dibromo compounds can qualify for useful spectrophotometric determinations.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Formation of Hydrazine in Electric Discharge Decomposition of Ammonia[1,2]

BY JOHN C. DEVINS[3] AND MILTON BURTON

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In the decomposition of ammonia in a d.c. electric discharge in the pressure range 0.6-11 mm., hydrazine and nitrogen (as well as hydrogen) are produced by apparently unconnected processes. Nitrogen is produced uniformly throughout the discharge while hydrazine is produced significantly only in the positive column. Nitrogen yield is not substantially affected by back reaction while hydrazine yield is limited, at least in part, by back reaction which appears to involve atomic hydrogen. Catalysis of H atom removal (by platinum-coating the wall of the discharge tube) increases over-all hydrazine yield. Maximum 100 e.v. yields reported are $G(N_2) \sim 0.8$ and initial $G(N_2H_4) \sim 2.5$; the latter may have been exceeded. Effects of pressure, temperature, surface-to-volume ratio, X/p, and general character of discharge are discussed and suggestions are offered as to detailed mechanism and methods of modification of the yields. Substantially, all the primary chemical effects involve only relatively low excited states of ammonia, with energies far less than those required for ionization and probably below optically attainable levels.

Symbols Used Throughout Paper

H, hydrazine collected, mole sec.$^{-1}$ × 10^9
$\dot{N}$, nitrogen collected, mole sec.$^{-1}$ × 10^9
$\dot{\mathbf{H}}$, $d\dot{H}/dx$, mole sec.$^{-1}$ cm.$^{-1}$ × 10^9
$\dot{\mathbf{N}}$, $d\dot{N}/dx$, mole sec.$^{-1}$ cm.$^{-1}$ × 10^9
$\dot{N}_n$, nitrogen prod. in the cathode zones, mole sec.$^{-1}$ × 10^9
$G(\mathbf{H})$, number of molecules of hydrazine produced per 100 e.v. in positive column at $x = 0$
$G(\mathrm{N})$, number of molecules of nitrogen produced per 100 e.v. in positive column (this value is constant throughout the positive column unless otherwise specifically stated)
$G_n(\mathrm{N})$, number of molecules of nitrogen produced per 100 e.v. in negative glow
F, flow rate (cc. sec.$^{-1}$) measured at N.T.P.
i, discharge current, ma.
p, pressure, mm.
R, radius of discharge tube, cm.
T, temperature of discharge tube, °C.
V, discharge potential, volts
V_n, cathode fall, volts
x, interelectrode distance, cm.
X, dV/dx, volt cm.$^{-1}$
Y, initial energy yield of hydrazine at $x = 0$, g. k.w.h.$^{-1}$

1. Introduction

In the work here reported an investigation of the processes occurrent in the low pressure d.c. glow discharge through ammonia has yielded information on optimum conditions required for the production of hydrazine. In certain respects the conclusions agree with recent expressions of Ouchi and his colleagues.[4] We concur, for example, on the limited role of ions in the total chemical process but differ in more detailed considerations of the energetics and also in interpretation of the mechanism of the decomposition and of formation of products. We agree that the evidence clearly shows the reactions necessary for hydrazine production to occur in the positive column as contrasted with the negative glow.

Unlike the negative glow, the positive column of a glow discharge[5] is an essentially uniform plasma. The molecular temperature is close to ambient, while the ionic temperature is only slightly higher. The electrons have a drift velocity in the direction of the field of $\sim 10^5$ cm. sec.$^{-1}$ superimposed upon a random velocity distribution, usually thought to be nearly Maxwellian[4a] with an average energy of the order of 1 e.v.[6] Chemical reaction is initiated by interaction of sufficiently energetic electrons with molecules at about room temperature.

In principle it is possible, with knowledge of the energy distribution of electrons in a discharge plasma and the pertinent collision cross-sections, to determine the relative rates of production of all states conducive to reaction. Lunt and Meek[4g] have performed such calculations for the relatively simple case of hydrogen, but they are excessively difficult for a gas like ammonia. By contrast, essentially simple experiments do, however, lead to some potentially valuable physical and chemical conclusions.

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(1) Paper presented before Division of Physical and Inorganic Chemistry, Meeting of American Chemical Society at Los Angeles, Calif., March 17, 1953.

(2) Detailed data of this paper have been deposited as Document number **4181** with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm, to Chief, Photoduplication Service, Library of Congress.

(3) Olin Research Fellow at the University of Notre Dame.

(4) Part I: (a) K. Ouchi and Y. Watanabe, *J. Electrochem. Soc. Japan*, **17**, 285 (1949); (b) K. Ouchi, *ibid.*, **20**, 164 (1952); (c) **20**, 168 (1952); (d) **20**, 209, 212 (1952); (e) K. Ouchi and T. Takamatsu, *ibid.*, **20**, 266, 268 (1952); (f) **20**, 378 (1952); (g) **20**, 381 (1952). These articles are in Japanese accompanied by introductions and abstracts in English. (h) Part I is also paraphrased in English; *cf.* K. Ouchi, *Science Reports of the Research Institutes, Tôhoku University*, **A-4**, 203 (1952). A wide variety of discharge phenomena is discussed. (i) Parts II and III of the same subject "The Chemical Reaction by the Glow Discharge in Ammonia Gas" have appeared accompanying a complete reprint of Part I (with different pagination) in a single report not identified as to source or publisher. Apart from introductions and abstracts, these parts are in Japanese.

(5) For extensive discussion of the glow discharge and its various details, and review of much pertinent literature, *cf.* L. B. Loeb, "Fundamental Processes of Electrical Discharge in Gases," John Wiley and Sons, Inc., New York, N. Y., 1939: (a) p. 585; (b) p. 578; (c) Chap. XI; (d) p. 566. (e) A more qualitative description including some recent literature is given in K. G. Emeleus, "The Conduction of Electricity through Gases," John Wiley and Sons, Inc., New York, N. Y., third edition, 1951; (f) M. J. Druvesteyn and F. M. Penning, *Rev. Modern Phys.*, **12**, 87 (1940); (g) R. W. Lunt and C. A. Meek, *Proc. Roy. Soc.* (*London*), **A157**, 146 (1936).

(6) (a) H. Wiener and M. Burton, THIS JOURNAL, **75**, 5815 (1953). (b) See also section 4.2.

