The Reactions of Singlet NH Radicals with Methyl and Ethyl Alcohols in the Liquid Phase

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The reactions of the singlet NH($a^1\Delta$) radicals with alcohols were studied by the photolyses of hydrogen azide in liquid methyl and ethyl alcohols at the temperature of Dry Ice–methyl alcohol and at 0 °C. The main products were nitrogen, ammonia, and oxime ethers; acetaldehyde oxime O-ethyl ether from ethyl alcohol and formaldehyde oxime O-methyl ether from methyl alcohol. The relative yields of the products were independent of the changes in the reaction temperature and in the concentration of the hydrogen azide examined. Methoxyamine or ethoxy-amine, a possible insertion product of the singlet NH into the O–H bond of alcohol, was detected as a form of oxime ether by the reactions with the aldehyde eventually formed. It was concluded that the singlet NH radicals can effectively insert into the O–H bond of the alcohol.

Recently, it was shown that the singlet NH radicals, NH($a^1\Delta$), inserted into the C–H bonds of hydrocarbons and carboxylic acids to form amines and amino acids respectively and added to the double bond of olefins to form aziridines.[1-7] These reactions are essentially the same as those observed in the reactions of O(^{1}D) and CH$_2$(^{1}A$_1$).[8,9] An insertion reaction into the O–H bond of an alcohol may be expected to occur; however, the reaction has not been examined in the case of NH.

In order to investigate the reactions of methylene with alcohol, Ogoshi and Takezaki photolyzed ketene in the presence of methyl alcohol vapor at 40 °C. The main products were dimethyl ether and ethyl alcohol. If these products were formed by the insertion into the C–H and O–H bonds of methyl alcohol, the efficiencies of these two processes should be almost equal.[10] Using diazomethane as the source of methylene, Kerr *et al.* found that the insertion of methylene into the O–H bond of alcohol was more efficient than that into the primary C–H bond and reported the values of the relative efficiencies as follows: 21.8 (methyl alcohol), 21.2 (ethyl alcohol), 14.9 (isopropyl alcohol), and 10.9 (*t*-butyl alcohol).[11]

The present paper reports the results obtained in the photolyses of hydrogen azide in liquid methyl and ethyl alcohols at the temperature of Dry Ice–methyl alcohol and at 0 °C.

Experimental

The experimental methods and the apparatus used were essentially the same as those described in the previous papers.[1-3]

Ethyl alcohol (Amakasu Kagaku Sangyo Co., 99.5%) and methyl alcohol (Tokyo Kasei Co., 99.5%) were used after having been degassed at −60 °C and −80 °C respectively and distilled at room temperature *in vacuo*. Further purified ethyl alcohol was also used to check the possibility of interference by acetaldehyde, *i. e.*, ethyl alcohol was treated with Ag$_2$O for several days and distilled from NaOH solution. The alcohols were stored under vacuum after purification. Hydrogen azide was prepared and purified by the method described in the previous papers.[1-3] Methyl alcohol-d_4 (Merck Sharp and Dohme, Canada Ltd.) was used without further purification except for low temperature distillation *in vacuo*. 2-Amino-1-ethanol and methoxyamine hydrochloride were purchased from the Tokyo Kasei Co. and used as supplied.

A Pyrex tube of 10 mm o.d. was used as a reaction cell. About 1 ml of a methyl or ethyl alcohol solution of hydrogen azide was irradiated with a medium pressure mercury lamp (Toshiba H400-P) at 0 °C or at the temperature of Dry Ice–methyl alcohol. Uncondensable products at −196 °C were analyzed with a combination of a Toepler pump, a gas buret, and a CuO furnace at 300 °C. The volatile products at room temperature were transferred in a trap containing NaOH coated glass wool *in vacuo* together with the reactants. After the treatment with NaOH, the products uncondensable at −40 °C (ethyl alcohol) or −60 °C (methyl alcohol) were analyzed by GLC using a column packed with Amine 220 on NaOH coated Celite 545 (Gasukuro Kogyo Co., 5 m in length). For the analysis of less volatile products, a KOH solution of methyl alcohol was added to the reaction mixture and directly injected into a gas chromatograph equipped with FID (Hitachi 023). A column packed with Tenax GC (Gasukuro Kogyo Co., 1 m in length) was used. *s*-Butyl alcohol was used as the standard. For the identification of the products, a GC-mass spectrometer (Nichiden Varian, TE 600) and an NMR (Varian 390) were used.

