[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

Effect of Strong Electric Fields on the Radiochemical Decomposition of Gaseous Ammonia[1]

BY MICHAEL J. MCGUINNESS, JR.,[2] AND HARRY ESSEX

A paper by Essex and Smith[3] presented the results of ion yields in the alpha ray decomposition of ammonia in electric fields. This work has been continued with measurements at lower pressure and at higher field strength. The effects of these changes on the ion yield are significant as regards the mechanism of the alpha ray decomposition and on the products of the reactions between electrons and ammonia molecules.

The ion yields were determined by the saturation current method, the rate of ion production being determined from the saturation current across the ionized gas and the rate of decomposition of the gas by the increase in pressure of the gases, nitrogen and hydrogen, uncondensed by liquid air. Previous papers from this Laboratory have shown that the saturation current method gives ion yields which, when account is taken of the effect of the difference in intensity of irradiation, agree with the ion yields determined by the more indirect methods of "homogeneous irradiation" and "central irradiation" used by others.

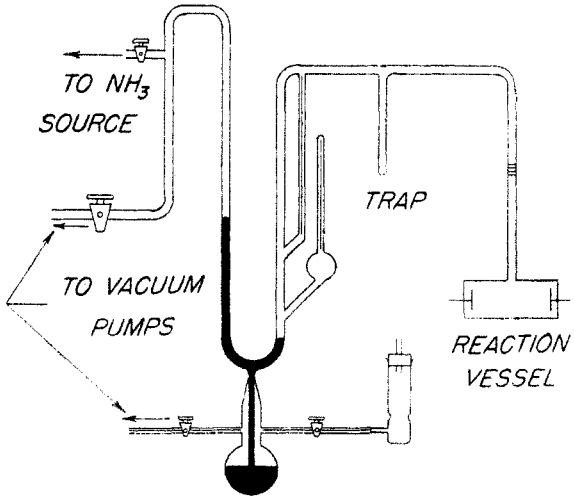

Fig. 1.

Experimental

The apparatus is shown in Fig. 1. The radioactive material, mesothorium, was placed in a small depression in the reaction vessel. The vessel was fitted with platinum electrodes as shown. Ammonia, guaranteed by the manufacturers to be not less than 99.95% NH_3, was dispensed from a solution in ammonium thiocyanate, dried over metallic sodium and purified by repeated condensation in the indicated trap at liquid-air temperature, followed each time by evacuation of uncondensed gases. The ammonia gas at about 20 cm. was finally enclosed by the mercury seal. The reaction vessel was surrounded by an air-bath maintained at $24.7 \pm 0.2°$.

Circular thin copper shields were cemented to the outside of each end of the reaction vessel with a nitrocellulose cement containing silver filings to improve electrical contact. The shield at the low potential end was electrically insulated from the lead to the electrode. Currents to electrode and shield were measured separately. At the highest potentials the current to the shield was about 2% of that to the plate and was included in the ion current since preliminary experiments showed the conductivity through and over this glass to be negligible. The shields prevented sparking between glass and electrode edges.

During a run the field strength was kept constant except that at intervals of about twenty-four hours the saturation current was measured and the residual pressure ($N_2 + 3H_2$) determined with the McLeod gage after freezing out ammonia in the trap. At the end of a run the ammonia was frozen out, the system evacuated, the mercury seal closed and a new run started at another field strength. In many of the runs the field strengths were far higher than necessary for saturation.

The results are presented in Table I and the ion yields (M/N) are plotted *vs.* field strength in Fig. 2. The experi-

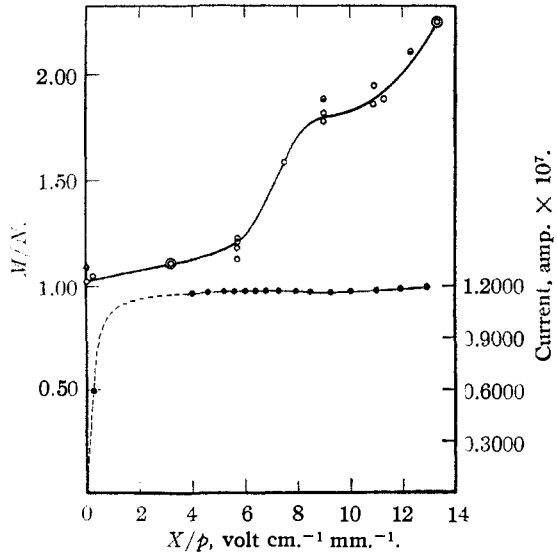

Fig. 2.—Comparison of ion yield with plate current: O, ion yield; ◒, short run; ●, plate current.

