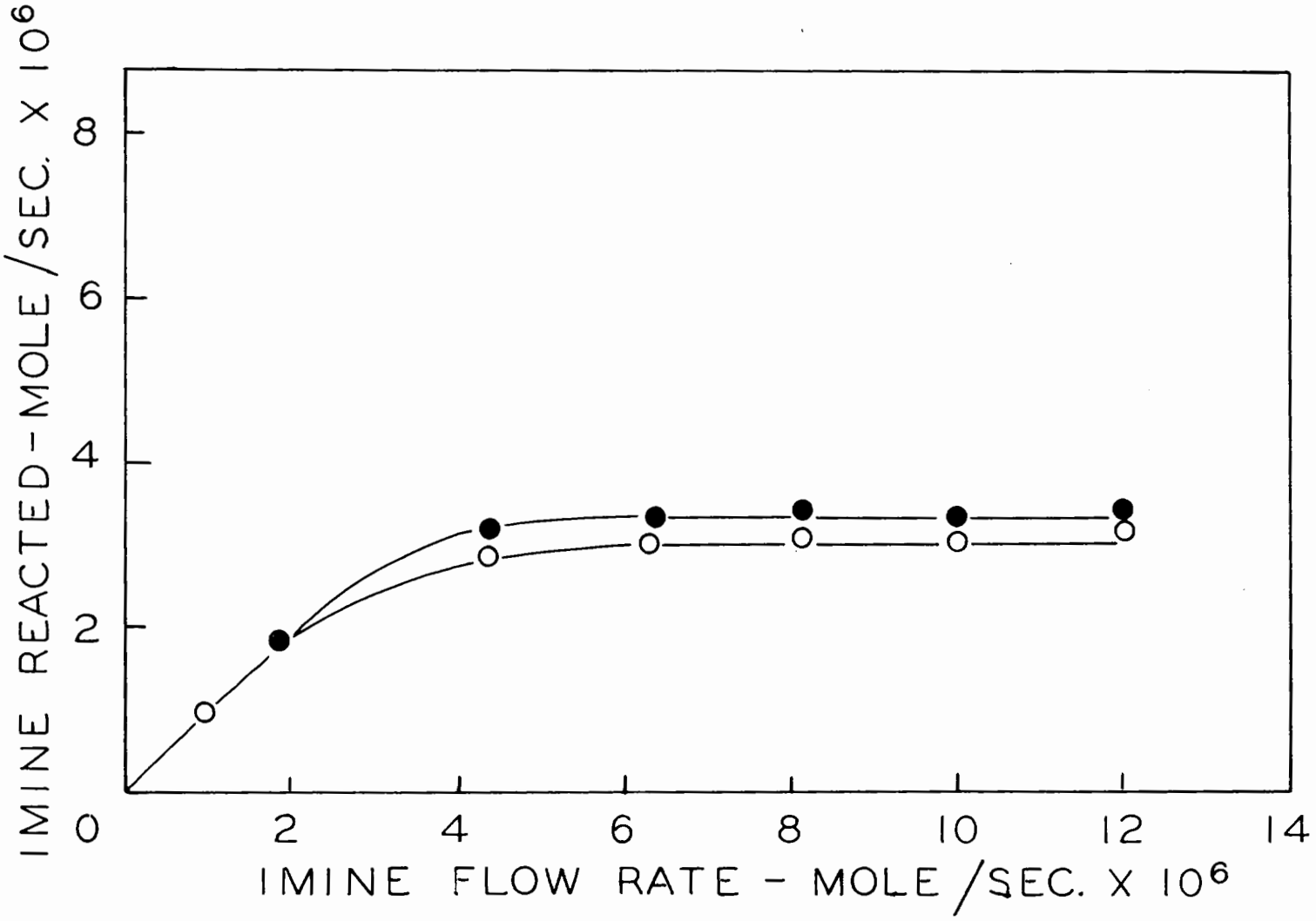
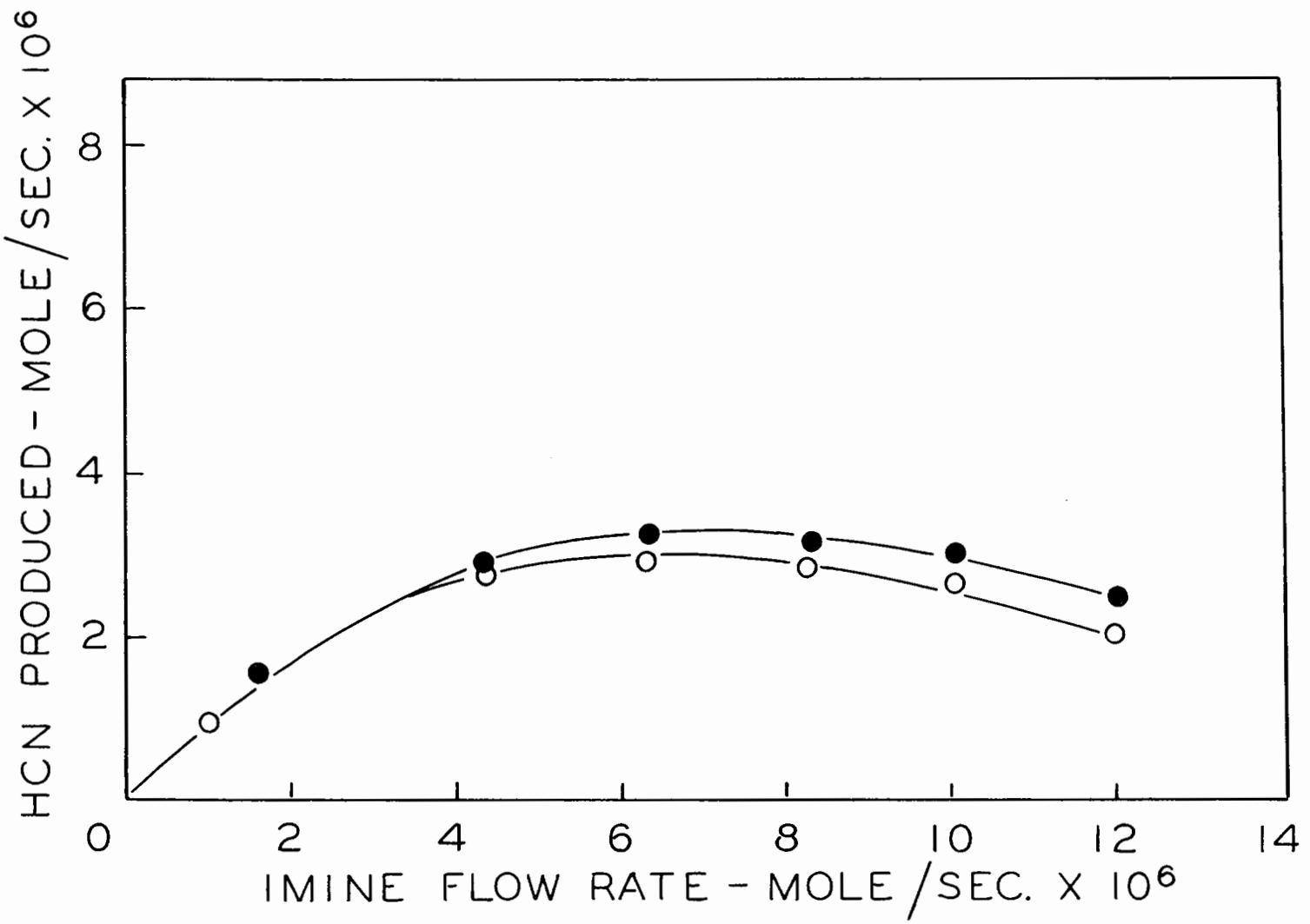

IMINE REACTED - MOLE /SEC. X 10⁶
0
2
4
6
8
IMINE FLOW RATE - MOLE /SEC. X 10⁶
2
4
6
8
10
12
14

Figure 7

HYDROGEN CYANIDE PRODUCED IN THE REACTION
OF 2-METHYL ETHYLENIMINE WITH H-ATOMS

○ HCN at 70°C.

● HCN at 284°C.


HCN PRODUCED - MOLE/SEC. X 10⁶
0
2
4
6
8
10
12
14
IMINE FLOW RATE - MOLE/SEC. X 10⁶

The reaction at room temperature was investigated by detailed analysis of the products of reaction. The methods for separation and identification of the products were similar to those described previously. The analytical data are given in Table IX and plotted in figure 8. The non-condensable products of the reaction were estimated by gas chromatography as outlined before, and are shown in figure 8.

It is evident from Table IX and figure 8 that the yields of ethane and ammonia attained a constant value, while the production of methane went through a maximum as the flow-rate of imine was increased.

C. 1-3 Propylenimine

The production of HCN and the consumption of imine were determined for different imine flow-rates in an unheated reaction vessel and at 300°C. As with the other reactions studied, no reaction flame was observed, but the temperature of the reaction zone in the unheated vessel increased to as much as 170°C. with increase in imine flow-rate. For reactions at both temperatures, the yield of HCN increased linearly with the reactant flow-rate, and attained a limiting value which was independent of further increase in flow-rate. The production of HCN from this reactant, unlike that from 2-methyl ethylenimine, was markedly

TABLE IX

PRODUCTS FROM THE REACTION OF 2-METHYL ETHYLENIMINE WITH HYDROGEN ATOMS

Flow Rate - micromoles per second

Temp. 70°C.

