The Reactions of Hydrogen Atoms with Methylamine Initiated by Ionizing Radiation

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In a previous paper1) dealing with the radiolysis of methylamine in the gas phase, it has been shown that the main volatile products are hydrogen, ammonia and methane, and that the most important primary process is the formation of hydrogen atoms by the dissociation of the N–H bond, though there is a small amount of unscavengeable hydrogen formation. Even after the study, however, there was still uncertainty concerning the position of the abstractable hydrogen atoms (the N–H and C–H hydrogen) in the secondary process. It became desirable, therefore, to clarify this step by an investigation using isotopic methylamines (CH_3ND_2 and CD_3NH_2) or by the measurement of the activation energy of the process.

The activation energy of the hydrogen abstraction from ethyleneimine by methyl radicals produced photochemically was found to be 4.8 kcal./mol. by Brinton and Volman;2) this value is much lower than the values for any C–H type abstraction, found by Trotman-Dickenson and Steacie.3) Therefore, they suggested that it is the N–H hydrogen atoms which are active in methane formation. Thynne4) has also studied the reaction of methyl radicals with a deuterated methylamine, CH_3ND_2; he observed a very low activation energy (5.7 kcal./mol.) for the N–H abstraction, while the value was 9.0 kcal./mol. for the C–H abstraction.

The present paper is concerned with the activation energy of the reaction of hydrogen atoms with methylamine; we used ethylene as a hydrogen atom scavenger in the radiolysis of methylamine.

Experimental

The preparation and purification of methylamine and ethylene have been previously described.1) Gaseous samples, involving 300 mmHg of methylamine and various amounts of ethylene, were irrradiated in a 500 ml. Pyrex cyrindrical vessel fitted with a breakable seal and graphite-coated electrodes in order to measure the saturation ion current during γ-irradiation.

Irradiations were carried out using a 5000-curie ^{60}Co source at various temperatures up to 152°C. The conversion was kept lower than 0.1%. A conventional vacuum line was used to degas the irradiation samples and to analyze the products.

The other experimental details have been described previously.1)

Results and Discussion

On the basis of the mechanism elucidated for the radiolysis of methylamine at room temperature,1) the following main reactions appear to be acceptable representations of the initial steps:

$$CH_3NH_2 \rightsquigarrow H + CH_3NH\cdot \tag{1}$$

$$\rightsquigarrow H_2 + CNH_3 \tag{2}$$

$$\rightsquigarrow \cdot CH_3 + \cdot NH_2 \tag{3}$$

$$H + CH_3NH_2 \rightarrow H_2 + CNH_4 \tag{4}$$

$$2CNH_4 \rightarrow NH_3 + C_2NH_5 \tag{5}$$

Reaction 3 was supposed not to be important at room temperature, because of the low yields of methane and ethane.

The yield of methane, however, increased at higher temperatures, as is shown in Fig. 1 while the ion-pair yield of hydrogen decreased. These temperature dependencies of the products may be interpreted as showing that the precursors, which will give hydrogen atoms or molecules at lower temperatures, prefer to dissociate to amino and methyl radicals (reaction 3), thus leading to

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1) S. Takamuku and H. Sakurai, This Bulletin, **38**, 791 (1965).

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

3) A. F. Trotøanm-Dickenson and E. W. R. Steacie, ibid., **18**, 1097 (1950); **19**, 163, 169, 329 (1951).

4) J. C. J. Thynne, *Proc. Chem. Soc.*, **145** (1963).

TABLE I. ION-PAIR YIELDS OF THE PRODUCTS AND THE RATE CONSTANT RATIOS (k_4/k_6)

Temp. °C	$(M/N)_{H_2}$	$(M/N)_{H_2(1)}$	Radical %	$(M/N)_{CH_4}$	$(k_4/k_6)\times 10^2$
20	3.10	2.50	81	0.10	1.05
50	2.91	2.30	79	0.14	1.51
80	2.64	2.11	80	0.27	1.71
152	2.46	2.02	82	0.68	3.60

the formation of methane at high temperatures. Another possibility is that the precursors are collisionally deactivated as the pressure increases at a high temperature (the pressure of the irradiation sample was kept constant, 300 mmHg, at room temperature). The increase in methane yield may be explained as due to the thermal degradation of the primary radicals, thus producing methyl radicals.

