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The Photodecomposition of Ammonia

BY HENRY J. WELGE AND ARNOLD O. BECKMAN

Introduction

Although the photodecomposition of ammonia was one of the first photochemical reactions to be studied carefully and the initial investigation of Warburg[1] has been followed by many others, the nature of the reaction has remained in doubt. The results of the various investigations are summarized in Table I.

TABLE I

SUMMARY OF PREVIOUS INVESTIGATIONS

Photochemical unless otherwise noted

Date	Investigator	NH_3 pressure, mm.	Minimum products for H_2 detn., mm. $\times 10^3$	H_2 yield, %	N_2H_4 yield	Quantum yield
1911	Warburg	45–900				0.25
1926	Kuhn[2]	5–900				.2 –0.5
1926	Dickinson and Mitchell[3]	0– 1	5	70 (sens.) 87 (dir.)		
1927	Bates and Taylor[4]		40	96 (dir.) 89 (sens.)	Amt. small	
1931	Koenig and Brings[5]	250			Small amt.	
1932	Gedye and Rideal[6]	44			0–57% of NH_3 decomp.	
1932	Wiig and Kistiakowsky[7]	0–760	15	75		.24
1934	Ogg, Leighton and Bergstrom[8]	1– 9	Large	75		.14
1935	Wiig[9]	0–900	20	75		.10– .33

Several investigators obtained as products only hydrogen and nitrogen in 3:1 molal ratio and a quantum yield of about 0.25 molecule of ammonia decomposed per quantum absorbed. Others obtained higher hydrogen to nitrogen ratios and still others obtained hydrazine in varying amounts.

The present investigation includes a study of the reaction products and determination of the quantum yields for both the direct photochemical decomposition and the mercury sensitized decomposition. Evidence is presented which makes possible a reconciliation of some of the apparently conflicting data of earlier investigations and which sheds new light on the nature of the decomposition. The results are of particular interest when the amount of decomposition is small; in some cases the partial pressure of the non-condensable products was as low as 10^{-4} mm. of mercury.

Materials and Apparatus

Commercial anhydrous ammonia, free from hydrazine and hydroxylamine, was drawn under vacuum into a storage bulb containing C. P. potassium hydroxide and was purified by repeatedly freezing in a liquid air trap and pumping off the non-condensable gases. Several samples of ammonia from different sources were used during the course of the investigation with completely concordant results.

Most of the apparatus employed has been described previously.[10,11] The vacuum system included mercury diffusion pump, McLeod gage, quartz fiber gage, a reaction cell of quartz (attached to the rest of the system through a quartz–Pyrex graded seal), a storage bulb for the ammonia, and several stopcocks and mercury cut-offs. The cut-offs were so placed that no stopcocks were included in that part of the system in which measurements were made.

The direct decomposition of ammonia was studied with the aid of radiation from a high-voltage condensed spark between water-cooled aluminum electrodes. Energy for the spark was supplied by a 13,000-volt, 10-kva. transformer with a 0.1-mf. condenser placed in parallel with the spark. The sensitized decomposition was produced by the 2537 Å. resonance radiation from a water-cooled quartz mercury arc. Radiation of wave length shorter than 2400 Å. was removed by an acetic acid filter.

In the quantum yield experiments monochromatic radiation, vacuum thermopiles and high-sensitivity galvanometers were used. The thermopiles had fused quartz windows attached with wax and were continuously evacuated by an oil diffusion pump. Monochromatic radiation was

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(1) Warburg, *Sitzber. preuss. Akad. Wiss.*, 746 (1911).

(2) Kuhn, *J. chim. phys.*, **23**, 521 (1926).

(3) Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

(4) Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

(5) Koenig and Brings, *Z. physik. Chem.*, 541 (1931).

(6) Gedye and Rideal, *J. Chem. Soc.*, 1158 (1932).

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

(8) Ogg, Leighton and Bergstrom, *ibid.*, **56**, 318 (1934).

(9) Wiig, *ibid.*, **57**, 1559 (1935).

(10) Wenner and Beckman, *ibid.*, **54**, 2787 (1932).

(11) Myers and Beckman, *ibid.*, **57**, 89 (1935).

obtained by means of a quartz monochromator and was focused on the vane of one of the thermopiles, T_t (transmission). The fused quartz reaction cell, provided with plane windows, was inserted in this light path. The front window of the cell, attached at an angle of 45°, reflected a fraction of the incident radiation onto the vane of the second (reflection) thermopile, T_r. A recording device provided continuous records for both thermopiles.

