[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

The Photolysis of Solutions of Alkali Metals in Liquid Ammonia

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The classical researches of Kraus and his co-workers[1] on the electrical properties of solutions of metals in liquid ammonia, and the study of their absorption spectra by Gibson and Argo[2] have indicated, beyond serious doubt, the constitution of these solutions. The evidence indicates that the metal is dissociated into the corresponding positive ion and an electron (two electrons in the case of alkaline earth metals) which becomes associated with the solvent. The degree of solvation is a maximum at low concentration.

At slightly elevated temperatures, or in the presence of catalysts, the dissolved metal reacts with the solvent, yielding the metal amide and hydrogen. The metal ion probably plays little part in this reaction, which may be considered as taking place between the electrons and the solvent, with the production of amide ion and hydrogen. In the absence of catalysts, such as metallic oxides and hydroxides, the reaction is very slow at ordinary temperatures.

It has been reported by Joannis[3] that sunlight produces an appreciable acceleration of this reaction. Evidence reported here indicates that this effect was probably due to heating. The authors have, however, observed a definite photochemical reaction in the short ultraviolet. When pure liquid ammonia is exposed to light of the same spectral region which causes the decomposition of gaseous ammonia (2300 Å.), no observable change is produced; but when metallic solutions are so exposed, a reaction occurs, with the production of amide ion and hydrogen. As will be shown, the existence of such a reaction, and its quantitative study, is of interest not only in itself, but also in relation to the photodecomposition of gaseous ammonia, and the results of such a study are reported in the present paper.

Experimental Details

Light Source.—A condensed spark discharge served as the source of ultraviolet light for most of the work, although a quartz mercury arc was used in some of the preliminary qualitative experiments. The spark gap was of new design, whose details are indicated in Fig. 1. The spark passed between the tapered edges of two rotating disks A,A′, mounted on hollow shafts B,B′, through which cooling water was circulated. To provide insulation, the cooling water circuit was broken by sprinklers with a fall of several feet. The frames holding the shafts were movable, so that the gap length could be

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(1) Kraus, "Properties of Electrically Conducting Systems," A. C. S. Monograph No. 7, 1922.

(2) Gibson and Argo, THIS JOURNAL, **40**, 1327 (1918).

(3) Joannis, "Recherches sur le sodammonium et la potassammonium," Paris, 1906.

adjusted by means of screws I,I′. A separation of about 1 cm. was usually employed. The shafts were belt driven in opposite directions at the rate of several hundred r. p. m. by a $^{1}/_{4}$ h. p. motor. Electrical contact was made through heavy carbon brushes L,L′, connected to the terminals of a 0.010 mfd. oil-immersed condenser across the secondary of a rebuilt 5 k. w. x-ray transformer. By this means one to two discharges per half-cycle were obtained across the gap. A vacuum cleaner hose mounted close behind the spark drew off objectionable fumes. The gap was readily demountable, which allowed cleaning and reoiling of bearings and interchange of electrode disks. Cobalt and cadmium electrodes were used for most of the investigation. The latter eroded slowly and required occasional returning. The rotation and cooling of the electrodes rendered the spark quite steady in position and intensity.

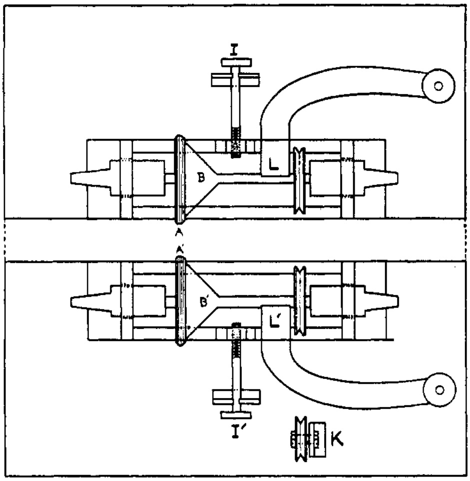

Fig. 1.—Spark gap with rotating water-cooled electrodes.

Monochromator.—Monochromatic light was obtained from the spark by a quartz optical system. The split Bakelite panel holding the electrodes was mounted in a wooden housing box, the spark being vertical. The box was fastened to slotted brass bars allowing it to slide on a brass track, which in addition carried a condensing lens, slit and collimating lens, and was pivoted under the front face of a large Cornu prism. By rotating the track and adjusting the position of the spark and of the first slit the desired spectral line could be focused sharply upon the exit slit. Light from this was focused by a small fluorite lens upon the thermopile slit. The reaction cell (*vide infra*) was interposed directly in front of the thermopile. A shutter on the box housing most of the optical system was operated by a remote control.