(1) This paper is from the doctoral dissertation of Michael J. McGuinness, Jr., Syracuse University, 1941, and was presented at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Present address: Battelle Memorial Institute, Columbus, Ohio.

(3) Essex and Smith. *J. Chem. Phys.*, **6**, 188 (1938).

TABLE I

ION YIELDS IN AMMONIA

Temperature 24.7°, pressure 20 cm.

Duration, hours	Residual pressure change, mm.	Saturation current, amp. × 10^8	M/N	Potential diff. between electrodes, kv.	X/P, volt, cm.$^{-1}$ mm.$^{-1}$
23.62	0.00763	12.03	1.09	0	0
304.15	.0905	11.90	1.02	0	0
175.73	.0537	11.82	1.05	0.5	0.25[a]
210.4	.0677	11.68	1.12	6.4	3.2
185.5	.0608	11.88	1.12	6.4	3.2
43.08	.01436	11.70	1.16	11.4	5.7
43.70	.01398	11.81	1.10	11.4	5.7
		Average, for last two runs	1.13	11.4	5.7
162.22	.0579	11.73	1.23	11.4	5.7
91.38	.0319	11.67	1.21	11.4	5.7
29.23	.0092	11.69	1.09	11.4	5.7
		Average, for last two runs	1.18	11.4	5.7
34.92	.0135	11.59	1.35	11.4	5.7
170.00	.0578	11.68	1.18	11.4	5.7
		Average, for last two runs	1.21	11.4	5.7
76.92	.0363	11.84	1.62	15.0	7.5
63.43	.0287	11.80	1.56	15.0	7.5
		Average, for last two runs	1.59	15.0	7.5
191.4	.0980	11.69	1.78	18.0	9.0
47.27	.0260	11.81	1.89	18.0	9.0
364.3	.193	11.83	1.82	18.0	9.0
96.17	.0524	11.90	1.86	21.8	10.9
169.55	.0961	11.81	1.95	21.8	10.9
55.27	.02703	10.93	1.81	22.6	11.3
193.00	.1052	11.50	1.92	22.6	11.3
		Average, for last two runs	1.90	22.6	11.3
43.65	.0261	11.78	2.11	24.6	12.3
62.2	.0405	11.80	2.24	26.6	13.3
91.8	.0600	11.84	2.24	26.6	13.3
		Average, for last two runs	2.24	26.6	13.3
138.47	.0903	11.80	2.24	26.6	13.3

[a] Current to plate during this run equal to one-half of saturation current.

mental errors are naturally greater in the shorter runs. Figure 2 also shows a typical current *vs.* field strength curve. The ion yields reported here were obtained at intensities of ionization similar to those in the experiments carried out in this Laboratory[3] on ammonia at pressures in the neighborhood of one atmosphere. The nature of the method, depending upon saturation current measurements, precludes the use of higher intensities of irradiation where saturation is obtainable only at extremely high voltages, if at all. The ion yield 1.03 (weighted) obtained in the absence of a field at 20 cm. may be compared with the value 1.37 previously obtained[3] at 62 cm. and 30°. Luyckx[4] also observed a decrease in ion yield with decrease in pressure in the alpha ray decomposition of ammonia. He found that the effect was greater the lower the intensity of irradiation. Since the lowest intensity of irradiation he used was greater than that employed in these experiments, quantitative comparison is not possible.

(4) Luyckx, *Bull. soc. chim. belg.*, **43**, 117 (1934).