Imine Introduced	Products recovered							Recovery %	
	C_2H_6	CH_4	NH_3 free	NH_3 bound	HCN free	HCN (Imine) complex	Imine free	N	C
300	90	160	-	15	100	90	-	103	87
600	150	400	-	30	20	200	100	105	105
1000	180	420	-	30	-	200	470	96	101
1200	180	360	-	10	-	200	680	97	97

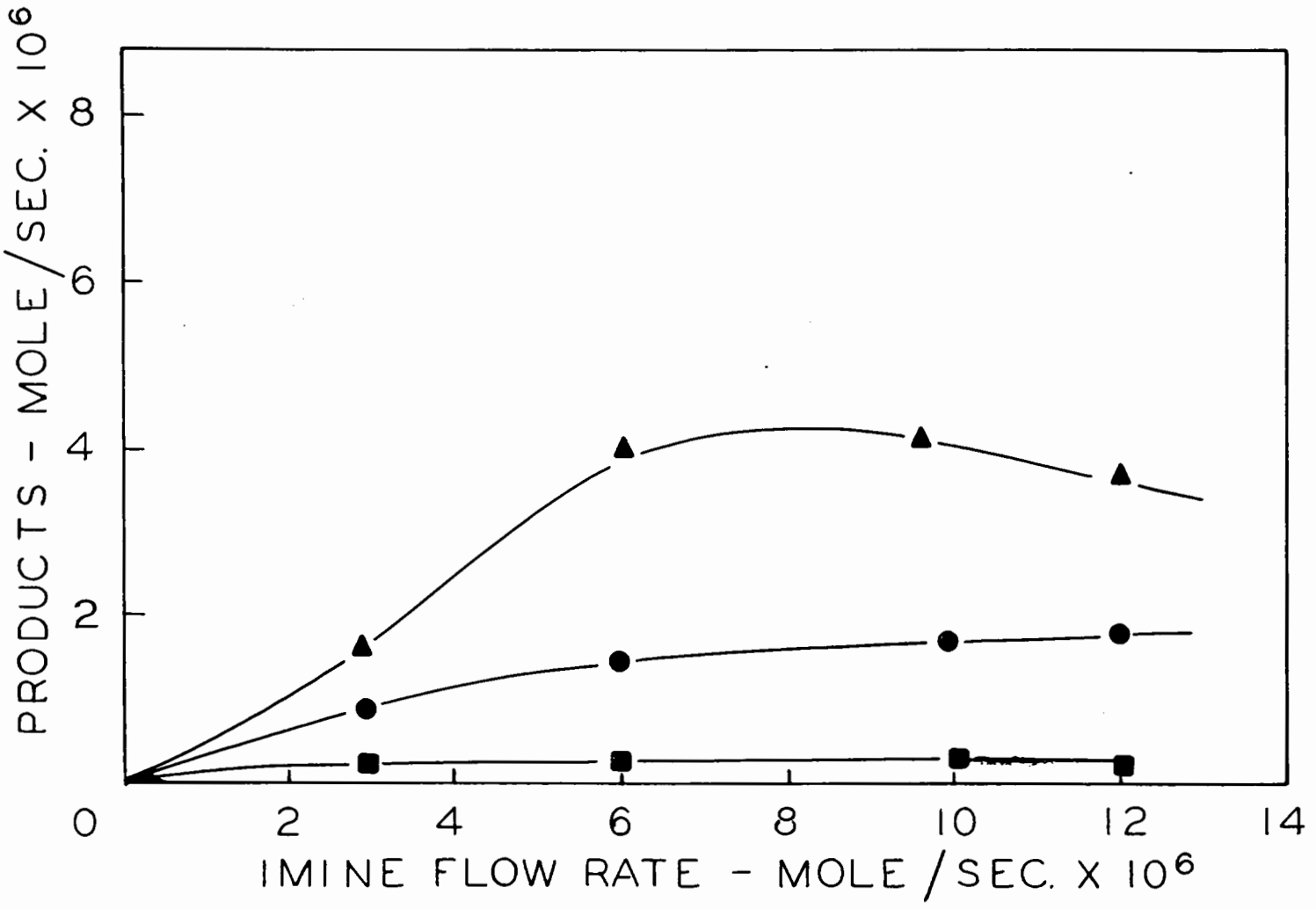
Figure 8

PRODUCTS OF THE REACTION OF 2-METHYL ETHYLENIMINE WITH H-ATOMS AT ROOM TEMPERATURE

▲ Methane

● Ethane

■ Ammonia


PRODUCTS - MOLE/SEC. X 10⁶
0
2
4
6
8
2
4
6
8
10
12
14
IMINE FLOW RATE - MOLE/SEC. X 10⁶

increased by an increase in temperature. The data for the two temperatures are given in Table X and plotted in figures 9 and 10.

At each temperature, and at sufficiently high imine flow-rates, the amount of imine reacted attained a constant value, which was less than the available H-atom flow-rate (10.8 micromoles per second).

The course of the reaction in the unheated vessel (temperature = 150°C.) was investigated by detailed analysis of the products for various flow-rates.

The analyses with the LeRoy still were quite similar to those outlined previously. However, it is interesting to note that, as observed with methyl-, ethyl-, and dimethylamine (87,107), a fraction was isolated in the present study which gave titration for neither base nor cyanide ("No titre fraction"). On further investigation, this fraction was identified by infra-red spectroscopy to be CH_3CN. This was quantitatively estimated as follows.

The products of the reaction were absorbed, as usual, in distilled water and then rendered acidic by dilute H_2SO_4. The solution was heated to 40°C. and a stream of nitrogen was bubbled through the solution. The issuing

TABLE X

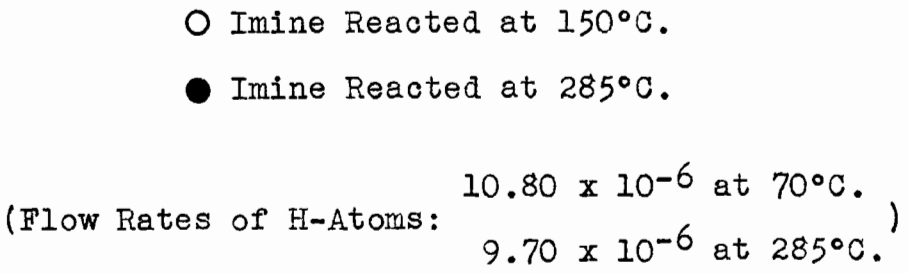
REACTION OF 1-3, PROPYLENIMINE WITH H-ATOMS

Flow Rate - micromoles per second

Temp. °C.	Imine Introduced	Imine Reacted	HCN Produced
	3.0	1.30	0.65
150±3	6.0	2.10	0.70
	10.0	3.50	0.75
	14.0	4.40	0.70
	16.0	4.45	0.75
330±4	3.0	2.0	2.0
	6.0	3.40	2.0
	10.0	5.35	2.10
	14.0	5.70	2.05

