of bicarbonate at 31.98°, and nowhere requires for its formation more than 3.74% of bicarbonate in the solution.

3. Four invariant temperatures for the ternary system have been found between the temperature of the ternary eutectic at —3.32 and 35.27°.

NEW YORK CITY

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. V. THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA BY RELATIVELY SHORT WAVE LENGTHS

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Very few photochemical studies in the far ultraviolet have been carried out. In a previous paper[1] a report was made of a study of the photochemical decomposition of anhydrous oxalic acid in the far ultraviolet. It was found, qualitatively, that the decomposition proceeded more rapidly with light transmitted by fluorite than with light transmitted by quartz.

The present work was undertaken with the object of determining the quantum efficiency of the decomposition of ammonia in the region of wave lengths below that transmitted by quartz.

I. Experimental Method and Results

It is possible to use fluorite windows for studies of the effects of radiations of slightly shorter wave lengths than those transmitted by quartz. Quartz may be said to transmit, under ideal conditions and in thin layers, as far as 185mμ. Fluorite is considerably more variable in its characteristics and the data on its transmission do not agree among themselves. Fluorite transmits relatively well to about 150mμ and some authors report transmission as far as 100mμ.

Many authors have made spectroscopic investigations in the far ultraviolet. Methods of detection of the radiation were available which were far more sensitive than the ordinary methods which may be used in photochemical studies.

In the case of gas reactions, the rate of reaction can be determined by measurements of the pressure change. It is far more difficult to find a suitable light source, since the sources of light used by spectroscopists for studies in this region are usually too feeble to produce measurable photochemical effects unless the quantum efficiency of the reaction is high. In the present work two sources of light were tried. The first was a discharge tube of the type described by Hopfield.[2] This tube was used with both nitrogen and hydrogen, but the light emitted was found to be too feeble to produce

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[1] Noyes and Kouperman, THIS JOURNAL, **45**, 1398 (1923).

[2] Hopfield, *Phys. Rev.*, **20**, 573 (1922).

measurable decomposition of the ammonia. The second type was a condensed discharge through hydrogen. The spark gap was of tungsten and the hydrogen was passed through in a continuous stream. The spark was brought about by means of a $^1/_4$ kilowatt transformer with a secondary voltage of approximately 8000 volts. A capacity of approximately 0.003 microfarad was used. The tube was cooled by a rapid stream of water and the sputtering was greatly reduced by the rapid flow of hydrogen.

In the preliminary experiments an attempt was made to measure the ammonia decomposition directly with a McLeod gage. This was found not to be feasible.

The procedure finally adopted was to freeze out the ammonia with liquid air and measure the residual pressure with a McLeod gage.[3] The reaction chamber was 9 cm. in length and 2 cm. in diameter. The fluorite window was sealed on with a special vacuum wax and the bulb containing the spark gap was sealed directly to the other side of the window. There was, therefore, no air gap between the source of light and the reaction vessel.

The ammonia used in these experiments was a commercial product. On issuing from the cylinder it passed over sodium hydroxide and then over calcium oxide in order to remove most of the moisture. It was next condensed in a bulb surrounded by carbon dioxide snow and ether. After an appreciable amount had condensed, ammonia was drawn out of the system by a water pump until about 25% of it had disappeared. The system was then shut off from the water pump and the carbon dioxide snow and ether placed around a second bulb containing metallic sodium. After the ammonia had distilled over to the sodium the system was evacuated for a few minutes and the ammonia distilled onto a second quantity of sodium contained in a third bulb. The sodium dissolved in the ammonia to give a deep blue solution which was permanent until the ammonia was distilled off. The ammonia was finally distilled onto ammonium nitrate which had been dried for a period of several hours at a high vacuum and a temperature of 105°. The ammonia from this solution was used as needed.

In order to obtain the effect of radiation transmitted by fluorite but not by quartz, a quartz window was used in part of the experiments. The window was of clear crystalline quartz with a thickness of about 3 mm.

TABLE I

RATE OF DECOMPOSITION OF AMMONIA (WITH QUARTZ WINDOW)

Init. press. of NH_3, mm.	Init. residual press. mm. × 10^3	Final residual press. mm. × 10^3	Time, min.	dp/dt, mm. × 10^3/min.
240	1.423	8.208	406	0.01669
150	0.146	1.778	79	.02066
250	0.821	5.700	271	.01800
			Average	.01845

Since the volume of the entire apparatus was 670 cc. and since one mole of ammonia gives two moles of decomposition products, the rate of decomposition of ammonia when quartz windows are used is found to be ($T = 25°$) 3.32×10^{-10} moles per minute.