Discussion

Effect of Pressure.—It frequently has been assumed that alpha ray induced decompositions are entirely the result of recombination of ions. By measuring the ion yield at constant pressure and temperature as a function of field strength, it is possible to calculate the fraction of the decomposition which in the absence of a field is consequent on recombination of ions and the fraction of the decomposition due to other mechanisms. At field strengths sufficient for saturation, recombination cannot occur. But practical saturation is obtained only at such high fields that, as our previous work has shown, decomposition by a new mechanism, probably by electron collisions, has begun. However, half saturation is obtained

at field strengths only a small fraction, often about one-tenth of those necessary for saturation and the ion yield due to ion recombination should be twice the difference between the ion yield in no field and at half saturation. The ion yield due to other mechanisms is obtained by difference.

In this way Essex and Smith[3] calculated in the decomposition of ammonia at 30° and 62 cm. that 30% of the decomposition is consequent on ion recombination. But the data here presented show that at 24.7° and 20 cm. pressure and under very similar conditions as regards vessel size and intensity of irradiation, the ion yield at no field is 1.03 and at half saturation 1.05. These yields are identical within the experimental error and show that at this lower pressure, none of the alpha ray decomposition is consequent on ion recombination, *i. e.*, that the decomposition is entirely due to other mechanisms. It seems probable that at the lower pressure all of the ions reach the walls by diffusion and are there discharged. The only effect of low fields is to change the location of ion discharge from the walls to the electrodes. Assuming that recombination takes place entirely in alpha ray tracks which extend completely across the vessel at all pressures and that the diameter of the track and the rate of diffusion of ions show the pressure dependence to be expected, it is easily shown that the fraction of the ions recombining in the gas is proportional to the $^5/_2$ power of the pressure. Comparing the fraction of the ions which combine at 20 cm. and 62 cm. pressure

$$\frac{\text{fraction combining at 20 cm.}}{\text{fraction combining at 62 cm.}} = \frac{20^{5/2}}{62^{5/2}} = \frac{1}{17}$$

which makes plausible the implications of these experiments that at 20 cm. in a vessel of this shape and size, most of the ions are neutralized at the walls.

At 30° and 62 cm. pressure the total ion yield in the absence of a field was 1.37, the ion yield due to recombination of ions 0.40 and that due to other mechanisms 0.97. Comparing the latter figure with 1.03 it is seen that pressure has little or no effect on that portion of the reaction due to mechanisms other than ion combination.

Effect of Electric Field.—The first effect of increasing the field strength across ionized ammonia is to remove ions before they recombine, which often results in decomposition, or reach the walls by diffusion. The increase in ion yield at higher field strength is due to collisions of electrons with ammonia molecules as, at the pressures of these experiments, the energy of molecular ions is increased by the field but slightly above the thermal energy of the molecules. The ion yield curve (Fig. 2) is therefore an electron yield curve but with the electron yield scale undetermined since the ratio of electrons to molecular negative ions is unknown. High energy electrons are known to split the ammonia molecule with attachment of the electron to one or the other fragment.

Bradbury[5] passed electrons through ammonia at pressures from 3 to 97 mm. Negative molecular ions appeared at $X/p = 7.5$ at which value he estimated the average energy of the electrons to be 4 volts. A gas uncondensable by liquid air was formed upon the appearance of negative ions. Four volts is approximately the energy of dissociation of NH_3 either to NH_2 and H or NH and H_2. Bradbury postulated one or the other of the reactions

$$NH_3 \longrightarrow NH_2^- + H$$
$$NH_3 \longrightarrow NH^- + H_2$$

Mann, Hustrulid and Tate[6] analyzed with the mass spectrograph the ions formed in ammonia at very low pressures by electrons of controlled energies. The only negative ions found were NH_2^- and H^-. The onset of formation of both ions occurred at electron energies very close to the excitation potential, 6 e. v. The disagreement between Bradbury and Tate as to the minimum energy necessary for electron attachment (4 and 6 e. v., respectively) may be inherent in their methods of attack. Bradbury's method was excellent for detecting ions at small probability of formation due to the fact that he was using much higher pressures than are possible in mass spectrometric methods. His calculations provided the average energy of the electrons, but, regarding the actual energies of the individual electrons, little information is available since the distribution function has not been satisfactorily determined. Therefore, as Bradbury has stated,[7] his results do not show convincingly that electrons of energies less than 6 e. v. do become attached. Tate and his co-workers,[6] on the other hand, were operating at such low pressures that although the energy of the electrons could be known accurately, attachment would not be detectable if the probability of attachment were small.