Figure 9

RELATION BETWEEN AMOUNT OF 1-3 PROPYLENIMINE REACTED AND IMINE FLOW RATE AT DIFFERENT TEMPERATURES



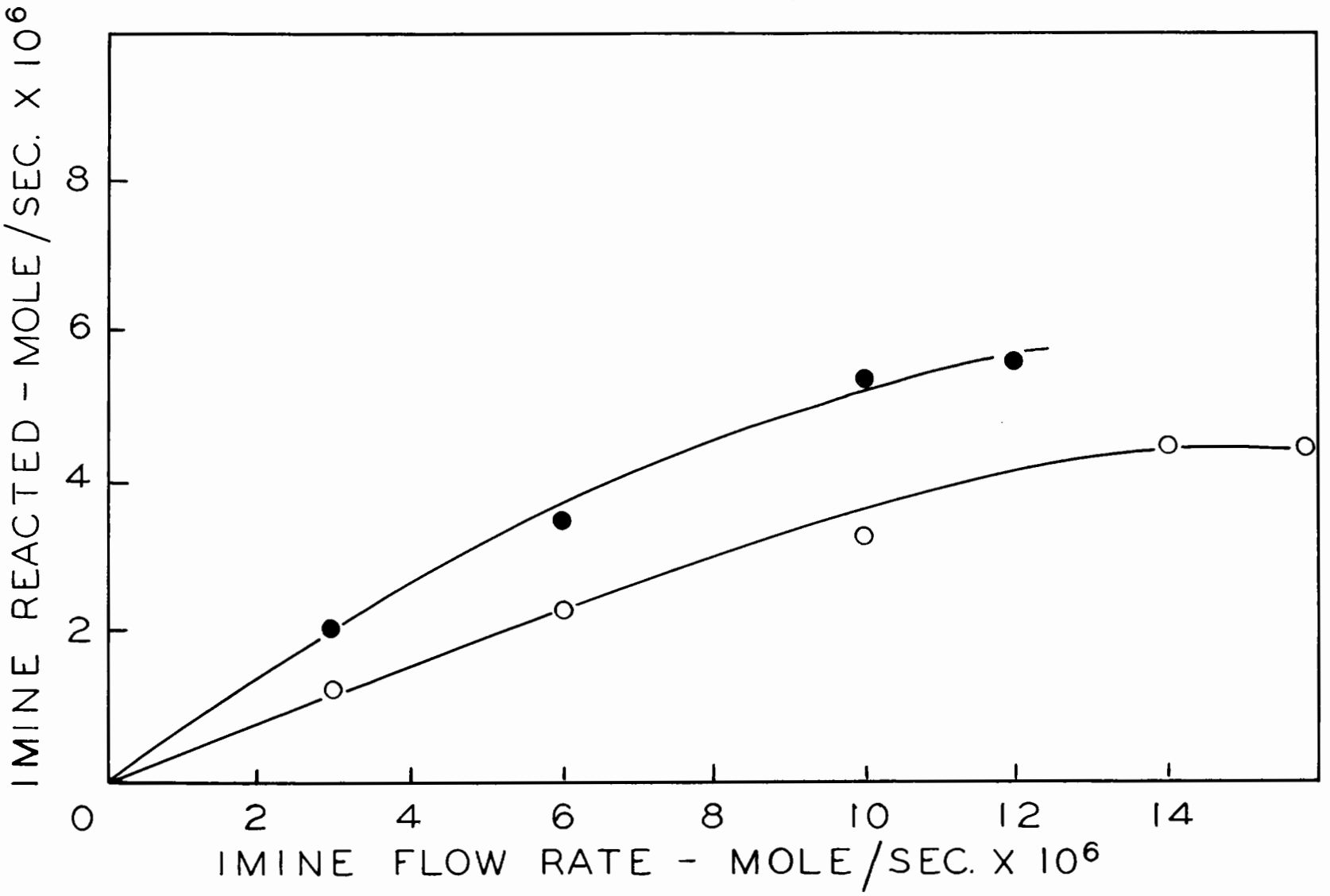
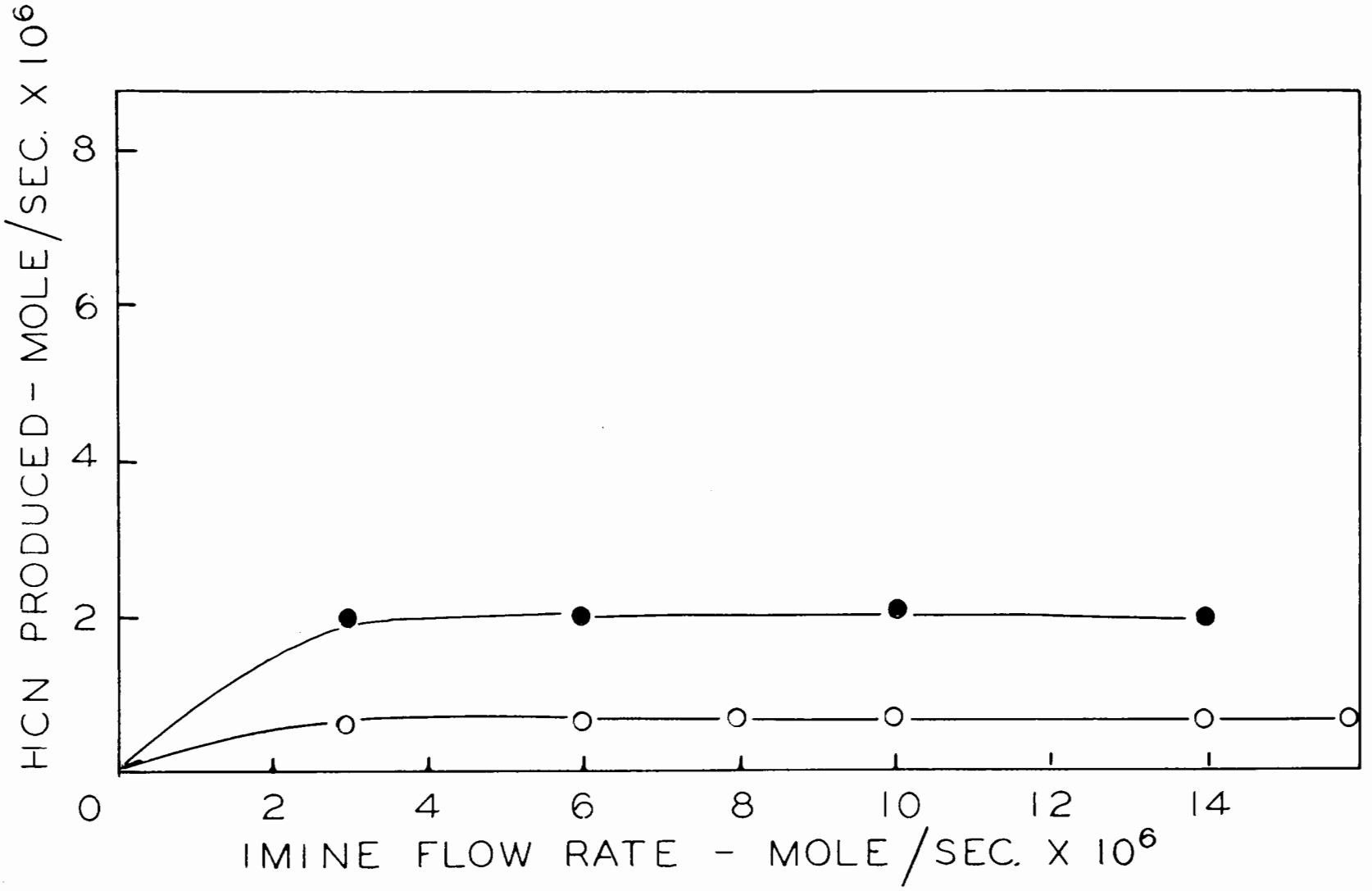

IMINE REACTED - MOLE/SEC. X 10⁶
0
2
4
6
8
2
4
6
8
10
12
14
IMINE FLOW RATE - MOLE/SEC. X 10⁶

Figure 10

RELATION BETWEEN PRODUCTION OF HCN AND FLOW RATE OF 1-3 PROPYLENIMINE AT DIFFERENT TEMPERATURES

○ HCN at 150°C.

● HCN at 284°C.


HCN PRODUCED - MOLE/SEC. X 10⁶
0
2
4
6
8
0
2
4
6
8
10
12
14
IMINE FLOW RATE - MOLE/SEC. X 10⁶

gases were passed through an absorber containing 2 N NaOH solution frozen by dry ice-acetone mixture. The frozen contents of the closed trap were allowed to come to room temperature, and then heated to 60°C. to hydrolyse HCN and any CH_3CN that might have been trapped. The resulting ammonia was led into a known volume of standard H_2SO_4, and the total ammonia determined by back-titration with standard alkali. This total ammonia is the sum of ammonia produced directly in the reaction, plus ammonia resulting from hydrolysis of HCN plus ammonia resulting from hydrolysis of CH_3CN. Since the first two quantities were known from independent estimations, the amount of CH_3CN in the sample could be readily calculated. This is essentially the method adopted by Rabinovitch and Winkler (111) for the hydrolysis of alkyl nitriles.

The non-condensable products of the reaction were analysed with a mass-spectrometer. The quantitative analyses of the various products are summarized in Table XI and represented in figures 11 and 12. The separation of C_2 and C_3 unsaturated hydrocarbons from the corresponding saturated ones was effected by absorbing the fraction in a 5 per cent solution of mercuric sulphate in dilute H_2SO_4 which absorbs only the unsaturated fraction.

TABLE XI

PRODUCTS OF REACTION OF 1-3 PROPYLENIMINE WITH H-ATOMS

Flow Rate - micromoles per second

Temp. 150°C.

Imine Flowed	C_2H_6	C_2H_4	CH_4	HCN free	HCN bound	CH_3CN	NH_3 free	NH_3 bound	C_3H_8	C_3H_6	Imine recovered	% Recovery N	% Recovery C
300	60	50	-	-	55	-	45	15	-	-	140	110	97
600	180	75	50	-	50	20	60	20	15	20	325	85	99
1000	200	120	30	-	50	100	130	20	20	20	600	92	100
1400	300	150	15	-	55	110	160	15	20	25	900	80	100
1600	300	165	-	-	50	110	185	20	15	20	1100	86	97

Figure 11

EFFECT OF FLOW RATE OF 1-3 PROPYLENIMINE ON THE AMOUNT OF IMINE REACTED AND ON THE YIELDS OF HCN AND CH_3CN AT 150°C.

● Imine Reacted.

■ HCN Produced.

▲ CH_3CN Produced.

