CHEMISTRY LETTERS, pp. 1151-1154, 1973. Published by the Chemical Society of Japan

THE THERMAL DECOMPOSITION OF CH_3NH_2 IN SHOCK WAVES

Yoshiaki HIDAKA, Ko SAITO, and Hitoshi YAMAMURA
Department of Chemistry, Faculty of Science,
Hiroshima University, Higashisenda, Hiroshima 730

The thermal decomposition of CH_3NH_2, diluted in Ar, has been studied behind reflected shock waves over the temperature range 1600 - 2100 K by the application of infrared emission techniques. It was found that apparent activation energy in the CH_3NH_2 decomposition was 38.6 kcal/mol.

Hitherto, the thermal decomposition of CH_3NH_2 has been studied at temperatures below 1000 K by several researchers. Among these investigations, Jolly$^{1)}$ showed that the decomposition proceeded with stages as follows,

$$CH_3NH_2 \longrightarrow 2H_2 + HCN$$
$$CH_3NH_2 + H_2 \longrightarrow CH_4 + NH_3.$$

Carter$^{2)}$ showed that the decomposition was initiated by a surface reaction. His experimental results were not reproducible precisely since the reaction was influenced by the surface of reaction vessel as reported by Jolly.

In this paper, investigations of the thermal decomposition of CH_3NH_2, diluted with Ar, in the reflected shock waves have been carried out over the temperature range 1600 - 2100 K. The reaction processes in the decomposition are studied by observing the time history of each infrared emission at wavelengths 2.8 - 3.8μ though the direct assigment of each infrared emission for each reaction product at higher temperatures is difficult in practice.

Experimental

A conventional bursting diaphragm shock tube (2-in. i.d.) was used as reported elsewhere.$^{3)}$ The test tube was evacuated to less than 2 x 10^{-4} torr before each run. Time-resolved measurements were made with infrared emissions at the position of 1 cm upstream from the end plate of the test tube. Infrared emission of each wavelength from 2.8 - 3.8μ which was selected by a monochrometer with a spectral interval of 0.05μ, was detected by a InSb element at 77 K and its output signal was recorded by a synchroscope. The time constant of this detecting system was about 10 μsec. A 5% mixture of CH_3NH_2 in Ar was prepared from high purity Ar (99.998%) and from the CH_3NH_2 purified by trap to trap distillation. The initial pressure of the sample gas introduced in the test tube was from 10 to 50 torr.

Results and Discussion

The time history curves of infrared emission observed in each different wavelength from 2.8 - 3.6μ are shown in Fig. 1 (a) - (e). The emission above 3.5μ

becomes gradually weaker with increasing wavelength, and the signals become negligible at 3.8μ. The emission below 3.0μ becomes weaker with decreasing wavelength until it disappears completely at 2.7μ. The records above 3.3μ are completely different from those below 3.2μ, that is, the former shows an exponential decay immediately after shock heating and the latter shows a steady increase with time.

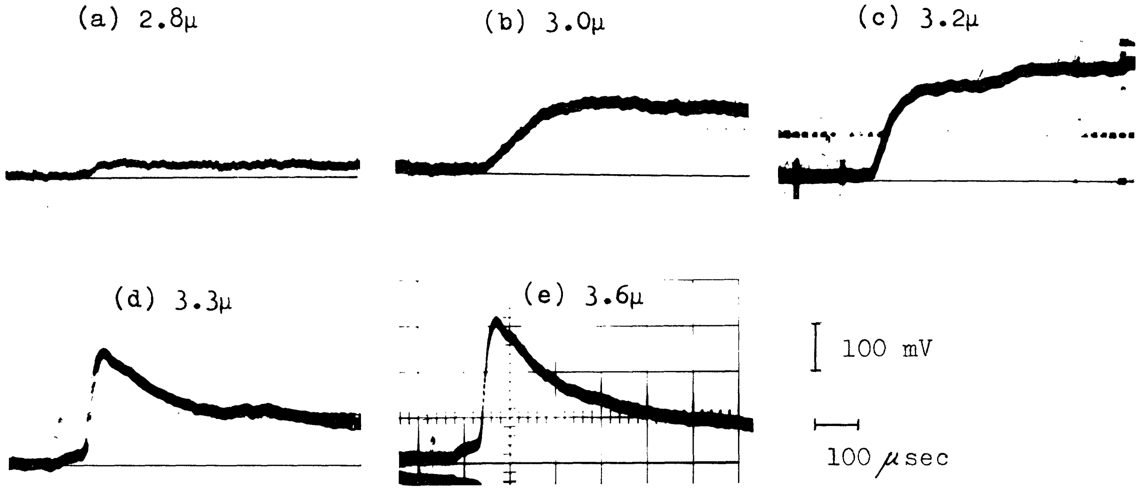

Fig. 1. Typical records of infrared emission for each wavelength at about 1900 K.

The exponential decay curves above 3.3μ are analogous to those which have been observed in the decomposition of the molecules such as HCl, NH_3 and CO_2 etc..3,4) The decay curves will show the decrease of the CH_3NH_2 concentration by the decomposition, because this molecule has a C-H streching band at 3.4μ at room temperature.