Results

The products obtained in the photolysis of hydrogen azide in liquid methyl or ethyl alcohol were fractionated into three parts; uncondensable products at −196 °C, products more volatile than the solvent, and the less volatile products than the reactants. The uncondensable product at −196 °C was nitrogen for both methyl and ethyl alcohols. A negligibly small amount of hydrogen was also formed. The yield was less than 2% of that of nitrogen. No methane formation was detected by the mass spectrometric analysis. Ammonia formation was observed in the second fraction both for methyl and ethyl alcohols. From this fraction, formaldehyde oxime O-methyl ether and methoxyamine were detected in the case of methyl alcohol. The yield of the latter was about 1/100 of that of the former. No formaldehyde was detected. The identification of formaldehyde oxime O-methyl ether was based on the following results:

a) The molecular weight of the product was 59. The mass spectrum is shown in Table 1.

b) The product did not form a salt with hydrogen azide as well as with hydrogen chloride.

c) This product was also obtained without treat-

TABLE 1.   MASS SPECTRA OF FORMALDEHY DE OXIME O-METHYL ETHER
AND ACETALDEHYDE OXIME O-ETHYL ETHER

m/e	Formaldehyde oxime O-methyl ether			Acetaldehyde oxime O-ethyl ether
	$NH+CH_3OH$	$CH_2O+CH_3ONH_2$	$NH+CD_3OD$	$NH+C_2H_5OH$
15	15	13		74
18			16	10
26				15
27	28	22		46
28	100	100	34	38
29	66	65		93
30	22	26	100	30
31	72	65		13
32			11	
34			43	
40				13
41				63
42				100
43				13
44	53	53	16	23
46			35	
59	85	83		79
62			20	
64			46	
72				10
87				18

TABLE 2.   THE YIELDS OF AMMONIA AND FORMALDEHYDE OXIME O-METHYL ETHER RELATIVE TO THAT OF NITROGEN OBTAINED IN THE PHOTOLYSIS OF HYDROGEN AZIDE IN LIQUID METHYL ALCOHOL

[HN₃] mol dm⁻³	Photolysis time min	NH₃/N₂	FM/N₂^a)
0.033^b	60	0.28	0.24
0.036^b	60	0.24	0.16
0.073^b	60	0.34	0.28
0.105^b	60	0.24	0.19
0.143^c	60	0.34	0.22
0.147^b	15	0.29	0.26
0.145^b	30	0.29	0.22
0.152^b	60	0.34	0.30
0.154^b	60	0.41	0.20
0.152^b	90	0.40	0.24
0.144^b	120	0.25	0.30
0.210^b	60	0.37	0.26
Average		0.32±0.06	0.24±0.05

a) FM=Formaldehyde oxime O-methyl ether. b) Experiments at the temperature of Dry Ice–methyl alcohol. c) Experiments at 0 °C.

ment with NaOH.

d)   When methyl alcohol-d_4 was used, the molecular weight of the product increased to 64. This result suggested that the product had five hydrogen atoms.

e)   The mass spectrum and the retention time of GLC of this compound agreed with those of the product obtained by the reaction of methoxyamine hydrochloride with KOH and formaldehyde. (see Table 1).

TABLE 3.   THE YIELDS OF AMMONIA AND ACETALDEHYDE OXIME O-ETHYL ETHER RELATIVE TO THAT OF NITROGEN OBTAINED IN THE PHOTOLYSIS OF HYDROGEN AZIDE IN LIQUID ETHYL ALCOHOL

[HN₃] mol dm⁻³	Photolysis time min	NH₃/N₂	AE/N₂^a)
0.054^b)	60	0.32	0.25
0.099^b)	30	0.30	0.21
0.091^c)	60	0.31	0.21
0.097^b)	60	0.41	0.18
0.102^b,d)	60	n.d.^e)	0.21
0.103^b)	60	n.d.^e)	0.21
0.106^b)	90	0.30	0.23
0.153^b)	60	0.36	n.d.^e)
Average		0.33±0.04	0.22±0.02

a) AE: Acetaldehyde oxime O-ethyl ether. b) Experiments at the temperature of Dry Ice–methyl alcohol. c) Experiments at 0 °C. d) Further purified ethyl alcohol was used. e) n.d.: Not determined.

