gated by others and so it is made highly probable that this explanation applies to the great majority of anomalies previously described. Their common occurrence indicates that the low-temperature, reversible, inhibition of enzymes plays an important role in biological processes, both *in vivo* and *in vitro.*

RECEIVED JANUARY 6, 1949

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Electrolysis of Solutions of *m*-Dinitrobenzene in Liquid Ammonia

BY J. D. FARR, C. C. BARD AND G. W. WHELAND

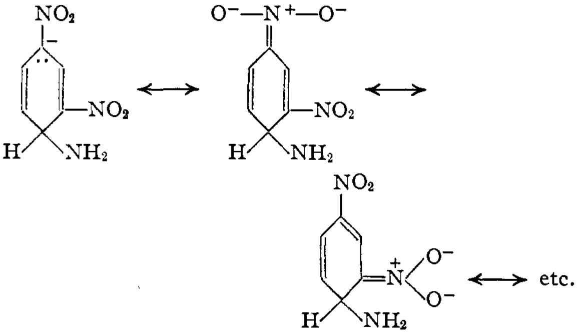
When *m*-dinitrobenzene is dissolved in liquid ammonia, there is obtained a deep purple solution which is a good conductor of the electric current. Other aromatic compounds with two or more meta nitro groups behave similarly; moreover, the ammonia solvent can be replaced by hydrazine or by ethylenediamine without obvious change in the properties of the solution.

The state of the dissolved nitro compound has been considered by several investigators.[1,2] Thus, by means of transference experiments in liquid ammonia, Field, Garner and Smith[1] showed that the color resides in an organic anion; on prolonged electrolysis, the solution surrounding the cathode ultimately consists of only the pure solvent. These authors reported, however, that there is no evolution of gas at either electrode and that, after the electrolysis, the nitro compound can be recovered unchanged. On the basis of these observations, they concluded that the ionization equilibrium in ammonia must be representable by some such equation as

$$C_6H_4(NO_2)_2 + 2NH_3 \rightleftarrows [C_6H_4(NO_2)_2]^- + 2NH_3^+$$

Thus, the cation and anion, when discharged at the corresponding electrodes, become identical, respectively, with the solvent and the uncharged solute. If, on the other hand, the cation were the ammonium ion, NH_4^+, hydrogen would have to be evolved at the cathode, or else the nitro compound would have to be reduced (or both). This same conclusion was supported also by Walden.[2]

In the work reported below, the electrolysis of the solution of *m*-dinitrobenzene in liquid ammonia was carefully re-examined. It was found that, contrary to the results of Field, Garner and Smith, hydrogen is evolved at the cathode, nitrogen is evolved at the anode, and the nitro compound is extensively reduced. It is therefore evident that the possible existence of an *ammonium* salt in the solution can again be considered. Although conclusive evidence regarding the constitution of this salt is lacking, a reasonable suggestion is that the anion may have the resonating structure



or the like.[3]

Experimental

Apparatus.—The electrolyses were carried out independently by two of the authors (J. D. F. and C. C. B.), with different apparatuses; an interval of approximately three years elapsed between the two sets of measurements. In the first series of measurements (J. D. F.), the apparatus was that shown in Fig. 1. In the second series of measurements (C. C. B.), the apparatus differed from the foregoing only in the use of the electrolysis cell shown in Fig. 2.[4] The two arms A of this cell were connected to the vacuum line by a common junction at the same point at which the cell D of Fig. 1 was attached.

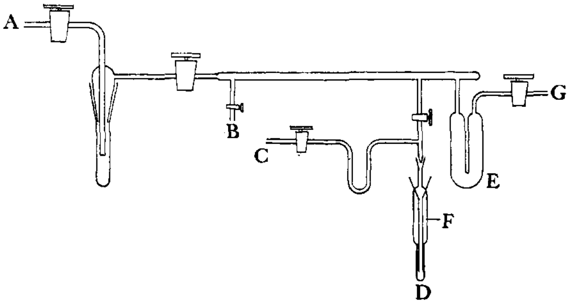


Fig. 1.—Apparatus used in the electrolysis of solutions of *m*-dinitrobenzene in liquid ammonia: A, to pumping system; B, to McLeod gage; C, to Töpler pump; D, electrolysis cell; E, U-tube; F, Pt electrode; G, ammonia inlet.

