The nitromethane–sodium hydroxide solutions were made up at various ionic strengths with NaCl as indicated in paragraph 6, and the rate constants measured. Table IV gives the results. The slope is about 0.6 positive. A positive slope can result only if two ions of like charge are involved. The charge on the ions must be integral and, in this case, it must be concluded that two negative ions of unit charge are involved. As pointed out by La Mer,[11] in many other cases the deviations from the Brönsted equation are only as to magnitude, without effect on the sign of the slope. The data show that two negatively charged ions react to form methazonate ion and that each ion probably carries a unit charge.

Acknowledgment.—The authors wish to express their indebtedness to Professor Milton Burton for discussions of the results.

CHINA LAKE, CALIF.

The Photolysis of Ammonia in the Presence of Propane and Oxygen[1]

BY H. GESSER[2]

The photolysis of ammonia in systems with propane and oxygen both individually and combined was studied. Hydrogen atoms and NH_2 radicals from the primary dissociation of ammonia abstract hydrogen from propane at high propane pressures, high temperatures and at low intensity. The products, H_2, N_2, C_3H_6, isoproylamine, 2,3-dimethylbutane, do not give a material balance because of polymer and C_9 formation. Oxygen cleans up the primary hydrogen atoms and reacts with NH_2 radicals by a proposed reaction sequence to produce nitrogen. The three component system is complicated by the formation of acetone which subsequently competes with ammonia for part of the incident light. The photolysis of ammonia in a static system at $-80°$ shows that hydrazine is probably not a product. Reactions are proposed to account for the experimental results.

Introduction

The mechanism whereby ammonia decomposes photochemically, though the subject of many thorough investigations,[3] is not completely understood. The most recent studies[4] have not entirely eliminated doubt concerning the step by which nitrogen is formed.

It was hoped that by the addition of foreign gases (other than hydrazine) it would be possible to clarify certain steps in the mechanism and perhaps obtain information about reactions of the NH_2 radical. The systems chosen were ammonia and propane, ammonia and oxygen, and ammonia, oxygen and propane.

Experimental

The apparatus was of the conventional type used in this Laboratory and was constructed free of stopcocks (except for some preliminary work with ammonia and propane). The analytical units consisted of a furnace containing copper and copper oxide and maintained at 210° for the analysis of mixtures of hydrogen and nitrogen, and of oxygen and nitrogen: a copper oxide furnace of quartz maintained at 700° for the combustion of the isopropylamine and ammonia fraction; a platinum wire unit for the analysis of hydrogen in the presence of nitrogen and excess oxygen; a hydrogenator with a P_2O_5 absorber to remove the last traces of ammonia from the propane and propylene fraction prior to analysis of propylene in the hydrogenator.

It was difficult to separate isopropylamine[5] quantitatively from ammonia. A combustion method was developed to determine isopropylamine in the presence of ammonia. The propane fraction was distilled from the ammonia fraction at $-150°$ by means of a Le Roy still.[6] The ammonia and isopropylamine were then distilled from the remaining C_6 fraction at $-110°$ and oxidized in the copper oxide furnace at 700°. The nitrogen produced was pumped off through a trap immersed in liquid nitrogen. The water formed was used as a carrier by means of which the gases were cycled through the furnace several times. It was found necessary to heat the U-traps on either side of the furnace to prevent formation of any stable compound between the ammonia, carbon dioxide and water. The carbon dioxide was separated from the water, measured and corrected for the blank from the impurity in ammonia.

Ammonia was prepared by mixing J. T. Baker C.P. ammonium chloride and Merck Reagent Grade sodium hydroxide pellets and warming. The gas was dried by passage through a column of potassium hydroxide pellets, repeatedly degassed at $-140°$, and distilled into the storage bulb from $-110°$. The gas prepared in this manner proved to be of high purity and upon combustion was shown to contain 0.04% carbon.

Propane was Phillips Research Grade certified as 99.99% pure and was fractionated by bulb to bulb distillation. The middle third was retained and was shown within the limits of analysis to be free of unsaturated and higher hydrocarbons.