Experimental Method

Since the decomposition products were very small in amount, it was essential to keep the system thoroughly outgassed. This was achieved by almost continuous evacuation during the investigation. The reaction system would retain for hours a vacuum better than 10^{-6} mm.

In experiments to determine the composition of the non-condensable products, a sample of purified ammonia was irradiated and the pressure and composition of the products not condensable in liquid air were determined by combined use of the McLeod and quartz fiber gages. These products were assumed to contain only hydrogen and nitrogen; it has been shown[12] that this method of analysis gives accurate results with such mixtures. The quartz fiber gage was calibrated frequently, using both nitrogen and hydrogen.

Quantum yields were measured by an absolute method. In each experiment the ratio of the transmission and reflection thermopile readings with the empty cell was first determined. The purified ammonia was then admitted and irradiated, a continuous photographic record being taken of both thermopile readings. Liquid air was applied and the pressure and composition of the non-condensable products determined. Calibrations of the quartz fiber gage were alternated with quantum yield runs. Blank experiments were also run, in some of which the shutter of the monochromator remained closed throughout the experiment; in others the shutter was opened as usual but the ammonia was kept frozen. The sensitivity of the transmission thermopile was measured frequently with the aid of standardized carbon lamps supplied by the Bureau of Standards. The transmission factors of the rear window of the cell and of the window of the transmission thermopile for the radiations used were determined experimentally.

Experimental Results

Products of the Photochemical Decomposition.—When the amount of ammonia decomposed was relatively large (*i. e.*, partial pressure of products greater than 0.05 mm.) the non-condensable products contained approximately 75% hydrogen and 25% nitrogen, in agreement with the results reported by several of the previous investigators (Table I). However, when the amount of decomposition was successively decreased, the percentage of hydrogen increased, approaching 100% in the limiting case. The data for the photochemical decomposition are represented by the circles in Fig. 1, in which the ordinates are the percentages of hydrogen in the non-condensable decomposition products and the abscissas are the total pressures of the non-condensable products as measured with the McLeod gage. The lowest pressure on which accurate analyses could be made was about 3×10^{-4} mm.

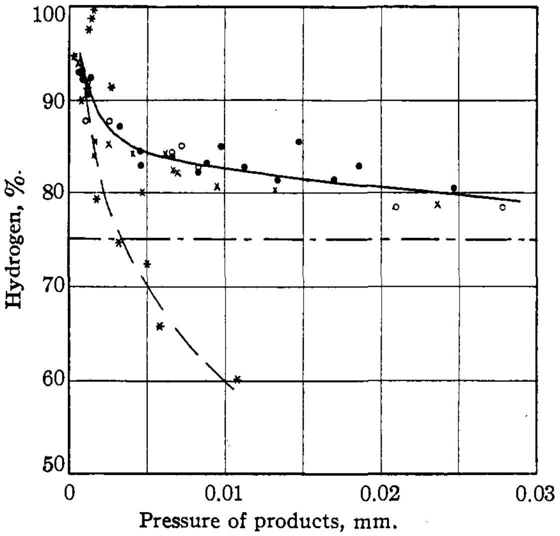

Fig. 1.—Composition of the non-condensable gases: ●, direct photochemical decomposition, 4 mm. NH_3; ○, direct photochemical decomposition, 20 mm. NH_3; *, mercury sensitized decomposition, 4 mm. NH_3, fresh cell; ×, mercury sensitized decomposition, 20 mm. NH_3.

To prove that the results could not be attributed to easily decomposed impurities in the ammonia, experiments were made not only with fresh samples of ammonia but also with the residual ammonia remaining from previous experiments, in which large amounts of decomposition had taken place and in which 75% hydrogen had been obtained. In all cases, the percentage of hydrogen was considerably greater than 75% for very small amounts of decomposition and decreased progressively toward 75% as the amount of decomposition was increased.

Percentages of hydrogen in excess of 75% indicate the formation of hydrazine during decomposition. Varying amounts of hydrazine in the decomposition products of ammonia have been reported by certain investigators who used a flow method. Thus Bates and Taylor[4] and Koenig and Brings[5] obtained small amounts of hydrazine, while Gedye and Rideal[6] reported hydrazine yields ranging from 0 to 57% of the amount stoichiometrically possible from the amount of ammonia decomposed. Other investigators obtained no evidence of hydrazine formation.