Thermopile–Galvanometer System.—Light intensity was measured with a line thermopile constructed by one of the authors in this Laboratory, following the details given in an earlier paper.[4]

The thermopile was connected to a Leeds and Northrup high sensitivity galvanometer by leads enclosed in a grounded iron sheath. The ballistic method of reading the galvanometer was employed, a thirty-ohm resistance being inserted in the circuit to give the proper damping. Careful experiments showed the thermopile to be sufficiently uniform in sensitivity to integrate correctly the intensity of a non-homogeneous beam falling on its surface. Horizontal integration was obtained by moving the pile with a millimeter screw. Three settings separated by the width of the slit sufficed to integrate the beam completely, about 80% of the total deflection being obtained at the central setting. Calibration with radiation standards of the Bureau of Standards was carried out in the usual fashion. The response was found to be a linear function of intensity over the entire range of deflections employed in the course of the subsequent work.

Reaction Cell and Pressure Gage.—The apparatus for containing the liquid ammonia to be investigated is shown in Fig. 2a. It will be observed that it was small and easy of transport. As all work was at room temperature, the apparatus was required

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(4) Leighton and Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

to withstand a pressure of over eight atmospheres. The cell, "a," was constructed from clear Vitreosil tubing 12 mm. in diameter, and had a capacity of 4 cc. It was attached through a graded seal to the remainder of the apparatus, which was of Pyrex. The amount of reaction was determined by freezing out the ammonia in cell "a" with liquid air, and measuring the pressure of non-condensed gas (hydrogen or nitrogen) in the closed system with a micro McLeod gage, b. This was operated by a glass plunger, c, containing a piece of soft iron, magnetically controlled by a solenoid slipped over the closed leg. To work the gage the plunger was forced down, thus displacing mercury and causing it to rise into the bulb, b. The mercury levels were read to 0.01 mm. with a Wilson traveling microscope. The gage was capable of indicating pressures up to 2.5 mm. with an accuracy of about 0.005 mm.

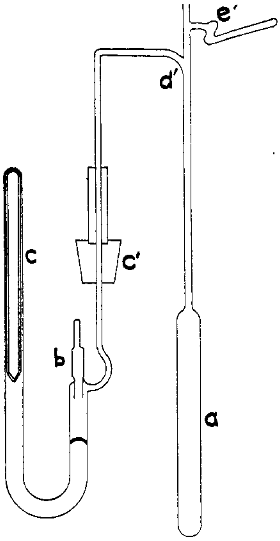

Fig. 2a.—Reaction cell and pressure gage.

For quantitative experiments, the apparatus was held by a clamp in a fixed position with the cylindrical silica cell immersed in a water-filled jacket with plane parallel quartz sides. The cell was held vertically by glass plates at top and bottom with snugly fitting holes. This water jacket was mounted on a brass plate with holes fitting over pegs in the thermopile track, so that it could be readily removed but brought back to a position in which the light beam traversed the diameter of the cylindrical cell. Inasmuch as fused silica and water have nearly identical refractive indices at the wave lengths employed, refraction at the cylindrical interface was negligible. The same was true of the silica–liquid ammonia interface. The convergent beam was quite narrow, and suffered very little spreading in traversing the water jacket with the immersed liquid-filled cell.

Gas Line.—The line used in evacuating the reaction apparatus and obtaining ammonia samples is shown in Fig. 2b. The reaction apparatus was sealed on at A. By two diffusion pumps backed with an oil pump the line could be evacuated to pressures too small to be read on a McLeod gage ($<10^{-6}$ mm.). The interchangeable ground joint B was used for glass blowing, releasing pressure, etc. The trap H allowed condensation and final drying of ammonia by sodium introduced through the ground joint.

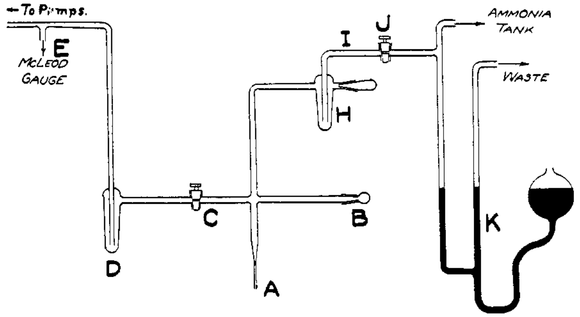

Fig. 2b.—Gas train for preparing materials and filling cell.