In order to calculate the quantum efficiency it is necessary next to determine the light intensity. Since the pressures used were relatively low and the fraction of the total intensity absorbed was small, it would be difficult to use the ordinary methods of determining light intensities.

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[3] The vapor pressure of solid ammonia has been measured by Karwat, *Z. physik. Chem.*, **112**, 486 (1924). Extrapolation by means of his equation shows that at liquid-air temperatures the vapor pressure is less than 10^{-6} mm.

TABLE II

RATE OF DECOMPOSITION OF AMMONIA (WITH FLUORITE WINDOW)

Init. press. of NH_3, mm.	Init. residual press., mm. × 10^3	Final residual press., mm. × 10^3	Time, min.	dp/dt, mm. × 10^3/min.
185	2.043	10.62	188	0.04560
175	0.00	3.037	100	.03037
180	0.091	13.15	375	.03483
180	17.81[a]	25.13	223	.03283
			Average	.03591

[a] In this experiment a quantity of air was purposely admitted. It seems to show that neither oxygen, nitrogen nor water vapor affects the decomposition markedly. Kuhn[4] had previously shown that nitrogen and water vapor are without effect.

From the above data it is found that 6.470 × 10^{-10} moles of ammonia are decomposed per minute when fluorite windows are used.

Accordingly, a photochemical method was finally adopted. Warburg[5] has determined the quantum efficiency for the formation of ozone from oxygen. Since oxygen absorbs in the same region as ammonia, it should be possible to obtain a good measure of the light intensity by means of this reaction.

Warburg[5] finds that two molecules of ozone are formed per quantum absorbed. His values never quite attain this figure, but he used relatively high pressures and the quantum efficiency would approach two molecules per quantum at atmospheric pressure. From theoretical considerations, also, this value is probable.[6] The mechanism may be pictured as a direct dissociation of oxygen with subsequent addition of the two atoms formed to normal molecules.

A calculation based on the data of Landsberg and Predwoditileff[7] shows that for all wave lengths less than 214mμ the absorption by ammonia is practically complete under the conditions of the experiments described. Few accurate quantitative data on the absorption of radiation by oxygen in this spectral region are available. Kreusler[8] has determined the absorption coefficient of oxygen at two different wave lengths, 186mμ and 193mμ. Bloch and Bloch[9] have measured the wave lengths of many absorption lines of oxygen with a quartz spectrograph from 195.75 to 186.48mμ. Warburg[5] at high pressures has obtained ozone at a wave length of 253mμ.

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[4] Kuhn, *Compt. rend.*, **177**, 956 (1923); **178**, 708 (1924); *J. chim. phys.*, **23**, 521 (1926).

[5] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1914**, 872; **1915**, 230.

[6] See Franck, *Trans. Faraday Soc.*, **21**, 536 (1926); Born and Gerlach, *Z. Physik*, **5**, 433 (1921); Hogness and Lunn, *Phys. Rev.*, **27**, 737 (1926); Birge and Sponer, *ibid.*, **28**, 259 (1926).

[7] Landsberg and Predwoditileff, *Z. Physik*, **31**, 544 (1925).

[8] Kreusler, *Ann. Physik*, **6**, 412 (1901); See Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, **1923**.

[9] Bloch and Bloch, *Compt. rend.*, **158**, 1161 (1914); *Le Radium*, **11**, 99 (1914).

Recently, Hopfield and Leifson[10] have studied the absorption spectrum of oxygen, using a layer 2.5 cm. in thickness at atmospheric pressure and the continuous spectrum of hydrogen as a background. They find sixteen clearly-resolved bands between 195 and 176mμ and a great absorption band from 175 to 130mμ. The conclusion may be drawn from the various lines of evidence mentioned that the absorption by oxygen under the conditions of these experiments would be very nearly complete for wave lengths below those transmitted by quartz and down to the limit of fluorite.

It would be possible, therefore, to determine the number of quanta emitted per second in this region of the spectrum by the source of light used in these experiments if oxygen could be passed through the reaction vessel and the amount of ozone formed determined. A similar calculation could not be made for the range of wave lengths transmitted by quartz, since the absorption bands of ammonia and of oxygen do not coincide.

Hydrogen shows only a faint continuous spectrum between 240 and 168mμ, since there is no many-lined spectrum in this region.[11] Since hydrogen at a pressure of one atmosphere begins to absorb strongly at 160mμ,[12] the wave lengths transmitted by fluorite and not by quartz in these experiments lie mainly in the region between 190 and 160mμ. In addition, fluorite transmits slightly better than quartz for the wave lengths slightly longer than 190mμ. The effect of this on the results will be discussed later.

