$Co(NH_3)_5Cl^{++}$ as compared to $Co(NH_3)_4OH_2 \cdot Cl^{++}$, but the former undergoes chloride release in aqueous solution at a rate only a few times greater than the latter,[33] as against a factor of 60 or more in the corresponding carbonato compounds. The explanation must be that, while each substitution event (whether by HCO_3^- or H_2O) results in carbonate exchange in N_5, H_2O substitution for H_2O in the bicarbonato-aquo species, which results in no carbonate exchange, may well be the favored path.[34] Furthermore, the dynamic

(33) D. R. Stranks in "Modern Co-ordination Chemistry" (ref. 29), p. 129.

(34) Since only the immediately adjacent water molecules of the solvent sheath can take part in the substitutions, the geometry of the transition states for the H_2O/H_2O and H_2O/HCO_3^- reactions may be almost identical, differing only by small shifts in the O–H, O–C and O–Co bond distances. The more easily attainable orientation, assumed here to be that for H_2O/H_2O exchange, will thus be favored at the expense of the other, especially as labilization of the OH_2 ligand by the adjacent basic O_3CH ligand[35] will assist in formation of this "more favorable" transition state.

(35) It is significant that water exchange between water solvent and the cis-Co(en)$_2$OH·H$_2$O $^{-+}$ ion occurs at 25° at a rate over 50 times greater than

equilibrium of reaction 1 provides an additional non-carbonate-exchange reaction path which is not available to the N_5 complex.

The tn_2 complex undergoes carbonate exchange an order of magnitude more slowly than do the other bidentate carbonato complexes. This is logically explained in terms of the reduced value of K_1 for tn_2, since the rate constants of both types of carbonate substitution reactions include the factor $K_1(H_2O)/K_1(H_2O) + 1$. Equilibrium isotope effects, hydrogen-bonding and spectral evidence for a relatively small K_1 value in tn_2 have been discussed above.

the rate of the corresponding reaction of the cis-Co(en)$_2$(H$_2$O)$_2$$^{+3}$ ion (W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961)), and over 400 times greater than for cis-Co(en)$_2$NH$_3$·H$_2$O $^{-3}$ (D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962)). This commonly observed hydroxide-induced labilization of the adjacent ligand (see ref. 33) can be expected to be paralleled by a similar effect by the strongly basic bicarbonate group.

The Photochemistry of Methylamine[1]

BY JOE V. MICHAEL[2] AND W. ALBERT NOYES, JR.

Hydrogen, methane, nitrogen, ethane, ammonia, ethylenimine, dimethylamine, azomethane and a polymer have been identified as products in the photochemical decomposition of methylamine. Quantum yields of most of these products have been determined under a variety of experimental conditions at room temperature. By use of CH_3ND_2 and of CD_3NH_2 as well as by use of scavengers it has been shown that the main primary process is the elimination of a hydrogen atom. This is followed by abstraction from the substrate to form hydrogen gas. Other steps in the mechanism are suggested and evidence for some of them presented.

The photochemistry of methylamine has been extensively studied.[3] The results were not always in good agreement.

Methylamine is a photochemically interesting molecule. There is some direct production of molecular hydrogen in the primary process following absorption by methanol vapor.[4] An analogous reaction in methylamine would be possible.

Methylamine probably shows a predissociation type spectrum.[5] By analogy with NH_2 the reactions of CH_3NH with oxygen and with nitric oxide might also prove to be interesting.[6,7]

The photochemistry of methylamine is complex, a fact to be expected from the difficulties in interpreting results on the photolysis of ammonia.[8] The main primary process is the formation of hydrogen atoms, but there may be small amounts of dissociation to

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Contract AF49(638)-679.

(2) National Science Foundation Coöperative Fellow, 1959–1960; Eastman Kodak Company Fellow, 1960–1961; National Science Foundation Predoctoral Fellow, 1961–1962.

(3) H. J. Emeléus and H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 3370 (1931); H. J. Emeléus and L. J. Jolley, *J. Chem. Soc.*, 1612 (1935); O. C. Wetmore and H. A. Taylor, *J. Chem. Phys.*, **12**, 61 (1944); C. I. Johnson and H. A. Taylor, *ibid.*, **19**, 613 (1951); J. S. Watson and B. deB. Darwent, *ibid.*, **20**, 1041 (1952). For reviews see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 382, and E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 244, 636.

(4) R. P. Porter and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 2307 (1959).

(5) See H. J. Emeléus and L. J. Jolley, ref. 3. A. B. F. Duncan, *Phys. Rev.*, **47**, 822 (1935), and R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935), have discussed ammonia spectrum and bands.

(6) H. Gesser, *J. Am. Chem. Soc.*, **77**, 2626 (1955).

(7) A. Serewicz and W. A. Noyes, Jr., *J. Phys. Chem.*, **63**, 843 (1959).

(8) Cf. C. C. McDonald and H. E. Gunning, *J. Chem. Phys.*, **23**, 532 (1955).

methyl and amine radicals as well as to form molecular hydrogen.

Experimental

An unfiltered Hanovia S-100 was used for all experiments. Since polymer formed on the front window of the cell, it was necessary to clean the cell after each run.

The radiation was not monochromatic. All of the wave lengths between 1940 and 2440 Å. are probably absorbed by methylamine.

