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THE FORMATION OF HYDROXYLAMINE BY INSERTION OF THE NH($^1\Delta$) RADICAL INTO THE O-H BOND OF WATER

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The photolysis of hydrogen azide was examined in water. The main products were nitrogen and hydroxylamine. Hydroxylamine formed was converted into acetoxime by the reaction with acetone which was added after irradiation. The amount of acetoxime was analyzed with GLC. The results suggest that the NH($^1\Delta$) radical efficiently inserts into the O-H bond of water.

The NH singlet, NH($^1\Delta$), can be produced in the UV photolysis of hydrogen azide.[1)] We have examined the reactions of the NH singlet using the photolysis of hydrogen azide in liquid paraffins, olefins, carboxylic acids, and alcohols.[2-5)] The reactions of the NH singlet are similar to those of O(^1D) and $CH_2(^1A_1)$, the isoelectronic species of the NH radicals; i.e., the NH singlet inserts into the C-H bond of hydrocarbons and adds to the double bond of olefins. By the insertion into the C-H bond of carboxylic acids, amino acids are formed.[4)] In the case of methanol, formaldehyde oxime O-methyl ether is produced along with ammonia and nitrogen.[5)] The formation of formaldehyde oxime O-methyl ether was explained by the condensation reaction of formaldehyde with methoxyamine, which was a possible insertion product of the NH singlet into the O-H bond of alcohol. If the NH singlet inserted into the O-H bond, the formation of hydroxylamine would be expected in the reaction with water.

Hydroxylamine is known to react with acetone to form acetoxime.[6)] This reaction was used to detect hydroxylamine produced by the photolysis of hydrogen azide in water. The authentic sample of acetoxime was synthesized from acetone and hydroxylamine-hydrochloride (Koso Chemical Co.) in aqueous solution at room temperature. Acetoxime was analyzed with GLC using a column packed with Tenax GC (Gasukuro Kogyo Co., 1 m in length) at 100°C. The amount of acetoxime formed was determined by comparison of the peak area with that of methyl butyrate, which was added as a standard. The peak area of acetoxime relative to that of methyl butyrate is plotted in Fig. 1 as a function of initial amount of hydroxylamine relative to that of methyl butyrate added. The amount of hydroxylamine can be determined from the amount of acetoxime. The yields of acetoxime thus obtained were not affected by the presence of ammonia and hydrogen azide and also by elapse of time after the addition of acetone. Hydrogen azide was synthesized and purified by the method already described.$^{2)}$ Distilled water was used after having been degassed in vacuo.

An aqueous solution of hydrogen azide was prepared in a Pyrex tube of 12 mm o.d. in vacuo and irradiated with a medium pressure mercury lamp (Toshiba H400-P) at about 5 °C. The non-condensable product at -196°C was analyzed with a combination of a Toepler pump, a gas buret, and a CuO furnace at 300°C. The non-condensable product at -196°C was nitrogen. After the analysis of nitrogen, the seal of the reaction cell was cut off and about 0.1 cm^3 of acetone and a known amount of methyl butyrate were added

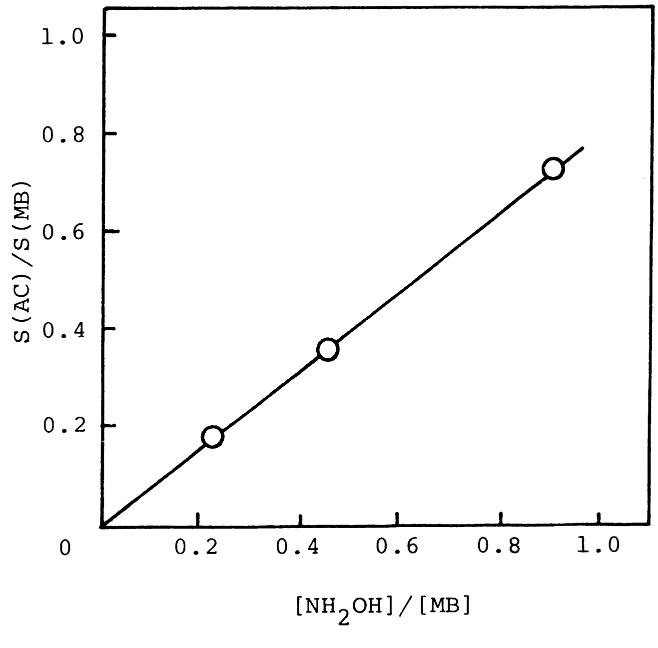

Fig. 1. Plots of S(AC)/S(MB) as a function of initial $[NH_2OH]/[MB]$.$^{a)}$

^{a}S(AC) and S(MB) represent peak areas of acetoxime (AC) and methyl butyrate (MB) respectively.

Table 1. Relative Yields of Hydroxylamine

$[HN_3]$ mol/dm^3	It$^{a)}$ min	$NH_2OH/N_2$$^{b)}$
0.05	30	0.79
0.10	30	0.65
0.11	30	0.75
0.15	30	0.74
0.15	30	0.79
0.21	15	0.65(0.78)
0.20	30	0.78(0.83)
0.20	60	0.88(0.67)
0.20	60	0.71
0.20	90	0.72

^{a}Irradiation time. ^{b}The values in the parentheses show the relative yields obtained one day after the addition of acetone.

using a micro syringe. The reaction mixture thus obtained was analyzed with GLC. The product observed was acetoxime. The identification of the product was based on the comparisons of its relative retention time and the mass spectrum with those of authentic acetoxime. The amount of hydroxylamine was estimated from that of acetoxime using the results shown in Fig. 1. Without the irradiation, no acetoxime formation was observed. The results obtained are summarized in Table 1. The relative yield of hydroxylamine to nitrogen was independent of the changes in the reaction time and also in the concentration of hydrogen azide examined and was 0.75 ± 0.07.