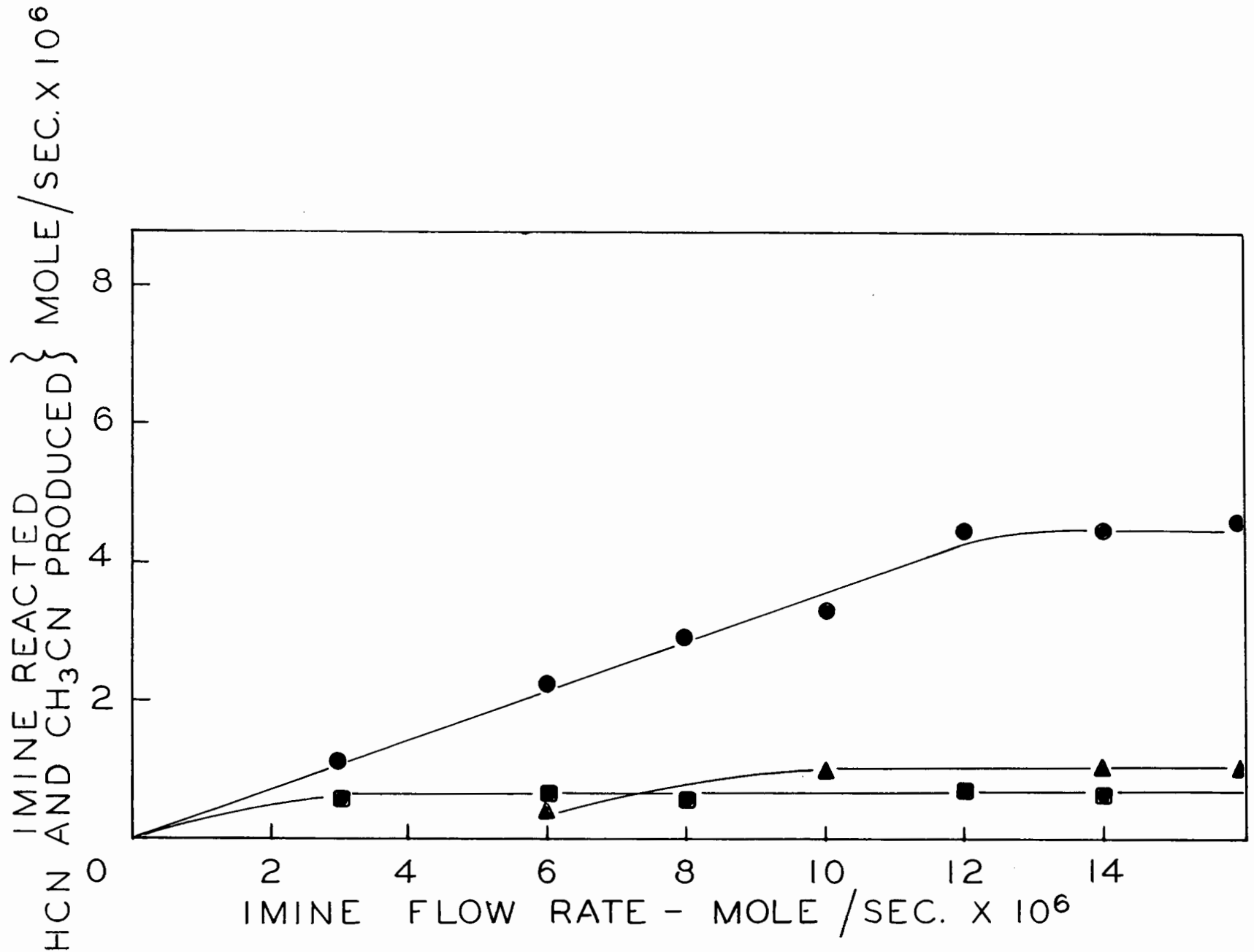
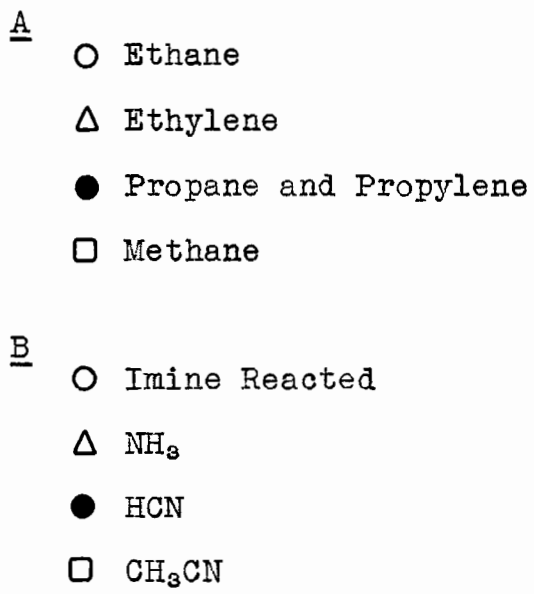
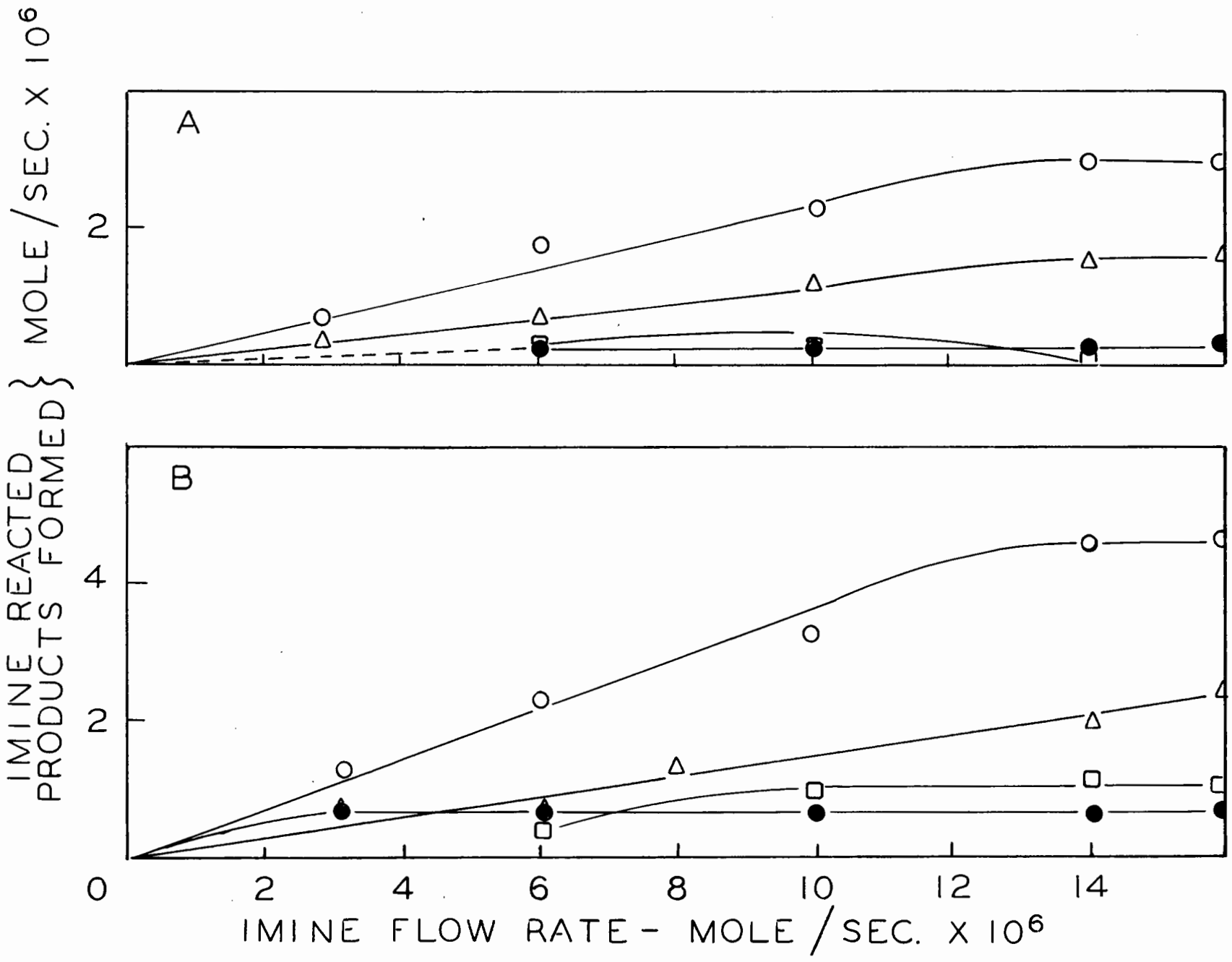

IMINE REACTED
HCN AND CH_3CN PRODUCED } MOLE/SEC. X 10^6
0
2
4
6
8
10
12
14
IMINE FLOW RATE - MOLE/SEC. X 10^6

Figure 12

EFFECT OF FLOW RATE OF 1-3 PROPYLENIMINE ON IMINE CONSUMPTION AND PRODUCT FORMATION AT 150°C.




A
B
2
4
0
2
4
6
8
10
12
14
IMINE REACTED
PRODUCTS FORMED
MOLE / SEC. X 10⁶
IMINE FLOW RATE - MOLE / SEC. X 10⁶

it is seen from the figures that the yield of the hydrocarbons and HCN levelled out as the imine flow-rate was increased. The production of methane (which was quite low compared with the other reactions studied) passed through a maximum.

COMPARISON OF THE THREE REACTIONS

There is little point in comparing the results obtained in the trimethylamine reaction with those obtained in the reactions of the imines, since the types of molecules involved are rather dissimilar. However, a brief comparison of the two imine reactions does seem appropriate.

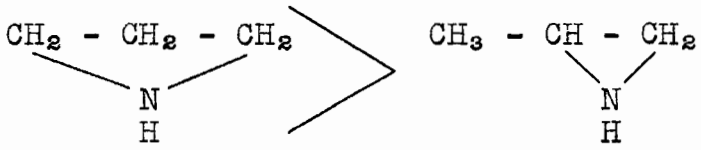
With 2-methyl ethylenimine the reactant consumption approximated the available H-atom flow-rate, while with 1-3 propylenimine the H-atom concentration exceeded consumption of the imine.

With 2-methyl ethylenimine, the yield of HCN went through a maximum, whereas with 1-3 propylenimine the production of HCN attained a limiting value as the imine flow-rate was increased.

The yield of methane from both reactions passed through a maximum, while the yields of ethane and ammonia levelled off as the flow-rates of the reactants were increased.

CH_3CN was detected, identified and quantitatively estimated only in the 1-3 propylenimine reaction, while ethylene was detected only in the 1-3 propylenimine reaction.

The exothermicity of the reactions appeared to be in the order



DISCUSSION

By analogy with other H-atom reactions that have been studied, it is probably reasonable to conclude that the primary step in the reactions of H-atoms with amines and imines should be an H-atom abstraction. The site of this abstraction is not definitely known. From the work of Watson and Darwent (68), and Trotman-Dickenson and Steacie (88), it would appear that (N-H) and (C-H) bonds are of comparable strength. On the other hand, the exchange experiments of Goldfinger and Lasareff (112) showed that deuterium of heavy water exchanged rapidly with methylamine and dimethylamine at the nitrogen site

$$CH_3\ NH_2\ HCl + D_2O \rightarrow CH_3\ ND_2.DCl$$

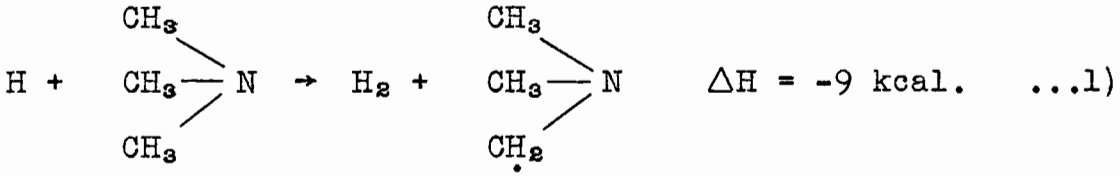
$$(CH_3)_2NH.HCl + D_2O \rightarrow (CH_3)_2\ ND.DCl$$

In previous studies in this laboratory of the reactions of imines and amines with H-atoms, it was assumed that, although H-atom abstraction might occur from either carbon or nitrogen in the primary process, it probably occurred somewhat more readily from the nitrogen. Hence the interest, as indicated previously, in studying the comparable reaction with trimethylamine where there is no hydrogen attached to the nitrogen atom.