Actinometry measurements were made by the hydrogen bromide–mercury vapor system in tandem with the photolysis cell. This actinometer is described in detail elsewhere.[9,10] One molecule of hydrogen is assumed to be formed per photon when mercury is present to react with the bromine. Quantum yields should be valid within 5%.

Reagents.—Methylamine was prepared from Eastman Kodak Co. White Label methylamine hydrochloride. It was recrystalized three times from water, and the amine was liberated by anhydrous calcium oxide.[11] The purity was 99.9%.

Methylamine-C-d_3 was prepared in the same manner as was methylamine. Methylamine-C-d_3 hydrochloride was supplied by Dr. R. J. Cventanović of the National Research Council, Ottawa, Can., to whom the authors are indebted. The purity determined by vapor phase chromatography of the final sample was 99.9% and the isotopic purity determined by mass spectrometry was at least 93%.

Methylamine-N-d_2 was obtained from Merck, Sharp, and Dohme of Canada, Ltd., and had a purity of 99.5%. The principal impurity was ND$_3$. The isotopic purity was at least 99%.

Ammonia was obtained from the Matheson Co., Inc. A middle third was taken from a bulb-to-bulb distillation. Vapor phase chromatography and mass spectrometry showed it to be 99.9% pure.

Azomethane was prepared by the method of Jahn and was purified by vapor phase chromatography.[12]

Research grade methane and ethane (Phillips Petroleum Co.) were used without further purification.

(9) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 83.

(10) W. A. Noyes, Jr., *J. Chem. Phys.*, **5**, 807 (1937).

(11) A. P. Gray and R. C. Lord, *ibid.*, **26**, 690 (1957).

(12) F. P. Jahn, *J. Am. Chem. Soc.*, **59**, 1761 (1937).

TABLE I

QUANTUM YIELDS AS A FUNCTION OF TIME

Cell volume, 191.4 ml.; room temperature; $P_{CH_3NH_2} = 140 \pm 5$ mm.; Hanovia S-100 lamp; Φ_{H_2} is assumed to be unity

Time, sec.	Φ_{NH_3}	Φ_{CH_4}	Φ_{N_2}	$\Phi_{C_2H_6}$	$\Phi_{(CH_3)_2N_2}$	$\Phi_{(CH_3)_2NH}$	$\Phi_{(CH_2)_2NH}$	$-\Phi_{CH_3NH_2}$
450	1.08	0.020	0.014	0.077	0.033	0.003	0.49	
900	1.11	.019	.013	.046	.036	.028	.57	
1800	1.04	.027	.013	.026	.041	.081	.55	
3636	1.07	.036	.010	.023	.027	.12	.42	
7200	1.04	.049	.013	.019	.025	.16	.30	2.2
10800	0.93	.051	.015	.028	.020	.15	.24	1.7
21762	1.03	.076	.013	.024	.019	.15	.17	1.9
	1.04 ± 0.04		0.013 ± 0.001					1.9 ± 0.2

Dimethylamine was prepared and purified in the same manner as was methylamine from Eastman Kodak Co. White Label dimethylamine hydrochloride. The purity was 99.9%.

Propylene (Phillips Petroleum Co.) was purified by taking a middle third from a bulb-to-bulb distillation.

Cylinder hydrogen and deuterium were used without further purification. Mass spectrometric analysis showed only trace impurities.

Hydrogen deuteride was prepared by the reaction of lithium aluminum hydride with heavy water. The sample was 98% pure as shown by mass spectrometric analysis.

Ethylenimine was obtained from Chemical Intermediates and Research Laboratories, Inc. A middle third was collected from a bulb-to-bulb distillation. Vapor phase chromatography and mass spectrometry showed the sample to be at least 99% pure.

Hydrogen bromide was obtained from the Matheson Co., Inc., and was used without further purification. The stated purity was 99.8%.

Procedure.—Methylamine was measured in a calibrated volume and transferred to the evacuated cell by distillation. The sample was allowed to stand at least 15 minutes before irradiation.

A conventional high vacuum distillation technique was employed to obtain all products except dimethylamine and ethylenimine. These two products were obtained from mass spectrometric analysis of the photolyzed mixture.

After the sample had been photolyzed, the break-seal was broken and the contents of the cell distilled into a trap at $-196°$. Fraction 1 contained the gases not condensed by solid nitrogen ($-215°$) and was oxidized over copper oxide at $220°$. Mass spectrometric analysis showed that hydrogen, methane and nitrogen were present. The hydrogen was determined as the difference between this fraction and the second fraction. Fraction 2: After oxidation the residue was measured and placed in a sample tube for mass spectrometric analysis. This fraction contained only methane and nitrogen. The mole fraction of each could be determined and, thus, the absolute amount of each component calculated. Fraction 3: The unreacted methylamine and products condensable by solid nitrogen were transferred to a LeRoy still maintained at $-165°$.[13] The gas was removed by a Toepler pump and measured. Analysis by the mass spectrometer showed this fraction to contain only ethane. Fraction 4 was obtained by distillation at $-78°$ and contained almost all of the unreacted methylamine. The sample was analyzed on a Perkin–Elmer model 154 vapor phase chromatograph with Column W. Polyethylene glycol was the solute phase and the stationary phase was powdered Teflon. The column was 2 meters in length. At relatively slow flow rates, the products were separated from the unreacted methylamine. Azomethane was eluted after 2 minutes and was determined by the mass spectrometer. At 3.5 minutes, ammonia, identified in the same way, was eluted. Methylamine was eluted at 7 minutes. The azomethane was determined by collection and chromatographic analysis with a Perkin–Elmer Column D. This is a 3-meter column of tetraisobutylene upon 60–80 mesh firebrick. Fraction 5: The final fraction was taken at room temperature. Mass spectrometric analysis showed that this sample contained dimethylamine and ethylenimine as well as unreacted methylamine. The quantitative results obtainable for dimethylamine and for ethylenimine were never reproducible because dimethylamine has a slight vapor pressure at $-78°$. Ethylenimine is adsorbed on glass so strongly that it was impossible to collect all of it.

