1025. *Glow-discharge Electrolysis. Part V.*[1] *The Contact Glow-discharge Electrolysis of Liquid Ammonia.*

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If liquid-ammonia solutions are electrolysed with a small thin wire anode immersed in them, then when the electric power dissipated is sufficiently great the anode becomes sheathed in vapour through which current passes by a type of glow-discharge. The chemical effects of this contact glow-discharge electrolysis have been investigated; hydrazine is the main product formed in solution, and the dependence of the yield on experimental variables has been studied. Electrolysis of ammonia–water mixtures by this technique also yields hydrazine in substantial amount provided less than 50% of water is present; increase in water content beyond this point causes the yield to decrease rapidly.

When the glow-discharge electrolysis of liquid ammonia described in Part IV [1] was being investigated, an experiment was performed in which the anode touched the surface of the electrolyte, and even so at a sufficiently high current density (c.d.) the liquid ammonia parted from the electrode and a glow-discharge was started and maintained. This result was investigated further by using thin platinum wire anodes immersed to a few centimetres' depth and a remarkable behaviour was observed. At first, on passage of a small current, conventional electrolysis took place with evolution of gas bubbles at the anode, and Ohm's law was obeyed with a relatively small cell voltage set up. However, when a sufficiently large current was passed the electrolysis became noisy with very vigorous gas evolution and a turbulent movement of the solution round the electrode, and the resistance increased. On still further increase in electric power a critical value was reached where a sharp change occurred; the potential across the cell increased to about 500 v and the current fell to about one-fifth of its former value, this change being accompanied by the formation of a greenish glow on the anode which appeared to extend a short distance into the solution through a vapour film which surrounded the electrode. In this last region hydrazine was formed in the solution, and this phenomenon of a luminous discharge at a high voltage at an anode immersed in a conducting solution is for convenience termed " contact glow-discharge electrolysis." It provides a very simple means of carrying out glow-discharge electrolysis, even at atmospheric pressure, and its investigation is described below.

Experimental

The same vacuum apparatus, cell, and gas-sampling system were used as previously described.[1] The electrical circuit was simplified since the discharge was started merely by rapidly increasing the applied voltage from the power supply so that the induction coil and ballast resistances could be dispensed with. The cathode was the same as before but the anode was a thin platinum wire (0·025 cm. diameter) which was immersed in 40 ml. of liquid ammonia so as to have 0·1 sq. cm. of metal in contact with the solution. The wire was kept vertical and was part of a much longer piece which was suspended above the solution. This was found by trial to be the most successful arrangement for the anode, and methods where the anode was sealed into glass failed because during electrolysis the wire tended to melt at the point where it emerged from the glass.

The general technique was to add a weighed amount of ammonium nitrate as electrolyte to the cell and to dissolve it in 40 ml. of liquid ammonia. The electrodes were inserted and the applied voltage increased until the critical point was passed. The voltage was then readjusted to give the desired current. After the required quantity of electricity had been passed as indicated by a gas coulometer, the electrolysis was stopped and the cell contents were analysed as previously described. The standard experimental conditions adopted were:

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[1] Part IV, preceding paper.

electrolyte, 40 ml. of 0·01M-solution of ammonium nitrate in liquid ammonia; pressure, atmospheric; anode, 0·1 sq. cm. of Pt wire, diameter 0·025 cm.; temperature, *ca.* −75°; current, 0·1 A.

RESULTS

Physical Characteristics of the Discharge.—In Fig. 1 A and B are shown the voltage–current graphs for the system at −75° at different pressures, and for different temperatures at 1 atm. pressure. They consist in general of three regions: at low voltages the current is linearly proportional to the applied voltage as expected; at voltages of more than 150 V there is an unstable region where current decreases while voltage rises; finally a stable region is entered where the anode is covered by the glowing discharge and the voltage is about 500 V. The general form of the voltage–current relation was independent of pressure and temperature, but the critical condition was most easily established at low pressures and high temperatures, and the final voltage was greater at higher pressures. In this glow-discharge region a limited variation of current was possible. The current had to be kept above about 0·07 A for the glow-discharge to be maintained, while above about 0·15 A the heat dissipated locally was sufficient to melt the electrode.