2. Experimental

2.1 **Chemicals.**—Reagents employed in this work included Matheson Co. ammonia labeled 99.5% pure and Eastman Kodak *p*-dimethylaminobenzaldehyde. Other reagents required in analysis of hydrazine were labeled C.P.; spectra obtained with the blank reagents agreed with those obtained by James.[7]

2.2 **Apparatus.**—Instability of the hydrazine produced in a glow discharge through ammonia necessitated employment of a flow system. Variation of the interelectrode distance results only in an increase in the length of the positive column, provided, of course, that the electrode separation is already great enough to support all the cathode regions.[4] Such variation can thus be employed to distinguish the reactions occurrent in the latter region (Crookes dark space, negative glow and Faraday dark space) from those in the positive column.

Figure 1 shows the discharge assembly. The electrodes E were flat circular tantalum disks, 0.7 cm. diameter and ~10 mils thick, spot-welded, through nickel, to tungsten leads. A glass shield S protected the cathode against possible striking of the discharge to the back surface and lead. The braided copper wire W served both as a cable for moving the anode, by means of a derrick arrangement actuated through the ground glass joint J, and as the electrical lead to the anode. The heavy capillary tube C acted as a weight and kept the anode centered in the discharge tube. The apparatus was readily dismantled for use of discharge tubes of various diameters with the same cathode and anode assemblies.

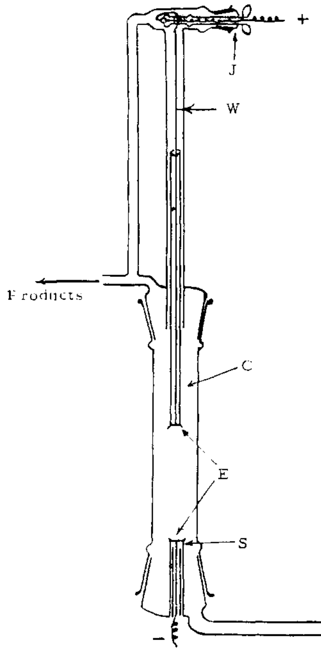

Fig. 1.—Details of discharge tube.

All measurements were made with a d.c. power supply of conventional design employing a 5000-volt center-tapped neon-sign transformer, two 266 half-wave rectifiers and a 30-henry choke with 8 mfd. condensers on the input and output sides as filter. The voltage was controlled by means of a Variac in the transformer primary, fine adjustment being obtained with a 20 K potentiometer in the cathode lead. The line voltage was stabilized with a Sola constant-voltage transformer.

2.3 **Technique.**—Figure 2 shows the complete system in schematic form. Erratic results during the early part of the investigation suggested the importance of removal of traces of water and oxygen from the system. The ammonia was predried with alumina in vessel A and stored over sodium at −78° in T_1. After a period never less than 24 hr. all gases non-condensable in liquid air were pumped off between repeated meltings, during repeated freezings of the solution with liquid air. Immediately prior to a run, the required amount of ammonia was distilled into T_2 immersed in liquid air, while S_6 was open, to remove the last traces of non-condensables.

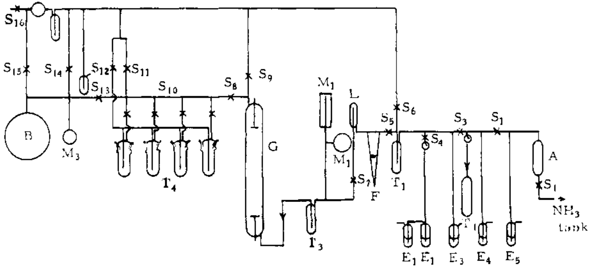

Fig. 2.—Diagram of apparatus for study of discharge decomposition of ammonia.

During a run the pressure to the right of L, an all-glass needle valve, was maintained at one atmosphere by allowing the ammonia in T_2 to rise to its boiling point, the excess gas being vented through vessels E_4 and E_5 containing dibutyl phthalate. The pressure in the reaction system was measured with a DuBrovin gage, M_2, or a McLeod, M_1, and the flow rate determined with flowmeter F. The vessel T_3 was maintained at −78° to remove mercury vapor.

Hydrazine was collected for a period of only 200 seconds. Consequently, to avoid effect of initial surges and unsteadiness in the discharge, the products were by-passed through S_{11} until the discharge had reached a steady state. The hydrazine and ammonia were then collected in one of the removable traps, T_4, surrounded by liquid air. With the four traps, four runs could be made before opening the system for determination of hydrazine production.

During a run, nitrogen and hydrogen were collected for 50 seconds in the 3-liter bulb B by closing S_{14} and S_{16} and opening S_{15}. Corrections (<10%) were applied for the gas present between S_{16}, S_{15} and the single stage diffusion pump D before collection was begun. The pressure in B as measured on the McLeod M_3 never rose sufficiently high appreciably to change the pumping speed, and thus the pressure on the low pressure side of the pump, during collection.

2.4 **Analysis.**—Hydrazine was determined colorimetrically as a complex with *p*-dimethylaminobenzaldehyde using the DU spectrophotometer. The method is described by James[7] from whose data we have calculated molecular extinction coefficients. $\epsilon_{460} = 1.40 \times 10^5$ and $\epsilon_{500} = 9.06 \times 10^3$ liter cm. mole^{-1} at 460 and 500 mμ, respectively, over the concentration range 0 to 10^{-5} *M* hydrazine. Our data show that Beer's law applies over the range 0 to 10^{-4} *M* giving $\epsilon_{460} = 1.46 \times 10^5$ and $\epsilon_{490} = 2.69 \times 10^4$ liter cm. mole^{-1}. At concentrations much above 10^{-4} *M*, appreciable departure from Beer's law occurs.

The yields of nitrogen and hydrogen were calculated separately from stoichiometry assuming them and hydrazine as the only products.

3. Results and Comments

3.1 **General Outline of Attack.**—The theory of the general physical and chemical processes which occur in an electric discharge is given in a paper by Wiener and Burton.[6] An experimental study requires information on (a) the various factors which may contribute to high potential gradient per unit pressure (*i.e.*, X/p) and (b) the effect of such gradients on the presumed elementary processes and the observed gross chemical effects.

The various features of an electric discharge reaction cannot all be varied independently at will. Pressure, X/p, access of ions to containing walls, rates of diffusion, half-lives of radicals and ions, and contributions of wall reactions are mutually interdependent and, while surface-to-volume ratio

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[7] W. A. James, Midwest Research Institute Report, "Quantitative Determination of Hydrazine Using the DAB Reagent Analytical Procedure."

does not, of course, affect pressure, it does affect all the others. On the other hand, the nature of the wall, the molecular temperature (within limits), the length of the positive column, and the transit time of the reactant gas can be varied without major effect on the electrical characteristics of the discharge.

In this work many of these conditions were varied, separately where practicable, in various different relationships where necessary. An attempt was made to relate purely physical factors and gross chemical effects.

