ring 38 g. (0.197 mole) of 1,1,2-trifluoro-2-chloro-1-nitro-2-nitrosoethane was added slowly during 0.5 hr. The reaction mixture was worked up as above. The product, 29 g., b.p. 95°/630 mm., n_D^{25} 1.3749, d_4^{25} 1.6699, gave an infrared spectrogram which was identical with that of 1,1,2-trifluoro-1-chloro-1,2-dinitroethane which was obtained directly from the reaction of trifluorochloroethylene with nitric oxide (see above).

Oxidation of 2-nitro-2-nitroso-1,1,1,2,3,3-hexafluoropropane. Thirty-four grams (0.15 mole) of 2,3-dinitro-1,1,1,2,3,3-hexafluoropropane was oxidized as in the preceding experiments with 15 g. (0.15 mole) of chromium trioxide in 50 ml. of glacial acidic acid and 25 ml. of concd. sulfuric acid. The product, 27 g., was worked up similarly and gave 5 g. of unchanged starting material, and 21 g. of 2,3-dinitro-1,1,1,2,-3,3-hexafluoropropane, b.p. 68–68.5°/630 mm., n_D^{25} 1.3222, d_4^{25} 1.6476. Mol. wt., Calcd. 242; found 240. The infrared spectrogram of this compound was identical with that of 2,3-dinitro-1,1,1,2,3,3-hexafluoropropane described above.

Chemical distinction between 1,2-dichloro-1,1,2-trifluoroethane and 1-nitro-1,1,2-trifluoro-2,2-dichloroethane. 1,2-Dichloro-1,1,2-trifluoro-2-nitroethane reacted vigorously at room temperature with zinc dust in either anhydrous pyridine or in dibutoxy tetraethylene glycol. 1-Nitro-1,1,2-trifluoro-2,2-dichloroethane did not react with zinc dust in either solvent at room temperature or at 50°. A partial reaction was brought about at 75–80° for 5 hr., but 60% of the starting material was recovered unchanged.

Tetrafluoroethylene and nitric oxide. Equivalent quantities of nitric oxide and tetrafluoroethylene were charged into an evacuated 12.5-l. glass vessel to 1 atm. pressure, (0.25 mole each). After 16 hr. at 20°, the pressure dropped to 0.5 atm. The flask was then repressured to 1 atm. with nitric oxide. After an additional 16 hr., the pressure dropped to 0.7 atm. The blue product was fractionated in a screen-saddle packed column. To the pot residue was added 10 cc. of water for hydrolysis of the remaining impurities. Deep-blue liquid, 21 g., accounting for 60 wt. % of the starting materials was obtained, b.p. 24.5–25.5°. The infrared spectrum showed an absorption of 6.17 μ (contrasted to 6.25 μ for R_fNO).

Anal. Calcd. for C_2ClF_4NO: C, 13.2; F, 41.0; N, 14.6. Found: C, 13.6; F, 41.2, N, 14.9. Mol. wt. (Dumas), Calcd. 179; found 176. NMR spectrum supports the structure $ONCF_2CF_2NO_2$.

The following condition favoring the formation of $ONCF_2CF_2NO_2$ was used. Equimolar quantities of nitric oxide and tetrafluoroethylene are charged into a 50-l. Pyrex vessel. After 16–24 hr. the pressure dropped to 0.5 to 0.6 atm. The contents of the vessel were sent through water scrubber, dried and collected in a Dry Ice trap, and the uncondensed material returned to the reactor. The reactor was then re-pressured with nitric oxide and the cycle repeated. Yields of 80–90% (based on tetrafluoroethylene consumed) were obtained.

BOULDER, COLO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Fluorinated C-Nitroso Compounds. II.[1] The Reaction of Nitric Oxide with Some Fluoroolefins in the Presence of Ferric Chloride

J. D. PARK, A. P. STEFANI,[2] AND J. R. LACHER

Received October 3, 1960

The fluorinated olefins tetrafluoroethylene, trifluorochloroethylene and 1,1-difluoro-2,2-dichloroethylene react with nitric oxide in the presence of anhydrous ferric chloride to give good yields of the nitrosoethanes $ClCF_2CF_2NO$, $ClCF_2CFClNO$, and $ClCF_2CCl_2NO$, respectively. Along with these compounds, which constitute the major part of the reaction mixture, are formed nitro-nitroso, nitro, and fully halogenated derivatives all of which have been isolated and characterized. Ferric chloride participates in the reaction by making chlorine available to the reacting system, and the ferric ion is reduced to the ferrous state.

The success of Haszeldine,[3] and of Banus[4] in preparing trifluoronitrosomethane and heptafluoronitrosopropane from the corresponding normal perfluoroalkyl iodides and nitric oxide, and also Brown's[5] extension of an earlier study[6] of the reaction of nitric oxide with unsaturated organic compounds demonstrated clearly the latent capacity of nitric oxide to behave as a free radical. This capacity of nitric oxide was known since Hinshelwood's[7] first kinetic studies with it, but was not exploited in organic reactions for the preparation of nitroso compounds until trifluoronitrosomethane and heptafluoronitrosopropane were synthesized.

From the results of our earlier studies reported in the first paper of this series it became evident that formation of nitroso compounds as major products in the interaction of nitric oxide with fluorinated olefins could not be effected in a static system under the conditions employed in these studies. The reaction was therefore adapted to a flow system in which the reactants, nitric oxide and fluoroolefin, were passed through a Pyrex tube packed with various finely divided solid surfaces which were expected to promote or catalyze the reaction.