In order to determine the intensity of the light, an exit tube was sealed to the reaction chamber as close to the window as possible. Dry oxygen was streamed through the tube, entering at the back and leaving at the end near the light source.

The quantity of ozone produced by the action of the light used was very small, so that it became necessary to devise a sensitive method for the determination of ozone. A colorimetric method was finally adopted. The oxygen issuing from the reaction vessel was led into a tube in such a manner that it came into contact with a piece of filter paper moistened with a solution of starch and potassium iodide. After the oxygen had streamed for a few minutes with the light on, the paper was observed to have become colored. The color, however, was brown instead of the blue usually associated with the starch-iodine complex. Several experiments were carried out with various oxidizing agents and it was finally found that solutions of hydrogen peroxide produced the same brown color. The equations for these reactions are as follows.[13]

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[10] Hopfield and Leifson, *Phys. Rev.*, **25**, 716 (1925).

[11] Lyman, "The Spectroscopy of the Extreme Ultraviolet," Longmans, Green and Co., London, **1914**, p. 75.

[12] Ref. 11, p. 71.

[13] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1922, Vol. I, p. 904, 940.

$$O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH$$
$$H_2O_2 + 2KI = I_2 + 2KOH$$

A number of starch-potassium iodide papers were prepared. To some of them a drop (weighed to within about 2%) of very dilute hydrogen peroxide was added. These served as standards. Others were exposed to the oxygen-ozone stream and the time which they required to develop a color that matched that of the standards was determined. Several sources of error might be mentioned. 1. The ozone formed might not be completely absorbed by the starch-potassium iodide papers. 2. The ozone might be partially decomposed by the ultraviolet light. The second of these errors is not serious.[11] However, both of these errors would produce an effect in the same direction, namely, the time of formation of the proper brown color would be increased. An idea of the error could be obtained by a variation of the rate of flow of the oxygen. Increase in the rate of flow produced no regular variation in the time required for a given darkening. The maximum variation was not over 20%, while the rate of flow was nearly tripled in some instances. In addition, two different concentrations of hydrogen peroxide were used, one three times the other, and the ratio of the average times for darkening is nearly the same as the reciprocal of the ratio of the concentrations.

The hydrogen peroxide solutions were made by diluting ordinary hydrogen peroxide to about 0.1 *N* and titrating with permanganate. This solution was subsequently diluted to 0.001591 *N* or 0.000530 *N*. In all of this work conductivity water was used. A fresh solution of hydrogen peroxide was prepared each day, although it was found that the solution could be kept fairly well in the dark. The oxygen was dried by phosphorus pentoxide before exposure to the light.

The weight of solution used was always 0.048 g., within about 2%. When the 0.001591 *N* solution was used with the fluorite window the average time for equivalent darkening was 30.10 minutes with a maximum deviation of 9.7%. With the 0.000530 *N* solution and fluorite window the average time was 10.07 minutes with a maximum deviation of 14.3%. With the 0.000530 *N* solution and the quartz window the average time was 36.21 minutes with a maximum deviation of 9.6%.

The ratio of the two concentrations used is 1:3.002, whereas the ratio of the average times is 2.989:1. One drop of the 0.000530 *N* solution is equivalent to 1.272×10^{-8} mole of ozone. The above figures give as a result, therefore, the production of 1.263×10^{-9} mole of ozone per minute when fluorite windows are used. A similar calculation with the more concentrated solution gives 1.268×10^{-9} mole per minute. For the quartz window it is found that 0.352×10^{-9} mole of ozone is formed per minute. The difference, or 9.14×10^{-10}, is the number of moles of ozone formed per minute by radiation transmitted by fluorite but not by quartz. If the assumption is now made[5] that two molecules of ozone are formed per quantum absorbed, it is found that 2.77×10^{14} quanta per minute are transmitted by fluorite in the region in which quartz does not transmit. Returning now to the photochemical decomposition of ammonia, it is found that 3.15×10^{-10} mole of ammonia is decomposed per minute by the radiation transmitted by fluorite but not by quartz. Multiplication by Avogadro's number (6.06×10^{23}) gives 1.91×10^{14} molecules of ammonia decomposed per minute. It is found, therefore, that on the average 0.690 molecule of ammonia is decomposed per quantum absorbed or, in other words, that 1.45 quanta are required on the average to decompose one molecule.