In the case of ethyl alcohol, a similar product, having a molecular weight of 87, was found to be formed in the second fraction along with ammonia. From the mass spectrum shown in Table 1, this product was identified to be acetaldehyde oxime O-ethyl ether. In the case of the mixture of methyl and ethyl alcohols, two new products were observed to be formed along with ammonia, formaldehyde oxime O-ethyl ether, and acetaldehyde oxime O-methyl ether. Their molecular weights were both 73. One of the new products gave the same mass spectrum and the retention time as those obtained

TABLE 4. THE YIELD OF 2-AMINO-1-ETHANOL RELATIVE
TO THAT OF NITROGEN OBTAINED IN THE PHOTOLYSIS
OF HYDROGEN AZIDE IN LIQUID ETHYL ALCOHOL[a]

$\dfrac{[\mathrm{HN_3}]}{\mathrm{mol\,dm^{-3}}}$	$[\mathrm{NH_2CH_2CH_2OH}]/[\mathrm{N_2}]$
0.099	0.16
0.101	0.06
0.102	0.07
0.150	0.13
Average	0.10 ± 0.05

a) Obtained at the temperature of Dry Ice–methyl
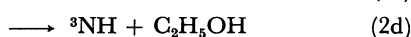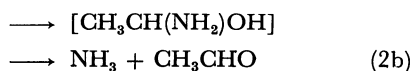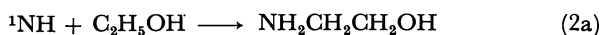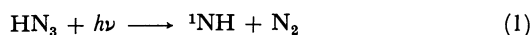alcohol with photolysis time of 60 min.

from the product formed by the reaction of methoxy-
amine hydrochloride with KOH and acetaldehyde. This
product was identified to be acetaldehyde oxime O-
methyl ether. The other was concomitantly identified
to be formaldehyde oxime O-ethyl ether. No acetal-
dehyde was detected in the case of ethyl alcohol.

From the less volatile fraction, no retrievable products
were obtained in the case of methyl alcohol. In the case
of ethyl alcohol, 2-amino-1-ethanol was observed to be
formed. The assignment was based on comparisons of
its mass spectrum and retention time with those of the
authentic sample. $\mathrm{CH_3CH=NCH_2CH_2OH}$, a possible
product formed by the reaction of 2-amino-1-ethanol
with acetaldehyde, could not be observed. The yield
of this product should be less than 1/10 of that of 2-
amino-1-ethanol, if any.

Tables 2, 3, and 4 show the yields of the products
relative to that of nitrogen obtained under various
experimental conditions. The relative yields were almost
constant for the changes in the concentration of hydrogen
azide and in the reaction temperature examined.

Discussion

As shown in Tables 2, 3, and 4, the relative yields
of the products were independent of the changes in the
concentration of hydrogen azide. This trend is similar
to those obtained in the cases of olefin and carboxylic
acid.[5-7] The following reaction mechanism can be
considered to explain the results obtained in the case of
ethyl alcohol:

$$\mathrm{HN_3} + h\nu \longrightarrow \mathrm{{}^1NH} + \mathrm{N_2} \tag{1}$$

$$\mathrm{{}^1NH} + \mathrm{C_2H_5OH} \longrightarrow \mathrm{NH_2CH_2CH_2OH} \tag{2a}$$

$$\longrightarrow \mathrm{[CH_3CH(NH_2)OH]}$$

$$\longrightarrow \mathrm{NH_3} + \mathrm{CH_3CHO} \tag{2b}$$

$$\longrightarrow \mathrm{C_2H_5ONH_2} \tag{2c}$$

$$\longrightarrow \mathrm{{}^3NH} + \mathrm{C_2H_5OH} \tag{2d}$$

$$\mathrm{C_2H_5ONH_2} + \mathrm{CH_3CHO}$$

$$\longrightarrow \mathrm{CH_3CH=NOC_2H_5} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{C_2H_5ONH_2} \longrightarrow \mathrm{CH_3CHO} + \mathrm{NH_3} \tag{4}$$

$$\mathrm{{}^3NH} + \mathrm{HN_3} \longrightarrow \mathrm{NH_2} + \mathrm{N_3} \tag{5}$$

$$\mathrm{NH_2} + \mathrm{HN_3} \longrightarrow \mathrm{NH_3} + \mathrm{N_3} \tag{6}$$

$$2\mathrm{N_3} \longrightarrow 3\mathrm{N_2} \tag{7}$$
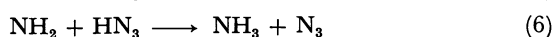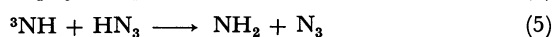
Here, ${}^1\mathrm{NH}$ and ${}^3\mathrm{NH}$ represent the NH radicals in the
singlet state ($\mathrm{a^1\Delta}$) and the triplet state ($\mathrm{X^3\Sigma^-}$) respec-
tively.