Oxygen was prepared by heating Merck Reagent Grade potassium permanganate and dried by passage through a trap immersed in liquid nitrogen. Analysis showed it to contain 0.03% nitrogen.

The light source was a Hanovia S-100 Alpine Burner. The beam was collimated by one quartz lens and a stop and passed over a droplet of mercury in a tube to reduce the photosensitized reaction. Negligible amounts of hydrogen were produced when propane alone was illuminated in this manner. The mercury lines observed below 2200 Å. were those at 1942, 1974 and 1995 Å. The ammonia bands lying closest to these lines are at 1974 and 1940 Å.[7] The de-

(1) This work was supported in part by a contract between the Office of Naval Research, United States Navy, and the Department of Chemistry, University of Rochester.

(2) National Research Council of Canada, Ottawa, Ontario, Canada. The author wishes to express his gratitude to the Celanese Corporation of America for a postdoctoral fellowship for 1952–1953, and to the Doctors Camille and Henry Dreyfus Foundation, Inc. for a postdoctoral fellowship for 1953–1954.

(3) For review see (a) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941; (b) P. A. Leighton, "Exposés de Photochimie," Hermann et Cie. Paris, 1938.

(4) (a) C. E. Herrick, Jr., Ph.D. Thesis, University of Rochester (1943); (b) M. Vanpée, Bull. soc. chim. Belg., 53, 179 (1944); (c) C. C. McDonald, A. Kahn and H. E. Gunning, J. Chem. Phys., 27, 908 (1954).

(5) Isopropylamine and 2,3-dimethylbutane were identified by means of mass spectrographic analysis as products in the ammonia-propane system. Acetone was similarly identified in the ammonia-oxygen-propane system. Unpublished work done in this Laboratory by Dr. L. S. Forster.

(6) D. J. Le Roy, Can. J. Res., B29, 492 (1950).

(7) A. B. F. Duncan, Phys. Rev., 47, 822 (1935).

TABLE I

PHOTOLYSIS OF AMMONIA-PROPANE MIXTURES

Cell unit volume, 73 cm.³; no stirring; illuminated volume, 49 cm.³.; rates are in molecules $\times$ 10^{-12} per second.

Time. sec.	$P_{C_3H_8}$. mm.	R_{H_2}	R_{N_2}	$R_{C_3H_7NH_2}$	$R_{C_3H_6}$	$R_{C_6H_{14}}$	ΔC_3	(R_{H_2}/R_{N_2})	$(R_{C_3H_6}/R_{C_6H_{14}})$
				$T = 26°$, $P_{NH_3} = 50$ mm.					
3600	0	50.2	20.3	..	..	...	..	2.5	..
3600	5.0	76.2	7.5	11ᵃ	2	19.3ᵃ	..	10.2	0.1
5820	10.7	74.5	5.4	14ᵃ	1.1	13.0ᵃ		13.8	0.08
7200	25.7	66.8	3.0	18ᵃ		3.8ᵃ		22.3	
85200	2.7	9.3	0.7	1		0.8	3.7	13.3	
				$T = 96°$, $P_{NH_3} = 62.5$ mm.					
86120	1.1	18.1	1.4	1.0		1.0	7	12.9	0.11
86400	3.0	20.5	1.0	2.5	0.2	1.8	11	21.5	
54000	7.5	33.6	1.0	6.0	0.3	2.4		33.6	0.12
54000	16.0	43.9	1.0	12.0	0.5	2.9		43.9	0.17
84000	1.0	9.7	0.5	1.0		1.5	4.9	19.4	
				$T = 200°$. $P_{NH_3} = 80$ mm.					
80400	1.0	17.4	1.6	4.0		2.2	11.2	10.4	

ᵃ Experimental error in analysis is large (about 30%) due to the small amounts of product.

cay in the intensity of the light source was of the order of 1 to 2% per hour. This is greater than for lines at longer wave lengths. The reaction cell was surrounded by a brass block and was electrically heated. The cell was 10 cm. long and 2.5 cm. in diameter and was totally illuminated in all experiments. The cell used in the experiments at −80° was of the same dimensions but in a vertical position and enclosed in a 2 inch diameter Pyrex jacket. The space between cell and jacket was filled with magnesium chips to a height 1 inch above the front window of the cell. This was done by means of an aluminum collar which fitted around the front end of the cell. The unit was immersed in a Dry Ice–acetone bath to a height of 4 inches above the cell. The Pyrex jacket was fitted with a quartz window and was evacuated to prevent condensation of moisture onto the cell window.

