Thus the coils must have some degree of flexibility; indeed, flow would otherwise scarcely be conceivable with such an overlapping of molecular domains as exists at a concentration of even 5×10^{-3} g./ml. Evidently in the more concentrated solutions the motion of a coil segment is determined largely by the resistance of its surroundings, the difficulty of bending of its own structure being small by comparison. A similar conclusion is reached from analysis of dynamic mechanical properties of these solutions at low frequencies.²⁶ Whether the flexibility is achieved by occasional hinges in the helix structure²⁷ is not clear.

In more dilute solutions, however, the inherent stiffness of the coil evidently becomes more important, and the character of the non-Newtonian flow is more consistent with that predicted for a very long rigid ellipsoid (or rod). The rotary diffusion coefficient estimated for this rigid structure is larger than that measured by flow birefringence in extremely dilute solution by a factor which is simply the relative viscosity. The concept of molecular rigidity agrees with conclusions from other measurements in extremely dilute solution, such as the lack of influence of salt on the intrinsic viscosity⁵ and the effect of solvent viscosity on flow birefringence.²⁸

Effect of Salt.—The coincidence of data with and without salt in the reduced-variable plot of Fig. 6 indicates that, at a concentration of 1.5×10^{-3} g./ml., salt affects the rates of all rotary diffusion processes to the same extent. Thus, the 8-fold drop in macroscopic viscosity occasioned by 0.2 M sodium chloride is accompanied by a similar drop in the resistance to motion of any coil segment through its surroundings. This is consistent with the view that the intramolecular resistance of

(26) F. E. Helders, J. D. Ferry, H. Markovitz and L. J. Zapas, THIS JOURNAL, **60**, 1575 (1956).

(27) J. D. Watson and F. H. Crick, Nature, 171, 737 (1953).

(28) H. Schwander and R. Cerf, Helv. Chim. Acta, 34, 436 (1951).

bending the coil itself is small by comparison at this SDNA concentration, and with the conclusion of Butler, Conway and James⁵ that the viscosity drop caused by electrolyte is related to long-range interionic attractions.

Effect of Glycerol.—That glycerol at a concentration of 50.4% causes an intramolecular change is indicated not only by the smaller relative viscosity (Fig. 3) but also by the different character of the non-Newtonian flow in dilute solution, which now resembles that of a shielded coil rather than that of a stiff ellipsoid or rod. This recalls the picture of denaturation of the SDNA molecule²⁹ as a partial unravelling of the stiff helix and approach toward a random coil configuration. It is also consistent with the observations of Schwander and Cerf,²⁸ who found that the rotary diffusion constant from flow birefringence was inversely proportional to solvent viscosity for moderate glycerol concentrations but abnormally large for glycerol concentrations over 40%. Evidence of a similar configurational change in concentrated ethanol solutions has recently been reported by Geiduschek and Gray.³⁰

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(29) P. Doty, Proc. 3rd Intern. Congress Biochem., Brussels, 1955, p. 135.

(30) E. P. Geiduschek and I. Gray, J. Am. Chem. Soc., 78, 879 (1956).

THE REACTIONS OF ETHYLENIMINE AND N-METHYLETHYLENIMINE WITH ATOMIC HYDROGEN AND THEIR RELATION TO COMPLEXES IN ACTIVE NITROGEN REACTIONS¹

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The reactions of hydrogen atoms with ethylenimine and N-methylethylenimine produce mainly hydrogen cyanide and methane in the temperature range 55 to 300° . Some C₂ hydrocarbons are also formed. The hydrogen atom attack probably gives rise to cyclic radicals which subsequently decompose to hydrogen cyanide. This would seem to give credence to the assumption that the attack of active nitrogen on an olefin may form a cyclic complex of structure similar to that of the cyclic ethylenimino radical, prior to the formation of HCN as the main product.

Of the many reactions of active nitrogen with organic compounds that have been studied in this Laboratory, most appear to involve the formation of a relatively long-lived complex between a nitrogen

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(2) Holder of a Cominco Fellowship.

atom and the organic molecule. Such a complex was regarded as an essential part of the mechanism even in the first quantitative investigation of the reaction of active nitrogen with ethylene,³ and forms the basis of a unified mechanism, outlined in a

(3) J. H. Greenblatt and C. A. Winkler, Can. J. Res., B27, 721 (1949).

recent review,⁴ for many analogous reactions.