The insertion of a singlet NH radical into the C–H
bond at the β position will give 2-amino-1-ethanol
(Reaction 2a). 1-Amino-1-ethanol may be formed by
the insertion into the C–H bond at the α position;
however, this compound is known to be unstable and
to decompose to acetaldehyde and ammonia (Reaction
2b). Ethoxyamine may be formed by the insertion
into the O–H bond of alcohol (Reaction 2c). Neither
ethoxyamine nor acetaldehyde formation was detected
in this study. Instead of these products, acetaldehyde
oxime O-ethyl ether was found to be one of main
products. This product may be formed by the condensa-
tion reactions of alkoxyamine and aldehyde (Reaction
3).[12] Reaction 4 is included in the mechanism in order
to take into account the possibility that ethoxyamine
is unstable and also k_{2b} is smaller than k_{2c}. This point
will be discussed later. Although ethoxyamine was
not detected in the case of ethyl alcohol, methoxyamine,
a possible insertion product into the O–H bond of
methyl alcohol, was detected as a minor product. This
difference might be explained by the difference in the
stability of the alkoxyamine.

Reaction 2d is included in the mechanism to explain
the fact that the amount of ammonia formed was more
than that of acetaldehyde oxime O-ethyl ether or
formaldehyde oxime O-methyl ether. The deactivation
process has been considered in the cases of hydrocarbons
and carboxylic acids.[1-7] The reaction of the triplet
NH radicals is assumed to be a hydrogen-atom abstrac-
tion from hydrogen azide (Reaction 5). The triplet
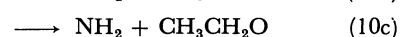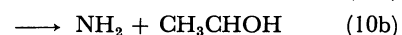NH radicals might also abstract a hydrogen atom from
ethyl alcohol;

$$\mathrm{{}^3NH} + \mathrm{CH_3CH_2OH} \longrightarrow \mathrm{NH_2} + \mathrm{CH_3CHOH}$$

$$\Delta H = 10\,\mathrm{kJ/mol^{13}} \tag{8}$$
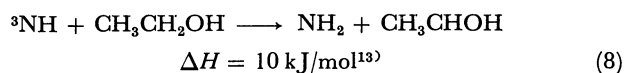
although the reaction is slightly endothermic. If
$\mathrm{CH_3CHOH}$ radicals abstract a hydrogen atom from
hydrogen azide;

$$\mathrm{CH_3CHOH} + \mathrm{HN_3} \longrightarrow \mathrm{CH_3CH_2OH} + \mathrm{N_3} \tag{9}$$

Reaction 8 followed by Reaction 9 would be
indistinguishable from Reaction 5.

In the above reaction mechanism, a hydrogen atom
abstraction by the singlet NH radicals was neglected:

$$\mathrm{{}^1NH} + \mathrm{CH_3CH_2OH} \longrightarrow \mathrm{NH_2} + \mathrm{CH_2CH_2OH} \tag{10a}$$

$$\longrightarrow \mathrm{NH_2} + \mathrm{CH_3CHOH} \tag{10b}$$

$$\longrightarrow \mathrm{NH_2} + \mathrm{CH_3CH_2O} \tag{10c}$$

All these reactions are energetically possible. If resultant
alcohol radicals abstracted a hydrogen atom from
hydrogen azide, Reactions 10's would be indistinguisha-
ble from Reaction 2d. If all these radicals recombined
with $\mathrm{NH_2}$, Reactions 10a—c would be hard to
discriminate from Reactions 2a—c, respectively. If
one of these assumptions were the case, it would
be difficult to estimate the extent of the participa-
tion of the abstraction reactions. In the intermediate
case, that is, if some of the alcohol radicals abstracted
a hydrogen atom and the rest recombined with $\mathrm{NH_2}$

radicals, the relative yields of the products should depend on the concentration of hydrogen azide. This case is most probable if the singlet NH radicals abstracted a hydrogen atom from alcohol. The concentration dependence observed, however, was different from that expected. Similar reaction mechanism may be considered in the case of methyl alcohol except for Reaction 2a.