Materials.—The ammonia was a synthetic product of high purity. It was stored over sodium (which removed water and traces of organic impurities) in a small steel cylinder with a delicate needle valve.

The sodium and potassium were pure Baker samples. The cesium was obtained from Professor Fogg, of the University of New Hampshire. The metals were melted in a vacuum and filtered through a fine constriction into thin-walled capillaries. Final purification was achieved by distillation as described below.

Procedure

Preparation of Alkali Metal Solutions in Ammonia.—The reaction apparatus in Fig. 2a was sealed to the gas line at A in Fig. 2b and evacuated to the lowest obtainable pressure (trap O was immersed in a solid carbon dioxide–acetone bath) while all parts not adjacent to the mercury were strongly heated to drive out adsorbed gases. Ammonia was then admitted at a pressure such that it escaped through the bubbler, K. The tip of the small side arm e′ (Fig. 2a) was heated, thus blowing out a hole from which ammonia issued rapidly, preventing ingress of air. The desired length of capillary filled with the proper metal was broken off in the ammonia stream and quickly inserted into the hole, whence it slid down to the small bulb. The projecting tubing was then sealed off, the pressure being momentarily released by unseating the cap of B. The system was again evacuated, and the side arm e′ was gently heated. In the high vacuum the metal vaporized without attacking the glass, and condensed as a bright mirror in the adjoining vertical tube, down which it was driven by careful heating.

During this distillation the small trap C′ in Fig. 2a was kept full of pulverized solid carbon dioxide to prevent diffusion of mercury vapor to the alkali metal. The system was again filled with ammonia gas. By swabbing the outside of the vertical tube d′ with cotton dipped in a solid carbon dioxide-acetone bath, ammonia was condensed and the metal washed down into the silica cell. The desired amount of liquid ammonia (usually 1–2 cc.) was then condensed in the latter. (The ammonia could be subjected to final drying with sodium in trap H (Fig. 2b), but this was usually unnecessary.) The ammonia was frozen in liquid air, and the system was again evacuated. The apparatus was sealed off a little below the side arm, e′ (Fig. 2a). The ammonia was then allowed to warm to room temperature.

The concentration of each solution was determined after completion of the experiments. The apparatus was weighed accurately and then opened without loss of glass by heating the tip where it was originally sealed off, the ammonia being cooled to a temperature slightly above the boiling point. After the slow escape of the ammonia the apparatus was again weighed, the loss representing ammonia. The Pyrex tube leading to the cell was severed, and a drop of water was admitted to decompose the residue of metal and amide. Traces of ammonia were removed by warming and repeated evacuation. The residual hydroxide was titrated in the cell with 0.0216 *N* hydrochloric acid (methyl red indicator). Using 0.610 for the density of liquid ammonia (the density of the fairly dilute solutions is practically that of the solvent) at 20°,[5] the normality of the solution was readily found.

Qualitative Observations on Pure Liquid Ammonia.—Samples of pure liquid ammonia were prepared in the apparatus by the above procedure (with omission of metal). By immersion of the silica cell in liquid air the pressure of ammonia was rendered negligible[6] and that of products of photodecomposition (nitrogen and hydrogen) could be measured with the gage. In all of the samples prepared the original pressure of noncondensed gas was negligible. The cell was then placed in the position of the first slit of the optical system and the total radiation from the spark was focused on it, the vapor

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[5] Cragoe and Harper, *Bur. of Standards Sci. Paper*, **420** (1921).

[6] From the data of Karwat, *Z. physik. Chem.*, **112**, 986 (1929). The vapor pressure of solid ammonia at liquid–air temperature was calculated to be less than 10^{-6} mm.

space being protected by a black paper jacket. Exposures up to an hour with light from zinc, aluminum, cobalt and cadmium sparks were made. In every case no increase of gas pressure could be detected after illumination. When the vapor space was exposed, in four minutes a pressure of 4 to 5 mm. was developed.

Qualitative Observations on Sodium Solutions.—The first solutions were prepared as above, but in the silica cell without attached gage. Since the metal solution is an intense blue and that of the amide a very pale yellow, color fading was used as the criterion of reaction. Carefully prepared solutions showed no noticeable color change on several days standing, in ordinary light. Exposure to intense radiation from a quartz mercury arc caused rapid fading, yielding finally the pale yellow amide solution. Solutions in glass vessels showed no such fading, indicating the active radiation to be of wave length shorter than 3000 Å.