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[12] Beckman and Dickinson, THIS JOURNAL, **50**, 1870 (1928).

Hydrazine, if present, might be expected to condense with the undecomposed ammonia when liquid air is applied to the freezing-out trap. In several experiments the trap containing the condensed material was removed from the vacuum system and the contents dissolved in dilute acid. Tests with iodate, ammoniacal silver, and gold chloride failed to give a positive indication for hydrazine. Since the amount of hydrazine theoretically present (calculated from the pressure and composition of the non-condensable gases, assuming that the hydrazine is the only other product formed in the decomposition) is not greatly in excess of the minimum amount capable of detection (about 10^{-8} mol) by these methods, and since hydrazine is known to be strongly adsorbed on glass and quartz, it appeared probable that failure to detect hydrazine was due to the fact that most of the hydrazine remained in the reaction cell. Consequently, tests were made in which acidified, de-aerated water was added directly to the reaction cell and the aqueous liquid withdrawn and tested for hydrazine with ammoniacal silver nitrate. Positive indications for hydrazine were obtained in all cases. Control experiments made under identical conditions except that the ammonia was not irradiated gave no tests for hydrazine.

Quantum Yield for the Photochemical Decomposition.—The results of the quantum yield determinations for the direct decomposition of ammonia, using monochromatic radiation of 1990 Å., are given in Table II. In these experiments the amount of decomposition was always very small and the percentage of hydrogen in the non-condensable gases was large, averaging about 95%. Assuming that hydrazine, hydrogen and nitrogen are the only products, this means that 16 molecules of ammonia decompose to give hydrogen and hydrazine for every molecule that decomposes to hydrogen and nitrogen. The number of molecules of ammonia decomposed may be found by means of the stoichiometric relation

$$N_{\mathrm{NH}_3} = 6(f - 0.667)N\frac{pV}{RT} \qquad (1)$$

where N is Avogadro's number, p is the total pressure of non-condensable gas and f is the mole fraction of hydrogen.

The number of quanta of 1990 Å. radiation absorbed may be calculated from the relation

$$N_{\mathrm{Q}} = \frac{(\beta D_{\mathrm{r}}S_{\mathrm{r}} - D_{\mathrm{t}}S_{\mathrm{t}})t}{\alpha_1\alpha_2 hc/\lambda} \qquad (2)$$

where β is the ratio of galvanometer deflections with the empty cell, D_{r} and D_{t} are the galvanometer deflections for the reflection and transmission thermopiles, S_{r} and S_{t} are the sensitivities of the transmission thermopile at deflections of D_{r} and D_{t}, *i. e.*, the number of ergs per second required to give unit deflection, t is the time of irradiation, α_1 and α_2 are the transmission factors for λ 1990 Å. of the rear window of the reaction cell and the window of the transmission thermopile, h is Planck's constant, c the velocity of light and λ is the wave length 1990 Å. The quantum yield is obtained by dividing N_{NH_3} by N_{Q}.

In the first four experiments listed in Table II the reaction cell was thoroughly outgassed by

TABLE II

QUANTUM YIELDS FOR THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA (λ = 1990 Å.)

Expt. no.	Pressure NH_3, mm.	Time, min.	Pressure products, mm. $\times 10^4$	H_2 in products, %	Molecules NH_3 dec. $\times 10^{-14}$	Quanta absorbed $\times 10^{-14}$	Quantum yield
6[a]	5.0	33	3.5	95.2	33.8	47.0	0.72
10[a]	12.7	29.75	3.6	91.5	29.9	41.0	.73
5[a]	30.3	46	6.1	96.5	60.9	76.4	.80
9[a]	111.2	24	3.86	92.9	34.2	51.8	.66
							Av. .70
18	2.2	29.5	4.2	94.5	39.45	46.55	0.85
17	5.9	28	5.65	96.8	57.5	61.25	.94
13	6.0	29	6.37	96.8	64.75	68.37	.95
11	13.8	18	4.63	92.67	40.95	51.95	.79
15	14.3	29	8.2	95.5	80.15	85.78	.94
12	29.3	23	6.4	94.45	60.2	69.55	.87
16	30.0	18.5	5.0	95.6	49.03	54.55	.90
14	60.7	19.5	4.46	94.1	41.4	55.77	.74
19	128.2	29.5	8.7	90.5	70.2	81.9	.86
							Av. .87

[a] Fresh cell used in first four experiments, cell walls saturated with hydrogen atoms for remaining experiments.