REACTION OF TRIMETHYLAMINE WITH H-ATOMS

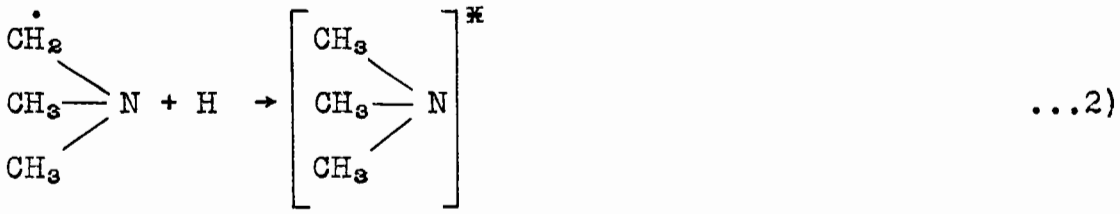
It will be recalled that the production of HCN at low flow-rates of amine was linear and increased only slightly with temperature. In these respects, this reaction closely resembled that of dimethylamine with H-atoms (107).

As in the similar reactions studied previously in this laboratory (79,87,107) the primary reaction is presumably an H-atom abstraction, of necessity from a methyl group, i.e.,



$$H + \begin{matrix} CH_3 \\ CH_3 — N \\ CH_3 \end{matrix} \rightarrow H_2 + \begin{matrix} CH_3 \\ CH_3 — N \\ \dot{C}H_2 \end{matrix} \qquad \Delta H = -9 \text{ kcal.} \qquad ...1)$$

The trimethylamine radical produced in reaction 1 could react further with H-atoms to yield the activated trimethylamine molecule,



$$\begin{matrix} \dot{C}H_2 \\ CH_3 — N \\ CH_3 \end{matrix} + H \rightarrow \left[\begin{matrix} CH_3 \\ CH_3 — N \\ CH_3 \end{matrix} \right]^* \qquad ...2)$$

which, because of the excess energy (85 kcal.) obtained by the formation of a (C-H) bond, might dissociate as follows

$$\left[(CH_3)_3N\right]^{*} \rightarrow CH_3 + (CH_3)_2\dot{N} \qquad \Delta H = -12 \text{ kcal.} \qquad ...3)$$

$$\rightarrow CH_4 + CH_3 - \dot{N} - \dot{C}H_2 \qquad \Delta H = -11.9 \text{ kcal.} \qquad ...4)$$

Reaction of the dimethylamine radical produced in reaction 3 with another H-atom would yield the corresponding activated dimethylamine,

$$(CH_3)_2\dot{N} + H \rightarrow \left[(CH_3)_2NH\right]^{*} \qquad ...5)$$

identical, of course, with the excited dimethylamine molecule in the reaction of dimethylamine with H-atoms studied previously (107). The excited dimethylamine of reaction 5 might dissociate,

$$\left[(CH_3)_2NH\right]^{*} \rightarrow CH_3 + CH_3NH \qquad \Delta H = -20 \text{ kcal.} \qquad ...6)$$

$$\rightarrow CH_4 + CH_3N \qquad \Delta H = -17 \text{ kcal.} \qquad ...7)$$

or it might, perhaps, be stabilized

$$\left[(CH_3)_2NH\right]^{*} + M \rightarrow (CH_3)_2NH + M \qquad ...8)$$

where M is a third body (trimethylamine, hydrogen or the wall of the vessel). The presence of dimethylamine in

the reaction products is therefore not surprising.

As in the previous studies of the corresponding reactions with other amines, the production of HCN may be explained by dissociation of CH_3N radicals,

$$CH_3N \rightarrow HCN + H_2 \qquad \Delta H = -48 \text{ kcal.} \quad ...9)$$

produced either in reaction 7 or by further reaction of H-atoms with the methylamino radical (CH_3NH) produced in reaction 6, i.e.,

$$CH_3NH + H \rightarrow CH_3N + H_2 \quad ..10)$$

The slight increase in HCN yield with increase of temperature would reasonably correspond to increased dissociation of the excited dimethylamine to CH_3N radicals, and their subsequent dissociation to HCN, at higher temperatures.

It is suggested that the decrease in HCN yield beyond the maximum, with increase in amine flow-rate, is to be attributed at least partially to increased recombination of CH_3N radicals

$$2\ CH_3N \rightarrow C_2H_6 + N_2 \quad ..11)$$

before they suffer dissociation to give HCN, since some free nitrogen is found in the products at higher flow-rates

of amine. However, the increase in production of ammonia at higher amine flow-rates suggests that decrease in HCN yields under these conditions might also result from a reaction such as

$$\begin{matrix} CH_3NH \\ CH_3NH \end{matrix} \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!NH + NH \qquad \Delta H = -1 \text{ kcal.} \qquad ..12)$$

followed by reaction of the (NH) radical with molecular hydrogen to yield NH_3. It is of interest, perhaps, that reaction 12 would also supplement reaction 8 in contributing to the observed production of dimethylamine in the system.

The following reactions would probably account for methane production

$$CH_3 + H + M \rightarrow CH_4 + M \qquad ..13)$$

$$CH_3 + H_2 \rightarrow CH_4 + H \qquad ..14)$$

$$CH_3 + \begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!\!N \rightarrow CH_4 + \begin{matrix} \dot{C}H_2 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!\!N \qquad ..15)$$

The decrease and final levelling-out of methane yield after the maximum might be due to the replacement of reaction 13 by the slower abstraction reaction 15, for which the activation energy is about 9 kcal., which would predominate at

higher amine flow-rates. Reaction 14 may not be significant below 300°C.

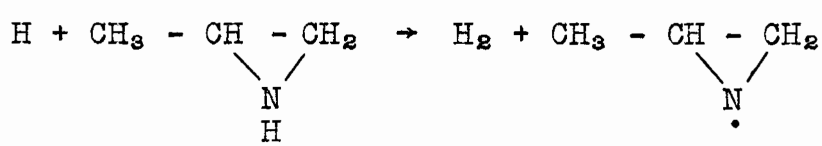
The curve for "amine reacted" (fig. 5) represents the combined extents to which trimethylamine and dimethylamine suffered reaction, since these two were not separated in establishing this curve. To explain the decrease in total amine reacted at higher amine flow-rates, it seems necessary to assume that trimethylamine is a better third body than hydrogen for collisional stabilization of the excited trimethyl- or dimethyl- amines of reactions 2 and 5. Effectively, this means that, at the higher flow-rates, the amine may cause catalytic recombination of H-atoms.

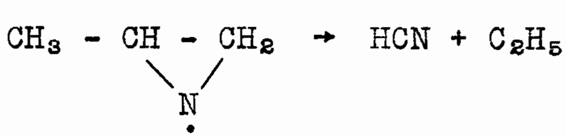
It is interesting to note that if, at high flow-rates of amine and relative deficiency of H-atoms, reaction 3 were followed only by reaction 5 and stabilization of the resulting dimethylamine, then methane and ethane, but no HCN, could be produced. Such a condition would presumably be approximated at high amine flow-rates. Actually, if methane production at such flow-rates were mainly by reaction 15 and relatively slow, ethane would become a major product of reaction at sufficiently high amine flow-rates, and this appears to be true experimentally.

<u>REACTION OF 2-METHYL ETHYLENIMINE WITH H-ATOMS</u>

It may be recalled that, at lower flow-rates of imine, the rates of imine consumption and HCN production were linear with imine flow-rate and essentially independent of temperature. Examination of the products of the reaction reveals that HCN, methane and ethane were obtained as major products and these attained limiting values at an imine flow-rate of 6 to 7 micromoles per second (fig. 7, 8 and 9). Also, the maximum HCN produced corresponded roughly to one-half the H-atom flow-rate.

As in the reactions of H-atoms with other imines, it may be reasonably assumed that the primary process involves abstraction of a hydrogen atom from a nitrogen atom, followed by the dissociation of the residual radical. The mode of this dissociation presents a problem, but since no trace of ethylene was found as a product of the reaction, it seems almost necessary to assume that the dissociation resulted in the formation of an ethyl radical, rather than ethylene, i.e., the following sequence,


...1)


$\Delta H = -38.4$ kcal ...2)
overall

Since disproportionation of ethyl radicals would yield some ethylene, while their recombination would produce butane, which was also absent from the products, it is necessary to assume that practically all the ethyl radicals formed in reaction 2 are destroyed by the fast "cracking" reaction

$$C_2H_5 + H \rightarrow 2\ CH_3 \qquad \ldots 3)$$

This overall mechanism is supported by the fact that two H-atoms are used up for every mole of imine consumed and that the maximum HCN yield corresponds to about one-half the H-atom flow-rate (5.7 micromoles per second).