Further experiments were made with the cell attached to the gage. Long standing under ordinary conditions produced only very small amounts of gas. Illumination for a few minutes with the full radiation from a cadmium spark resulted in a considerable gas pressure. The gas produced was almost completely combustible by hot copper oxide (contained in a small side arm, heated externally), indicating it to be practically pure hydrogen.

Quantitative Study of Photolysis of Alkali Metal Solutions.—The reactions were thereafter followed by measuring the pressure of evolved hydrogen. The liquid air was kept at a definite mark on the tube leading to the cell, and the space thus immersed was assumed to be at 90°K. The short section of tubing leading from the liquid air to the mouth of the Dewar vessel was assumed to be at 190°K.—the approximate mean of room and liquid air temperatures. (Any error in this assumption should be insignificant because of the small fraction of the total volume involved.) The temperature of the gage and remaining tubing was taken as 293°K. At the conclusion of each set of experiments the volumes of the above sections were measured. From the volume of the liquid air cooled space it was necessary to subtract the volume of solid ammonia, found from its weight (*vide supra*) and the density at 90°K., 0.836.[7] A slow thermal reaction was found, and was corrected for by making blank experiments of the same duration as the exposures. The observed pressure increase was subtracted from that resulting from illumination. This correction was irregular, but always small (0.01–0.04 mm.) and was significant only in experiments in which the quantum efficiency was small. This "thermal reaction" was probably due chiefly to catalysis by mercury vapor from the gage. Since the amount of photochemical reaction was always too small to affect the concentration appreciably, several successive runs could be made on one solution, thus reducing the labor of preparation.

Since the reaction was

$$\mathrm{M} + \mathrm{NH_3} \longrightarrow \mathrm{MNH_2} + {}^1/_2\mathrm{H_2}$$

the number of alkali metal atoms (and ammonia molecules) reacting was

$$\frac{2NP}{R}\left(\frac{V}{293} + \frac{V'}{190} + \frac{V'' - X}{90}\right)$$

where P is the corrected pressure increase, N Avogadro's number, R the gas constant, X the volume of solid ammonia and V, V' and V'' are the respective volumes of the different sections of the apparatus.

Exposures of fifteen minutes were usually employed. The light intensity was determined before and after each exposure and the mean was taken as the average. In no case was the drift more than a few per cent. At each wave length used measurements were made with the thermopile of the fraction of light transmitted by the water jacket

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[7] McKelvey and Taylor, *Bur. of Standards Sci Paper*, **465** (1923).

filled with water and by the jacket containing the silica cell filled with water. The interfacial losses were calculated from Fresnel's law. The quartz plates were found to show no appreciable absorption at any of the wave lengths employed. From the results of the measurements were calculated the fractions absorbed by the water layer between the quartz plate and silica cell, and by one wall of the silica cell. In all runs light reaching the solution was totally absorbed, and reflection at the silica–liquid ammonia interface could be neglected.

The transmission of the quartz thermopile window for ultraviolet light was assumed to be that calculated from Fresnel's law, since the thin quartz plates used were found to show no appreciable absorption. The transmission for the standard lamp radiation was 0.91. The above data, together with the calibration of the thermopile–galvanometer system, sufficed to calculate the total light energy and hence (from the known wave length) the number of light quanta absorbed by the solution.

Experimental Results

The qualitative studies indicate that the quantum efficiency for the photodecomposition of pure ammonia in the liquid phase must be negligibly small.

The quantum efficiency of the photoreaction of sodium, potassium and cesium with liquid ammonia was measured at various concentrations and at wave lengths 2313, 2194, 2144 Å. (Cd spark), 2550, 2397 and 2286 Å. (Co spark). The results are compiled in Table I. The values of Φ, the quantum efficiency, are the number of alkali metal atoms (or ammonia molecules) reacting per quantum.

It will be seen that the check determinations are in fair agreement, particularly for the larger values of Φ. For the smaller values the experimental error is greater, and the agreement is not as good. As regards the absolute accuracy of the values obtained, it is believed that no serious consistent errors were present. The general trend of the results indicates that adsorption of hydrogen by solid ammonia cannot be large, a result which the work of Wiig and Kistiakowsky[8] confirms. The accuracy of the over-all procedure was checked by separate determinations of the quantum efficiency of hydrogen bromide decomposition, using essentially the same apparatus and method. Within the limits of error this was found to be 2.0, in agreement with the accepted value.