3.2 Physical Characteristics of the Discharge.—With discharge current of 2–8 ma. and pressure of 1–10 mm. all zones of the d.c. discharge in ammonia are clearly visible in a darkened room. The negative glow is blue and the positive column green with no visible striations. The latter is separated from the walls by a dark space of 3–8 mm. dependent on the pressure. Small bright glowing spots present on the anode decrease in number at higher pressures.

Figure 3 shows how the voltage necessary for maintenance of discharge varied both with discharge length and current in this work. The extrapolations to zero interelectrode distance indicate a normal cathode fall less than 500 volts in all the cases studied (*cf.* Ouchi and Takamatsu[4e]). After more than a year of intermittent operation, cathodic sputtering onto the glass shield S (see Fig. 1) resulted in an increase of effective cathode area; the minimum extrapolated voltage under such conditions dropped to 350 volts. A.D.I. Tables 2 and 3[2] show that the cathode drop, V_n, increases markedly at pressures below about 3 mm. at 2 ma. current. The data correspond to the reasonable value[5b] $j_n/p^2 \sim 4 \times 10^{-4}$ amp. cm.$^{-2}$ mm.$^{-2}$, where j_n is the normal cathode current density.

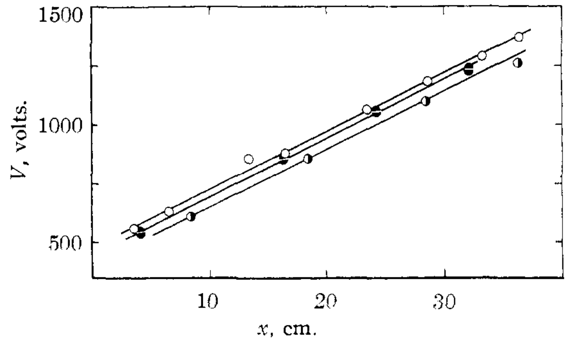

Fig. 3.—Typical relationships between voltage, interelectrode distance and current: R(A) = 1.37 cm.; p = 3 mm.; F = 2.28 cc. sec $^{-1}$. Legend: ○, 2 ma.; ●, 1 ma.; ◑, 0.6 ma.

Figure 3 also shows the typical linear variation of voltage (independent of current) with interelectrode distance, x, in the positive column. This linear variation indicates a uniform positive column and thus a constant rate of primary reaction per unit volume independent of column length. (Ouchi,[4d] on the other hand, appears of the opinion that a maximum rate of primary reaction occurs in the center of the positive column.) Except when otherwise indicated, the field strength X in the positive column was constant throughout its length.

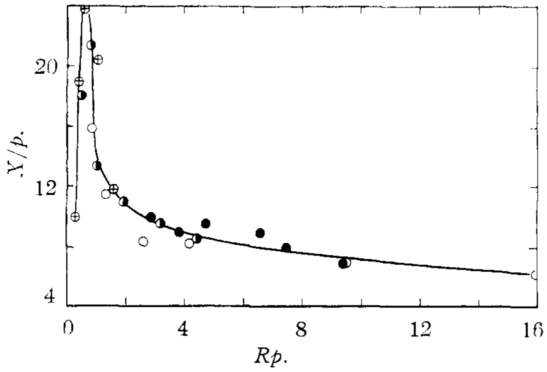

Fig. 4.—Influence of discharge tube radius on X/p as a function of Rp. The points represent a variety of currents in the range 0.6 to 6 ma. except for the points ⊕ which were all at 0.4 ma. Legend: tube radii ○ and ⊕ 1.35 cm.; ●, 0.94 cm.; ◑, 0.64 cm.

According to the analysis of Engel and Steenbeck,[5c] in which ion and electron recombination is governed principally by ambipolar diffusion to the walls, X/p should be a function of the product Rp for a particular gas, where R is the radius of the tube and p the pressure. Figure 4 indicates the validity of the relationship. The points corresponding to the largest tube at a current of 0.4 ma. may be quantitatively unreliable, for X in these cases was not constant throughout the length of the tube through the whole pressure range. They are included only as further evidence for the existence of a maximum in X/p at low values of Rp. (These particular data represent the values of X only over the initial range of interelectrode distance x; in that range they were constant.) The maximum in X/p is not presently understood and has severely restricted the range of X/p over which investigation of the reaction could be made. In simultaneous studies of the plasma using a Langmuir probe,[8,9] the characteristics of which were recorded on an oscilloscope, a sudden change in the pattern was observed at this point. The characteristic curve changed shape, became less stable, and was accompanied by large-amplitude oscillations. An examination of the cathode current to the discharge, using an oscilloscope, indicated that over the whole pressure range plasma oscillations were present. They had a frequency of ~50 kc. and a peak to peak amplitude of ~10% of the d.c. current. The power supply voltage showed no similar a.c. component and attempts to eliminate the oscillations by series inductances and by-pass condensers were unsuccessful.

The curve to the right of the maximum is similar to that found for other gases and is of the form to be expected from the analysis of Engel and Steenbeck.

3.3 Dependence of Nitrogen and Hydrazine Formation on Discharge Length.—Figure 5 shows typical curves for the amount of nitrogen, $\dot{N}$, and hydrazine, $\dot{H}$, produced per second with various discharge lengths, x, measured as the distance be-

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(8) I. Langmuir and H. Mott-Smitt, Jr., *Gen. Elec. Rev.*, **26**, 731 (1923).

(9) *Cf.* I. Langmuir and H. A. Jones, *Science*, **59**, 380 (1924).

tween electrodes. The slopes of these curves, denoted by $\dot{\mathbf{N}}$ and $\dot{\mathbf{H}}$, represent the rate of production of nitrogen and hydrazine per cm. length of positive column per second. The discontinuity in $\dot{H}$ at $x = 20$ cm. with a discharge current of 1 ma. was caused by insertion of a platinum probe at this point. The effect is discussed in sections 3.4 and 3.7. The extrapolation of $\dot{H}$ to zero at a positive intercept of x is probably due to the finite extension of the cathode zones. The value $x \sim 1.5$ cm. is of the order to be expected from visual observations of the cathode zones.

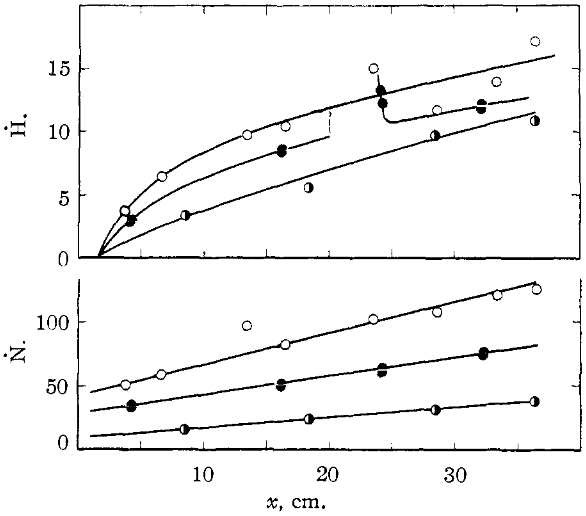

Fig. 5.—Typical curves for hydrazine and nitrogen production as a function of interelectrode distance and current. In the 1 ma. runs a probe was inserted at $x = 20$ cm. Conditions and legend as in Fig. 3.