Next, the thermal decomposition of CH_3I was studied for the comparison of the infrared emission curves. The records at wavelengths below 3.2μ in the CH_3I decomposition were analogous to those in the CH_3NH_2 decomposition, although CH_3I has not the absorption band at these wavelengths. Hence, it appears that the time history curves below 3.2μ in the decomposition of CH_3I (and also CH_3NH_2) represent the increment of the products.

Hydrocarbons, NH_3, N_2H_4, HCN and H_2 etc. are expected as the products of the CH_3NH_2 decomposition.1,2) Among these molecules, NH_3 and N_2H_4 which are expected to have infrared emissions below 2.8μ were not observed under the observing conditions in this study. HCN, C_2H_4 and C_2H_6 have infrared absorptions at 3.6, 3.3 and 3.4μ respectively at room temperature, but the emissions from these molecules seem to be concealed behind the strong emission of CH_3NH_2.

Hartig5) reported that in the thermal decomposition of CH_4 the infrared emission at 2.9 - 3.0μ may be based on the intermediates such as CH_3, CH_2 and other C-H species. On the other hand, it was ascertained that at the temperatures above 1700 K in shock waves, the main products in the CH_4 decomposition are C_2H_2 and H_2.6,7) From these facts and from the consideration that the decomposition of CH_3NH_2 is analogous to that of CH_4, it is seen that the emission at 3.0μ in the

CH_3NH_2 decomposition (Fig. 1b) is mainly based on C_2H_2 molecules which have the absorption at 3.04μ at room temperature.

The time history curves observed at wavelengths 3.3 - 3.7μ indicate exponential decay with time (Fig. 1d and e). In the region 3.3 - 3.4μ, however, the decay rate is somewhat smaller than that obtained at above 3.5μ. This fact can be explained by the contribution of the products such as CH_4, C_2H_4 and C_2H_6. On the other hand, since the decay curves obtained above 3.5μ fall to zero level at the time sufficiently after the shock front (~500 μsec), the emission intensity can be assumed as the variation of only the CH_3NH_2 concentration. It is found that the decay rate depends on the temperature and the concentration of the reactant. The decomposition rate is described by $-d(CH_3NH_2)/dt = k(CH_3NH_2)^{3/2}$. This is represented in Fig. 2. A plot of the rate constant k vs. 1/T is shown in Fig. 3. From the straight line, k is given to be $2.64 \times 10^{11} \exp(-38.6\ \mathrm{kcal/RT})\ l^{\frac{1}{2}}mol^{\frac{1}{2}}sec^{-1}$.

Since the C-H and C-N bond energies in CH_3NH_2 are, respectively, 97 and 79 kcal/mol, initial step of the decomposition will probably be

$$CH_3NH_2 \longrightarrow CH_3 + NH_2. \qquad (1)$$

This initiation reaction is followed by

$$\begin{aligned} CH_3 + CH_3NH_2 &\longrightarrow C_2H_6 + NH_2 \\ &\searrow CH_4 + \text{radical} \end{aligned} \qquad (2)$$

$$NH_2 + CH_3NH_2 \longrightarrow CH_3 + N_2H_4 \qquad (3)$$

$$2CH_3 \longrightarrow C_2H_6. \qquad (4)$$

By applying the stationary state treatment to CH_3 and NH_2 we find for the rate of disappearance of CH_3NH_2

$$-\frac{d(CH_3NH_2)}{dt} = 2\left[k_1 + k_2\left\{\frac{2k_1(CH_3NH_2)}{k_4}\right\}^{1/2}\right](CH_3NH_2).$$

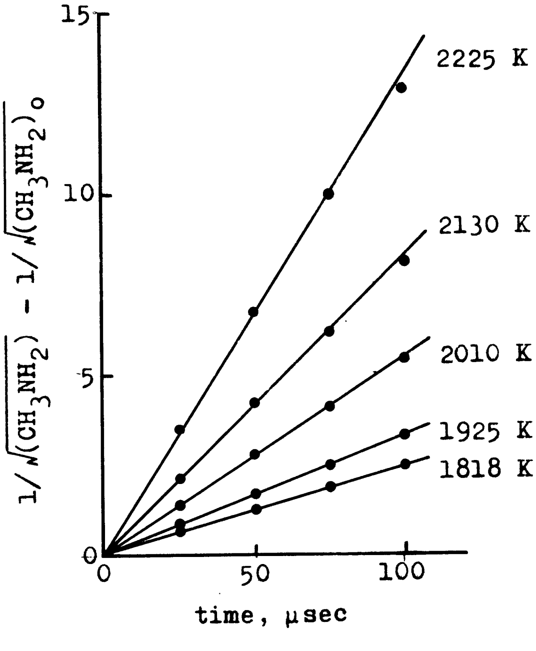

Fig. 2. Data reduction assuming $-d(CH_3NH_2)/dt \propto (CH_3NH_2)^{3/2}$.