TABLE I

Expt.	Metal	Normality of soln.	λ, Å.	Exposure, sec.	Quanta abs. $\times 10^{-17}$	Corr. press. H_2, mm.	Φ
1	Na	0.0017	2313	900	7.211	0.047	0.047
				900	7.418	.030	.029
				900	7.280	.049	.049
						Average	.042
2	Na	.0060	2313	900	7.537	.072	.068
				855	6.952	.048	.049
				900	6.443	.053	.059
						Average	.059

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(8) Wiig and Kistiakowsky, THIS JOURNAL, 54, 1806 (1932).

TABLE I (*Concluded*)

Expt.	Metal	Normality of soln.	λ, Å.	Exposure, sec.	Quanta abs. × 10^{-17}	Corr. press. H_2, mm.	Φ
3	Na	0.0131	2313	900	7.396	0.150	0.164
				900	7.501	.116	.125
						Average	.144
4	Na	.0536	2313	900	7.164	.230	.272
				900	7.153	.200	.237
						Average	.254
5	Na	.0096	2397	900	7.506	.136	.147
				900	7.891	.120	.123
						Average	.135
6	Na	.0422	2397	900	7.204	.157	.185
				900	7.324	.155	.180
						Average	.182
7	Na	.1055	2397	900	7.057	.200	.244
				900	6.664	.160	.227
						Average	.236
8	Na	.0389	2550	900	7.150	.036	.042
				900	7.122	.010	.011
						Average	.026
9	Na	.0389	2286	900	6.924	.193	.230
				900	6.708	.205	.253
						Average	.242
10	Na	.0389	2194	900	3.797	.057	.124
				900	3.820	.056	.121
						Average	.122
11	Na	.0389	2144	900	2.941	.027	.077
				900	2.990	.030	.083
						Average	.080
12	K	.0040	2313	900	6.784	.047	.057
				900	7.174	.030	.034
						Average	.046
13	K	.0274	2313	900	7.171	.188	.222
				900	6.987	.151	.183
						Average	.202
14	Cs	.0080	2313	900	6.931	.018	.022
				900	6.503	.040	.052
						Average	.037
15	Cs	.0170	2313	900	6.622	.078	.108
				450	3.418	.036	.097
						Average	.102

It will be seen that the quantum efficiency for photolysis of alkali metal solutions in ammonia is a function of both concentration and wave length. The range of conditions is not as great as could be desired, but enough data have been obtained to reveal some very interesting relations. In Fig. 3 are plotted the values of the quantum efficiency against concentration for two wave lengths. At 2313 Å. the curve is seen to pass through the origin and apparently to approach an asymptote of unity or less at high concentrations. The values for sodium and potassium both lie on this curve, but those for cesium are lower. The curve at 2397 Å. is lower and flatter.

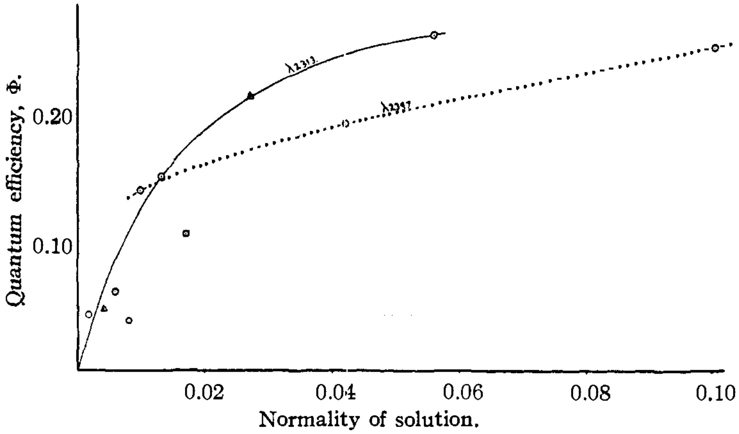

Fig. 3.—Quantum efficiencies for photolysis of liquid ammonia solutions of alkali metals at various concentrations: ⊙, sodium; △, potassium; ⊡, cesium.