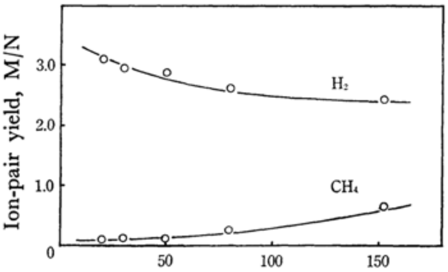

Fig. 1. Ion-pair yields of hydrogen and methane as a function of temperature (methylamine, 300 mmHg at a room temperature).

As was pointed out earlier,[1,5-7] when a radical scavenger (C_2H_4) is present in the system, it competes with methylamine (reaction 4) for hydrogen atoms:

$$H + C_2H_4 \rightarrow C_2H_5\cdot \tag{6}$$

The following equation was obtained by the steady-state kinetic treatment of hydrogen atom production:

$$\frac{1}{\varDelta(M/N)_H} = \frac{1}{(M/N)_{H(1)}} \cdot \frac{k_4[CH_3NH_2]}{k_6[C_2H_4]} + \frac{1}{(M/N)_{H(1)}} \tag{I}$$

where $\varDelta(M/N)_{H_2}$ is the difference in the ion-pair yield of hydrogen, without and with ethylene, and $(M/N)_{H(1)}$ is the ion-pair yield of hydrogen produced by reaction 1. Figure 2 shows that the results here obtained obey Eq. 1, even at high temperatures.

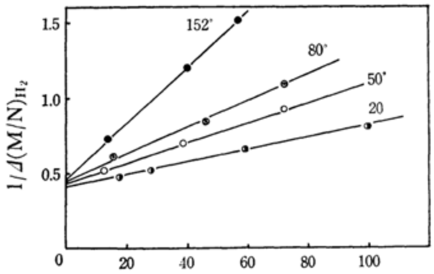

Fig. 2. Kinetic plot of the data from experiments with added ethylene at various temperatures (The total pressure 300 mmHg at a room temperature).

The rate constant ratios, k_4/k_6 and $(M/N)_{H(1)}$, calculated from these straight lines are summarized in Table I. From these results it is obvious that the relative importance of the radical process in the hydrogen formation is independent of the temperature, though the total hydrogen yield decreases slightly with the temperature.

Arrhenius plots of the rate constant ratios, k_4/k_6, give a fairly good straight line, as is shown in Fig. 3. This result is expressed by the equation:

$$\frac{k_4}{k_6} = 3.2\exp(-2.3/\boldsymbol{R}T) \tag{II}$$

By assuming the activation energy of the reaction 6 to be 1.9 kcal./mol.[7] and the log A value to be 12.9,[7] the following relation is obtained:

$$k_4 = 10^{13.4}\exp(-4.2/\boldsymbol{R}T) \tag{III}$$

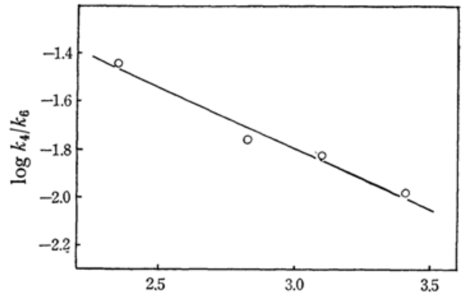

Fig. 3. Arrhenius plot of values of k_4/k_6.

The activation energy, 4.2 kcal./mol., estimated for the reaction 4 is considerably lower than the others reported for the C–H type abstractions. For example, the activation energies of the hydrogen abstraction from methane, ethane, propane and neopentane by hydrogen atoms were reported by

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5) R. A. Back, *J. Phys. Chem.*, **64**, 124 (1960).
6) T. J. Hardwick, ibid., **65**, 101 (1961).
7) K. Yang, *J. Am. Chem., Soc.*, **84**, (1961).

Steacie[8] to be 13, 9.5, 8.5 and 9.3 kcal./mol. respectively.

The present observation, therefore, supports the suggestion that the N–H bond is the acitive participant in the reaction 4, on analogy to the low activation energy for the abstraction of N–H hydrogen by methyl radicals.

Summary

The radiolysis of methylamine with and without ethylene has been investigated at various temperatures up to 152°C.

The relative importance of the radical process (80%) in the hydrogen formation is independent of the temperature, though there are a slight decreases in the total hydrogen formation at high temperatures.

The thermal hydrogen atoms thus formed in the primary process may be supposed to abstract mainly the N–H hydrogen atoms of methylamine, because the activation energy for the process has been observed to be 4.2 kcal./mol., much lower than any C–H type abstraction.

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[8] E. W. R. Steacie and W. R. Trost, *J. Chem. Phys.*, **16**, 361 (1948); E. W. R. Steacie and R. E. Rebbert, ibid., **21**, 1723 (1953).