The mass spectra always showed peaks in the $m/e = 35$-45 region but relative peak heights changed with conditions. The ratio of peak 45 to peak 44 was constant at 0.56 and compared favorably with the ratio for dimethylamine. The height of peak 45 was taken to measure dimethylamine. The spectrum after peaks due to dimethylamine were subtracted was identical, within experimental error, with the spectrum of ethylenimine. The ratio of peak heights in methylamine, peak 17/peak 31, is 0.0139. Thus, by using this ratio, the relative peak height for

(13) D. J. LeRoy, *Can. J. Res.*, **B28**, 492 (1950).

peak 17, due to ammonia, can also be calculated. Calibrations were made for ethylenimine, dimethylamine and ammonia in the presence of excess methylamine. A straight line relationship between the mole fraction and the parent peak fraction was obeyed, and it is believed that analyses performed in this way are fairly accurate.

Results

The photolysis of methylamine was studied as a function of time, intensity and pressure. The results are given in Tables I, II and III.

TABLE II

QUANTUM YIELDS AS A FUNCTION OF INTENSITY

Cell volume, 191.4 ml.; room temperature; $P_{CH_3NH_2} = 144 \pm 5$ mm.; Hanovia S-100 lamp; Φ_{H_2} is assumed to be unity

Time, sec.	Intensity[a]	Φ_{NH_3}	Φ_{CH_4}	Φ_{N_2}	$\Phi_{C_2H_6}$
7200	1.00	0.98	0.045	0.013	0.024
7572	0.56	1.05	.037	.005	.023
7200	.38	0.98	.029	.005	.026
12626	.15	1.10	.030	.004	.021
12600	.04	1.15	.028	.008	.026
		1.05 ± 0.06			0.024 ± 0.002

[a] Arbitrary units.

In all experiments a polymer formed on the front window and absorbed the photolyzing wave lengths. Rates of production of products appear to decrease with time even if they were truly time independent. Quantum yields for four runs in the range 1800 to 8900 sec. were determined with the hydrogen bromide–mercury vapor actinometer and indicate that Φ_{H_2} is close to unity in this time range. The values given in Table I are based on $\Phi_{H_2} = 1.0$ for the complete time range.

The hydrogen quantum yield was constant and independent of intensity. Since Φ_{H_2} is near unity the hydrogen yield is also assumed to be unity over the complete intensity range and the other product quantum yields are calculated from this assumption. These data are shown in Table II.

The hydrogen bromide–mercury vapor actinometer was used to obtain the quantum yields as a function of pressure. These data are shown in Table III.

The rates of production and the isotopic distributions of the products formed in the photolysis of CD_3NH_2 and CH_3ND_2 are given in Table IV. The photolysis was also studied in the presence of the scavengers: propylene, oxygen and nitric oxide. The data are given in Table V.

Azomethane was photolyzed in the presence of CD_3NH_2 and of CH_3ND_2 at 3130 Å. and room temperature. In both cases CH_3D and CH_4 were observed. This indicates that CH_2NH_2 and CH_3NH radicals are both formed by methyl abstraction.

Attempts to characterize the polymer were made. The formula calculated from material balance seemed to change from C_2NH_5 to C_2NH_4 as a function of time, but product determinations are not accurate enough to state this conclusively. The empirical formula determined from combustion analysis was $(C_2N_2H_3)_x$,

TABLE III

QUANTUM YIELDS AS A FUNCTION OF PRESSURE

Cell volume, 191.4 ml.; room temperature; time, 7200 sec.; Hanovia S-100 lamp; hydrogen bromide–mercury actinometer

$P_{CH_3NH_2}$, mm. Hg	Φ_{H_2}	Φ_{NH_3}	Φ_{CH_4}	Φ_{N_2}	$\Phi_{C_2H_6}$	$\Phi_{(CH_3)_2N_2}$	$\Phi_{(CH_3)_2NH}$	$\Phi_{(CH_2)_2NH}$	$-\Phi_{CH_3NH_2}$
138.3	0.90	0.93	0.042	0.011	0.023	0.018	0.14	0.27	1.8
98.9	.89	.89	.042	.011	.024	.019	.13	.22	2.1
49.7	.95	.96	.047	.020	.027	.016	.15	.16	1.8
23.5	.83	.78	.053	.038	.044	.007	.14	.088	1.8
16.1	.79	.68	.053	.041	.041	.004	.15	.071	1.7
4.4	.62	.27	.045	.049	.055	.005	.084	.040	0.9