TABLE III

QUANTUM YIELDS FOR THE SENSITIZED DECOMPOSITION OF AMMONIA (λ = 2537 Å.)

Expt. no.	Pressure NH_3, mm.	Time, min.	Pressure products, mm. $\times 10^4$	H_2 in products, %	Molecules NH_3 dec. $\times 10^{-14}$	Quanta absorbed $\times 10^{-14}$	Quantum yield
26	0.25	26	0.32	(95.0)[a]	2.14	44.45	0.05
25	.60	21	.51	(95.0)[a]	3.4	34.85	.10
24	1.3	21	.64	(95.0)[a]	4.28	38.5	.112
19	1.4	23.65	.84	(95.0)[a]	7.55	48.2	.156
23	2.1	21	.78	(95.0)[a]	5.24	41.7	.125
18	4.9	21	1.01	(95.0)[a]	6.45	48.6	.133
28	8.3	21	1.15	(95.0)[a]	7.55	66.4	.114
29	8.3	39	0.88	(95.0)[a]	5.78	54.3	.105
17	14.3	16	.87	(95.0)[a]	5.58	43.73	.127
16	38.5	21	1.35	(95.0)[a]	8.7	80.0	.109
22	103.3	26	1.78	(95.0)[a]	11.77	109.5	.107
31a	3.1	150	7.45	94.7	68.7	445	.154
31b	3.1	212	10.6	96.7	105.3	628	.168
30a	8.5	100	4.56	84.7	34.55	359	.096
30b	8.5	145	7.5	93.0	64.2	520	.123
27a	20.6	100	3.88	90.0	30.0	360	.083
27b	20.6	240	9.57	95.0	90.3	865	.104
						Av. =	.12

[a] For these experiments the hydrogen in the non-condensable products was assumed to be 95%. For the remaining experiments the percentage of hydrogen was determined by analysis.

baking and evacuating prior to the experiment. Since it is known that hydrogen readily "cleans up" on fresh quartz surfaces,[13] it was felt that the observed quantum yields (av. = 0.70) might be low for that reason. Therefore, for the remainder of the experiments, prior to the admission of ammonia to the cell, hydrogen at a pressure of a few millimeters in the presence of mercury vapor was irradiated for several hours with intense mercury resonance radiation, followed by thorough evacuation. With such treatment of the cell, the observed quantum yields rose to an average value of 0.87. Blank experiments showed that irradiation of the empty treated cell produced negligible amounts of gas, proving that the increased quantum yield was not due to outgassing of adsorbed hydrogen. In Fig. 2 the quantum yields for the direct decomposition of ammonia are represented by the circles. The yields seem to approach unity as a limit and are not affected by changes in ammonia pressure nor the amount of products, when the latter is less than 10^{-3} mm.

Mercury Sensitized Decomposition.—The products of the sensitized decomposition were the same as in the direct decomposition. The percentage of hydrogen in the non-condensable products again varied from nearly 100% down to about 75% as the amount of decomposition increased, as shown in Fig. 1, where the crosses represent sensitized decompositions. It will be noticed that the same curve fits either type of decomposition, except when the ammonia pressure is low and a fresh cell is used. In this event, hydrogen is cleaned up on the walls to such an extent that its fraction in the gases drops considerably below 0.75 on continued irradiation with λ 2537 Å. When hydrogen alone is similarly irradiated in the cell, its pressure slowly falls off.

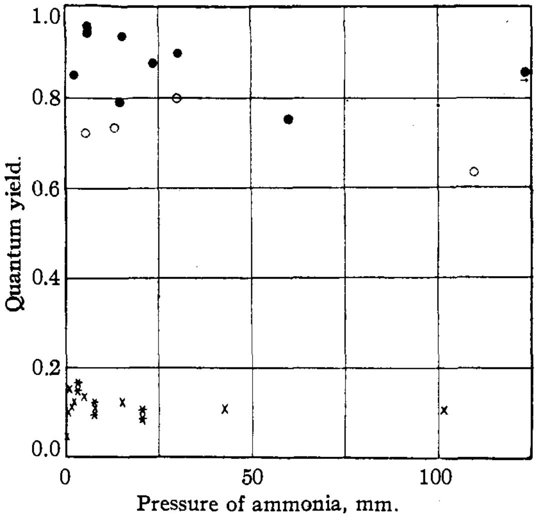

Fig. 2.—Quantum yield of the photodecomposition of ammonia: ○, direct decomposition, fresh cell; ●, direct decomposition, cell saturated with H atoms; *, sensitized decomposition; ×, sensitized decomposition, 95% H_2 assumed.