In some experiments when oxygen was present at low pressures an all glass magnetically operated stirrer was used to circulate the gases and prevent depletion of reactants in the cell. The extent of decomposition of ammonia was always kept below 1% and usually below 0.1%.

Results

The Photolysis of Ammonia in the Presence of Propane.

—Preliminary experiments showed that R_{H_2}/R_{N_2} (where R refers to rate in molecules per second) increased with increase in propane pressure. Figure 1 shows the effect of propane pressure on these rates at 35 and 100°. The rates have been corrected for the decay in lamp intensity which was followed by measuring the decrease in $(R_{H_2} + R_{N_2})$ for ammonia alone. In Table I are recorded results of experiments in which, where possible, complete analyses of the known products were made. In some cases, at low pressures of propane, the amount of propane consumed was measured. This is expressed as ΔC_3 and is equivalent to $-(R_{C_3H_8} + R_{C_3H_6})$. R_{H_2} is approximately proportional to intensity in the NH_3-C_3H_8 system, but the ratio R_{H_2}/R_{N_2} increases both at 35° and at 100° with decrease in intensity.

Photolysis of Ammonia at −80°.

—Two experiments were made at 21 and 5 mm. pressure of ammonia during which the walls of the reaction vessel were cooled to −80°. R_{H_2}/R_{N_2} was 2.98 and 3.00, respectively, whereas this ratio at room temperature in the same vessel was 2.93 and 3.03. There is thus no significant variation under conditions such that hydrazine might be expected to condense on the walls.
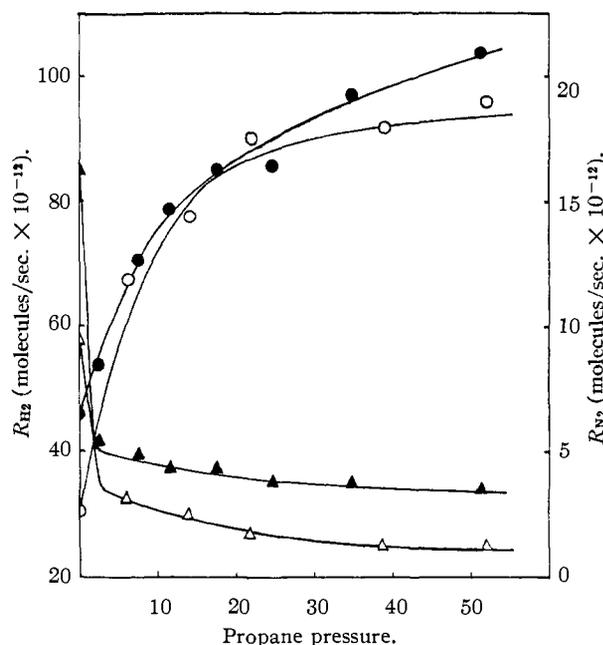
Fig. 1.—Rates of hydrogen and nitrogen formation from ammonia as a function of propane pressure: ●, R_{H_2} at 35°; ▲, R_{N_2} at 35°; ○, R_{H_2} at 100°; △, R_{N_2} at 100°; (cell unit volume = 75 cm.³; no stirring; illuminated volume = 49 cm.³); ammonia pressure = 50 mm.

The Photolysis of Ammonia in the Presence of Oxygen.

—The experimental results of the photo-oxidation of ammonia are listed in Table III. Preliminary experiments indicate that by adding oxygen to ammonia it is possible to double R_{N_2}. However, when the gases are stirred no such effect is observed and little, if any, hydrogen is formed. When pure ammonia is photolyzed following a photoöxidation experiment, R_{H_2}/R_{N_2} shows a marked decrease from 3 and an increase in R_{N_2} is observed. Continued photolysis shows a gradual increase in the value of the ratio R_{H_2}/R_{N_2} to 3 and a decrease in R_{N_2}.