Materials.—The ammonia used as solvent was a commercial product, stored over sodium in steel cylinders.

---

[1] M. J. Field, W. E. Garner and C. C. Smith, *J. Chem. Soc.*, **127**, 1227 (1925).

[2] P. Walden, *Z. physik. Chem.*, **A168**, 419 (1934).

[3] *Cf.* N. V. Sidgwick, T. W. J. Taylor and W. Baker, "The Organic Chemistry of Nitrogen," Oxford University Press, Oxford, 1937, pp. 259 ff., for a discussion of the presumably analogous complexes formed between polynitro compounds and alkali alkoxides.

[4] For a somewhat similar cell, see S. Goldschmidt and F. Nagel, *Ber.*, **64**, 1744 (1931).

The *m*-dinitrobenzene was likewise a commercial product; it was purified by the method of Wyler[5] and then sublimed *in vacuo*.

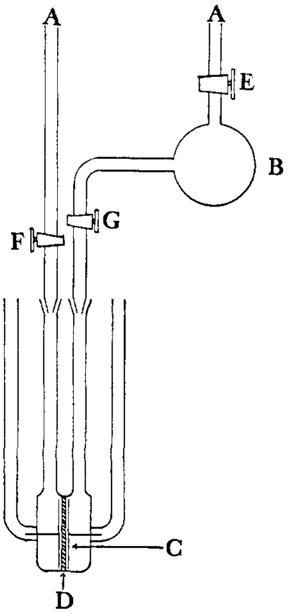


Fig. 2.—Cell used when the gases evolved at the two electrodes were collected separately: A, to line; B, expansion bulb; C, Pt electrode, 25-mm. diameter and 5-mm. separation between electrodes; D, coarse Pyrex fritted disk, 32-mm. o. d.

Procedures.—In the first series of measurements, the sample of *m*-dinitrobenzene was placed in the electrolysis cell, and the line was evacuated to 10^{-5}–10^{-6} mm. for several hours. Ammonia was then condensed in the U-tube E (Fig. 1), which contained metallic sodium. The ammonia was subsequently distilled into the electrolysis cell. The ammonia solution of *m*-dinitrobenzene which was thus formed was twice degassed by being evacuated while frozen in liquid nitrogen. The electrolysis was then carried out at the boiling point of liquid ammonia with an applied potential of 18 volts. The amount of current which passed through the solution was measured by means of a silver coulometer. In agreement with Field, Garner and Smith,[1] the color was observed always to migrate toward the anode. After the electrolysis was completed, the solution in the cell was frozen with liquid nitrogen, and the mixture of gases which had been evolved at the two electrodes was transferred by means of a Töpler pump to a buret, where its volume was measured over mercury.

In the second series of measurements, the following modifications were adopted. The solvent was degassed while still in the U-tube E of Fig. 1, since the electrolysis cell of Fig. 2 was nearly always broken if its contents were frozen in liquid nitrogen and then allowed to warm up. The electrolysis was carried out at −70° in a bath containing Dry Ice and methanol. The applied potential was 100 volts. During the electrolysis, the stopcock E above the expansion bulb B (Fig. 2) was kept closed so that the gases could not become mixed. Since the volumes of the gases formed at the two electrodes were different, there was a tendency for the pressures in the two arms of the cell to become unequal, and hence for the level of the solution to rise in one arm and to fall in the other. This undesirable tendency was overcome by having the surface of the methanol in the cooling bath at the same level as that of the solution in the cell. Then, if the solution in one arm of the cell rose, it was partially removed from the bath and hence became slightly warmed. The resulting increase in the vapor tension of the ammonia in that arm then compensated the pressure difference which had caused the original change in levels. In this way, the solutions in the two arms were automatically held at nearly the same height. After the electrolysis was completed, the gas evolved in the arm at the left of Fig. 2 was transferred from the cell to the line. Since, as noted above, the solution in the cell could not safely be frozen, the U-tube E (Fig. 1) was cooled in liquid nitrogen, and ammonia was distilled into it from the left arm of the cell, which was open to the line. When this arm had been sufficiently well swept out by the stream of ammonia the stopcock F was closed, and the gas was pumped by the Töpler pump away from the frozen ammonia and into the buret. In a similar way, the gas evolved in the right arm of the cell was transferred to the line, with stopcock F closed and stopcocks E and G open; and then to the buret, with all stopcocks closed.