To some extent, particularly at low imine flow-rates, the radical produced in reaction 1 might react with a second H-atom, as postulated for methyl-, ethyl-, dimethyl- and trimethylamine (87,107), and dissociate as follows

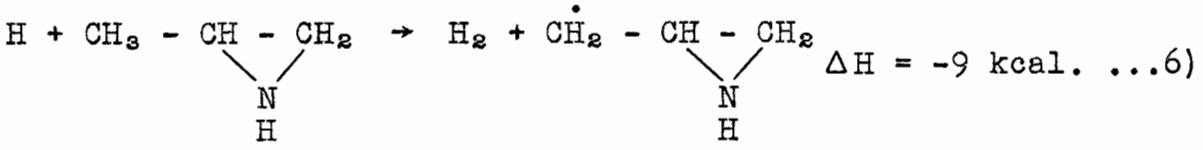
$$H + CH_3 - \underset{\bullet}{N}(CH) - CH_2 \rightarrow \left[CH_3 - \underset{H}{N}(CH) - CH_2\right]^{*} \rightarrow HCN + 2\ CH_3 \qquad \Delta H = 0 \qquad \ldots 4)$$

$$\rightarrow HCN + C_2H_6 \qquad \Delta H = -84 \text{ kcal} \qquad .5)$$

However, the results of the present investigation are quite similar to those for the corresponding reactions of ethylenimine (79) where HCN was quantitatively recovered from the

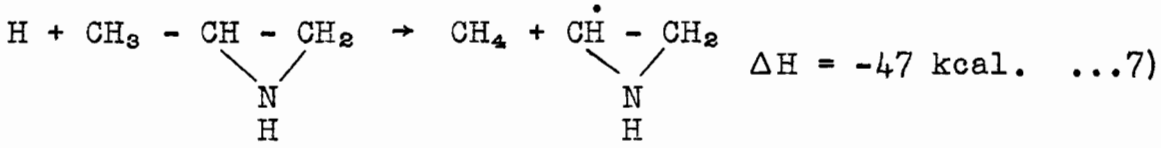
imine consumed, and in these reactions, the mechanism appeared to involve dissociation of radicals directly, as in reaction 2. It seems likely, therefore, that reactions 1 and 2 are the main reactions in the H-atom attack on the present reactant.

Abstraction of a hydrogen atom might also occur from the methyl group of the imine, i.e.,



It is not possible to stipulate the relative extents of H-atom abstraction from C-H and N-H sites, but the previous argument would seem to apply to either case, i.e., the resulting radical apparently must dissociate without formation of ethylene. It seems reasonable, however, that dissociation of the radicals formed in reactions 1 and 6 might well behave similarly, since they are isomeric.

The reaction



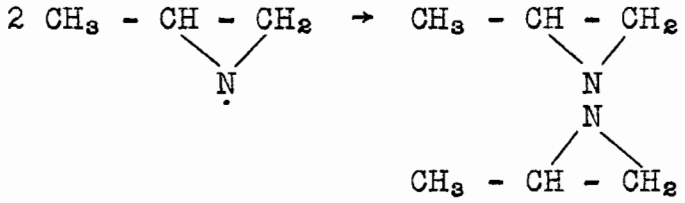
need not be seriously considered since few, if any, reactions are known where CH_3 abstraction is preferred to abstraction of

an H-atom in such reactions. From a survey of H-atom reactions (15), it appears that the only reaction where methane might be formed in the primary process is

$$H + CH_3 - Hg - CH_3 \rightarrow CH_4 + CH_3 Hg$$

where $D(CH_3 Hg - CH_3)$ is only 51 kcal. (113).

The slight decrease in HCN yield from the 2-methyl ethylenimine - H-atom reaction after the maximum (fig. 7), is probable due to some recombination of radicals



...8)

at high imine flow-rates, to produce traces of relatively non-volatile materials and perhaps traces of N_2 (as found) and higher hydrocarbons (insufficient for detection) by decomposition of the dimer. The slower decrease in HCN yield after the maximum, with increase in temperature of the reaction vessel, is readily explained by an increased decomposition of the imine radical (reaction 2) relative to its recombination (reaction 8).

Ethane could result from the following reactions

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \qquad ...9)$$

$$C_2H_5 + CH_3 - \underset{\diagdown\ \underset{H}{N}\ \diagup}{CH - CH_2} \rightarrow C_2H_6 + CH_3 - \underset{\diagdown\ \underset{\bullet}{N}\ \diagup}{CH - CH_2} \qquad ..10)$$

the C_2H_5 and CH_3 radicals being produced in reactions 2 and 3 respectively. However, reaction 10 is probably not of great significance, even at high imine flow-rates, owing to the fast destruction of ethyl radicals by H-atoms (reaction 3).

The observed increase and final levelling-out of ethane production with increase in imine flow-rate might be expected from an increased rate of recombination of methyl radicals to a limiting value as the rate of imine consumption is increased.

Methane was probably produced by the reaction

$$CH_3 + H + M \rightarrow CH_4 + M \qquad ..11)$$

together with reactions of the type

$$CH_3 + CH_3 - \underset{\diagdown\ \underset{H}{N}\ \diagup}{CH - CH_2} \rightarrow CH_4 + CH_3 - \underset{\diagdown\ \underset{\bullet}{N}\ \diagup}{CH - CH_2} \qquad ..12)$$

Reaction 11 would be mainly responsible for methane production at low flow-rates of imine (excess H-atoms), while reaction 12 might be expected to predominate at high flow-rates of imine. The maximum in methane production might

result from replacement of reaction 11 by the slower abstraction reaction 12. If this were true, it might be expected that methane production would attain a limiting value (as with trimethylamine) if the imine flow-rate were sufficiently high (above those investigated) that reaction 12 would become responsible for practically all methane production.

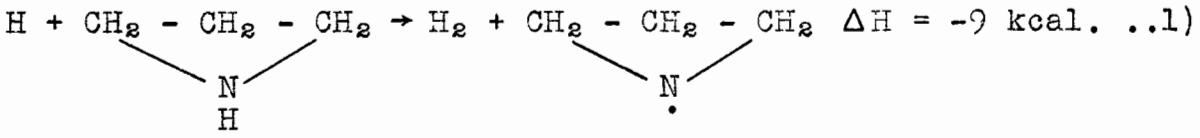
The relatively temperature-independent consumption of imine and production of HCN are consistent with a rapid reaction that consumes virtually all the available H-atoms. If the proposed reactions 1 and 2 give a reasonably correct interpretation of the overall reaction, it is obvious that these have low activation energies and that the imino radical, $CH_3 - CH - CH_2$ (N•), is comparatively unstable. As with ethylenimine (79), the imine consumption at higher flow-rates of imine and at 275°C, may be taken as a measure of H-atom flow-rate.

REACTION OF 1-3 PROPYLENIMINE WITH H-ATOMS

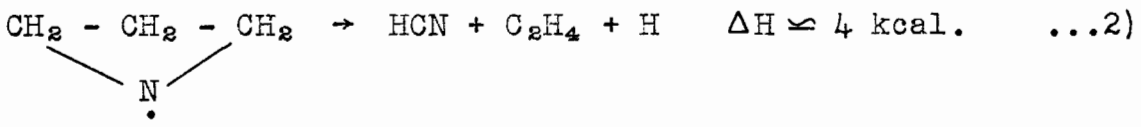
The reaction of 1-3 propylenimine with H-atoms was characterized by a low yield of HCN (about 15 per cent of the imine reacted at room temperature), relatively high yields of ethane, ethylene, ammonia, the recovery of methyl cyanide as a product, and the production of small

amounts of propane, propylene, and methane. All the reaction products except ammonia attained limiting values, as did also the consumption of imine as the imine flow-rate was increased. Ammonia production appeared to increase with imine flow-rate.

As before, the primary reaction probably involves abstraction of an H-atom at the nitrogen atom,



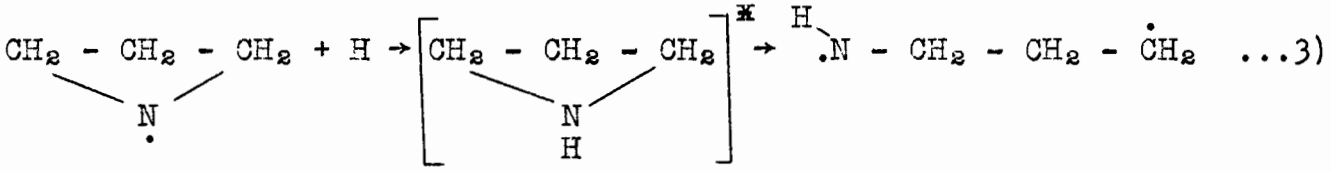
which might be followed by



The limited production of HCN at room temperature indicates, however, that reaction 2 was of rather limited significance. This conclusion implies that the propylenimine radical is considerably more stable than the corresponding radical derived from 2-methyl ethylenimine. This is to be expected, since the strain in the 4-membered ring should be less than that in the 3-membered ring.

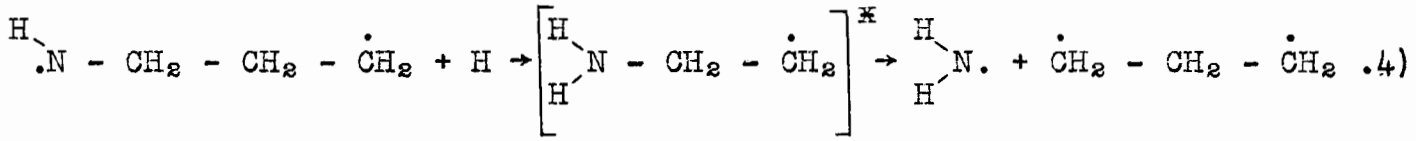
As a consequence of its longer life time, the radical from reaction 1 should have a greater opportunity

than the 2-methyl ethylenimine radical to react further with an H-atom and be converted to a bi-radical through the excited imine,



...3)

Hydrogen atoms may then react with the bi-radical at different sites. One mode of H-atom addition (perhaps at the nitrogen atom) might result in the following sequence:



.4)

The NH_2 radical could then react with an imine molecule or with an H-atom to yield ammonia. Recovery of appreciable amounts of ammonia among the reaction product indicates that this reaction is quite significant and may proceed at the expense of reaction 2.

The trimethylene radical produced in the reaction 4 might be expected to isomerize at the walls of the reaction vessel to produce propylene (114) some of which might be hydrogenated to propane, and both these hydrocarbons were found in the reaction products. The fact that the (N-C) bond is weaker than the (C-C) bond would probably favour reaction 4 and the production of a considerable quantity

of ammonia (fig. 13b).