Although the complex probably would have different structures in different types of reactions, an early suggestion⁵ was that it might be cyclic in the reactions of active nitrogen with unsaturated hydrocarbons, *e.g.*, for ethylene, the structure

$$\underset{N}{\text{H}_2\text{C}}\underset{N}{\overset{\text{C}}{\longrightarrow}}\text{C}\text{H}_2$$

seemed probable. After an investigation of the active nitrogen reactions with the butenes,⁶ and during a study of the mercury photosensitized decomposition of ethylenimine at the Illinois Institute of Technology, Dr. C. Luner proposed that the reaction of hydrogen atoms with ethylenimine be investigated, since it might produce a radical similar to the conjectural cyclic complex of ethylene with atomic nitrogen, and that if this occurred, hydrogen cyanide might be expected as a main product of the hydrogen atom-ethylenimine reaction. This possibility initiated the present investigation.

Experimental

Ethylenimine and N-methylethylenimine of research grade were supplied by Brickman and Co., Montreal, and were used after single bulb-to-bulb distillations. The apparatus was a conventional fast flow system

The apparatus was a conventional fast flow system similar to that used in the studies with active nitrogen,^{3,7} except that the discharge was continuous rather than condensed. The discharge tube and reaction vessel were "poisoned" with 4% phosphoric acid from which excess water was subsequently removed by evacuation. Experimental procedures, including analysis for hydrogen cyanide, were essentially similar to those described previously. Unreacted imine was determined by titration with standard sulfuric acid solution to the methyl red end-point. Samples of the non-condensable products were removed from the gas stream with a Töpler pump.

In all experiments, the flow rate of molecular hydrogen was 7.6 \times 10⁻⁵ mole/sec., corresponding to a pressure of 0.73 mm. in the reaction vessel, while hydrogen atom concentrations of about 6.5% at 60° and 5% at 250° have been estimated.

Results and Discussion

Hydrogen cyanide was indeed recovered as a main product from the reactions of hydrogen atoms with ethylenimine and N-methylethylenimine. The results are summarized in Figs. 1 and 2. Comparison of the graphs shows that very nearly one mole of HCN was formed for each mole of either imine destroyed.

At low flow rates of ethylenimine, the rates of imine consumption and HCN production were linear with flow rate and independent of temperature, while at high flow rates, the amounts of ethylenimine reacted or HCN formed remained constant at each temperature. Such behavior is typical of a fast reaction in which either reactant is completely consumed in an excess of the other so that the hydrogen atom concentrations are probably given approximately by the plateau values for ethylenimine destruction. Concordant estimates of the atom concentrations were made on the basis of the amounts of HCl produced in the reaction of atomic

(4) H. G. V. Evans, G. R. Freeman and C. A. Winkler, Can. J. Chem., 34, 1271 (1956).

(5) G. S. Trick and C. A. Winkler, ibid., 30, 915 (1952).

(6) H. Gesser, C. Luner and C. A. Winkler, ibid., 31, 346 (1953).

(7) H. Blades and C. A. Winkler, ibid., 29, 1022 (1951).



Fig. 1.—Hydrogen cyanide produced and ethylenimine consumed in the reaction of hydrogen atoms with ethylenimine.

hydrogen with ethyl chloride at 60, 120 and 275°. Thus, to a first approximation, it may be assumed that at high flow rates each H-atom reacted with a molecule of ethylenimine to give one HCN.

Formation of hydrogen cyanide as the main product can be explained by the reaction

$$H + \underbrace{\overset{H_2C \longrightarrow CH_2}{\underset{H}{\overset{N}{\overset{N}{\overset{}}}}}_{H} \longrightarrow H_2 + HCN + CH_3$$

 $\Delta H = -15 \text{ kcal.}^{\$} \quad (1)$

in which the primary step is probably abstraction of the imine hydrogen

$$H + \underbrace{H_2C - CH_2}_{H} \longrightarrow H_2 + \underbrace{H_2C - CH_2}_{N}$$
$$\Delta H = -6 \text{ kcal.} (2)$$

followed by decomposition of the ethylenimino radical.

$$\frac{H_2 C \longrightarrow CH_2}{N} \longrightarrow HCN + CH_3 \cdot \Delta H = -9 \text{ kcal.} (3)$$

Additional reactions of the type

$$H + \underbrace{H_2C \longrightarrow CH_2}_{N} \longrightarrow H_2 + \underbrace{HC \longrightarrow CH_2}_{N}$$

might be expected to occur at low flow rates, although at high flow rates, mechanisms involving

(8) Heats of reaction were calculated using the following values: accepted heats of formation of gaseous substances⁹ at 25°; heat of formation of ethylenimine = 25 kcal.¹⁰ Heats of formation have been estimated for N-methylethylenimine and the ethylenimino radical by assuming that $D_{C_{2}H_{4}N-H} \approx 97$ kcal. and $D_{C_{2}H_{4}N-CH_{8}} \approx 73$ kcal. It has also been assumed that the dissociation energy of the N-N bond in the dimer of the ethylenimino radical is roughly equivalent to D-(N-N) in hydrazine.¹¹

(9) U. S. Natl. Bur. Standards, Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, 1952.

(10) R. A. Nelson and R. S. Jessup, J. Research Natl. Bur. Standards, 48, 206 (1952).