The analyses of the gases were carried out in the conventional ways; the oxygen was absorbed by alkaline pyrogallol, the hydrogen was determined by explosion with oxygen, and the nitrogen was obtained by difference.

Results

The results of the electrolyses are summarized in Table I and in Table II. The fact that, in each instance, the amount of nitrogen evolved at the anode was slightly less than that calculated is in agreement with some analogous results of Goldschmidt and Nagel.[4] The amount of hydrogen evolved at the cathode was always a small fraction of that calculated. The ratio of observed to calculated volumes of hydrogen varied from approximately 1:50 to 1:2; in general, this ratio was greatest when the current density was lowest and when the solution was most dilute. The conclusion that the lowness of the yield of hydrogen is due to reduction of the *m*-dinitrobenzene is supported by the fact that the recovered nitro compound was dark colored and gave a positive test for an aromatic amine (by diazotation and coupling with β-naph-

TABLE I

ELECTROLYSES[a] OF *m*-DINITROBENZENE IN LIQUID AMMONIA

Faraday	Total volume[b] of gas collected	Volume[b] O_2 calcd.	Volume[b] O_2 obs.	Volume[b] H_2 calcd.	Volume[b] H_2 obs.	Volume[b] N_2 calcd.	Volume[b] N_2 obs.
0.000586	4.95	0.0	0.0	6.56	2.90	2.19	2.05
.001068	9.45	.0	.0	11.93	5.68	3.98	3.77
.000460	2.46	.0	.0	5.15	1.11	1.72	1.35
.001205	11.27	.0	.0	13.50	6.73	4.50	4.54

[a] The experiments reported in this table were performed by J. D. Farr with the apparatus of Fig. 1. Each solution was prepared from about 0.1 g. of *m*-dinitrobenzene in 6–7 cc. of ammonia. [b] All volumes are in cc. and are corrected to 0° and 760 mm.

TABLE II

ELECTROLYSES[a] OF *m*-DINITROBENZENE IN LIQUID AMMONIA

Faraday	Volume[b] H_2 evolved at cathode[c] calcd.	Volume[b] H_2 evolved at cathode[c] obs.	Volume[b] N_2 evolved at anode[d] calcd.	Volume[b] N_2 evolved at anode[d] obs.
0.0154	173.1	3.3	57.7	53.8
.00989	110.7	4.8	36.9	35.5
.00874	93.7	6.2	32.9	31.1
.01004	112.5	13.7	37.5	33.5
.0186	204.6	25.0	68.2	61.5

[a] The experiments reported in this table were performed by C. C. Bard with the cell shown in Fig. 2. In order to keep the conductivity high, each solution was saturated with respect to *m*-dinitrobenzene and contained considerable quantities of the undissolved solid. In this way, currents of 60–100 milliamperes were obtained at 100 volts. [b] All volumes are in cc. and are corrected to 0° and 760 mm. [c] No oxygen or nitrogen was evolved at the cathode. [d] No oxygen or hydrogen was evolved at the anode.

---

(5) O. Wyler, *Helv. Chim. Acta*, **15**, 23 (1932).

thol).[6] Although no definite product of the reduction could be either isolated or identified, a black and obviously impure material could be extracted from the recovered *m*-dinitrobenzene with 10% aqueous hydrogen chloride, and then precipitated from the extract by the addition of a base.

The solutions of *m*-dinitrobenzene in hydrazine and in ethylenediamine were found to be unstable at room temperature since the colors, which were initially formed, soon faded. The natures of the decompositions were not studied, however, and no electrolyses in these solvents were carried out.

Summary

Contrary to the report of Field, Garner and Smith, the electrolysis of *m*-dinitrobenzene in liquid ammonia gives hydrogen at the cathode and nitrogen at the anode. The nitro compound is also partially reduced. It is therefore probable that such a solution contains an *ammonium* salt. A reasonable structure for the anion is suggested.