In Fig. 4 Φ is plotted against wave length for a fixed concentration. There is a definite long wave threshold, in agreement with the qualitative

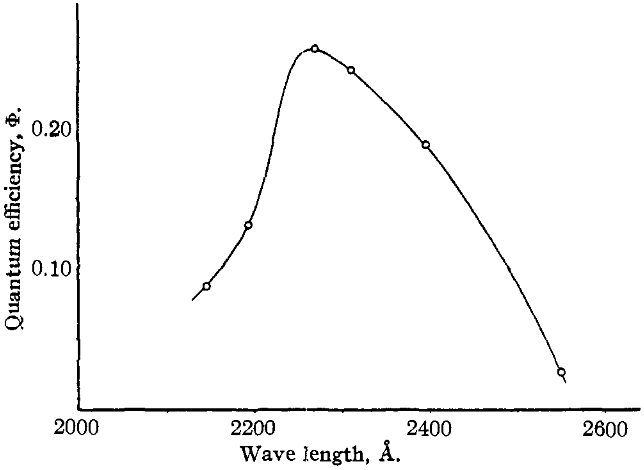

Fig. 4.—Quantum efficiencies for photolysis of a 0.0389 *N* solution of sodium in liquid ammonia at various wave lengths.

observations as to the ineffectiveness of light of long wave lengths. It should be pointed out that the falling off of Φ at short wave lengths may be due partly to the smaller intensity of the light employed. No direct observations as to the effect of intensity were made. Also it is possible that the values at the short wave lengths are somewhat in error, since they are based on rather small amounts of reaction.

For aid in interpreting the above results, the absorption spectra of pure ammonia, both liquid and gas, and of solutions of sodium and potassium in liquid ammonia were investigated. The silica cell immersed in the water jacket at 20° was used for the liquids. For work with the metals the cell was attached to a graduated side arm so that measured dilutions could be made. The continuous spectrum from a hydrogen discharge tube was used as a source. The spectra were photographed with a large quartz spectrograph. Pure liquid ammonia was found to be quite transparent to wave lengths longer than 2500 Å. Below this the absorption increased quite rapidly and became total at about 2350 Å. The last absorption band of the gas is at 2260 Å.,[9] so the liquid absorbs to considerably longer wave lengths than the gas. Solutions of sodium and potassium were found to show identical absorption, consisting of a fairly strong continuum throughout the ultraviolet region. The absorption apparently decreased slightly toward short wave lengths but extended to the region absorbed by the pure solvent.

Solutions of sodium and potassium amides in liquid ammonia were also investigated and found to show very strong continuous absorption throughout the ultraviolet with a pronounced maximum of absorption near the long wave threshold. For sodium amide the long wave length threshold was at 3800–3900 Å. (depending on concentration), and the maximum at 3400 Å. For potassium amide the threshold was 3950–4150 Å., and the maximum at 3420 Å. The absorption of both is thus seen to extend into the violet, which accounts for the pale yellow color of the solutions. Potassium amide solution is distinctly more yellow to the eye than sodium amide, in agreement with the longer wave length threshold for the former. It is interesting to observe that when these amide solutions are cooled to $-33°$ they become perfectly colorless. The recession of the threshold toward shorter wave length with decreasing temperature is to be expected.

Discussion

The diffuse banded absorption spectrum of gaseous ammonia and many facts concerning its photodecomposition led Bonhoeffer and Farkas[10] to postulate that the excited ammonia molecule undergoes spontaneous dissociation within a time small as compared with the period of rotation of the molecule—the process being termed predissociation. Evidence that the dissociation products are a hydrogen atom and NH_2 radical was

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[9] Leifson, *Astrophys. J.*, **63**, 73 (1926).

[10] Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337 (1928).

found by Gieb and Harteck,[11] who detected hydrogen atoms in photodecomposing ammonia.

Taking a dissociation of the ammonia molecule as the primary process, the results of the present investigation are capable of interpretation by the following simple mechanism

$$\begin{aligned}
NH_3 + h\nu \longrightarrow (NH_3') \longrightarrow H + NH_2 \qquad & (1)\\
H + NH_2 + NH_3 \longrightarrow NH_3 + NH_3 \qquad & (2)\\
2H + NH_3 \longrightarrow H_2 + NH_3 \qquad & (3)\\
NH_2 + \theta(NH_3)_x \longrightarrow NH_2^- + xNH_3 \qquad & (4)\\
NH_2^- + M^+ \longrightarrow MNH_2 \qquad & (5)
\end{aligned}$$