Table III presents results obtained when pure ammonia was photolyzed in the presence of "ox-

TABLE II
PHOTOLYSIS OF AMMONIA-OXYGEN MIXTURES

Illuminated volume, 49 cm.^{3}; reaction temperatue, 27°. Rates are in molecules $\times 10^{-12}$ per second.

Time, sec.	Po_2 in cell. μ Initial	Final	R_{H_2}	R_{N_2}	$-R_{O_2}$	$\left(\frac{R_{H_2}}{R_{N_2}}\right)$	$\frac{-(R_{O_2}/}{R_{N_2})}$

Preliminary experiments; cell unit vol., 73 cm.^{3}, no stirring ammonia pressure, 50 mm.

60,000	0	0	26.5	8.8		3.01	
60,000	587	444		15.6	5.3		
30,660	0	0	(38.6)			<3	
28,800	595	38		19.8	43.9		
45,570	660	208		19.0	23.2		

Cell unit vol., 213 cm.^{3}; stirring; ammonia pressure, 50 mm.

6,000	0	0	41.1	16.8		2.45	
10,000	401	323	<2.3	19.6	55.3		2.82
10,000	0	0	40.4	19.2		2.10	
10,000	440	361	<2.3	19.7	55.2		2.75
10,000	0	0	39.5	18.1		2.18	
10,000	0	0	40.7	15.8		2.58	
54,000	0	0	39.0	13.6		2.87	
10,000	0	0	37.6	12.3		3.05	

Cell unit vol., 214 cm.^{3}; stirring: trap at $-80°$ between cell and mercury float valve; ammonia pressure 45 mm.

10,000	0	0	29.2	9.6		3.04	
10,000	423	355	<1.8	15.1	48.6		3.22
10,000	0	0	32.4	12.9		2.51	
10,000	428	238	<1.5	16.4	47.4		2.89
10,000	0	0	32.6	15.1		2.16	

ide" coated walls. After the first experiment, the lamp was changed and the walls coated by photolyzing a stirred mixture of 50 mm. of ammonia and about 0.5 mm. oxygen for about 16 hours at room temperature prior to each experiment, thereby increasing the "oxide" on the walls.

TABLE III
PHOTOLYSIS OF AMMONIA WITH "OXIDE" COATED WALLS

Ammonia pressure, 50 mm.; stirring; reaction temperature 26°; cell unit volume, 214 cm.^{3}; illuminated volume 49 cm.^{3} (rates are in molecules $\times 10^{-12}$ per second).

Time, sec.	R_{H_2}	R_{N_2}	R_{H_2}/R_{N_2}
12,000^a	12.9	4.0	3.10
7,800	25.2	10.1	2.50
7,200	25.7	11.1	2.34
7,200	24.0	11.7	2.05
10,800	26.4	12.7	2.08

^{a} Old lamp.

TABLE IV
PHOTOLYSIS IN AMMONIA–PROPANE–OXYGEN MIXTURES

Ammonia pressure, 50 mm.; propane pressure, 50 mm.; reaction temperature, 35°; illuminated volume, 49 cm.^{3}; cell unit volume 220 cm.^{3}; illumination time, 200 min.; stirring.

Po_2 in cell. μ Initial	Final	R_{H_2}	R_{N_2}	$-R_{O_2}$	R_{CO}	$R_{Acetone}$ molecules/sec. $\times 10^{-12}$	Remarks
0	0	84.4	1.7				
444	660	22.3	5.2	118	2.6	25	Oxygen dosed into cell
0	0	57.5	1.5			0.5	Acetone not removed from reactants
0	0	67.6	1.3				Reactants free from acetone

The Photolysis of Ammonia in the Presence of Propane and Oxygen.

—Preliminary experiments at 35° showed that hydrogen and acetone were produced and that R_{N_2} decreased when propane was added to the ammonia–oxygen system. A detailed examination of the products at 200° showed that carbon monoxide and methane were produced in appreciable quantities. This made the analysis of hydrogen by the platinum wire method subject to large error. The results of experiments at 35° are recorded in Table IV. Before the last experiment the acetone was separated from the ammonia and propane by distillation at $-110°$.