(11) M. Szwarc, Chem. Revs., 47, 75 (1950).



Fig. 2.—Hydrogen cyanide produced and N-methylethylenimine consumed in the reaction of hydrogen atoms with N-methylethylenimine.

successive H-atom reactions would seem to be of relatively little importance since only one hydrogen atom is consumed in forming each molecule of HCN.

Mass spectrometric analyses¹² of the non-condensable products of the ethylenimine reaction showed methane to be present in appreciable quantities, as given in the table.

Temp., °C.	Imine flow, mole/sec. \times 10 ⁸	Methane flow, mole/sec. $\times 10^6$
55	5.7	1.8
	9.6	2.4
118	2.9	1.7
	5.3	3.1
271	2.9	1.5
	7.5	2.5

Methane could be formed by reaction of methyl radicals, produced in reaction 3, with any excess hydrogen atoms. The amounts of methane found at very low ethylenimine flow rates, where only a fraction of the available H-atoms were required to react with the imine, were in close agreement with the differences between the estimated atom concentrations and the amounts of imine destroyed. But for this concordance it might appear that the methane results at high flow rates imply true atom concentrations considerably higher than those estimated.

If there were an appreciable steady state concentration of ethylenimino radicals, the thermodynamically favorable reaction

$$CH_{3} + \bigvee_{N}^{H_{2}C \longrightarrow CH_{2}} \longrightarrow CH_{4} + HCN + CH_{2}$$
$$\Delta H = -25 \text{ kcal.} (4)$$

might take place. This reaction has the advantage that migration of a hydrogen atom within the

(12) We are grateful to Dr. H. I. Schiff, of this department, for permission to use the mass spectrometer, and to Mr. G. J. O. Verbeke for the analyses. ethylenimino radical is unnecessary. It might be favored at high imine flow rates if ethylenimino radicals were concentrated near the jet through which ethylenimine entered the reaction vessel. However, this reaction would hardly compete successfully with the combination of hydrogen atoms and methyl radicals, especially in the presence of excess H-atoms at low imine flow rates, and it seems unlikely that a large proportion of the HCN could be formed in this way. Some of the methane formation might be attributed to reaction 4, followed by subsequent hydrogenation of methylene radicals.

Since production of methane at lower flow rates of imine $(2.9 \times 10^{-6} \text{ mole/sec.})$ was found to be essentially the same at 118 and 271°, and the values for higher flow rates (>5.3 $\times 10^{-6}$ mole/sec.) showed no consistent trend with temperature, it would appear that there was no significant temperature coefficient for methane production. This indicates that the reaction

$$CH_{3} + \underbrace{\overset{H_{2}C \longrightarrow CH_{2}}{\bigvee}}_{H} \longrightarrow CH_{4} + \underbrace{\overset{H_{2}C \longrightarrow CH_{2}}{\bigvee}}_{N}$$

 $\Delta H = -4 \text{ kcal.} (5)$

which has an activation energy of 4.8 kcal./mole,¹³ did not occur appreciably. Furthermore, if reaction 5 occurred extensively, followed by reaction 3, ethylenimine consumption and HCN production would no longer be equivalent to the hydrogen atom concentration, as required by the experimental stoichiometry expressed by reaction 1. The required stoichiometry could be maintained if ethylenimino radicals formed a dimer or reacted with methyl radicals to form N-methylethylenimine to an extent equivalent to the ethylenimine destroyed by reaction 5. However, neither N-methylethylenimine nor dimer was detected by mass spectrometric analyses of a single sample which showed that, apart from HCN and unreacted ethylenimine, the condensable products contained only small amounts of C₂ hydrocarbons (probably ethane and ethylene).

The difference between the amounts of imine destroyed and HCN produced may be due to the reactions

$$2 \xrightarrow{H_2C \longrightarrow CH_2} \xrightarrow{H_2C} N \xrightarrow{H_2C} N \xrightarrow{H_2C} N \xrightarrow{H_2C} X \xrightarrow{H_2C} X \xrightarrow{H_2C} X \xrightarrow{H_2C} X \xrightarrow{H_2CH_2} X \xrightarrow{H_2CH_2} X \xrightarrow{H_2CH_2} X \xrightarrow{H_2CH_2} X \xrightarrow{H_2C} X \xrightarrow{H_2$$

which have been suggested by Brinton and Volman,¹³ although the dimer of the ethylenimino radical was not detected in the present study. Increase of temperature would favor reaction 3 and the corresponding decrease in ethylenimino radical concentration would be prejudicial to the second order reactions 6 and 7. This would explain the observation that, with increasing temperature, the amount of HCN produced accounted for a slightly larger fraction of the ethylenimine decomposed.

(13) R. K. Brinton and D. H. Volman, J. Chem. Phys., 20, 25 (1952).