TABLE IV

RATES OF FORMATION OF PRODUCTS FROM DEUTERATED METHYLAMINES

Cell volume, 191.4 ml.; room temperature; time, 7200 sec.; Hanovia S-100 lamp

Compound	Pressure, mm.	$R_{H_2}{}^a$	R_{NH_3}	R_{CH_4}	$R_{C_2H_6}$	R_{N_2}	$R_{(CH_2)_2NH}$	$R_{(CH_3)_2NH}$
CH_3NH_2 (1)	142.7	35.8	37.2	1.4	0.8	0.4		
CD_3NH_2 (2)	138.2	23.0	22.2	2.3	1.0	1.4		
CH_3ND_2 (3)	141.6	38.0	38.6	1.2	1.2	0.4		
CD_3NH_2 (4)	127.9						6.3	2.7
CH_3ND_2 (5)	34.8						~12	~8

ISOTOPIC COMPOSITION OF PRODUCTS

	Hydrogen	Ammonia	Methane	Ethane	Azomethane	Ethylenimine	Dimethylamine
	$0.44\ H_2$	$1.00^a\ NH_3$	$0.24\ CD_4$	$0.89\ C_2D_6$	$>0.90\ (CD_3)_2N_2$		
(2)	$.48\ HD$		$.74\ CD_3H$	$0.11\ C_2D_5H$			
	$.08\ D_2$		$.02\ CD_2H_2$				
	$.16\ H_2$		$.45\ CH_3D$	$1.00\ C_2H_6$	$>0.72\ (CH_3)_2N_2$		
(3)	$.81\ HD$		$.55\ CH_4$				
	$.03\ D_2$						
(4)		$0.52\ NH_2D$				$C_2ND_5{}^b$	$(CD_3)_2NH^b$
		$.48\ NH_3$					
		$.39\ ND_3$				$C_2NH_5{}^b$	$0.5\ (CH_3)_2ND$
(5)		$.42\ ND_2H$					$0.5\ (CH_2D)(CH_3)ND$
		$.19\ NDH_2$					

All rates are in moles sec.$^{-1}$ × 10^{10}. ^{a} Probably incorrect since this ammonia was collected from a vapor phase fractometer and if any water was present a rapid exchange would occur. ^{b} The compound indicated is the major isotopic isomer.

and the infrared spectrum indicated the presence of N—H, C—H and possibly C≡N bonds. Since the sample was obtained after long irradiation, the polymer may have been degraded by radiation. The polymer was highly soluble in water and in methanol and had a yellow-brown color. Absorption extended from 5500 to below 2000 Å.

Other workers have reported that the polymer hydrolyzes to formaldehyde.[14,15] Quantitative tests for formaldehyde by the Matsukawa method[16] were performed on water solutions of the polymer. The quantum yields of formaldehyde formation were 0.019, 0.039 and 0.043. The bulk of the polymer does not hydrolyze to formaldehyde. Moreover the absorption spectrum was unchanged by allowing the water solution to stand for long periods of time.

Discussion

The spectrum of methylamine seems to be quite diffuse.[17] By analogy with ammonia[5] one may assume that the observed bands in methylamine are truly diffuse. The primary dissociation yield should be close to unity[18] except possibly at high pressures.

The following possible primary dissociations of methylamine may be considered.
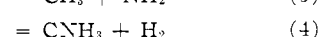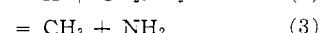
(14) See ref. 3, H. J. Emeléus and L. J. Jolley.

(15) See ref. 3, O. C. Wetmore and H. A. Taylor.

(16) D. Matsukawa, J. Biochem. (Tokyo), 30, 386 (1939).

(17) G. Herzberg and R. Kölsch, Z. Elektrochem., 39, 572 (1933); H. J. Emeléus and L. J. Jolley, J. Chem. Soc., 1612 (1935); V. Henri and W. Lasareff, J. chim. phys., 32, 353 (1935); T. Förster and J. C. Jungers, Z. physik. Chem., B36, 387 (1937); H. J. Emeléus and H. V. A. Briscoe, J. Chem. Soc., 127 (1937); E. Tannenbaum, E. M. Coffin and A. J. Harrison, J. Chem. Phys., 21, 311 (1953).

(18) See ref. 9, p. 370.

$$CH_3NH_2 + h\nu = H + CH_3NH \quad (1)$$
$$= H + CH_2NH_2 \quad (2)$$
$$= CH_3 + NH_2 \quad (3)$$
$$= CNH_3 + H_2 \quad (4)$$

Reaction 4 is written by analogy with methanol.[4] The fragment CNH_3 might have any one of the forms: $CHNH_2$, CH_2NH, CH_3N.

Either 1 or 2 must be the principal primary process, although both may occur. The reason for this is found in the very large decrease of hydrogen yield in the presence of scavengers (particularly propylene and oxygen). This conclusion agrees with earlier work.[3]

The decision between 1 and 2 might be based either on results with the isotopic compounds CH_3ND_2 and CD_3NH_2 or upon the character of secondary reactions which might arise from the two different radicals CH_3NH and CH_2NH_2.