Since hydrogen azide is a weak acid, $K = 2 \times 10^{-5}$ (25°C), hydrogen azide solution contains not only H_3O^+ and N_3^- but also hydrogen azide molecules. The absorption spectrum of the hydrogen azide solution was almost similar to that obtained in the gas phase.7) Therefore, it is considered that the photolysis of hydrogen azide in aqueous solution gives the singlet NH and nitrogen as well as that in the gas phase.1) The concentration dependence of hydrogen azide on the relative yield, as shown in Table 1, is similar to those obtained in the cases of olefins, carboxylic acids, and alcohols.3-5) The experimental results can be accounted for by the following mechanism:

$$\begin{aligned}
HN_3 + h\nu &\rightarrow {}^1NH + N_2 && (1)\\
{}^1NH + H_2O &\rightarrow NH_2OH && (2)\\
&\rightarrow {}^3NH + H_2O && (3)\\
{}^3NH + HN_3 &\rightarrow NH_2 + N_3 && (4)\\
NH_2 + HN_3 &\rightarrow NH_3 + N_3 && (5)\\
2\,N_3 &\rightarrow 3\,N_2 && (6)
\end{aligned}$$

Here, ^1NH and ^3NH represent NH radicals in the first excited singlet state, $^1\Delta$, and the ground triplet state, $^3\Sigma^-$, respectively. Reaction 3 is included in the mechanism in order to explain the observed relative yield of hydroxylamine. In the above reaction mechanism, the hydrogen-atom abstraction from water by ^3NH or NH_2 is neglected, because the bond-dissociation energy of water (D(H-OH) = 498 kJ/mol) is larger than that of hydrogen azide ($D(H\text{-}N_3)$ = 356 kJ/mol).8) If ^3NH and/or NH_2 abstracted a hydrogen atom from water, OH radicals would be formed:

$$\begin{aligned}
{}^3NH + H_2O &\rightarrow NH_2 + OH && (7)\\
NH_2 + H_2O &\rightarrow NH_3 + OH && (8)
\end{aligned}$$

The OH radical may abstract a hydrogen atom from hydrogen azide and/or be converted to OH^-:

$$\begin{aligned}
OH + HN_3 &\rightarrow H_2O + N_3 && (9)\\
OH + N_3^- &\rightarrow OH^- + N_3 && (10)
\end{aligned}$$

Reactions 7 and 8 followed by Reaction 9 or 10 are indistinguishable from Reactions 4 and 5. An alternative reaction mechanism for the formation of hydroxylamine is as follows:

$$^{1}NH + H_2O \rightarrow NH_2 + OH \qquad (11)$$

$$NH_2 + OH \rightarrow NH_2OH \qquad (12)$$

If this mechanism was important for the hydroxylamine formation, the yield of hydroxylamine should decrease with an increase in the concentration of hydrogen azide, because of the competition between Reactions 12 and 5 or 8. As shown in Table 1, this is not to be the case.

Egami and his co-workers have proposed that the reactions of hydroxylamine and formaldehyde in modified sea media are important for the chemical evolution.9) Since the NH singlet is known to be formed from ammonia in the vuv photolysis or in the electric discharge, the formation of hydroxylamine by the insertion of the NH singlet into the O-H bond of water might be important on the primordial earth.

References

1) H. Okabe, "Photochemistry of Small Molecules," John Wiley and Sons, New York (1978), p. 193.
2) S. Tsunashima, M. Hotta, and S. Sato, Chem. Phys. Lett., 64, 435 (1979); S. Tsunashima, J. Hamada, M. Hotta, and S. Sato, Bull. Chem. Soc. Jpn., 53, 2443 (1980); J. Hamada, S. Tsunashima, and S. Sato, ibid., 55, 1739 (1982).
3) T. Kitamura, S. Tsunashima, and S. Sato, Bull. Chem. Soc. Jpn., 54, 55 (1981); J. Hamada, S. Tsunashima, and S. Sato, ibid., 56, 662 (1983).
4) S. Sato, T. Kitamura, and S. Tsunashima, Chem. Lett., 1980, 687; S. Tsunashima, T. Kitamura, and S. Sato, Bull. Chem. Soc. Jpn., 54, 2869 (1981).
5) J. Kawai, S. Tsunashima, and S. Sato, Bull. Chem. Soc. Jpn., 55, 3312 (1982).
6) L. Fieser and M. Fieser, "Organic Chemistry," Reinhold Publishing Co., New York (1956), p. 211.
7) J. R. McDonald, J. W. Rabalais, and S. P. McGlynn, J. Chem. Phys., 52, 1332 (1970).
8) CRC Handbook of Chemistry and Physics, 63, F-196 (1982-1983).
9) M. Nishizawa and F. Egami, Bull. Chem. Soc. Jpn., 55, 2689 (1982) and references therein.

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