It is difficult to estimate the accuracy of this figure for the quantum efficiency. The determination of the quantity of ozone should not be in doubt by more than 10%. The values for the rate of decomposition of ammonia show good agreement with one exception. The actual numerical value may probably be written as 1.45 ± 0.50 quanta per molecule if the assumptions made in this work are justified. The assumption that both oxygen and ammonia absorb completely in the region between 190 and 160mμ seems to be justified on the basis of the best data available. The effect of the slightly better transmission of fluorite in the region between 190 and 220mμ would be to make the number of quanta absorbed per molecule too high rather than too low in the region under consideration.

II. Discussion of Results

The calculations made above are based on the assumption that the photochemical decomposition of ammonia proceeds according to the equation

$$2NH_3 = N_2 + 3H_2 \tag{1}$$

This reaction has apparently been assumed by Warburg[14] and by Kuhn.[4] The former found that four quanta are absorbed per molecule decomposed in the spectral region 214–202.5mμ. The latter for the same spectral region found that 2.2 quanta are absorbed per molecule decomposed but that as the light became more nearly monochromatic (210–206.3mμ), about ten quanta were required on the average to make one molecule decompose.

More recently, Dickinson and Mitchell[15] and Taylor and Bates[16] have studied both the direct photochemical decomposition of ammonia and the decomposition sensitized by mercury vapor. No measurements of the quantum efficiency were made by either of these authors. There are some slight disagreements between the researches of these authors, but both are in agreement that more hydrogen is obtained in the noncondensable gases during the direct (unsensitized) photochemical de-

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[14] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1911**, 746; **1912**, 216.

[15] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); Mitchell and Dickinson, THIS JOURNAL, **49**, 1478 (1927).

[16] Taylor and Bates, *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

composition than would be obtained if equation (1) were obeyed. This may indicate, perhaps, the formation of hydrazine. Taylor and Bates report that the non-condensable gases contain 96% of hydrogen, while Dickinson and Mitchell report 87% of hydrogen. Since Taylor and Bates used a dynamic method, while Dickinson and Mitchell used a static method, the discrepancy may be due to subsequent photochemical decomposition of hydrazine if it is left exposed to radiation. Since a static method was used in the experiments herein reported, and, in addition, a shorter wave length than that used by the other authors, the decomposition to nitrogen and hydrogen probably represents the majority of the reaction. In case hydrazine were formed, the number of molecules decomposed per quantum would be larger than that given above.

We may state, however, with a good deal of assurance that the quantum efficiency for the decomposition of ammonia is higher in the region 190–160mμ than it is in the region of the spectrum employed by Warburg[14] and by Kuhn.[4] Kuhn also reports that the quantum efficiency increases with the temperature and that at 500° only 0.3 quantum is absorbed per molecule decomposed. On the basis of the following heats of reaction

$$2NH_3 = N_2 + 3H_2 - 23{,}000 \text{ cal.}$$
$$H_2 = 2H - 84{,}000 \text{ cal.}$$
$$N_2 = 2N - 140{,}000 \text{ cal.}$$

Kuhn has calculated that the dissociation

$$NH_3 = N + H + H_2$$

involves the absorption of about 124,000 calories. This corresponds to light of about 230mμ in wave length. Kuhn proposes a mechanism to account for the various observed facts. The criticism to which this mechanism is open is that the heats of dissociation used are probably too small. Witmer[17] gives 100,000 calories per mole as the heat of dissociation of hydrogen obtained from an analysis of band spectra. Birge and Sponer[6] give about 260,000 for nitrogen. While little confidence can be placed in mechanisms based on the sort of calculation referred to, it may be of interest to list those reactions which are possible and those which are not possible, using as a basis these more recent values for the heats of dissociation of hydrogen and of nitrogen. For a wave length of 208mμ, corresponding to 137,000 calories per mole, it is found that the following reactions are possible

$$h\gamma + NH_3 = NH_3^* \qquad (2)$$
$$NH_3^* + NH_3 = N_2 + 3H_2 + 114{,}000 \text{ cal.} \qquad (3)$$
$$NH_3^* + NH_3 = N_2 + 2H_2 + 2H + 14{,}000 \text{ cal.} \qquad (4)$$
$$NH_3^* + H = N_2 + 2H_2 + 45{,}500 \text{ cal.} \qquad (5)$$
$$NH_3^* + H_2 = 2H + NH_3 + 37{,}000 \text{ cal.} \qquad (6)$$
$$NH_3 + N = N_2 + H_2 + H + 68{,}500 \text{ cal.} \qquad (7)$$

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[17] Witmer, *Phys. Rev.*, **28**, 1221 (1926).