Another mode of H-atom addition, (e.g., at a carbon atom) might result in a different sequence of reactions such that CH_3CN might be produced:

$$H + \overset{H}{\underset{}{\diagdown}}N - CH_2 - CH_2 - \dot{C}H_2 \rightarrow \left[\overset{H}{\underset{}{\diagdown}}N - CH_2 - CH_2 - CH_3\right]^{*} \rightarrow CH_3 + H_2 + CH_3CN \quad ...5)$$

Alternatively, dissociation of the H-atom adduct might yield ethylene, which appears to be a primary product of the reaction since it is present in the products at all flow rates of the imine

$$\left[\overset{H}{\underset{}{\diagdown}}N - CH_2 - CH_2 - CH_3\right]^{*} \rightarrow HCN + C_2H_4 + H_2 + H \quad ...6)$$

The comparatively low yield of HCN suggests that reactions 4 and 5 compete favourably with reactions 2 and 6, to yield ammonia and CH_3CN at the expense of HCN.

Ethane could be formed by the following reactions

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \quad ...7)$$

$$C_2H_4 + H \rightarrow C_2H_5 \quad ...8)$$

$$C_2H_5 + H \rightarrow 2\ CH_3 \quad ...9)$$

$$C_2H_5 + H + M \rightarrow C_2H_6 + M \quad ..10)$$

The levelling-out of ethane production would be expected as the supply of H-atoms became exhausted at higher flow rates of imine.

It is interesting to note that this reaction, unlike that of 2-methyl ethylenimine with H-atoms, shows a rather marked temperature dependence. It seems reasonable to ascribe the difference in behaviour of the two imines to the probable difference in stability of the radicals formed by H-atom attack on the parent molecule, as indicated previously. Obviously, if the greater stability of the radical from propylenimine is associated with a greater activation energy for its conversion to HCN or other products, an increase of temperature might well increase considerably the formation of products from propylenimine without a corresponding increase in the products from the reaction of 2-methyl ethylenimine.

THE NATURE OF THE ACTIVE NITROGEN - PROPYLENE COMPLEX

As indicated earlier, it was hoped that a comparative study of the H-atom reactions with 2-methyl ethylenimine and 1-3 propylenimine might give some information about the nature of the complex formed in the propylene-nitrogen atom reaction. Careful consideration of the results suggests that this has probably been realized.

The H-atom reactions with 1-3 propylenimine, like the reaction of active nitrogen with propylene, but unlike the H-atom reaction with 2-methyl ethylenimine, yielded ethylene as a primary product. From this, it might appear that the radical, $CH_2 - CH_2 - CH_2$ (N), rather than the

radical, $CH_3 - CH - CH_2$ (N), corresponds to the propylene-

nitrogen atom complex. However, the yield of HCN from the H-atom propylenimine reaction (15 per cent) was grossly inadequate to support such an inference, since HCN is a major product from the attack of active nitrogen on propylene (115).

To account for the relatively high yield of HCN and the complete absence of ethylene in the hydrogen atom attack on 2-methyl ethylenimine, it appears necessary to assume, as outlined earlier, that the radical, $CH_3 - CH - CH_2$ (N),

dissociates into HCN and an ethyl radical. The propylene-Nitrogen atom complex, on the other hand, must dissociate to form HCN and ethylene to account for these two major products of this reaction. At first sight, the discrepancy

suggests that the methyl ethylenimine radical must also be rejected as a possible counterpart of the propylene-nitrogen atom complex. However, it must be remembered that, unlike the H-atom reaction with the imine, attack of a nitrogen atom on propylene must form a highly energetic complex. The dissociation products of this complex might well be HCN and an excited ethyl radical, which would, however, dissociate immediately into ethylene and a hydrogen atom.

It appears reasonable to conclude, therefore, that the radical $CH_3 - CH(\cdot N) - CH_2$, the intermediate in the H-atom reaction with 2-methyl ethylenimine, might well be taken to represent the complex formed in the reaction of propylene with active nitrogen.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The production of HCN from the reaction of H-atoms with trimethylamine, 2-methyl ethylenimine and 1-3 propylenimine has been studied at different temperatures in a Wood-Bonhoeffer fast flow system. The flow of hydrogen was kept constant for each experiment, while the flow-rates of the reactants were varied over a wide range. The products of these reactions were examined in some detail (using appropriate quantitative analytical methods) for the room temperature reactions.

2. The trimethylamine - H-atom reaction was found to have the following characteristics:
   a) Dimethylamine was recovered among the products of the reaction.
   b) HCN production was linear at low amine flow-rates, went through a maximum with increase in flow-rate, and eventually decreased to zero at higher amine flow-rates.
   c) The products of the reaction were mainly methane, with smaller quantities of ethane, HCN and ammonia.
   d) The amine consumption was less than the available H-atom flow-rate at both temperatures.

3. The 2-methyl ethylenimine - H-atom reaction was found to behave as follows:
   a) About 90 per cent of the imine consumed was converted to HCN.
   b) The yield of HCN went through a maximum as the imine flow-rate was increased.
   c) Considerable quantities of methane and ethane and smaller amounts of ammonia were recovered in the reaction products in addition to HCN. No ethylene was recovered at any flow-rate of the imine.
   d) Imine consumption was lower than the available H-atom flow-rate at room temperatures and approximated the H-atom flow-rate at 275°C.

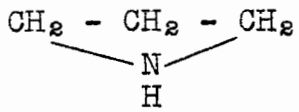
4. The 1-3 propylenimine - H-atom reaction had the following salient features:
   a) The yield of HCN was probably lower than that for any of the similar reactions studied in this laboratory.
   b) Increase of temperature had a pronounced effect on HCN production.
   c) CH_3CN was recovered in the reaction product and it might well be the 'No titre' fraction reported in the earlier work (87,107).
   d) Ethylene was recovered at all imine flow-rates. The ethane recovered in the reaction products might have resulted from the secondary reactions of ethylene.

e) Considerable quantities of ammonia were recovered in the reaction products.

f) Only a very small quantity of methane and traces of nitrogen were found among the non-condensable products of the reaction.

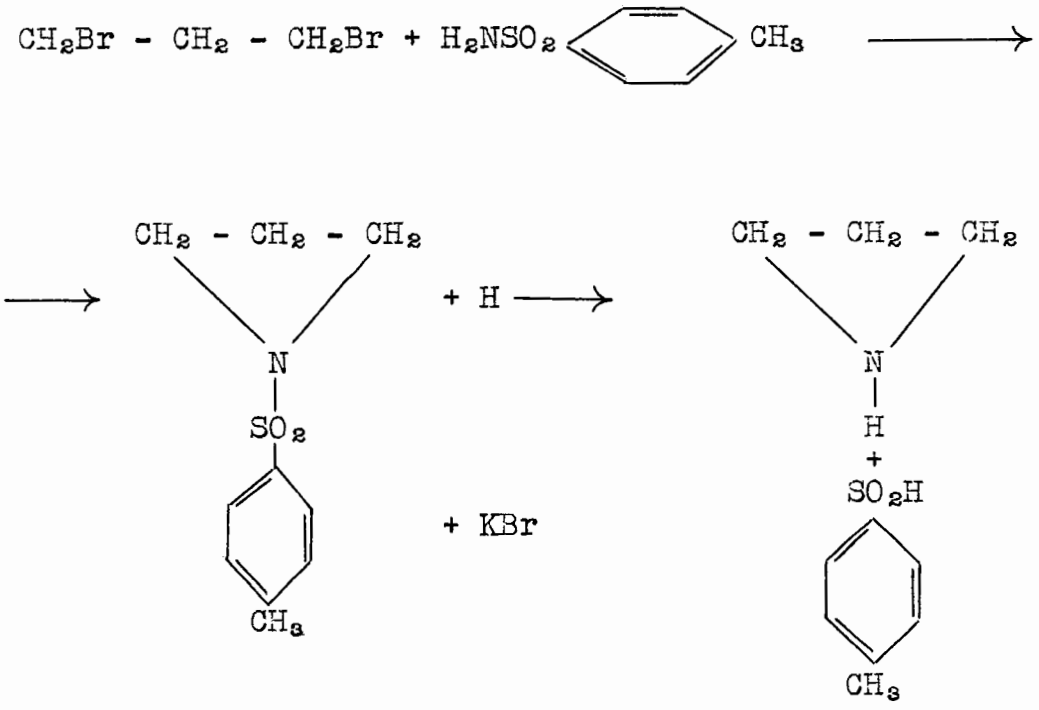
APPENDIX A

PREPARATION OF 1-3 PROPYLENIMINE (AZETIDINE)



Summary

The method consisted in reacting 1-3 dibromopropane with para-toluenesulphonamide in KOH solution and effecting a reductive cleavage, i.e.,



(p-Toluene sulphinic acid)

Procedure

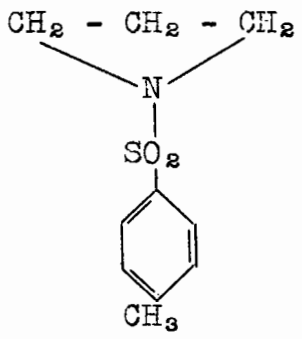
480 gm. of para-toluenesulphonamide were mixed with 1020 ml. of 16 per cent potassium hydroxide solution and 600 gm. of 1-3 dibromopropane. The mixture was refluxed for

4 hours with an efficient reflux condenser. When the solution was almost neutral, an additional 500 ml. quantity of 16 per cent KOH was added and refluxed until the resulting solution was neutral. This procedure was repeated until the resulting solution was again neutral. Experience proved that this refluxing with excess of KOH over a long period of time was very important, and required about 8 hours on each occasion.