3.4 Effect of Current.—Although X was independent of discharge current over the range 0.6 to 2 ma., the slopes of the $\dot{N}$ lines and the initial slopes of the $\dot{H}$ curves in Figure 5 show that both $\dot{\mathbf{N}}$ and $\dot{\mathbf{H}}$ increase nearly linearly with discharge current. The laws of increase are not greatly different for these series of experiments; *i.e.*, rate of production of nitrogen and the initial rate of production of hydrazine are both approximately proportional to the discharge current and thus to the amount of primary reaction. The range of current investigated was limited at the high end by the region of abnormal cathode fall, where heating of the cathode led to erratic results, and at the low end by instability of the discharge.

3.5 Reaction Zone.—The flow rate in these experiments varied from 10^2 to 5×10^2 cm. sec.$^{-1}$. Thus, unless the lifetime of the radicals or active intermediates involved in formation of ultimate products is larger than about 10^{-2} sec., most of the reaction would occur in the discharge.

Evidence in regard to the locale of reactions which determine hydrazine formation has been obtained by inserting an electrically unconnected flat circular probe 1 cm. in diameter vertically in (not across) the discharge tube. Figures 5 and 6 show a marked increase in hydrazine formation when the probe was in the discharge near the anode end, but no effect was observed when the probe was only a few millimeters upstream from the anode (*i.e.*, outside of the discharge). This effect was established by many repetitions, and it also was established (see section 3.8) that coating the walls with platinum produces a large increase in $\dot{\mathbf{H}}$ throughout the discharge tube. These results strongly indicate that any intermediates leading to hydrazine formation do not persist more than a few millimeters beyond the discharge. Figure 5 shows no similar effect on the rate of nitrogen production.

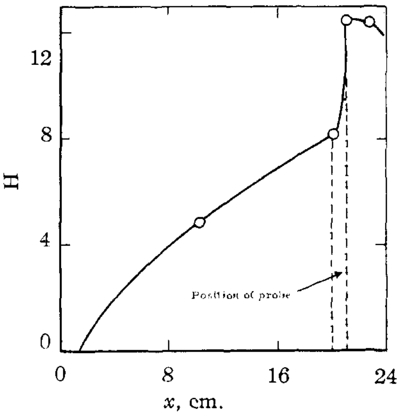

Fig. 6.—Effect of unconnected platinum probe on hydrazine formation in the positive column: current 1 ma.; pressure 3 mm.; discharge tube radius 1.37 cm.; flow rate 2.28 cc. sec.$^{-1}$.

3.6 Hydrazine Destruction and Steady-state Concentration.—Figure 7 shows the effect of fourfold increase in flow rate on rate of hydrazine production. The results are in agreement with the concept that hydrazine is destroyed in the discharge and that longer residence times favor hydrazine destruction (*cf.* Ouchi, *et al.*[4]). The fact that at the higher flow rate $\dot{\mathbf{H}}$ extrapolates to a positive value at $x = 0$ suggests the possibility that hydrazine is formed in the negative glow and under these conditions some escapes before complete decomposition.

The data in A.D.I. Table I (relating to a tube of 0.64 cm. radius) when compared with those of Fig. 7 show that with a discharge tube of smaller diameter smaller hydrazine concentrations are obtained. The data also show that at higher pressures higher hydrazine concentrations are attained. A steady-state hydrazine concentration is reached at relatively small interelectrode distances for low flow rates.[9] Several anomalously high results are evident in Fig. 7 as well as the A.D.I. Table I. The differences are well beyond experimental error in measurements and must represent lack of control in the reaction. Variations in the nitrogen yields were considerably smaller. For two runs at 3.08 mm. pressure in a 0.64 cm. radius tube, the calculated average steady-state hydrazine concentrations were 7.2×10^{-9} and 7.1×10^{-9} mole liter^{-1} (*i.e.*, at temperature and pressure of the experiment), values which agree within experimental error. The results of A.D.I. Table I show that $\dot{\mathbf{N}}$ is independent of flow rate and also that at lower pressures (0.83–1.6 cm.) more hydrazine may be produced with shorter positive columns.

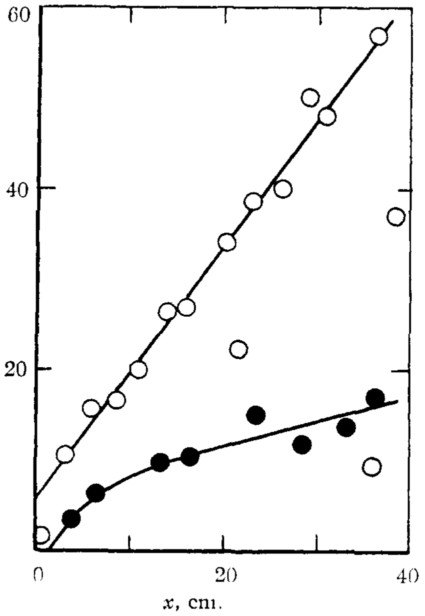

Fig. 7.—Effect of flow rate on hydrazine formation: current 2 ma.; pressure 3 mm.; discharge tube radius 1.37 cm.; flow rate: ○, 10.8 cc. sec.$^{-1}$, ●, 2.28 cc. sec.$^{-1}$.

3.7 Energy Efficiency as a Function of Pressure and Discharge Diameter.—Values of $G(\mathbf{H})$ and $G(\mathbf{N})$, respectively, the numbers of molecules of hydrazine and nitrogen produced per 100 e.v. of energy input to the positive column, are shown in Fig. 8 as function of pressure for three different tube radii. The data are taken from A.D.I. Tables 2–4. Here $G(\mathbf{H})$ was determined from the initial value of $\dot{\mathbf{H}}$ at $x = 0$ and thus represents the maximum value when no hydrazine has been decomposed. The value $G(\mathbf{N})$ was determined from the constant value of $\dot{\mathbf{N}}$ over the length of the column, and the power input was calculated using the measured discharge current and voltage gradient. The points for nitrogen production in the 2.73 cm. diameter tube at 0.4 ma. are again included only as confirmatory evidence for the maximum in $G(\mathbf{N})$ at low pressures. Like X in these experiments, $\dot{\mathbf{N}}$ changed with x and initial values were used. As is indicated in section 3.6, at the lower pressures a steady-state hydrazine concentration was reached at the smallest values of x employed and no estimate of the initial rate of hydrazine formation could be made. In view of the small steady-state concentration, however, it is likely to be small.