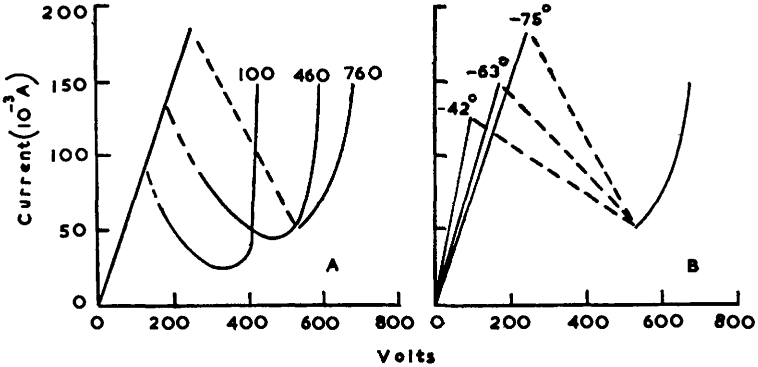

FIG. 1. Current-voltage graphs (A) at different pressures (mm.) at −75°, and (B) at different temperatures at 1 atm. pressure.

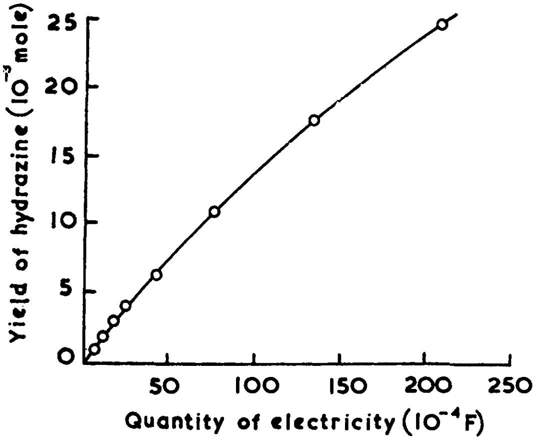

FIG. 2. Influence of quantity of electricity on yield of hydrazine.

Chemical Effects of Contact Glow-discharge.—Hydrazine was produced under the glow-discharge conditions and in Fig. 2 is shown the yield plotted against quantity of electricity passed for the standard experimental conditions. The curve is very similar to that found for glow-discharge electrolysis with the vapour-phase anode[1] but the actual yield is smaller.

Thus in the present case the initial yield of hydrazine is about 1·8 moles/faraday as against 2·5 moles/faraday with the vapour-phase anode.

Influence of Experimental Variables.—Pressure. The yield of hydrazine was almost independent of the pressure as shown by the results in Table 1 for a series of electrolyses of 28½ min. duration over the pressure range 0·1—2 atm.; the quantity of electricity passed in each experiment was 17 × 10^{-4} faraday and other conditions were standard.

TABLE 1.

Influence of pressure.

Pressure (mm.)	100	300	336	550	755	1520
Yield of hydrazine (10^{-3} mole)	3·05	3·35	3·32	3·30	3·07	2·82

Current. Increase of current raised the hydrazine yield slightly. This is shown by the results in Table 2 for currents in the range 0·07—0·15 A under standard conditions with 17 × 10^{-4} faraday passed.

TABLE 2.

Influence of current.

Current (A)	0·07	0·10	0·15
Yield of hydrazine (10^{-3} mole)	2·23	3·07	3·13

Temperature. The yield of hydrazine was not much affected by temperature, although there was perhaps a slight tendency for the yield to decrease at higher temperatures, as shown in Table 3; standard conditions and the same quantity of electricity were again used.

TABLE 3.

Influence of temperature.

Temperature	−75°	−46°	−33·5°
Yield of hydrazine (10^{-3} mole)	3·07	2·85	2·90

Electrolyte concentration. Table 4 shows the yield obtained with several electrolytes at different concentrations under standard conditions with the usual quantity of electricity.

TABLE 4.

Effect of electrolyte concentration.