Under the conditions in which the first term can be neglected we have

$$-\frac{d(CH_3NH_2)}{dt} = 2k_2\left(\frac{2k_1}{k_4}\right)^{1/2}(CH_3NH_2)^{3/2}.$$

The experimental activation energy obtained on the basis of a 3/2 -order reaction is found to be 38.6 kcal/mol. If we use the simple scheme described above, this should be equal to $E_2 + (E_1 - E_4)/2$. The value of E_2 is known to be 8.4 kcal for the CH_4 formation, while $E_4 = 0$. If the bond energy of 79 kcal is taken as the minimum value of E_1, the calculated value is 48 kcal, which is larger than the experimental value by about 10 kcal. Possible reasons for this descrepancy are thought to be as follows: 1) at the high temperatures above 1500 K the actual process may be more complex than the above simple scheme, although the 3/2 -order in (CH_3NH_2) for the decomposition rate can be explained by this scheme, 2) if the ir emission at 3.5μ involves the emission of some products, the deviation of the decomposition rate due to its effect becomes larger at higher temperatures and consequently the apparent activation energy becomes lower. However, as mentioned already, this second consideration is not reasonable.

As the elementary reaction of the CH_3NH_2 decomposition, many other reactions which involve small radicals and atoms are considered. However, according to the scheme containing these reactions the calculation of the apparent activation energy gives a value higher than 48 kcal. Thus, at the present state, the scheme (1) - (4) is thought to be most probable.

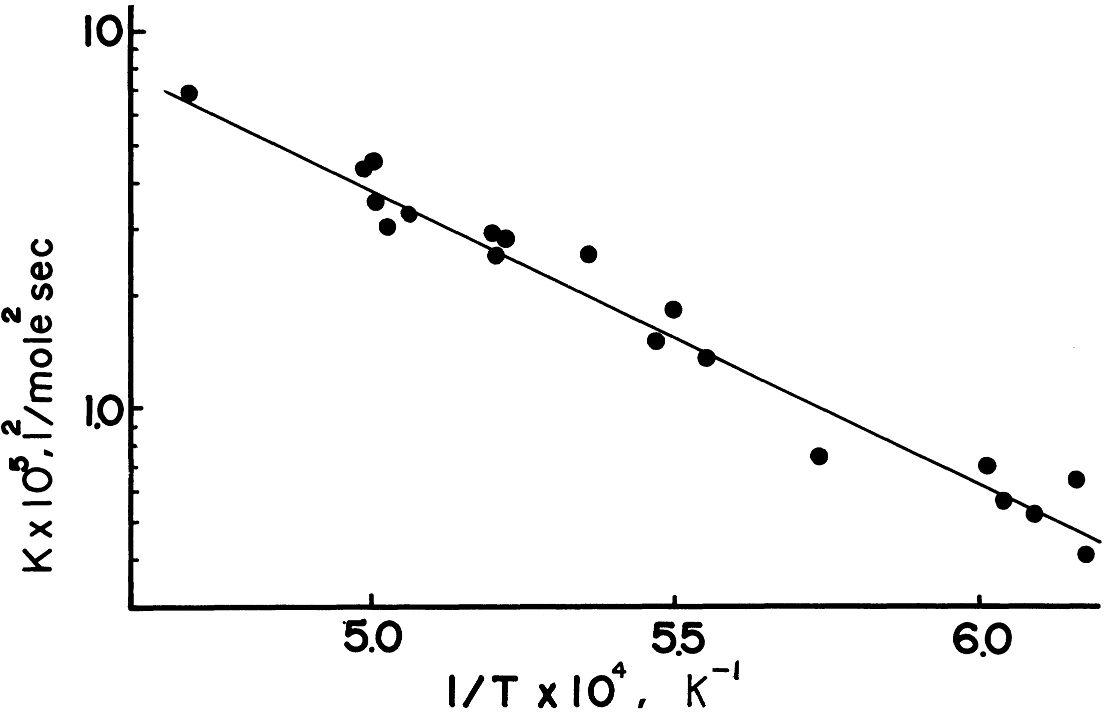

Fig. 3. Determination of apparent activation energy assuming $-d(CH_3NH_2)/dt = k(CH_3NH_2)^{3/2}$.

References

1) L. J. Jolly, J. Chem. Soc., 1957 (1934).

2) A. G. Carter, P. A. Bosanquet, C. G. Silcoks, M. W. Travers, and A. F. Wilshire, ibid., 495 (1939).

3) Y. Hidaka and H. Yamamura, J. Sci. Hiroshima Univ., A-35, 53 (1971).

4) E. S. Fishburne, K. R. Bilwakesh, and R. Edse, J. Chem. Phys., 45, 160 (1966); T. A. Jacobs, N. Coven, and R. R. Giedt, ibid., 46, 1958 (1967).

5) R. Hartig, J. Troe, and H. Gg. Wagner, Thirteenth Symposium (International) on Combustion, p. 147, The combustion Institute (1971).

6) G. B. Skinner and R. A. Ruehrwain, J. Phys. Chem., 63, 1736 (1959).

7) T. Asaba, K. Yoneda, and T. Hikita, Kogyo Kagaku Zassi, 66, 1438 (1963).

(Received August 2, 1973)