Comparison of Fig. 8 with Fig. 4 shows a striking parallelism between nitrogen production and X/p. Efficiency of hydrazine formation, on the other hand, increases over most of the range for which X/p decreases. Figure 8 shows that in the pressure range 3 to 8 mm. no appreciable change in efficiency of nitrogen production occurs, while the initial efficiency of hydrazine production more than doubles. Over this range X/p is very nearly constant. Consequently, it is expected that the rates of all primary reactions should be constant.

Figure 9 shows curves of $G(\mathbf{H})$ and $G(\mathbf{N})$ plotted directly against X/p for the three discharge tubes. The two points on the curves for $G(\mathbf{N})$ showing marked departures from the curves correspond to values to the left of the maxima in Fig. 8, and are thus in the region of instability for the discharge. The curves indicate that $G(\mathbf{N})$ and $G(\mathbf{H})$ are functions not only of X/p but of the tube radius as well. The efficiency for hydrazine production decreases markedly at lower pressures even though

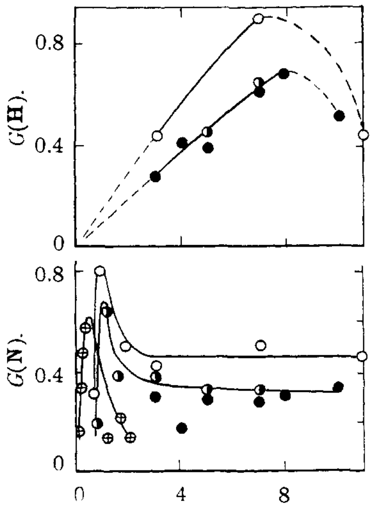

Fig. 8.—Effect of discharge tube radius on relation between pressure and energy efficiencies for nitrogen and initial hydrazine production under a variety of conditions. Legend as in Fig. 4.

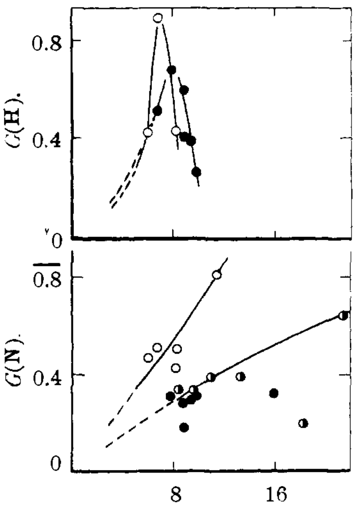

Fig. 9.—Effect of discharge tube radius on relation between X/p and energy efficiencies for nitrogen and initial hydrazine production under a variety of conditions. Legend as in Fig. 4.

TABLE I

EFFECT OF TEMPERATURE AND OF PLATINUM-COATED WALLS ON DISCHARGE REACTION

Tube Radii, R(B) = R(C) = 0.64 cm. Tube C has platinum coated walls. F = 4.56 cc. sec.$^{-1}$ except in run 58, for which F = 3.10 cc. sec.$^{-1}$.

Run	Tube	p	i	T	X	$(X/p)_{25}$	$\dot{N}$	G(N)	$\dot{H}$	G(H)	V_n	N_n	G_n(N)	Y
54	B	6.70	4.00	100	65.0	12.2	7.45	0.28	12.7	0.47	410	74.0	0.44	5.6
55	B	8.30	4.00	200	58.0	11.1	13.2	.55	21.3	.89	420	54.5	.31	10.6
52	B	8.70	4.00	200	57.3	10.4	6.93	.29	21.3	.90	405	63.0	.37	10.7
53	B	10.80	4.00	350	65.0	12.6	6.09	.23	21.3	.79	420	57.6	.33	9.5
56	C	5.05	2.00	RT*	63.7	12.6	3.00	.23	33.4	2.5	385	28.0	.35	30
57	C	7.00	4.00	RT*	63.7	9.1	8.03	.30	96	3.6	385	56.5	.36	43
58	C	3.08	2.00	RT*	37.7	12.2	2.72	.35	15.4	2.0	543	49.0	.44	23

* Room temperature.

X/p and, thus, presumably the efficiency of primary excitation are increasing.[10] These facts strongly suggest the importance of wall reactions involving the intermediates in the reaction.

3.8 Platinum-coated Walls.—The data from experiments with platinum probes did not establish whether the effect was prevention of hydrazine destruction or catalysis of its formation. Experiments were therefore made in a discharge tube whose walls were coated with platinum, so that initial values of $\dot{\mathbf{H}}$ could be obtained. Maintenance of nearly constant voltage gradient on the walls minimizes electrical disturbances in the plasma. Consequently, the platinum coating was deposited in the form of rings 1 cm. in length, separated 0.2 to 1 mm. for insulation purposes.

The platinum was deposited as a uniform film by thermal decomposition of Hanovia "Liquid Bright Platinum No. 0.505" painted on the inside of the tube. This coat was covered by a thin layer of paraffin wax on which circular scratches were made at 1-cm. intervals. The exposed platinum was then dissolved in aqua regia, and the paraffin removed with carbon tetrachloride.

The results are shown in Table I. Comparison of the energy efficiencies with those for the unplatinized tube (A.D.I. Table 3) shows that the platinum markedly catalyzes hydrazine formation but has little effect on production of nitrogen. The ratio X/p (referred to pressure at 25°) increased slightly in the platinized tube. Figure 9 indicates that $G(\mathbf{H})$ increases with increasing pressure, *i.e.*, with decreasing X/p. Thus, together these two sets of data are inconsistent with the theory that $G(\mathbf{H})$ reflects directly the energy efficiencies of the primary process.

Comparison may be made in this place to some results of Ouchi. Hydrazine yields reported herein (*e.g.*, either $G(\mathbf{H})$ or Y in Table **I**) are initial values in the positive column where hydrazine decomposition does not occur. They do not include energy losses in the negative glow. In Ouchi's work on ammonia flowing transverse to a 50 cycle a.c. discharge[4c] (thus removing the products rapidly from the region of their formation) he obtains a maximum yield of hydrazine of ~11 g. k.w.h.$^{-1}$. However, this figure is based on total energy input including loss in the negative glow and is not properly to be compared with our maximum value, 43 g. k.w.h.$^{-1}$, in the presence of a catalyst. In his work on interrupted discharge,[4b] Ouchi reports a maximum yield of 47.0 g. k.w.h.$^{-1}$ at a hydrazine concentration of 0.013%.[11]

3.9 Effect of Temperature.—The results shown in Table I indicate that $G(\mathbf{H})$ increases with increasing temperature from 25 to 350°, to a saturation, or perhaps a maximum, value. Any change in $G(\mathbf{N})$ is certainly less marked.