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(13) Cario and Franck, *Z. Physik*, **11**, 161 (1922).

The quantum yield of the sensitized decomposition was, however, much smaller than that of the direct decomposition, having an average value of 0.12, as shown in Table III, and in Fig. 2, where the crosses again represent sensitized decompositions. This value of the yield was independent of the amount of decomposition, if small, and of the ammonia pressure, except below 1 mm., where it fell rapidly to zero.

Discussion

The primary process in the photochemical decomposition of ammonia may be assumed to be a dissociation, since the absorption spectrum of ammonia is of the predissociation type,[14,15] involving the rupture of one of the hydrogen–nitrogen bonds.

$$NH_3 + h\nu \longrightarrow NH_2 + H$$

The most direct experimental evidence for this primary process is the work of Geib and Harteck,[16] who showed that the photochemical decomposition products of ammonia could effect the conversion of para to ortho hydrogen and therefore presumably contained hydrogen atoms.

In the lower limit of small amounts of decomposition, the products are substantially only hydrogen and hydrazine. The following mechanism accounts for their formation

$$\begin{aligned} NH_3 + h\nu &\longrightarrow NH_2 + H \\ H + H + M &\longrightarrow H_2 + M \\ NH_2 + NH_2 + M &\longrightarrow N_2H_4 + M \end{aligned}$$

This mechanism accounts satisfactorily for the additional experimental fact that the quantum yield is unity, independent of ammonia pressure. Other reaction steps assumed by previous investigators[4,7,8] are not needed. In particular, the reaction

$$H + NH_2 + M \longrightarrow NH_3 + M$$

leading to the re-formation of ammonia, does not play an important role, since the quantum yield is nearly unity.

The decomposition, with the exception of the primary process, probably proceeds heterogeneously on the walls of the reaction vessel at the low pressures of these experiments. Hydrogen atoms are known to be strongly adsorbed on glass[17] and are probably also adsorbed on quartz. The fact that no reducing substance was obtained in freezing-out traps may be taken as evidence that either NH_2 or N_2H_4 or both are adsorbed on the cell walls.

A little of the hydrazine will probably be decomposed by the hydrogen atoms, as shown by Dixon,[18] even when its amount is small. The decomposition of hydrazine in this way will give ammonia and some nitrogen, thus slightly reducing the hydrogen fraction below 100% and reducing the quantum yield below the value of unity. With larger amounts of products the effect is exaggerated, and the lower quantum yields obtained by previous investigators may be due in part to this effect. There is general agreement in recent investigations[7,9] that the non-condensable gaseous products contain 75% hydrogen and 25% nitrogen when relatively large amounts of products are obtained. These percentages also appear as the limiting values in the present experiments as the amount of decomposition successively increases. For small amounts of decomposition, however, the percentage of hydrogen is much greater, a fact which has a marked influence upon the calculation of the quantum yields. From equation 1 above, it is to be seen that for a given volume of non-condensable gas, the calculated number of ammonia molecules decomposed will be four times as large when the gas is 100% hydrogen as when it is 75% hydrogen. If the quantum yields given above in Table II had been computed on the assumption that the non-condensable gas consisted of 75% hydrogen and 25% nitrogen, the calculated quantum yields would have been reduced to approximately 0.25, in agreement with the results of others. Since the analyses showed that the non-condensable gas was substantially all hydrogen, the actual quantum yields are much larger, nearly unity.

The marked change in the composition of the products in the region of small amounts of decomposition illustrates a point which is often overlooked in photochemical investigations. Because of the difficulties which usually attend the analysis of the small amounts of products obtainable from quantum yield experiments, it is a common practice to get relatively large amounts of products for analysis, often radically changing the intensity of radiation, degree of monochromatization, concentration of the reactants, etc., from the conditions of the quantum yield experiments. Yet it is usually assumed that the reaction follows the

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(14) Leifson, *Astrophys. J.*, **63**, 73 (1926).

(15) Dixon, *Phys. Rev.*, **43**, 711 (1933).

(16) Geib and Harteck, *Z. physik. Chem.*, Bodenstein Festband, 849 (1931).