The results of the present investigation are in contrast to those obtained in earlier studies with ethylenimine. Brinton and Volman¹³ found that the products of the reaction of methyl radicals with ethylenimine were methane, nitrogen, ethylene and the dimer of the ethylenimino radical, while Luner¹⁴ found similar products, as well as hydrogen and small amounts of hydrogen cyanide, from the mercury photosensitized decomposition of ethylenimine. More detailed study of the various systems would seem to be necessary to explain the different types of behavior observed.

Hydrogen atoms attacked N-methylethylenimine much more slowly than ethylenimine. The rates of methylethylenimine destruction and hydrogen cyanide production increased with temperature throughout the range of flow rates used.

Samples of the non-condensable products of the methylethylenimine reaction were analysed with the mass spectrometer to obtain the results

Temp., °C.	Imine flow, mole/sec. \times 10 ⁶	Methane flow, mole/sec. \times 10 ⁶
67	4.3	2.5
	11.6	3.0
300	2.7	1.7
	2.7	1.4
	7.2	1.1
	11.6	0.7

Very small amounts of nitrogen were found in all samples.

The amounts of methane produced at about 300° preclude the possibility that all the HCN is formed in the reaction

$$H + \underbrace{H_2C - CH_2}_{N} \longrightarrow CH_4 + \\CH_3 \\H_2C - CH_2 \\N \longrightarrow CH_4 + HCN + CH_3 (8)$$
$$\Delta H = -38 \text{ kcal.}$$

since this would give at least one mole of methane for each mole of HCN. Thus, the occurrence of the reaction

$$H + C_{3}H_{7}N \longrightarrow H_{2} + C_{3}H_{6}N \longrightarrow H_{2} + HCN + C_{2}H_{5} \quad (9)$$
$$\Delta H = -27 \text{ kcal.}$$

is indicated. It is considered likely that a hydrogen atom is abstracted from the methyl group rather than from one of the carbons in the ring, since subsequent rearrangement would necessitate the migration of a hydrogen atom only, instead of a methyl group.

Ethyl radicals, formed in reaction 9, could then undergo "atomic cracking"

(14) C. Luner, private communication.

$$H + C_2 H_3 \longrightarrow 2CH_3$$
(10)

with formation of some methane by the reactions

$$H + CH_{2} \longrightarrow CH_{4}$$
(11)

$$CH_3 + C_2H_3 \longrightarrow C_2H_4 + CH_4$$
(12)

The amounts of methane obtained, particularly at high temperature, were larger than could be reasonably accounted for solely on the basis of reactions 9 to 12 although these reactions would explain the observed trend toward lower methane production at high imine flow rates, where fewer H-atoms would be available for secondary reactions. The formation of small amounts of nitrogen suggests, however, that reaction 8 does take place to some extent and that some of the ethylenimino radicals thus formed undergo reactions 6 and 7. Honco it is apprent thet both practing 8 and

7. Hence, it is apparent that both reactions 8 and 9 occur, although there is little doubt that the latter is predominant.

Mass spectrometric analysis of the condensables showed that very small amounts of C_2 hydrocarbons were produced at 53°, although considerable quantities were formed at 303°, presumably at the expense of methane production.

Small amounts of various higher hydrocarbon products were detected with the mass spectrometer. Their occurrence is probably due to combination of the alkyl radicals

$$\begin{array}{c} \mathrm{CH}_{3} + \mathrm{C}_{2}\mathrm{H}_{5} \longrightarrow \mathrm{C}_{3}\mathrm{H}_{8} \\ \mathrm{2C}_{2}\mathrm{H}_{5} \longrightarrow \mathrm{C}_{4}\mathrm{H}_{10} \end{array} \tag{13}$$

and to the disproportionation reactions 12 and

$$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \tag{15}$$

Second-order rate constants were calculated for the methylethylenimine reaction in terms of both the consumption of the imine and the production of hydrogen cyanide, for streamline and turbulent flow. Mean values of the frequency factor and activation energy, obtained from the Arrhenius plots, were found to be

$$A = 3 \times 10^{12} \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$$

 $E = 4.8 \pm 0.5 \text{ kcal./mole}$

These refer to the over-all production of hydrogen cyanide and destruction of methylethylenimine.

Formation of hydrogen cyanide as a main product in the ethylenimine reaction suggests that the transition state in the reaction of active nitrogen with ethylene may be simulated by the ethylenimino radical. This gives considerable credence to the view that analogous cyclic collision complexes are formed in the other active nitrogen reactions with unsaturated hydrocarbons. The ethylenimino radical apparently also occurred in the reaction of hydrogen atoms with N-methylethylenimine although HCN was produced mainly by the decomposition of another cyclic radical. This suggests that other radicals containing nitrogen may tend to decompose to hydrogen cyanide at low pressures.