CHICAGO 37, ILLINOIS RECEIVED JANUARY 20, 1949

---

[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 2nd edition, 1940, pp. 50f.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

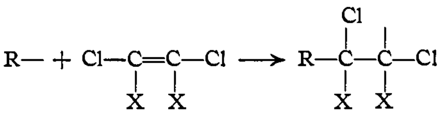
Peroxide-induced Condensation of Saturated Hydrocarbons with Polychloroethylenes

BY LOUIS SCHMERLING AND JAMES P. WEST

Chlorovinylation of saturated hydrocarbons by polychloroölefins occurs when the reactants are heated with a catalytic amount of an organic peroxide at a temperature at least as high as the decomposition temperature of the peroxide. The chain reaction which is involved in this reaction may be indicated as

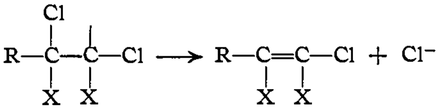
(1) $R'OOR' \longrightarrow 2R'O\text{—}$ (*e. g.*, $R' = t\text{-}C_4H_9$ or C_6H_5CO)

(2) $R'O\text{—} + RH \longrightarrow R\text{—} + R'OH$

(3) 

$$R\text{—} + Cl\text{—}\underset{X}{C}=\underset{X}{C}\text{—}Cl \longrightarrow R\text{—}\overset{Cl}{\underset{X}{C}}\text{—}\overset{|}{\underset{X}{C}}\text{—}Cl$$

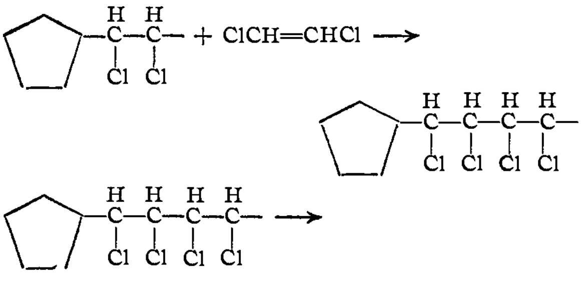
(X = Cl or H) (A)

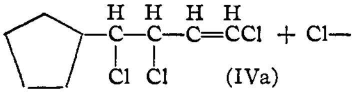
(4) 

$$R\text{—}\overset{Cl}{\underset{X}{C}}\text{—}\overset{|}{\underset{X}{C}}\text{—}Cl \longrightarrow R\text{—}\underset{X}{C}=\underset{X}{C}\text{—}Cl + Cl^-$$

(5) $Cl\text{—} + RH \longrightarrow R\text{—} + HCl$

The alkyl radical formed as in step 5 begins a new cycle as in step 3. The radical (A) may lose a chlorine atom as in step 4 or it may add to a second molecule of the polychloroethylene to yield high-boiling products. Such high-boiling products were actually obtained but were not investigated except in the case of the reaction of cyclopentane with *trans*-dichloroethylene (expt. 6)





(IVa)

Not only isoparaffins but also *n*-paraffins undergo the condensation reaction. Even propane may be employed: 1,1-dichloro-3-methyl-1-butene and 1,1,2-trichloro-3-methyl-1-butene, respectively, may be prepared in quite satisfactory yields by the reaction of this paraffin with tri- and tetrachloroethylene. The products seem to contain more or less of the products involving the intermediate formation of the *n*-propyl radical.

Cycloparaffins behave similarly. Those which were investigated include cyclopentane, cyclohexane and methylcyclohexane.

Data for the various experiments are summarized in Table I. The best yields of chloroölefin based on the peroxide were about 5 or 6 moles per mole of peroxide charged. Since each mole of peroxide theoretically furnished 2 moles of initiating radicals, it may be concluded that the longest reaction chains involved about three cycles. Longer chains could probably have been obtained by more efficient utilization of the peroxide, for example, by adding it to the reaction mixture gradually. This is indicated by the fact that the reaction of methylcyclohexane with trichloroethylene in the presence of 0.005, 0.015 and 0.046 mole, respectively, of *t*-butyl perbenzoate at 115° resulted in the formation of 6.2, 4.7 and 1.8 moles of (dichlorovinyl)-methylcyclohexane per mole of peroxide; on the other hand, the actual yields of product based on the trichloroethylene were, respectively, 10, 23 and 28%. The decrease in chain length with increase in the concentration of peroxide seems to indicate that one of the chain-terminating reactions involved is hydrogen (or chlorine) transfer between the condensation intermediates (A) to yield a saturated and an unsaturated compound. "Dimerization" of these radicals may also occur.