Discussion

The primary dissociation of ammonia almost certainly follows the equation

$$NH_3 + h\nu = NH_2 + H \qquad (1)$$
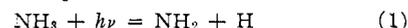
The primary quantum yield is unknown but is presumably high since the spectrum is truly diffuse. Atom recombination to form H_2 and reformation of ammonia from NH_2 and H must occur. The nitrogen-forming step is uncertain in spite of the large volume of work on ammonia decomposition. The present results are consistent with

$$2NH_2 = N_2 + 2H_2 \qquad (2)$$
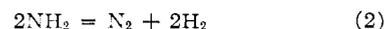
since the data in Table III show R_{H_2}/R_{N_2} to approach 2 when presumably the hydrogen atoms from the primary process are removed mainly at the walls.

The intermediate formation of hydrazine and its subsequent reactions to form nitrogen are often postulated. Certainly hydrazine can be a principal product in a flow system.[4c] There are ways of explaining this fact without predicting hydrazine as a necessary intermediate in a static system. It must be assumed, however, that the nitrogen-forming step is not known although reaction (2) may describe adequately what occurs for the purpose of the present discussion. The experiments with the walls at $-80°$ indicate the ratio of hydrogen to nitrogen to be 3 under conditions such that hydrazine, if formed, should be removed on the walls. Experiments at 80° with "oxide coated" walls did not show ratios below 2.5 so that the evidence for any single nitrogen forming mechanism is not conclusive.

If propane is added to the ammonia both H atoms and NH_2 radicals apparently abstract hydrogen atoms from the propane

$$H + C_3H_8 = H_2 + C_3H_7 \qquad (3)$$
$$NH_2 + C_3H_8 = NH_3 + C_3H_7 \qquad (4)$$
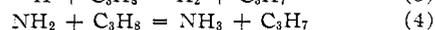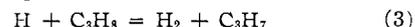
The limiting case with sufficient propane would make R_{H_2}/R_{N_2} infinite. Propane and propyl-(mainly isopropyl)-amine will be formed by the reactions

$$H + C_3H_7 = C_3H_8 \qquad (5)$$
$$NH_2 + C_3H_7 = C_3H_7NH_2 \qquad (6)$$
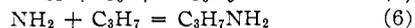
If reaction (3) proceeds quantitatively one molecule of hydrogen would be formed per primary dissociation and the rate of hydrogen formation at constant ammonia pressure will become constant and independent of propane pressure. This is found to be approximately true at 100° but constancy is less easily approached at 35° (Fig. 1).

If the propyl radicals undergo addition and disproportionation (in addition to (5) and (6))

$$2C_3H_7 = C_6H_{14} \qquad (7)$$
$$= C_3H_6 + C_3H_8 \qquad (8)$$
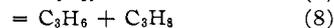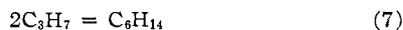
one obtains the following material balance equations

$$R_{H_2} - 3R_{N_2} = R_{C_3H_7NH_2} + R_{C_6H_{14}} + R_{C_3H_6} \qquad (9)$$
$$-R_{C_3H_8} = R_{C_3H_7NH_2} + 2R_{C_6H_{14}} + R_{C_3H_6} \qquad (10)$$
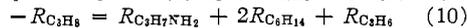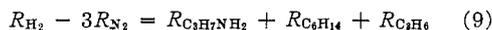
These equations are found not to be obeyed. Mass spectrographic analyses[8] showed 2,3,3,4-tetramethylpentane and an octene to be the principal products volatile above $-80°$. Reactions leading to such products may be postulated, usually by the addition of propyl radicals to propylene, but further speculation on this point is not warranted.

The existence of side reactions makes difficult the use of competitive rates to obtain ratios of rate constants. The ratio k_8/k_7 has values from 0.08 to 0.17 (Table I) which are lower than the 0.5 obtained at room temperature.[9] This can be explained by side reactions which use up propylene.