Electrolyte	0·005	0·01	0·1	0·4	1·0M
	Yield of hydrazine (10^{-3} mole)				
NH_4NO_3	2·78	3·07	3·75	—	4·26
KNO_3	—	2·29	2·65	2·97	—
$CH_3{\cdot}CO_2NH_4$	—	2·65	2·91	—	—

In contrast to the results obtained with a vapour-phase anode,[1] the yield increases appreciably with rise of electrolyte concentration.

The Stationary Concentration of Hydrazine.—The differential hydrazine yield under standard conditions at various hydrazine concentrations was determined as described previously,[1] and Fig. 3 shows the results. As with the vapour-phase anode, the yield drops with increasing hydrazine concentration, showing that the glow-discharge can initiate a decomposition of hydrazine, and ultimately a stationary hydrazine concentration is achieved. This occurred at about 1·0M which is substantially less than with the vapour-phase anode.[1] The stationary concentration was decreased by increase in electrolyte concentration, and slightly by rise of temperature; pressure seemed to have little effect.

Analysis of Gaseous Products and the Material Balance.—The gas evolved contained only nitrogen and hydrogen, the latter being in excess of the amount to be expected from the complete dissociation of ammonia. When the hydrogen equivalent to the hydrazine formed was allowed for, a material balance was achieved within the limits of experimental error. As in the previous investigation,[1] considerable decomposition of ammonia other than that leading to hydrazine seems to occur, and the results indicated that only about one-quarter of the total ammonia decomposed was involved in the hydrazine producing reaction.

Glow-discharge Electrolysis of Ammonia–Water Mixtures.—The contact glow-discharge electrolysis of a complete range of water–ammonia mixtures was studied under standard conditions, and some experiments with the mixtures containing most water were also made at 0°; the usual quantity of electricity was passed. The mixtures were made either by distilling appropriate quantities of ammonia into aqueous ammonia (*d* 0·880) in the cell, the latter being cooled meanwhile by liquid nitrogen, or for mixtures containing less than 35% of ammonia the aqueous ammonia was diluted with water. After electrolysis the solutions were evaporated and neutralised, or simply neutralised where the ammonia was present in small amount, and analysed for hydrazine, hydrogen peroxide, and hydroxylamine. Only in the electrolysis of aqueous solutions containing no ammonia was hydrogen peroxide detected, and in no experiment could a reaction for hydroxylamine be found. Hydrazine was formed in yields dependent on the ammonia content, as shown in Fig. 4. The yield of hydrazine remained almost constant with increase in water content until the solution contained more than 50% of water. Increase in water beyond this point caused the yield to decrease rapidly, and it was zero, of course, for 100% water. In the region of low ammonia content, increase in temperature to 0° resulted in an increase in hydrazine yield.

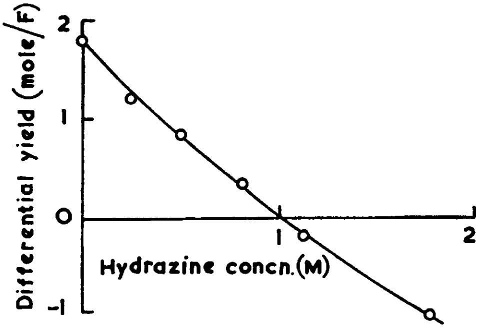

FIG. 3. Influence of hydrazine concentration on differential yield.

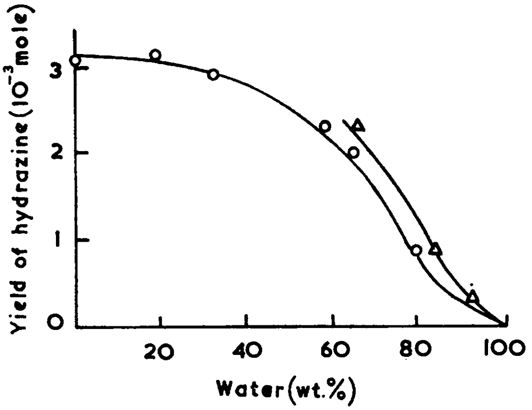

FIG. 4. Hydrazine yields in ammonia–water mixtures.
○, −75°. △, 0°.