The contents of the flask were cooled and a stream of air was drawn through the solution which was evaporated by suction. The purpose was to evaporate the alcohol formed in the reaction. In practice this was too laborious and accordingly the procedure was modified by heating the solution to 70°C. and drawing a constant stream of air through it for about 8 hours. This treatment produced a white 'paste' and the supernatant solution became clear. There was no danger of excessive evaporation since only the 'paste' was of interest.

After the contents of the vessel had been allowed to cool, the supernatant liquid was <u>decanted</u> (not filtered) from the paste which was then washed several times with 300 ml. portions of distilled water to remove the potassium bromide, which was tested by $AgNO_3$ solution. The paste was then washed with 300 ml. portions of ethanol until the

solution, which originally was yellow, became colourless. Immediate white crystals of



(N, 1-3 propylene para-toluenesulphonamide)

were formed. The yield was very good. The material was recrystallised from ligroin and the melting point of the dried material was 120°C. It was dried under vacuum and weighed.

The dried white powder (N, 1-3 propylene para-toluenesulphonamide) was dissolved in 25 times its weight of iso-amyl alcohol (density = 0.812). The mixture was refluxed with an efficient condenser for about 4 hours, the solution was allowed to cool and metallic sodium, equal in amount to three times the weight of the white powder, was added in small quantities with special care that the solution did not get sufficiently warm to cause significant loss of imine (b.p. 70°C). Moreover, the reflux condenser was removed for minimum time during each addition of metallic sodium (W. Marckwald suggests using metallic sodium equivalent

to twice the amount of white powder. However, experience has shown that complete reduction requires metallic sodium equivalent to approximately 3 times the weight of white powder). The solution turned foggy white and the addition of sodium was stopped when there was some metallic sodium left behind. The addition of metallic sodium produced sodium iso-amylate and hydrogen.

The solution was allowed to cool after all the sodium had been added, and enough water was then added to destroy the unreacted sodium. The solution was now poured into a separatory funnel and addition of water was continued with constant shaking until all the sodium iso-amylate had disappeared and two distinct layers were formed.

The lower aqueous alkaline layer contained sodium hydroxide, amyl alcohol, the imine, and water. The top layer contained amyl alcohol and the imine. The bottom layer was distilled to remove most of the imine and some iso-amyl alcohol.

The residue from the distillation (consisting mainly of amyl alcohol and sodium hydroxide) was discarded. (In the method of W. Marckwald, this residue was used again, but experience in the present study indicated that it was a main source of introducing amyl alcohol into the free imine with

which it formed an azeotrope).

The distillate from the bottom layer was combined with the top layer (containing amyl alcohol and imine) and the mixture was shaken with dilute sulphuric acid until the solution was slightly acidic. Two layers were formed with amyl alcohol as the top layer.

The slightly acidic lower aqueous layer, which contained the imine in the salt form, was shaken several times with 300 ml. portions of anhydrous ether to remove small quantities of amyl alcohol. An air stream was then drawn through the solution (acidic solution containing the imine in the salt form) to remove the ether (about 3 hours).

The solution was cooled with ice and mixed, with continuous shaking, with a fresh, concentrated, chilled solution of sodium-hydroxide (W. Marckwald used "residue" here). The imine was liberated as a thin upper layer and sodium sulphate was deposited at the bottom. Imine and water were distilled together at 80-100°C. To make sure that all the imine distilled over, an excess 100 ml. was collected at 100°C.

The distillate was saturated with KOH pellets in a separatory funnel, (care being taken that the solution did not get too warm to lose the imine) and the imine was again

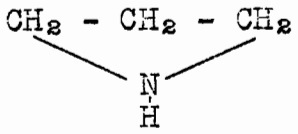
liberated as a thin upper layer. It was distilled over barium oxide and finally distilled twice over metallic sodium and stored over KOH pellets, b.p. 69-72°C.

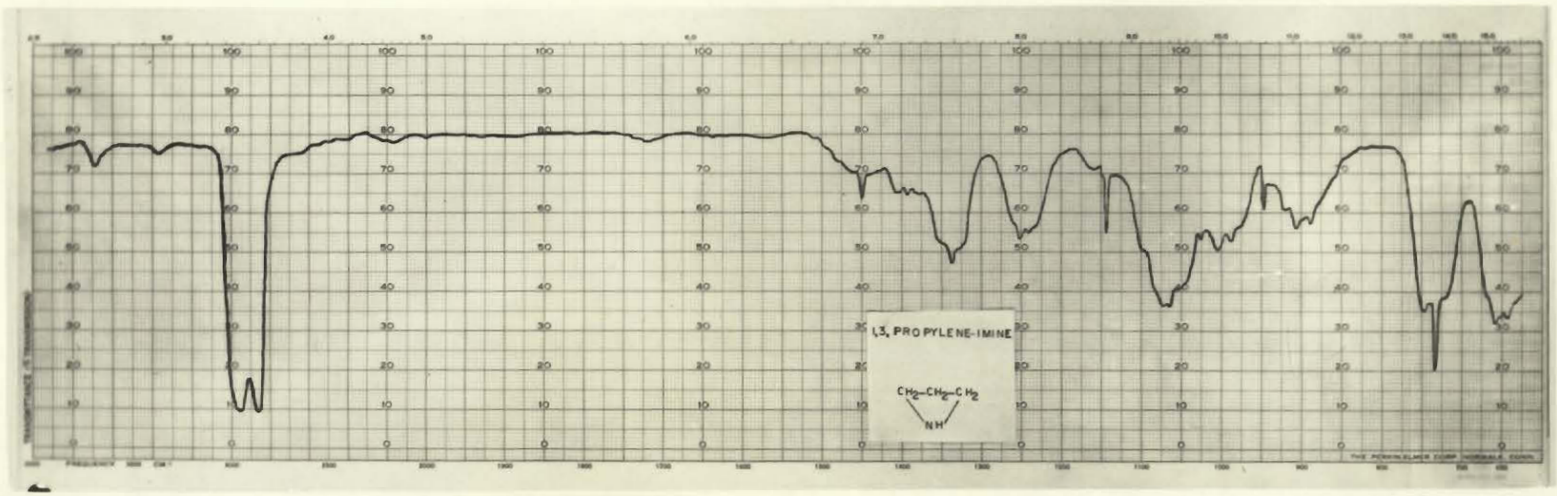
The imine is characterized by its ammoniacal odour and the formation of white fumes when it is exposed to moist air.

The impurity most likely to be present in the final product is iso-amyl alcohol. The purity of the imine was determined by infra-red spectroscopy. The presence of CH_2 bands and absence of CH_3 bands, indicated that no detectable iso-amyl alcohol was present as an impurity. The infra-red spectrum is shown in figure 13.

Figure 13

I. R. SPECTRUM OF 1-3 PROPYLENIMINE




1,3, PROPYLENE-IMINE
CH2–CH2–CH2
NH

APPENDIX B

CALCULATION OF HEATS OF REACTIONS

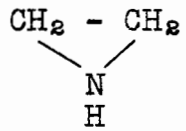
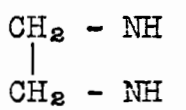
Some established values of heats of formation of gaseous substances at 25°C. are given in Table XII. Most of these values were taken from the United States National Bureau of Standards compilation (116). Some bond dissociation energies, most of which have been taken from Swarc (121) are given in Table XIV. In Table XIII are listed the heats of formation of radicals that have been estimated by using values of the appropriate bond dissociation energies.

The heat of a reaction may be calculated as the sum of the heats of formation of the products minus the sum of the heats of formation of reactants; or very approximately, it is equal to the sum of the dissociation energies of the bonds broken minus the sum of the dissociation energies of the bonds formed.

It may be mentioned that these data are not exact, but they do give an indication whether a given reaction is energetically favourable or not.

TABLE XII

HEATS OF FORMATION* AT 25°C.

	ΔH_f kcal/mole	Source
H	52.089	
NH	77±2	(117)
NH_2	41±2	(117)
NH_3	-11.04	(117)
HCN	31.2	
CH_3	32	
CH_4	-17.889	
C_2H_4	12.496	
C_2H_5	24.5	(118)
C_2H_6	-20.236	
CH_3NH_2	- 6.7	
$CH_3.CH_2.NH_2$	-11.6	
$(CH_3)_2NH$	- 6.6	
$(CH_3)_3$ N	-10.9	(119)
	26	(120)
	-13.86	

* From U.S. National Bureau of Standards, Circular 500 (116), except as noted.

TABLE XIII

ESTIMATED HEATS OF FORMATION AT 25°C.

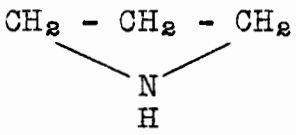
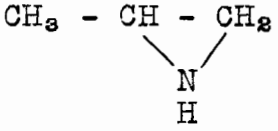
	ΔH_f kcal/mole	
CH_3NH	36	
CH_2NH_2	36	
CH_3N	79	
$CH_2{:}N$	$\sim$ 43	
$CH_3.CH_2.NH$	31	
$CH_3.CH.NH_2$	31	
$CH_3.CH_2.N$	74	
$(CH_3)_2N$	36	
$CH_3.CH_2.NH$	36	
$CH_3N{:}CH_2$	$\sim$ 18	
$CH_3.CH{:}NH$	$\sim$ 13	
	$\sim$ 40	(rough approximation)
	$\sim$ 46	

TABLE XIV

BOND DISSOCIATION ENERGIES *

	D kcal/mole	Source
H - H	103	(15)
H - NH_2	104±2	
$(CH_3)_2N$ - H	~ 95	Rough approximation
$(CH_3)_2N$ CH_2 - H	~ 95	
CH_3 - H	101.5	(118)
CH_3 - CH - CH_2 (N, H)	~ 95	Rough approximation
$(CH_2)_3N$ - H	~ 95	
CH_3 - NH_2	79	
NH_2 - NH_2	60±4	
$(CH_2)_3N$ - H	~ 95	Rough approximation

* From Swarc (121) except as noted.

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