Inspection of the results in Table IV indicates that H_2, HD and D_2 are all formed to greater or lesser extents from both deuterated methylamines. This agrees qualitatively with earlier work.[19] Abstraction from the CD_3 and from the NH_2 parts of the methylamine molecule would seem to be of equal importance for CD_3NH_2, but abstraction from the CH_3 seems to be preferred to abstraction from the ND_2 in CH_3ND_2. Nevertheless HD is the main hydrogen from both deuterated methylamines. Reaction 1 must account for at least 75% of the primary process and 2 is estimated to occur to about 10% of 1.

Reference to Table V indicates that none of the scavengers suppresses hydrogen formation completely.

(19) See ref. 3, J. S. Watson and B. de B. Darwent.

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TABLE V

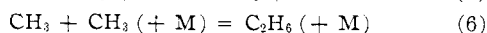PHOTOCHEMICAL REACTIONS OF METHYLAMINE IN THE PRESENCE OF SCAVENGERS

</div>

Light source, (unfiltered) Hanovia S-100; cell volume, 193.0 ml. (for A), 191.4 ml. (others); constant intensity within 10 to 15% in each section; room temperature

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A. Propylene

</div>

Time, sec.	Compound	Methylamine, mm.	Propylene, mm.	R_{H_2}	R_{CH_4}	R_{N_2}	R_{NH_3}
7200	CH_3NH_2	97.6	0.0	43.1	2.1	0.5	43.2
8316	CH_3NH_2	91.8	177.9	4.3	1.6	.8	~13
7635	CH_3ND_2	110.0	202.7	3.7[a]	1.4[b]	.4	
8438	CH_3NH_2	113.7	205.2	4.4	1.5	.6	
7200	CD_3NH_2	84.2	160.0	2.1[c]	2.4[d]	1.8	

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B. Oxygen

</div>

Time, sec.	CH_3NH_2, mm.	O_2, mm.	R_{H_2}	R_{CH_4}	$R_{C_2H_6}$	R_{NH_3}	R_{N_2}	$R_{(CH_3)_2N_2}$	$-R_{O_2}$	$-R_{CH_3NH_2}$
3922	148.0	6.5	20.6	Pr.	0.0	49.6	Pr.[d]	Pr.	35.2	211.6
7200	149.1	35.8	2.0	0.0	.0	43.2	Pr.	Pr.		212.5
7204	148.0	14.0	4.9	0.0	.0	50.5	Pr.	Pr.		171.7
7200	150.3	0.0	46.0	2.2	1.2	45.0	0.6	Pr.		
7200	146.8	.0	47.6	2.3	1.2	40.2	.4	1.4		84.9
7200	142.7	.0	35.8	1.4	0.8		.4	Pr.		
10110	146.3	74.1	2.2	0.0	.0		Pr.	Pr.		
7367	146.5	14.0	5.4	.0	.0		Pr.	Pr.	45.3	
7209	142.2	5.1	12.4	.0	.0		Pr.	Pr.	30.7	

(Av. R_{NH_3} for last four runs = 37.2)

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C. CD_3NH_2 with oxygen

</div>

7339	137.8	39.1	1.9[e]	0.0	0.0		Pr.	Pr.		136.2

<div align="center">

D. CH_3ND_2 with oxygen

</div>

7200	126.9	37.7	3.3[f]	0.0	0.0	40.3	Pr.	Pr.	83.6	

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E. Nitric oxide; time, 7200 sec.

</div>

Methylamine, mm.	Added gas, mm.	R_{H_2}	R_{CH_4}	R_{NH_3}	R_{N_2O}	R_{N_2}
150.1	11.9	7.41	0.47	15.8	3.96	37.2

<div align="center">

F. CH_3ND_2 and nitric oxide

</div>

94.5	38.8	5.99[g]	0.52[h]	11.8 ± 2.8	Pr.	57.5

All rates are in moles sec.$^{-1}$ $\times$ 10^{10}; Pr. stands for present but not determined quantitatively. [a] 0.38 H_2, 0.54 HD, 0.08 D_2. [b] 0.96 CH_4, 0.04 CH_3D. 2,3-Dimethylbutane was identified and was more than 70% 1,4-dideuterio-2,3-dimethylbutane. [c] 0.56 H_2, 0.18 HD, 0.26 D_2. [d] 0.21 CH_4, 0.61 CD_3H, 0.18 CD_4. The 2,3-dimethylbutane was essentially all undeuterated. [e] 0.42 H_2, 0.58 HD, 0.0 D_2. [f] 0.26 H_2, 0.68 HD, 0.06 D_2. [g] 0.30 H_2, 0.57 HD, 0.13 D_2. [h] 0.51 CH_3D, 0.49 CH_4.

The total yield of 4 is probably 0.1 as a maximum and all three possible eliminations of H_2 may occur with a slight preponderance of $CH_2NH + H_2$.