Since the average electron energy is a function of Xd, where d is the density, the pressure in these experiments was adjusted in an attempt to keep d constant at the value for 5 mm. and 25°. Consequently, the values of $(X/p)_{25}$ listed in Table I were calculated for purpose of comparison using the value of p for the same density at 25°. While, *a priori*, little effect of discharge temperature on electron temperature would be expected owing to the very large differences between the two, actually the ambipolar diffusion constant, and thus the electron temperature should increase somewhat with increasing molecular temperature. The effect, as manifested in an increasing value of X/p, is too small for detection.

Discussion

4.1 Background of Mechanism.—Direct conclusions from the data may be summarized as follows.

4.1.1 While nitrogen is produced in the negative glow no hydrazine escapes from this region (section 3.3). This result may mean either that hydrazine is not produced in the negative glow or that it is rapidly destroyed in this region of relatively high energy density. Similar conclusions were reported by Westhaver[12] and by Ouchi.[4c] The latter established in experiments with flow of gas perpendicular to the discharge that no significant yield of hydrazine emerged from the negative glow.

4.1.2 Since the field strength X, and thus X/p, are constant over the length of the positive column the rate of the primary processes should be constant. The steady decrease in $\dot{\mathbf{H}}$ with increasing x (section 3.3) therefore suggests that hydrazine or a precursor is disappearing in the discharge.

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[10] Increased X/p means increased energy gain in the mean free path of the electron. Thus, the average energy of the electrons is increased and this increase would result in an increased number of excited states leading to decomposition.

[11] *Cf.* also H. Schüler and V. Degenhart, *Z. Naturforschung*, **8a**, 251 (1953), who obtained a maximum yield of hydrazine of 11.11 g. k.w.h.$^{-1}$ in a 50-cycle discharge and of 13.8 g. k.w.h.$^{-1}$ in a 500-cycle discharge.

[12] J. W. Westhaver, *J. Phys. Chem.*, **37**, 897 (1933).

4.1.3 The simultaneous complete constancy of $\dot{\mathbf{N}}$ throughout the column (although $\dot{\mathbf{H}}$ decreased from the initial value approximately equal to $\dot{\mathbf{N}}$ in these experiments to less than $^1/_5$ of this value) indicates that the destruction of hydrazine or its precursor in the discharge does not lead to appreciable nitrogen formation (section 3.3).

4.1.4 The results of section 3.5 do not definitely establish the locale of formation either of nitrogen or of hydrazine. While our knowledge of the behavior both of free radicals and of excited molecules would evoke a reasonable doubt that they survive more than 10^{-2} sec. under the conditions of these experiments, these results signify merely that no devices used in these experiments beyond the discharge zone were able to affect the yields. This conclusion is different from that of Ouchi[4c] who interprets his results on the flow of ammonia perpendicular to a discharge as meaning that substantial formation of hydrazine (he suggests from $NH + NH_3$) occurs outside the discharge region in that case.

4.1.5 Occasional anomalous results are obtained[9] (section 3.6). According to the interpretation of section 4.4 (*cf.* section 3.7), surface reactions can play an important role in determination of hydrazine yield. The anomalies appear connected with an uncontrolled variation in the surface of the discharge tube.

4.1.6 The increased yield of hydrazine at lower pressure with shorter positive columns (section 3.6) may be caused by an expansion of the negative glow at the lower pressures with less hydrazine destruction in it or may merely reflect hydrazine normally formed in the negative glow and too small for observation when the relatively high yields found in the positive column at higher pressures dominate.

4.1.7 The results of Fig. 8 (*cf.* section 3.7) show that hydrazine and nitrogen are produced by essentially separate mechanisms involving different intermediates. We may note that the methods employed by Ouchi and his co-workers[4] precluded establishment of relationship or lack of relationship between nitrogen and hydrazine yields. Partly for this reason, their conclusions regarding mechanism are different from those presented herein.

4.2 Primary Processes in the Discharge.—While continued ionization of the gas is necessary to maintain an electric discharge (because the ions formed are constantly being neutralized) a minor fraction of the energy goes into this process. A major fraction is dissipated in electronic excitation[6a] and some of it is transferred in inelastic collisions into vibrational states of the molecules.[13] Thus, in principle, in the electric discharge the only primary physical processes of importance for chemistry are excitations. This theoretical principle is in agreement with the observations herein reported. In mass spectroscopic data[14] for ammonia the predominant peaks on bombardment by 100 volt electrons are NH_2^+ and NH_3^+ in the ratio 0.78:1. The appearance potentials are 15.7 and 10.5 e.v., respectively. The latter may be taken as the maximum value of the ionization potential of NH_3, $I_{max}(NH_3)$. The minimum corresponding value of the ionization potential, of the NH_2 free radical calculated from the 15.7 e.v. appearance potential and a bond dissociation energy for $NH_2–H$ $\sim$4.65 e.v.[15] is 11.05 e.v.; *i.e.* higher than $I_{max}(NH_3)$.

Details of the excited states of ammonia are not available. However, the lowest excited state attained by absorption of light is at 5.1 e.v. A virtual continuum of states exists to about 6.3 e.v.[16] It is reasonable to suppose that there are excited states, lower than 5.1 e.v., corresponding to triplet excitation.[6,17] No information is available on the lowest excitation level of NH_2, but the reasonable presumption is that it is a quadruplet level and that in view of the similarity of ionization potentials its energy is not greatly different from that of the lowest NH_3 level and is perhaps slightly higher. The characteristics of these lowest states are emphasized because, although they cannot be reached in light absorption, the selection rules for excitation by electron impact are not so restrictive.

An important conclusion from these considerations is that, in the gaseous mixture containing NH_3 and NH_2, molecules of the former are likely to be preferentially excited by impacting electrons, not only because of their relatively high concentration but because of their probably lower excitation potential.[6a]

The electron energy distribution in the discharge may be taken as approximately Maxwellian[5a]; the average energy distribution does not exceed $\sim$1.4 e.v.[18] Thus, relative to the number of electrons of energy adequate to excite NH_3 (to the lowest state reported in light absorption) the fraction of electrons with energy adequate to ionize NH_3 is $\exp[-(10.5 - 5.1)/1.4]$ or $\sim 1.8 \times 10^{-2}$. Correspondingly, the relative fraction with energy adequate to produce NH_2^+ from NH_3 is $\sim 8 \times 10^{-4}$. The values are calculated for comparisons involving the usual photochemically excited states; if the unknown lower triplet state is used as reference these values are decreased. In precise calculation of the relative numbers of ions and excited entities, the cross-sections for the excitation processes must, of course, be included. However, the

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(13) *Cf.* H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, 1952, p. 279.