The following reactions are found to be impossible:

$$NH_3 + h\nu = N + H + H_2 - 54{,}500 \text{ cal.} \quad (8)$$

$$NH_3^* + N_2 = NH_3 + 2N - 123{,}000 \text{ cal.} \quad (9)$$

$$NH_3 + H = N + 2H_2 - 91{,}500 \text{ cal.} \quad (10)$$

Any mechanism based on these figures would be somewhat different from that given by Kuhn. If there were no dissipation of energy, the resulting quantum efficiency would be 2, but this would not be expected in any actual case. Equation (6) is similar to that offered by Dickinson and Mitchell to explain the inhibiting effect of hydrogen on the sensitized decomposition of ammonia. Equation (9) would explain, similarly, the lack of effect of nitrogen. Kuhn offers similar explanations.

It may be of interest to point out the relation of the decomposition of ammonia to the ideas expressed by Franck.[6] Ammonia in the gaseous state is doubtless made up almost entirely of non-polar molecules and the electron orbits of the molecule probably have little similarity to the electron orbits of nitrogen or hydrogen atoms. The heat of dissociation, as in the case of oxygen, would be high. Dissociation, as in oxygen, can follow the absorption of radiation only through the agency of collisions. In this case the probability of dissociation after collision would be a function of the electron energy levels at the time of collision, and the potential energy of the nuclear system would not vary greatly. Thus, we can see qualitatively that the shorter the wave length used, the greater the chance of dissociation. The apparent deviation from the Einstein Law of Photochemical Equivalence may be satisfactorily explained in this manner. One would expect that the quantum efficiency would approach unity at the point where continuous absorption begins. In line with the results herein reported, the quantum efficiency increases for short wave lengths and may be unity for the short wave lengths of the region studied.[18]

With regard to the nature of the particular dissociation process involved, we may offer only speculations since the band spectrum of ammonia has never been thoroughly analyzed. If the process involves the removal of one hydrogen, then two NH_2 groups might add to each other with the production of hydrazine. This would seem to be a most unlikely occurrence with low light intensities. If hydrazine is formed it would be more reasonable to explain it as a result of a collision of one NH_2 group with a normal ammonia with the resultant production of monatomic hydrogen and hydrazine. It seems somewhat more reasonable to expect that the collision between an excited ammonia molecule and a normal molecule would lead to a more profound decomposition with production of nitrogen and hydrogen.

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[18] See "Molecular Spectra in Gases," by Kemble, Birge, Colby, Loomis and Page, *Bull. Nat. Res. Council*, Vol. XI, Part 3, No. 57 (1926), for a full discussion of the relation of band spectra to dissociation.

Summary

1. The photochemical decomposition of ammonia by relatively short wave lengths has been studied. It is found that for the approximate region of the spectrum between 190 and 160mμ, 1.4 quanta are absorbed per molecule decomposed. This is based on the assumption that two molecules of ozone are produced from oxygen per quantum absorbed. The quantum efficiency is higher in this region of the spectrum than that found by other authors in the neighborhood of 210mμ.

2. A short theoretical discussion is given. It does not seem possible to give a mechanism for the reaction which is free from all criticism, but with the use of thermal data it is possible to indicate which reactions might be possible. The increase in quantum efficiency with increase in frequency of radiation receives a reasonable qualitative explanation on the basis of recent theories of band spectra.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 38]

THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER

IV. KINETICS AT 100 AND 220°, THE TEMPERATURE COEFFICIENT BETWEEN 0 AND 220°, AND SUMMARY

BY ROBERT N. PEASE AND CARL A. HARRIS

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Previous work[1] on the hydrogenation of ethylene in the presence of copper has shown that at 0° the rate is increased by excess of hydrogen but decreased by excess of ethylene, while at 200° the rate indicates an approximation to a bimolecular reaction, in which case proportionate increases in rate are caused by excess of either hydrogen or ethylene. Obviously, at some intermediate temperature the reaction rate should be independent of the ethylene concentration and proportional to the hydrogen concentration alone. We have thought it worth while to investigate this case and at the same time to obtain additional data on the higher temperatures. Further, we have taken occasion to measure rates at a series of temperatures between 0 and 200° in order to obtain the conventional heat of activation of this reaction.

The apparatus and general method of procedure have been fully described in previous papers.[1b] Suitable gas mixtures were made up in a calibrated gas buret and run into the evacuated catalyst chamber. The rate of reaction was then followed by the pressure decrease at constant volume.

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[1] (a) Grassi, *Nuovo Cimento*, [6] **11**, 147 (1916); (b) Pease, THIS JOURNAL, **45**, 1198, 2235 (1923).