Assuming the above reaction mechanism, the following relations can be expected to hold:
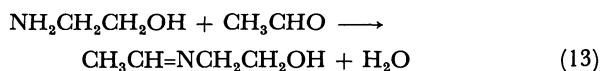for the case of ethyl alcohol,

$$([NH_2CH_2CH_2OH] + 4[NH_3]$$
$$- 2[CH_3CH=NOC_2H_5])/[N_2] = 1.0 \qquad (11)$$

for the case of methyl alcohol,

$$(4[NH_3]-2[CH_2=NOCH_3])/[N_2] = 1.0 \qquad (12)$$

Using the values shown in Tables 2, 3, and 4, the left-hand-sides of Eqs. 11 and 12 were calculated to be 1.0 ± 0.1 and 0.81 ± 0.13 respectively; i.e., the total yields of the products observed were successfully explained by the above mechanism.

Similar to alkoxyamine, 2-amino-1-ethanol may react with acetaldehyde:

$$NH_2CH_2CH_2OH + CH_3CHO \longrightarrow$$
$$CH_3CH=NCH_2CH_2OH + H_2O \qquad (13)$$

Reaction 13, however, should be unimportant under the present experimental conditions, since the material balance was good and no $CH_3CH=NCH_2CH_2OH$ formation was observed in the ethyl alcohol solution.

In the case of propionic acid, the singlet NH radicals inserted into the C–H bonds of α and β positions with almost equal rates.[6,7] For the insertion into the C–H bonds of paraffin, however, the relative rates of the insertion into the primary, secondary, and tertiary C–H bonds were 1.0, 1.9, and 2.3 respectively.[3] That is, the insertion rate slightly depends on the strength of the C–H bond. If this relation held in the case of ethyl alcohol, k_{2b} would be equal or slightly larger than $(2/3)k_{2c}$. The amount of acetaldehyde formed by Reaction 2b should be almost equal to that of 2-amino-1-ethanol. The yield of 2-amino-1-ethanol was about a half of that of acetaldehyde oxime O-ethyl ether. This was the main reason why Reaction 4 was included in the mechanism. The validity of Reaction 4 is unknown at present. Another possible assumption is that the singlet NH radicals can abstract two hydrogen atoms at once from ethyl alcohol to form ammonia and acetaldehyde:

$$^1NH + C_2H_5OH \longrightarrow NH_3 + CH_3CHO \qquad (14)$$
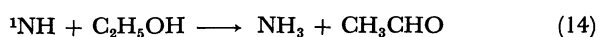
Reaction 14 is indistinguishable from Reaction 2b. Similar reactions which involve the abstraction of two hydrogen atoms have been considered in the case of the reactions of $O(^1D)$ with ethane or ethylene. The extent of the reaction is about 3% of the total $O(^1D)$ reactions in the liquid Ar.[14] For the case of the singlet NH, the concentration dependence of the ammonia formation could also be explained by the presence of the similar reaction in the case of the olefin, but not in the case of the paraffin. If Reaction 14 were included in the mechanism instead of Reaction 4, k_{2c} should be equal to $k_{2b}+k_{14}$ to explain the observed material balance.

In the above discussions, acetaldehyde was assumed to be formed by Reactions 2b and 4. Since acetaldehyde is known as a possible impurity in ethyl alcohol, it is possible to consider that the impurity affects Reaction 3. This possibility was, however, dismissed because of the following facts:

a)   No aldehyde was detected in this study, although this result does not conclusively eliminate the possibility of the presence of aldehyde, because of possible condensation reactions of aldehyde in the present analytical system.

b)   The amount of acetaldehyde oxime O-methyl ether did not decrease when more highly purified ethyl alcohol was used. (see Table 3).

c)   When the acetaldehyde was assumed to be an impurity, Eq. 11 should be changed to Eq. 15:

$$([NH_2CH_2CH_2OH] + [CH_3CH=NOC_2H_5]$$
$$+ 4[NH_3] - 3[NH_3]_{2b})/[N_2] = 1.0 \qquad (15)$$

Here, $[NH_3]_{2b}$ represents the amount of ammonia formed by Reaction 2b. If $[NH_3]_{2b}$ is assumed to be equal to $[NH_2CH_2CH_2OH]$, the left-hand-side of Eq. 15 becomes 1.3.

Assuming Reaction 4 and $k_{2a}=k_{2b}$, the relative efficiencies of Reactions 2a—d can be estimated to be 0.1_6, 0.1_6, 0.5_0, and 0.1_8 respectively. That is, the main reaction of the singlet NH with ethyl alcohol is the insertion into the O–H bond. For the case of methyl alcohol, the insertion into the C–H or O–H bond was calculated to be 85% of the reaction of NH radicals. The efficiencies could not be estimated seperately, because of the presence of Reaction 4. The insertion into the O–H bond, however, may be more important than the C–H bond of methyl alcohol.

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