DISCUSSION

It has been shown that the transition from conventional to contact glow-discharge electrolysis at a wire anode occurs abruptly as the voltage is increased, and the transition occurs at lower power dissipation if the pressure is decreased or the temperature of the solution is raised. This relates the ease of transition to the readiness of vaporisation of the solvent and suggests that in contact glow-discharge local heating at the electrode must produce a sheath of solvent vapour through which conduction takes place. Kellogg,[2] in seeking to imitate the anode effect found in molten electrolytes, showed that a similar phenomenon

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[2] Kellogg, *J. Electrochem. Soc.*, 1950, **97**, 133.

could be produced in aqueous solutions when the surface of the electrode reached the boiling point of water, although he did not use sufficiently high voltages for full glow-discharge to be established. Thus the present phenomenon may well be one of general occurrence in any conducting liquid under appropriate conditions although the detailed mechanism of the effect obviously needs further study. It is noteworthy that once contact glow-discharge is set up it is self-maintaining; if the vapour sheath should collapse for any reason and the liquid touch the electrode, then there is a surge in current and power dissipated bringing about further vaporisation. The electrode is undoubtedly hot under glow-discharge conditions, and a small increase in current serves to make it visibly red-hot.

Contact glow-discharge electrolysis could also be carried out with alternating instead of direct current, and with direct current making the electrode a cathode, but the working conditions were then much more critical since much of the energy dissipated in the discharge occurred at the metal surface instead of in the liquid, and the thin wires tended to melt readily.

In comparing the results of contact glow-discharge electrolysis with those where a vapour-phase anode at reduced pressure is used, the marked differences in the form of the discharge must be borne in mind. In contact glow-discharge the thickness of the vapour envelope is not known but it is probably much less than 1 mm. and it may well depend on experimental conditions. Thus the cathode fall of potential, which is of paramount importance, may differ from that observed with the vapour-phase anode where the discharge usually takes place over a much greater distance. Further, instead of a glow-spot of self-regulating area, in contact glow-discharge the area will be determined by the surface of the vapour sheath, and the c.d. may thus be very different from that in the glow-spot. When these differences are considered it is remarkable how very similar are the chemical effects of the two types of discharge in liquid ammonia, and this leaves little doubt that the chemical reactions occurring are similar in the two cases. If the same mechanism is adopted for contact glow-discharge, *i.e.*, the production of NH_2 radicals which undergo various competing reactions, then the results can be quantitatively interpreted as in the previous paper.[1] The treatment leads to an expression for the differential yield of hydrazine (G expressed in moles/faraday) as follows:

$$G = \frac{n}{2} \cdot \frac{A - [N_2H_4]}{A + B + [N_2H_4]} = 6{\cdot}0\,\frac{1{\cdot}0 - [N_2H_4]}{3{\cdot}4 + [N_2H_4]},$$

and this equation is in good agreement with the experimental results. The equation is closely similar to that found for the vapour-phase anode, and n has nearly the same value, but A and B are appreciably different. The difference implies that in contact glow-discharge electrolysis the stationary concentrations of NH_2 radicals and hydrogen atoms in the reaction zone are less than when the vapour-phase anode is used.

The variation of hydrazine yield with composition in ammonia–water mixtures is at first sight unexpected. However, if it is taken that there are three main species present in the mixtures, *viz.*, NH_3, NH_3,H_2O or NH_4OH, and H_2O molecules, and that NH_3 and NH_3,H_2O are equivalent in producing NH_2 radicals on collision with the initiating gaseous ions while the H_2O molecules simply function as diluents, then the explanation of the results is immediately apparent. The differential yield of hydrazine in a particular mixture should be given by

$$G_{\text{mixture}} = \frac{[NH_3] + [NH_3,H_2O]}{[NH_3] + [NH_3,H_2O] + [H_2O]}\,G_{\text{ammonia}}$$

Ignoring in the first instance the dissociation of the hydrate, the amount of water present would have to exceed 51% before free water molecules began to reduce the hydrazine yield substantially. In practice the position is complicated by the dissociation of the

NH_3,H_2O, and this will lead to a small decrease in the hydrazine yield as the amount of water increases, followed by a much more rapid decrease as the amount of water exceeds the stoicheiometric value for the hydrate.

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