The ion yield curve (Fig. 2) exhibits two poten-

(5) Bradbury, *J. Chem. Phys.*, **2**, 827 (1934).
(6) Mann, Hustrulid and Tate, *Phys. Rev.*, **58**, 340 (1940).
(7) Private communication.

tial ranges in which the rise in ion yield is rapid, the first of which is followed by a potential range in which the ion yield increases more gradually. It seems plausible to assume that non-resonant splitting and resonant splitting occur successively with increasing field, *e. g.*

$$(1)\quad NH_3 + e \begin{cases} \nearrow NH_2^- + H \\ \searrow NH_2 + H + e \end{cases}$$

and

$$(2)\quad NH_3 + e \longrightarrow NH_3^* + e \begin{cases} \nearrow NH_2^- + H \\ \searrow NH_2 + H + e \end{cases}$$

in which are included the possibility of failure of a molecular fragment to capture the electron. After an electron is captured by either mechanism, no further decomposition is possible by the ion (thereafter molecular) in its progress toward the electrode, which may explain the nearly horizontal portion of the curve. That the first increase in ion yield occurs at a value of X/p less than that ($X/p = 7.5$) at which Bradbury first observed negative ions is probably due to the fact that in these experiments no special precautions were taken to maintain the field uniform. Under such conditions as obtained in these experiments the field strength is considerably above the average in the neighborhood of the electrodes, especially at the cathode and at low potentials.

That considerable splitting of ammonia molecules without electron attachment occurs is apparent from the magnitude of the increase in ion yield with increase in field strength, from 1.03 to 2.24. Splitting with attachment could only result in an increase in ion yield of 1 unit if all negative ions were initially electrons and if no ammonia resulted from the recombination of the fragments. The work of Melville and Birse[8] indicates that only 43% of ammonia molecules which are split into NH_2 and H finally result in nitrogen and hydrogen. It would therefore appear that in the collisions of electrons with ammonia molecules approximately 2 molecules are split without attachment for each split with attachment; more than 2 in so far as negative molecular ions are produced by the action of the alpha rays, less than 2 to the extent that resonance splitting occurs by the second Tate mechanism

$$NH_3 + e \longrightarrow NH_3^* + e \longrightarrow N + H_2 + H^-$$

That no positive ions are produced by accelerated electrons in our experiments is evidenced by the appearance of the current–field strength curve which remains flat above the saturation voltage. Maximum energy of the electrons is therefore less than 10.5 e. v., the ionization potential of ammonia.

The reactions occurring in a field are also operative in the ordinary radiochemical decomposition (in the absence of a field) where energetic electrons are also present. The direct splitting reaction postulated by Bradbury would account for little of the decomposition since Mann, Hustrulid and Tate have shown it to be an improbable one. That portion of the reaction not consequent on recombination of ions probably results, largely, from resonance splitting (*e. g.* (2)).

Acknowledgment.—The liquid air used in this investigation was provided by the General Electric Company of Schenectady, New York, through the courtesy of Dr. L. M. Willey, to whom the authors wish to express their gratitude.

Summary

Ion yields in the alpha ray decomposition of gaseous ammonia at 25° and a pressure of 20 cm. have been determined over a wide range of field strengths. In the absence of a field none of the reaction is consequent on ion recombination under these experimental conditions. The increase in ion yield at high field strengths has been attributed to electron collisions. The electron collisions have been assumed to result in direct and resonance splitting of the ammonia molecule. The splitting of an ammonia molecule on collision with an electron does not involve electron attachment in the majority of such collisions.

(8) Melville and Birse, *Proc. Roy. Soc.* (London), **A175**, 164 (1939).

SYRACUSE, N. Y. RECEIVED APRIL 8, 1942