It appears probable that the triple collision with an ammonia molecule or other foreign molecule is necessary for the recombination of H and NH_2 (Equation 2), a conclusion also arrived at by Wiig and Kistiakowsky[8] in considering the mechanism for the photodecomposition of gaseous ammonia. In gaseous ammonia such triple collisions are comparatively rare, and the hydrogen atoms and amide radicals have opportunity to undergo other reactions leading to the eventual production of nitrogen and hydrogen. In the close packed liquid these triple collisions with the solvent molecules must be very frequent, with the result that there is a very large probability that the primary dissociation fragments will recombine before undergoing collisions with similar fragments from other molecules. This is attested by the observed fact that pure liquid ammonia undergoes no appreciable photodecomposition. Likewise it was observed by Kuhn[12] that aqueous solutions of ammonia undergo no photodecomposition—a fact readily explained by assuming that the solvent water molecules act as triple collision partners in promoting the recombination of H and NH_2. Of course this process of recombination in the very act of dissociation may be regarded simply as a deactivation of the excited molecule by collision with a molecule of the solvent. The important point is that there would be an appreciable time lag before the deactivation occurred, particularly since it is probable that only a small fraction of the triple collisions with foreign molecules would be effective in causing recombination of the fragments—a general characteristic of termolecular reactions.

In solutions of alkali metals, as was previously pointed out, the metal is almost completely dissociated into positive ions and solvated electrons. If the electron collides with the amide radical during the brief period before the latter recombines with the hydrogen atom, an amide ion results (Equation 4) and the hydrogen atom is set free to combine with another hydrogen atom. The electron thus acts as an acceptor for the NH_2 radical. Since the probability that an NH_2 radical will collide with electrons increases with the concentration of the latter, the quantum efficiency should increase regularly with concentration, starting at zero and approaching

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[11] Gieb and Harteck, *Z. physik. Chem.*, Bodenstein Festband, 849 (1931).

[12] Kuhn, *Compt. rend.*, **178**, 708 (1924).

unity asymptotically. This is seen to be the form of the curve in Fig. 3. At high concentrations other complicating factors probably enter in, and so it is not surprising that the apparent probable upper limit for Φ is less than unity. It will be observed that the positive ion plays no essential part in this mechanism, other than to eventually combine with the amide ion (since the metal amides are very weak electrolytes in ammonia). Hence the value of Φ should be independent of the metal. It will be observed that the values of Φ for sodium and potassium do fall on the same smooth curve. However, cesium shows abnormally low values. The explanation of this anomaly is uncertain. It seems improbable that cesium would be considerably less dissociated than sodium or potassium in ammonia, although there are no conductivity data to decide this point. A possible explanation of the behavior of cesium is given below in discussing the effect of wave length.

The variation of Φ with wave length is quite readily explained. By the above mechanism, only light absorbed by ammonia molecules is effective in producing reaction. However, in the alkali metal solutions the electron–ammonia complex also has a strong absorption, although no reaction is produced. Hence the pure ammonia and the electron complex compete for light energy. Since the quantum efficiency is necessarily based on the total light absorbed, light absorbed by the electron complex results in a corresponding decrease in Φ. It was found that the absorption of the electron–ammonia complex is about equally strong through the ultraviolet, whereas that of pure liquid ammonia shows a marked long wave threshold in the neighborhood of 2400 Å. It is to be observed that this absorption threshold coincides approximately with that for the reaction. A further bit of evidence is the variation of Φ with concentration at 2397 Å. At this wave length both the pure liquid and the electron–ammonia complex absorb an appreciable fraction of light. Increasing the concentration of the metal tends to increase Φ by the above mechanism. However, it also increases the fraction of light absorbed by the electron complex, and so decreases Φ. The partial counterbalancing of these two effects accounts for the smaller slope (*i. e.*, smaller increase of Φ with concentration) of the curve at 2397 Å. as compared with the curve of 2313 Å.

The falling off of Φ at shorter wave lengths is not so readily explained. If the effect is real (*vide supra*) it may be due to a strong absorption region of the undissociated fraction of the metal, causing an effect similar to that of the electron–ammonia complex at long wave lengths. Such an effect would be expected to be specific for the given metal, and the anomalous behavior of cesium may be due to some such cause.

The results of the present investigation may be regarded as constituting a direct detection of the NH_2 radicals as one of the products of photodecomposition of ammonia. The evidence seems to indicate that NH_2 radicals and hydrogen atoms combine by three-body collision in liquid ammonia. It therefore appears probable that this reaction takes place in the gas, and is one of the secondary reactions in the photodecomposition of gaseous ammonia.