The need for 3 is based on methane and ethane formation. The most logical reactions are

$$CH_3 + RH = CH_4 + R \qquad (5)$$
$$CH_3 + CH_3 (+ M) = C_2H_6 (+ M) \qquad (6)$$

Methyl radicals might be formed by secondary reactions, but no obvious ones can be suggested. Since (CH_4 to $2C_2H_6$) is always small compared to H_2, reaction 3 must have a yield much smaller than 1 plus 2. The relationship $R_{CH_4}/R_{C_2H_6}^{1/2} = k_5(RH)/k_6^{1/2}$[20] has been used to evaluate $k_5/k_6^{1/2}$ for methylamine[21] at higher temperatures. This relationship is usually not well obeyed at room temperature because of wall and other effects. Because of the low yields of methane and of ethane the data in the present instance are hardly accurate enough to test this equation, but quite obviously it is not obeyed. Moreover, the methane yield generally increases with time so that some product may have a more easily abstractable hydrogen atom than methylamine itself.
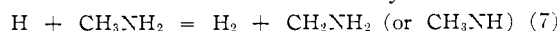
The primary yield for 3 is estimated not to exceed 0.05, but probably is not zero.

The total primary quantum yield is within experimental error of unity.

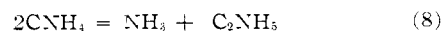Attention may now be directed to secondary reactions. The most prominent product other than hy-

(20) L. M. Dorfman and W. A. Noyes, Jr., J. Chem. Phys., 16, 557 (1948).
(21) A. F. Trotman-Dickenson and E. W. R. Steacie, ibid., 19, 329 (1951).

drogen is ammonia and the ratio H_2/NH_3 is 0.97 for twenty runs in Tables I–IV if one neglects the runs at low pressures where diffusion of hydrogen atoms to the walls may be important.

Reactions 1 and 2 must be followed by

$$H + CH_3NH_2 = H_2 + CH_2NH_2 \text{ (or } CH_3NH) \quad (7)$$

Thus every primary dissociation by 1 or 2 is accompanied by formation of two radicals which are either CH_2NH_2 or CH_3NH. There is no really satisfactory way of deciding whether CH_2NH_2 or CH_3NH is the more stable. The less stable radical may either rearrange to the more stable one or it may by abstraction from the substrate produce the more stable one. The data indicate that the rearrangement if it occurs is probably first order rather than second order since CD_3NDH is not formed in the photodecomposition of CD_3NH_2.

The ammonia producing reaction must involve two radicals of the empirical formula CNH_4. Thus tentatively one can write

$$2CNH_4 = NH_3 + C_2NH_5 \qquad (8)$$

C_2NH_5 is the empirical formula of ethylenimine which is identified as one of the products. If all radicals undergo 8 the yield of ethylenimine should be the same as the yield of ammonia. This is far from the case. On the other hand, the data in Table I indicate that the yield of ethylenimine decreases with time. The polymer must be primarily one of ethylenimine, but material balance requires the polymer to have an empirical formula close to C_2NH_4.

The manner in which ethylenimine is formed from two CNH_4 radicals is not certain. Possibly this is a wall reaction. The data in Table IV indicate $(CD_2)_2ND$ to be the major ethylenimine formed from CD_3NH_2 and $(CH_2)_2NH$ to be the major one formed from CH_3ND_2. Thus the hydrogen in the ethylenimine is mainly hydrogen from the methyl part of the methylamine. One can write as the main ethylenimine-producing reactions

$$2CND_3H = C_2ND_5 + NH_2D \qquad (9)$$

$$2CNH_3D = C_2NH_5 + ND_2H \qquad (10)$$

The data in Table IV show the major ammonia formed in each case to agree with the predictions of 9 and 10.

Dimethylamine is the product next in importance. It must be formed by a complex reaction. The reaction $CH_3NH + CH_3 = (CH_3)_2NH$ would be the logical way for dimethylamine to be formed, but there are not enough methyl radicals for this to be the case. Moreover if dimethylamine were formed in this way in competition with methane formation the yield should be intensity dependent. In Table III the number of quanta absorbed per milliliter per second will increase with the pressure and yet the yield is essentially independent of pressure. The yield does, however, increase with time and there is an induction period (Table I). Hence dimethylamine is probably formed by a slow thermal reaction, possibly from the polymer.

Azomethane is the remaining product of any importance. Its yield is low and is independent of time. It is, however, dependent markedly on pressure (Table III). Thus one is led to propose

$$CH_3N + CH_3NH_2 = CH_3N=NCH_3 + H_2 \qquad (11)$$
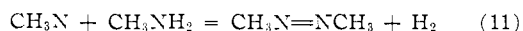
If 4 leads to appreciable amounts of CH_3N the yield of azomethane would be equal to the yield of 4 at high pressures. The data in Table I are in general agreement with this prediction. It would also be predicted that $CD_3N=NCD_3$ would be the azomethane from CD_3NH_2 and $CH_3N=NCH_3$ would be the azomethane from CH_3ND_2. The data in Table IV indicate this to be true.

The yield of nitrogen is small and is essentially independent of time and of intensity but does decrease with increase in pressure. The nitrogen-producing step in the photochemical decomposition of ammonia has probably never been fully established, although many authors tend to favor a reaction such as $N_2H_2 = N_2 + H_2$. The N_2H_2 is suggested to be formed by some such reaction as $H + N_2H_3 = H_2 + N_2H_2$.[8] In methylamine no hydrazine or substituted hydrazine could be detected, but the same is true in a static system with ammonia. Nevertheless there is good reason to believe that in ammonia hydrazine is formed but reaches a very low steady state due to rapid attack by radicals. In the present system the union of two CH_3NH radicals, or two NH_2 radicals or one CH_3NH and one NH_2 could lead to formation of a hydrazine. This could be followed by attack by hydrogen atoms to give $CH_3NN(H)CH_3$, N_2H_3 or $CH_3N(H)NH$, any one of which could be attacked by hydrogen atoms or other radicals. The first would give azomethane, the second could give nitrogen and hydrogen by the reactions suggested for the ammonia system and the third might possibly give ultimately methane and nitrogen. The data do not establish the mode of nitrogen formation.