(14) M. M. Mann, A. Hustrulid and J. T. Tate, *Phys. Rev.*, **58**, 340 (1940).

(15) According to Birse and Melville (ref. 22e), presence of ammonia does not affect the rate of the hydrogen-atom-induced conversion of *p* to *n* hydrogen. We are indebted to Professor Melville for the observation that this may mean a bond strength in ammonia substantially higher than that in hydrogen. On the other hand, as Dr. Darwent has suggested to us, the difference in rate is equally well ascribed to a steric factor ratio (for the H atom reactions with NH_3 and H_2, respectively) of $\sim 10^{-4}$.

(16) *Cf.* G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 181.

(17) *Cf.* the analogous case of water, K. Niira, *J. Phys. Soc. Japan*, **7**, 193 (1952); also G. G. Hall, *Proc. Roy. Soc.* (*London*), **A213**, 113 (1952); R. G. Parr, D. P. Craig and I. G. Ross, *J. Chem. Phys.*, **18**, 1561 (1950).

(18) This is certainly an upper limit. Using the approximate formula (ref. 5a), $E = Xe\lambda/2\alpha^{1/2}$, we adopt as values characteristic of this work $X = 63$ volt cm.$^{-1}$, $\lambda \sim 6.8 \times 10^{-3}$ cm., and the conservative low value $\alpha = 0.024$ (*cf.* ref. 13). Thus, the average energy of the electrons is $\sim$1.4 e.v.

present estimate shows clearly that relative to the number of chemically important excited entities, the number of ionized molecules is very low.

The model of Engel and Steenbeck[5c] involves ambipolar diffusion of the ions to the wall, where neutralization occurs. Although it might be expected that molecular ions would neutralize in the gas phase (because of the dissociative processes possible), Fig. 4 indicates that the Engel–Steenbeck model applies and that most of the ions neutralize on the wall. It is possible that neutralization of NH_3^+ on the wall may occur without dissociation, and indeed such an effect has been claimed by Smith and Essex.[19]

Measurements of the wall current made with a Langmuir probe indicate that the ratio of the number of molecules of ammonia decomposed to give products to the number of ions neutralized on the wall was between 30 and 60. Comparison of $G(\dot{\mathbf{H}})$ data (runs 56 of Table I and 48 of A.D.I. Table 3) indicate that the number of NH_2 radicals primarily produced is probably more than four times as large as those actually leading to products so that the ratio of ammonia molecules initially decomposed to ions neutralized on the wall may be between 120 and 240. Although the reliability of the probe data is questionable, the results should be correct to within an order of magnitude particularly with the probe operating near wall potential.

4.3 Paths of Reaction.—Apparently, hydrazine and nitrogen arise from two separate primary reactions (section 4.1.7). We denote by I and II the two paths which lead eventually to hydrazine and nitrogen, respectively. The variation of N_2 yield with pressure (Figs. 5 and 8) indicates that it reflects directly the change in the rate of attainment of path II although the dependence of $G(\mathbf{N})$ on both X/p and the radius of the discharge tube indicates that secondary wall reactions also affect the amount of nitrogen formation. Figures 8 and 9 indicate, however, that the efficiency of hydrazine formation as a function of pressure does not reflect change in efficiency of attainment of path I, since it is not to be expected that this will vary less regularly with X/p than does efficiency of attainment of path II. The dependence of $G(\mathbf{H})$ on both X/p and R, and the marked effect of platinized wall on $G(\mathbf{H})$ indicate importance of wall reactions. An analogous decrease in quantum yield with decreasing pressure below 100 mm.[20] is observed in ammonia photolysis. The apparent insensitivity of nitrogen yield to the platinum walls suggests that the wall reactions are either different from, or much less important than, those involved in hydrazine formation.

4.4 Secondary Reactions.—Considerations of the principle of microscopic reversibility rule out production of molecular products as well as free atoms from metathetical reactions of excited ammonia molecules, while photochemical evidence[21] on the other hand suggests the importance of NH_2 and H in the mechanism. Two obvious possible paths of decomposition are

$$NH_3 \rightsquigarrow (NH_3^*) \begin{cases} \longrightarrow NH_2 + H & \text{(I)} \\ \longrightarrow NH + H_2 & \text{(II)} \end{cases}$$

It is not possible to state whether such paths involve different excited states of ammonia, but, in any event, the state involved is probably a low-lying triplet level.[6a] Energy states lower than the NH_2–H bond dissociation energy (approximately 4.65 e.v.[15]) are inadequate for reaction I. The minimum energy required for II may be higher than for I because considerable distortion of the activated complex and a consequent potential energy hump are probably involved. The latter view fits the fact that $G(\mathbf{N})$ is generally less than $G(\mathbf{H})$, particularly in tubes with platinum-coated walls.

Of the variety of possible secondary reactions the results can be conveniently explained (consistently with ideas gained from photochemical evidence[21,22]) in terms of a rather simple pattern.

Reactions adequate to determine the yield of hydrazine are the forward reaction

$$NH_2 + NH_2 \xrightarrow[\text{or W}]{\text{M}} N_2H_4 \qquad (1)$$

and the back reactions

$$NH_2 + H \xrightarrow[\text{or W}]{\text{M}} NH_3 \qquad (2)$$

$$N_2H_4 \rightsquigarrow N_2H_4^* \longrightarrow 2NH_2 \qquad (3)$$

$$N_2H_4 + H \longrightarrow NH_2 + NH_3 \qquad (4)$$

Assumption of the last reaction is contrary to a reported collision yield[22d] of $\sim 10^{-7}$ but consistent with the fact that in photolysis of ammonia containing 0.1% hydrazine the hydrazine decomposes with a quantum yield greater than unity. Effects of X/p and pressure on relative rates of 1 and 2, respectively, determine hydrazine yield. Reaction 1 is favored by high X/p and reaction 2 by low pressure. Thus, at extremely low pressure both low X/p (*cf.* Fig. 4) and pressure combine to give low N_2H_4 yield; at slightly higher pressure, the effect is to increase probability of reaction 1 and to decrease the probability of reaction 2; at even higher pressure decrease in X/p is more important than increase in pressure and the effect is a maximum in the N_2H_4 yield (*cf.* Fig. 9).