With regard to the spectra of the alkali amides, they appear to furnish evidence as to the constitution of these molecules. The light absorbing species is almost certainly the undissociated molecule, since the amides are known from conductivity measurements[1] to be very weak electrolytes. Further, neither alkali metal nor amide ions would be expected to show appreciable absorption in the observed spectral region. Spectra of the type found for sodium and potassium amides are usually associated with the optical dissociation of the molecule. In this case the process is probably

$$\mathrm{MNH_2} \xrightarrow{h\nu} \mathrm{M} + \mathrm{NH_2}$$

If this is true the energy of the light quantum corresponding to the absorption maximum should be close to the upper limit of the dissociation energy. Only for sodium amide is it possible to calculate the dissociation energy thermochemically. The heat of formation of solid sodium amide was determined by de Forcrand[13]

$$\mathrm{NH_3(g)} + \mathrm{Na(s)} \longrightarrow {}^1/_2\,\mathrm{H_2(g)} + \mathrm{NaNH_2(s)} + 20{,}840 \text{ calories}$$

Taking

$$\mathrm{NH_3} \longrightarrow \mathrm{H} + \mathrm{NH_2} - 113{,}000 \text{ calories}^{14}$$
$$\mathrm{H} \longrightarrow {}^1/_2\,\mathrm{H_2} + 50{,}750 \text{ calories}$$

one finds

$$\mathrm{NaNH_2} \longrightarrow \mathrm{Na} + \mathrm{NH_2} - 83{,}000 \text{ calories}$$

This calculation takes no account of the energy differences in sublimation or solution of $\mathrm{NaNH_2}$ and Na, but is sufficient to show that the thermochemical value lies between the energy corresponding to the absorption maximum of $\mathrm{NaNH_2}$ at 3400 Å. (84,000 cal.) and the energy corresponding to the long wave length limit of absorption, approximately 75,000 calories.

It therefore appears probable that sodium amide is optically dissociated into a normal sodium atom and normal amide radical, and hence is ionically bound. Potassium amide is probably of similar constitution.

Summary

The photolysis of pure liquid ammonia and of solutions of sodium, potassium and cesium in liquid ammonia has been investigated. Pure liquid ammonia has been found to undergo no photodecomposition in short ultraviolet light, while illumination of the alkali metal solutions was shown to result in amide formation and evolution of gaseous hydrogen.

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(13) De Forcrand, *Compt. rend.*, **121**, 66 (1895).

(14) The reasons for selecting this value for the dissociation energy of ammonia will be given in a later communication.

The quantum efficiency was found to increase regularly with the concentration of the metal, but remained considerably smaller than unity at all concentrations studied. A distinct long wave length threshold was found for the quantum efficiency, and a maximum at around 2300 Å. Pure liquid ammonia was found to absorb light to considerably longer wave lengths than the gas, while solutions of metals and of metal amides show continuous absorption throughout the ultraviolet. The significance of these findings with respect to the photodecomposition of gaseous ammonia is discussed.

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The Photolysis of the Aliphatic Aldehydes.
II. Acetaldehyde

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In an earlier paper[1] the authors have summarized the general features of the photochemical decomposition and polymerization of the aliphatic aldehydes together with the results of a quantitative study of these reactions in the case of propionaldehyde. It was pointed out that the aldehydes present a favorable class of compounds for the study of the relations existing between absorption spectra and photochemical activity. In the aldehydes, three distinct absorption regions have been observed; bands with fine structure, diffuse bands or predissociation, and continuous absorption. These are more differentiated for acetaldehyde than for propionaldehyde, and this paper is concerned with a study of the photochemical reactions produced in acetaldehyde vapor by wave lengths falling in these different regions.

1. **The Absorption Spectrum of Acetaldehyde.**—The absorption band of acetaldehyde vapor which shows the phenomenon of predissociation extends from approximately 3480 to 2300 Å., with a maximum at about 2890 Å. The absorption coefficients have been determined by Smith,[2] and show a nearly symmetrical falling off on both sides of this maximum. Schou and Henri,[3] using a Hilger spectrograph, found that the region of absorption bands with distinct structure sets in, very faintly, at 3484 Å. and extends to the neighborhood of 3300 Å. Below 3300 Å. the structure grows gradually more diffuse and disappears entirely around 3080 Å. The diffuse bands were reported to continue to 2820 Å.

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(1) Leighton and Blacet, THIS JOURNAL, **54**, 3165 (1932).

(2) Smith, Carnegie Inst. Reports, **27**, 178 (1928).

(3) Schou, Doctorate Thesis, Les Presses Universitaires de France, Paris, 1928; Henri and Schou, *Z. Physik*, **49**, 774 (1928); Henri, *Trans. Faraday Soc.*, **25**, 765 (1929).