On the basis of the mechanism certain statements can be made: (1) At low pressures hydrogen atoms should disappear on the walls and yields of hydrogen and of ammonia should approach values one-half of those at high pressures. The trends are certainly in the direc-

tion predicted. (2) At both high and low pressures the ratio of methylamine disappearance to hydrogen formation should be two. The data in Tables I and III show this to be the case. (3) If hydrogen atoms abstract equally well from the CD_3 as from the NH_2 part of CD_3NH_2 and if deuterium atoms abstract mostly from the CH_3 part of the CH_3ND_2 molecule, one can calculate the isotopic compositions of the ammonias and of the hydrogens from the two deuteriomethylamines. The results agree as well as can be expected with predictions. (4) The isotopic composition of the ethylenimines produced from deuterated methylamines are in general agreement with the predictions provided CH_3NH radicals rearrange to CH_2NH_2 radicals and two CH_2NH_2 radicals to form ammonia and ethylenimine. (5) Azomethane is probably formed by reaction of CH_3N radicals with methylamine. (6) Dimethylamine and nitrogen are formed by reactions which are difficult to elucidate. (7) Ethane and methane must be formed from methyl radicals which originate presumably in part of the primary process.

In conclusion, a few remarks may be made about the three scavengers used: oxygen, propylene and nitric oxide. (A few experiments were also made with iodine as a scavenger, but the results were not deemed to be significant.)

There is no evidence that any of the three scavengers reduces the primary quantum yield and probably none changes its character. There is no evidence that a triplet state of finite duration is involved in the primary process.

Oxygen is the most effective scavenger for methyl radicals and at pressures of a few millimeters reduces the yields of methane and of ethane essentially to zero. The effect of oxygen on the hydrogen yield is also very large even though a third body is undoubtedly of importance in the reaction $H + O_2 = HO_2$. Nevertheless pressures of more than 35 mm. are required to reduce the hydrogen yield to less than 10% of its oxygen-free value (Table V). The residual hydrogen is almost certainly due to a small amount of reaction 4.

Propylene is a reasonably good scavenger for hydrogen atoms at pressures of about 200 mm. In the limit hydrogen formation is reduced to about 10% of its propylene-free value. It has long been recognized[22] that hydrogen atoms add to propylene to form isopropyl radicals and that these in turn combine to give 2,3-dimethylbutane. In this case ammonia formation is considerably reduced but not to zero.

Propylene when used with CD_3NH_2 gave mainly 2,3-dimethylbutane indicating superficially mainly 1 and a little 2. With CH_3ND_2, 1,4-dideuterio-2,3-dimethylbutane was 70% of the dimethylbutane formed, thus indicating approximately 87% formation of CH_3ND by 1 and 13% CH_2ND_2. The isotope effects on the reactions are not known, but agreement is fair with the composition of the hydrogens formed.

Nitric oxide is the least effective scavenger of the three and large amounts of nitrogen are formed when it is used. In fact, in mixtures of diethyl ketone and nitric oxide[23] and of acetaldehyde and nitric oxide[24] large amounts of nitrogen are produced. This fact seems not to have been explained even though much work has been done on radical–nitric oxide reactions.[7,25] Possibly CH_3NH reacts with NO to give CH_3OH and N_2. In the presence of nitric oxide and CH_3ND_2 the rates of formation of CH_3D and of CH_4 are nearly equal. Since there are two deuterium atoms and three hydrogen

(22) See E. W. R. Steacie, ref. 3, p. 441.
(23) J. E. Jolley, J. Am. Chem. Soc., **79**, 1537 (1957).
(24) C. S. Parmenter and W. A. Noyes, Jr., ibid., **85**, 416 (1963).
(25) See ref. 21, A. F. Trotman-Dickenson and E. W. R. Steacie, p. 111.

atoms in the parent molecule, these results may indicate some preference for abstraction of deuterium atoms or the presence of non-scavengable "hot" radicals. The former suggestion would seem to be somewhat contrary to expectations based either on zero point energy or bond strengths. Ethane formation is reduced essentially to zero in the presence of nitric oxide.

Oxygen does not reduce the ammonia yield. There must be a CNH_4 radical formed in the primary process, but since oxygen greatly reduces hydrogen formation a second CNH_4 radical is not formed to a large extent by abstraction of hydrogen atoms by hydrogen atoms. However other radicals formed by secondary reactions with oxygen may abstract hydrogen atoms. Abstraction by HO_2 is improbable, but further speculation

about secondary reactions involving oxygen seems to be fruitless.

Reaction 8 is probably the ammonia-forming reaction. If this reaction occurs when oxygen is present, CNH_4 radicals must not react with oxygen at all rapidly. An alternative would have CNH_4 react either with oxygen or with some other radical than CNH_4 to give ammonia. Reaction with oxygen would almost certainly be followed by secondary reactions to give more CNH_4 radicals.