Reactions adequate to determine nitrogen yield are

$$NH + NH_3 \longrightarrow N_2 + 2H_2 \qquad (5)$$

and the back reaction

$$NH + H_2 \xrightarrow[\text{or W}]{\text{M}} NH_3 \qquad (6)$$

Reaction 5 has been suggested by Ouchi,[4i] but although it would be expected to have an activation energy, the fact is that nitrogen yield is relatively insensitive to temperature (*cf.* Table I). Moreover, the work of Rice and Freamo[23a] on the free NH radical gives evidence only for

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(19) C. Smith and H. Essex, *J. Chem. Phys.*, **6**, 188 (1938).

(20) E. O. Wiig, THIS JOURNAL, **57**, 1559 (1935).

(21) *Cf.* W. A. Noyes, Jr., P. A. Leighton and G. K. Rollefson, "Exposes de Photochimie," Herman *et* Cie, Paris, Chap. III, 1938.

(22) (a) G. R. Gedye and E. K. Rideal, *J. Chem. Soc.*, 1160 (1932); (b) A. Kahn and H. E. Gunning, paper presented at American Chemical Society Meeting, Division of Physical and Inorganic Chemistry, Cleveland, Ohio, April, 1951; (c) H. J. Weleg and A. O. Beckman, THIS JOURNAL, **58**, 2464 (1936); (d) E. A. B. Birse and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A175**, 180 (1940); (e) **A175**, 187 (1940).

(23) (a) F. O. Rice and M. Freamo, THIS JOURNAL, **73**, 5529 (1951) (b) **75**, 548 (1953).

$$4NH \xrightarrow{W} NH_4N_3 \qquad (7)$$

They specifically note an inability to detect free NH in the electric discharge through ammonia even at low pressure. Unfortunately, there does not appear to be any direct evidence of reaction or absence of reaction in the gas phase between NH radicals, *i.e.*

$$NH + NH \longrightarrow N_2 + H_2 \qquad (8)$$

or between NH radical and some other molecule such as NH_3 or N_2H_4. Reaction 6 has a formal similarity to $CH_2 + H_2 \xrightarrow{M(?)} CH_4$, which appears to be rather well established.[6a,24]

Reactions between NH and NH_2 radicals are ruled out by the fact that the yields of N_2 and N_2H_4 (the products of the presumed reactions 2 and 5 or 8) are not interdependent (*cf.* section 4.1.7).

The catalytic effect of platinum walls on hydrazine formation suggests the importance of a reaction which can interrupt the back reaction, 2 or 4, *e.g.*,

$$H + H \xrightarrow[\text{or W}]{M} H_2 \qquad (9)$$

The effect of platinum walls is explained most simply by increase in the rate of reaction 9 and consequent decrease in rate of reaction 4.

4.5 Hydrazine Decomposition.—Hydrazine is rapidly destroyed in the discharge and nitrogen is not formed in this process (section 4.1.3). Steady-state concentrations were established at values less than 0.1 mole per cent. in the platinum-coated tube. The lowest excited state of hydrazine is probably triplet and the lowest significant excited state probably corresponds to the dissociation energy of the $H_2N–NH_2$ bond. This figure is given by Szwarc[25] as ~2.6 e.v. in rather good agreement with a value of 2.9 e.v. estimated from the 4.65 e.v. value of the $H–NH_2$ bond. Neglecting considerations of possible difference in cross-sections for the electronic interactions and assuming, as before, that the average electron temperature is about 1.4 e.v., it follows that the probability of production of $N_2H_4^*$ is at the most about 5 times that of attainment of path I. Thus, preferential excitation of N_2H_4 would not appear to be the limitation responsible for the relatively low concentration of hydrazine (*e.g.*, ~0.04 mole per cent. in Table I, run 56) obtain in this work, so that reaction 4 rather than reaction 3 would appear to be the major restriction on yield and steady-state concentration of hydrazine. This conclusion is contrary to the view of Ouchi.[4b]

4.6 Reaction in the Negative Glow.—Whether production of inappreciable quantities of hydrazine in the negative glow is due to its rapid destruction or to its substantial lack of formation in this region is not known. The average energy near the cathode edge is probably higher, while that near the anode edge lower, than that existing in the positive column.[5d] Evidence has been presented that at high flow rates some hydrazine does escape from this region.

The data in A.D.I. Tables 2 to 4 indicate a maximum energy efficiency for nitrogen production in the negative glow between 2 and 3 mm. pressure with a value approximately equal to that in the positive column at high pressures. The paucity of data available on the reaction and on the electron energy distribution in this region[4e,f,g] forbid discussion of mechanism. The situation is further complicated by the possibility that reactions occur in the Faraday dark space.[4c]

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[24] (24) C. E. H. Bawn and J. Milstead, *Trans. Faraday Soc.*, **35**, 889 (1939).

[25] (25) *Cf.* M. Szwarc, *Chem. Revs.*, **47**, 75 (1950). If a low NH bond dissociation energy is assumed for NH_3 (*cf.* footnote 14) the agreement is better.

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Polymer Production in Radiolysis of Benzene[1,2]

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Irradiation of liquid benzene with 1.5 Mv. electrons gives polymer as a non-volatile product with a 100 e.v. yield $G(C_6H_6 \rightarrow \text{polymer}) = 0.75$ independent of intensity and total energy input. Average molecular weight increases non-linearly with energy input; the maximum value observed was ~530. At the same time *G*(double bond formation) decreases linearly with input independent of intensity. In explanation of the results it is suggested that a fixed fraction of the primarily excited benzene molecules are excited to a particular energy level and then react to give polymer formation.

1. Introduction

Polymer is produced in electron-bombardment radiolysis of benzene with a 100 e.v. yield of benzene molecules converted to polymer, *i.e.*, $G(C_6H_6 \rightarrow \text{polymer})$, previously given as 0.76.[3] Little, however, has been published about its production or its nature. Such information, useful perhaps for elucidation of the mechanism of radiolysis of benzene and for clarification of some details of behavior of benzene mixtures, is presented in this report.

2. Experimental

The benzene used in this work was a portion of an exceptionally high-purity sample[4] previously employed in synthesis of benzene-d_6. Techniques of irradiation by 1.5 Mv. electrons are largely those described in an earlier paper.[4] However, for determination of polymer, the irradiation cells were necessarily modified by extension of the

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[1] (1) A contribution from the Radiation Project operated by the University of Notre Dame and supported in part by the Atomic Energy Commission under Contract AT(11-1)-38.

[2] (2) Abstract from a thesis presented to the Department of Chemistry of the University of Notre Dame by W. N. Patrick in partial fulfillment of requirements for the degree of Doctor of Philosophy.

[3] (3) J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

[4] (4) W. N. Patrick and M. Burton, *ibid.*, **58**, 424 (1954).