When oxygen is added to ammonia, hydrogen formation is suppressed but nitrogen formation is not. The reactions

$$NH_2 + O_2 = NO + H_2O \qquad (11)$$
$$NH_2 + NO = N_2 + H_2O \qquad (12)$$

have been suggested.[10] Reaction (12) must be rapid

(8) The author wishes to express his appreciation to Mr. R. C. Wilkerson and his group at the Celanese Corporation of America, Clarkwood, Texas, for performing the mass spectrographic analyses.

(9) (a) R. W. Durham and E. W. R. Steacie, *Can. J. Chem.*, **31**, 377 (1953); (b) F. E. Blacet and J. G. Calvert, THIS JOURNAL, **73**, 661 (1951).

(10) (a) C. H. Bamford, *Trans. Faraday Soc.*, **35**, 568 (1939); (b) H. E. Bacon and A. B. F. Duncan, THIS JOURNAL, **56**, 336 (1934).

compared to (11) if nitrogen formation is to be explained in this way.

The values of $-R_{O_2}/R_{N_2}$ agree with those obtained by Bacon and Duncan[10b] 2.7 to 3.

The system ammonia–oxygen–propane is undoubtedly complex. Acetone is one of the products and undoubtedly results from the isopropyl radical–oxygen reaction, but there is no evidence for or against the formation of an intermediate hydroperoxide. Acetone is also one of the main products in the hydrogen bromide–catalyzed oxidation of propane.[11]

Acetone has strong absorption bands near the mercury lines at 1942 and 1995 Å.[12] Thus acetone will reduce absorption by the ammonia and photochemically give carbon monoxide, methane and ethane. This fact prevented a determination of the competitition between oxygen and propane for hydrogen atoms. Small amounts of acetone markedly decreased the rate of hydrogen formation from ammonia, due undoubtedly to radiation being absorbed by the acetone.

(11) Z. K. Meizus and N. M. Emanuel, *Doklady Akad. Nauk. U.S.S.R.*, **87**, 241 (1952).

(12) W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, *J. Chem. Phys.*, **2**, 717 (1934).

ROCHESTER, N. Y.

The Study of Chlorine Atom Reactions in the Gas Phase

BY H. O. PRITCHARD, J. B. PYKE[1a] AND A. F. TROTMAN-DICKENSON[1b]

The rates of chlorine atom attack on the following compounds: methane, ethane, propane, 2-methylpropane, 2,2-dimethylpropane, cyclopentane, methyl chloride and ethyl chloride, have been related to the rate of the reaction Cl + H$_2$ → HCl + H. The rate factors listed in Table II were deduced from measurements made in the temperature range from 0 to 300°. The activation energies are lowest for those compounds which contain the weakest C–H bonds, but the activation energies and bond strengths are not linearly related. The most reactive compounds react with activation energies less than 1 kcal. No evidence is found for A (pre-exponential) factors greater than the collision rates.

The reactions of chlorine atoms with hydrogen-containing compounds are chain reactions, and as such their over-all rates are very sensitive to the presence of small traces of impurity, to the condition of the surface of the reaction vessel and, in photochemical systems, to the intensity of the absorbed light. Consequently the many attempts which have been made to determine rate constants for the elementary reactions of chlorine atoms have met with disproportionately little success. However, Tamura[2] was able to set an upper limit of 6

(1) (a) College of Forestry, N. Y. State University, Syracuse 10, N. Y.; (b) Chemistry Department, The University, West Mains Road, Edinburgh 9.

(2) M. Tamura, *Rev. Phys. Chem. Japan*, **15**, 86 (1941).

kcal. for the activation energy of reaction 1a.

$$Cl + CH_4 \longrightarrow HCl + CH_3 \qquad (1a)$$
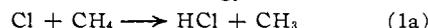
Schumacher and Wolff[3] obtained $E < 4.3$ kcal. for the similar reaction with chloroform.

The rate constant of reaction 1b is known accurately over the temperature range 273 to 1050°K.

$$Cl + H_2 \longrightarrow HCl + H \qquad (1b)$$
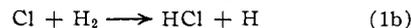
from the work of Ashmore and Chanmugam,[4a] Steiner and Rideal[4b] and Rodebush and Klingel-

(3) H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, **B25**, 161 (1934).

(4) (a) P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953); (b) H. Steiner and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A173**, 503 (1939).