Thus either 8 must occur even when oxygen is present or some radical, e.g., OH or CH_3O, reacts with CNH_4 to give ammonia and a complete molecule, viz., CH_2O or CH_3CHO. More work on this point would be desirable.

Halide Anions as Proton Acceptors in Hydrogen Bonding[1]

BY ADAM ALLERHAND[2] AND PAUL VON RAGUÉ SCHLEYER[3]

The effect of quaternary ammonium halides on the X–H stretching frequencies of methanol, propargyl bromide and several deuterated haloforms in inert solvents has been studied. Very large spectral shifts, attributed to X—H...anion hydrogen bonding, were observed. The magnitudes of these shifts depended to a marked extent on the halide anion, in the order $Cl^- > F^- > Br^- > I^-$. Variations in the cation had little effect with I^- and Br^-, but influenced the X—H...Cl^- shifts to a pronounced degree. Covalently bound halogen atoms were very much weaker proton acceptors and gave an inverse spectral shift order. A novel technique for investigating hydrogen bonding of CDX_3 to inorganic salts was studied, using acetone as solvent. Ionic salts such as NaI produced large spectral shifts in this system, but covalent salts such as $HgCl_2$ did not.

Intermolecular hydrogen bonding has been studied extensively by infrared spectroscopic methods.[4] In most cases the proton acceptor is a covalent compound containing an oxygen or nitrogen atom and the solvent is CCl_4 or another "inert" liquid. Despite the expectation that anions should give the strongest hydrogen bonds, only a few experimental results have been published in which an anion is the proton acceptor.[5–7] Most ionic compounds are not soluble in the usual infrared spectroscopic solvents, but some quaternary ammonium salts overcome this limitation. Lund[5] observed large spectral shifts $(\Delta\nu)$ between the "free" OH and NH stretching vibrational bands of several proton donors and the bands due to XH...anion association; with a common proton donor the magnitude of $\Delta\nu$ was found to vary with the nature of the anion in the ammonium salt. Bufalini and Stern[6] studied the behavior of the X–H stretching of methanol and other proton donors in the absence and presence of quaternary ammonium salts. In benzene solution at the concentrations of methanol employed in the absence of electrolyte, both methanol monomer and "dimer" bands were present. The addition of the ionic compound caused the disappearance of the "dimer" band and the appearance of a new absorption at a lower frequency, attributed to the methanol...anion complex; $\Delta\nu$ again was found to vary with the anion. A similar investigation has been reported recently by Hyne and Levy.[7] A solution of t-butyl alcohol in CCl_4 showed three bands, at 2.74, 2.86 and 2.96 μ,

assigned to monomer, "dimer"[8] and polymer, respectively. The polymer band was very weak, but the addition of tetrabutylammonium bromide caused a very marked growth in intensity of the 2.96 μ band. Although the possibility that this intense band was due to alcohol...anion hydrogen bonding was admitted, Hyne and Levy noted that the position of the new band corresponded to that of t-butyl alcohol polymer, and concluded that the most probable role of the ammonium salt was to stabilize the polymeric form of the alcohol by serving as nucleation centers for the aggregation of alcohol molecules. However, the reported dependence of the XH...anion stretching frequency on the nature of the anion[5,6] cannot easily be rationalized on the basis of enhanced proton donor association in the presence of ionic species, but can be readily explained if hydrogen bonding to the anion is occurring.

All previous investigations on the effects of ionic compounds on XH bands have employed spectrometers equipped with low resolution NaCl prisms and the frequencies observed were accurate only to ± 20 cm.$^{-1}$ or worse. In view of the ambiguity of interpretation summarized above and our interest in hydrogen bonding to covalently bonded halogen atoms,[9,10] we have studied the nature of XH...halide ion interaction using high resolution spectrophotometers.

Alcohols self-associate readily because they are both good proton donors and good proton acceptors. The shifts in ν_{OH} from monomeric to polymeric bands are very large. If by coincidence ν_{OH} for the polymer were approximately the same as ν_{OH} for the alcohol...anion hydrogen bonded species, it would be difficult to distinguish between the two, although the possibility of polymer formation could be reduced greatly by using very dilute solutions of alcohol.

(1) Paper VIII of a series on hydrogen bonding; paper VII, J. Am. Chem. Soc., 85, 371 (1963). This work was taken from the Ph.D. Thesis of Adam Allerhand, Princeton University, 1962.

(2) Merck Foundation Fellow, 1960–1961; Esso Foundation Fellow, 1961–1962.

(3) Alfred P. Sloan Research Fellow.

(4) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(5) H. Lund, Acta Chem. Scand., 12, 298 (1958).

(6) J. Bufalini and K. H. Stern, J. Am. Chem. Soc., 83, 4362 (1961).

(7) J. B. Hyne and R. M. Levy, Can. J. Chem., 40, 692 (1962); cf., J. B. Hyne, J. Am. Chem. Soc., 85, 304 (1963).

(8) M. Saunders and J. B. Hyne, J. Chem. Phys., 29, 1319 (1958); 31, 270 (1959); E. D. Becker, ibid., 31, 269 (1959).

(9) P. von R. Schleyer and R. West, J. Am. Chem. Soc., 81, 3164 (1959).

(10) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee and P. von R. Schleyer, ibid., 84, 3221 (1962).