(17) Bonhoeffer, *ibid.*, **113**, 199 (1924).

(18) Dixon, THIS JOURNAL, **54**, 4262 (1932).

same course in both cases. The present experiments show that this assumption must be viewed with suspicion. The safe plan is to perform the experiments leading to a deduction of reaction mechanism under the same conditions as the quantum yield experiments, or better still to combine them in the same experiments.

The mercury-sensitized decomposition differs from the photochemical decomposition in the nature of the primary processes and by the fact that marked fluorescence was observed.[3]

$$\begin{aligned} Hg + h\nu_1 &\longrightarrow Hg' \\ Hg' + NH_3 &\longrightarrow NH_3' + Hg \\ NH_3' &\longrightarrow NH_3 + h\nu_2 \\ NH_3' &\longrightarrow NH_2 + H \end{aligned}$$

The low quantum yield for the photosensitized decomposition may be attributed to fluorescence and suggests that the quantum of λ 2537 Å. (approximately 112,000 cal. per mole) is barely sufficient to produce decomposition.

Summary

The photochemical and mercury photosensitized decompositions of ammonia have been investigated in the region of very small amounts of decomposition. In contrast to the results obtained with large amounts of decomposition, namely, a quantum yield of 0.25 and gaseous products consisting of 75% hydrogen and 25% nitrogen, with small amounts of decomposition the quantum yield approaches unity and the gaseous products approach pure hydrogen, in the case of the photochemical decomposition. For the photosensitized decomposition a quantum yield of 0.12 was obtained.

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The Rearrangement of Acetylchloroaminobenzene in the Presence of Radioactive Hydrochloric Acid

BY A. R. OLSON, C. W. PORTER, F. A. LONG AND R. S. HALFORD

The mechanism of the Hofmann rearrangement of N-substituted aromatic amines has been under investigation, intermittently, over a period of sixty years. As early as 1881 Michael[1] advanced the theory that in the rearrangement of methylaniline hydrochloride into the hydrochloride of *p*-toluidine, the first step is a dissociation into methyl chloride and aniline. The methyl chloride is then supposed to act upon the aniline, substituting the methyl group for the para hydrogen atom. In 1920 Michael[2] reaffirmed this conclusion and referred to the dissociation mechanism as a "self-evident explanation."

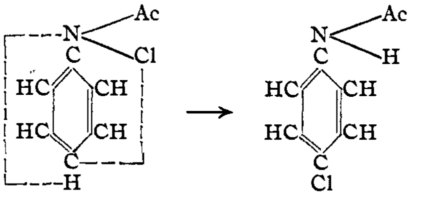
Orton and his colleagues[3] outlined a mechanism for the rearrangement of acetylchloroaminobenzene which has become almost universally accepted. They envisage the reaction as proceeding in three steps: (1) the hydrolysis of the chloroamine; (2) the production of chlorine from hydrochloric and hypochlorous acids; (3) the chlorination of acetanilide.

$$C_6H_5NClAc + H_2O \rightleftarrows C_6H_5NHAc + HClO \quad (1)$$

$$HClO + H^+ + Cl^- \rightleftarrows H_2O + Cl_2 \quad (2)$$

$$C_6H_5NHAc + Cl_2 \longrightarrow ClC_6H_4NHAc + H^+ + Cl^- \quad (3)$$

At the Richmond meeting of the American Chemical Society (1927) one of us presented the view that the arrangement is intramolecular.[4] It was postulated that a bond is formed between the chlorine atom and the para carbon atom while the chlorine is still attached to the nitrogen. Similarly it was assumed a bond is formed between the nitrogen atom and the para hydrogen atom in advance of any dissociation process. These weak bonds are represented by dotted lines in formula I. When molecules in state I become sufficiently activated the bonds represented by dotted lines become full valence bonds and the rearrangement is accomplished. In the Richmond



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[1] A. Michael, *Ber.*, **14**, 2105 (1881).

[2] A. Michael, THIS JOURNAL, **42**, 787 (1920).

[3] F. O. Chattaway and K. J. P. Orton, *Proc. Chem. Soc.*, **18**, 200 (1902); K. J. P. Orton and W. J. Jones, *Brit. Assn. Adv. Sci. Repts.*, 1910, p. 85; F. S. Kipping, *et. al.*, *Chem. News*, **108**, 155 (1913).

[4] C. W. Porter, paper read at the April meeting, 1927.