As Lewis acids of trivalent cations in the solid state are known to absorb nitric oxide reversibly, it was thought that with some of these acids, a temperature could be found at which nitric oxide and

---

[1] Paper I in this series, *J. Org. Chem.*, **26**, 3316 (1961).

[2] Present address, State University College of Forestry, Baker Hall, Syracuse 10, N. Y.

[3] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955).

[4] J. Banus, *J. Chem. Soc.*, 3755 (1953).

[5] J. F. Brown, *J. Am. Chem. Soc.*, **79**, 2480 (1957).

[6] G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944).

[7] J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc.*, **159**, 32 (1937).

the Lewis acid–nitric oxide complex would be in equilibrium:

$$MX_3NO \rightleftharpoons MX_3 + NO$$

At this equilibrium temperature nitric oxide might be activated and behave as a true free radical which would then attack an olefinic substance to initiate a chain reaction and perhaps form an α,β-dinitroso compound. Various trivalent metal Lewis-type acids were employed under diverse conditions but none, except ferric chloride gave satisfactory results. Finely divided anhydrous ferric chloride brought about a nearly quantitative reaction, but the nitroso compounds obtained were not those anticipated. Ferric chloride participated in the reaction by making chlorine available to the reacting system with a concurrent reduction of the ferric ion to the ferrous state. The major product of this type of reaction is a blue nitroso compound which results from the addition of the elements of nitrosyl chloride to the olefinic bond. Thus, tetrafluoroethylene, trifluorochloroethylene and 1,1-difluoro-2,2-dichloroethylene yielded 1-chlorotetrafluoro-2-nitrosoethane (I), 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane (II), and 1,2,2-trichloro-1,1-difluoro-2 nitrosoethane (III) respectively in yields ranging from 71 to 76% based on total weight of product. Accompanying the major product in each case were nitro compounds, nitro-nitroso compounds, and other compounds which are listed in Table I. The optimum conditions for a maximum yield of nitrosoethanes of the type $ClCF_2CX_2NO$ ($X = F$ or Cl) are a reaction temperature range of 45–75° and a throughput rate of one mole of olefin to about two moles of nitric oxide per twenty four hours. The reaction is sensitive to variations of temperature and of the ratio of reactants. Variations of these conditions affects the nature of the products and in particular the yield of the nitroso derivative. Higher temperatures favor the formation of the acyl fluoride $ClCF_2COF$, of nitro, and fully halogenated compounds at the expense of the respective nitrosoethanes.

The structure proof of I was based upon its physical constants, infrared spectra, and upon oxidation to 1-chlorotetrafluoronitroethane (VII) for which a good elemental analysis was obtained. VII, which was also obtained in the reaction, is a known compound.[8] The structure proof of II has been discussed in the first paper of this series. No structure proof was worked out for III; its structure is assigned as such on the basis of the evidence for the structure of II and on the basis of other free radical reactions of 1,1-difluoro-2,2-dichloroethylene. XVII is a nitro compound, but its most likely structure, 1-nitro-1,1-difluoro-2,2,2-trichloroethane has not been definitely established. The rest of the compounds in Table I are either known compounds[9–12] or have been discussed in our previous paper. The structures for V and XI were inferred from infrared spectra and by chemical means (see experimental section). Undoubtedly the analogous nitrite 1-chloro-1,1-difluoro-2,2-dichloroethyl nitrite was present in the products of the reaction of 1,1-difluoro-2,2-dichloroethylene with nitric oxide, but no attempt was made to isolate it at the present time.

Each of the products of these reactions is, as we have pointed out in our first paper, that which would be obtained by the addition to these olefins of nitrosyl chloride, nitryl chloride, chlorine, dinitrogen tetroxide, and nitrogen sesquioxide, respectively. Since it is conceivable and thermodynamically possible that nitric oxide may disproportionate to nitrogen and nitrogen dioxide[5,13] under favorable conditions, the formation of the compounds which presumably resulted by the addition of dinitrogen tetroxide and nitrogen sesquioxide to the double bond may easily be rationalized. An explanation, however, for the formation of compounds I, II, III, V, VII, and their analogues in similar reactions is not immediately evident.

During the course of this investigation it has been established that neither nitric oxide nor fluoroolefins will undergo a reaction other than adsorption (or perhaps complex formation: $NO + FeCl_3 \rightarrow FeCl_3NO$) when each was brought in contact with anhydrous ferric chloride. The point of interest here is that nitrosyl chloride could not be obtained from the interaction of nitric oxide with ferric chloride under the condition of the reaction outlined in the experimental section. Similarly, no effective addition of chlorine to an olefin could be brought about by ferric chloride under these conditions. Nitric oxide has been reported to react with ferric chloride at the sublimation temperature of the latter to form nitrosyl chloride and ferrous chloride.[14] Similarly, the ferric ion in the ferric chloride–nitrosyl chloride complex ($FeCl_4NO$) has been shown to undergo reduction to the ferrous state when treated with nitric oxide under pressure.[15]

$$FeCl_4NO + 2NO \longrightarrow FeCl_2NO + 2NOCl$$

These observations suggest that in the presence of a fluoroolefin, nitric oxide and ferric chloride react in the following manner to form nitrosyl chloride which then adds to the double bond:

---

(8) R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

(9) A. M. Lovelace *et al.*, *Aliphatic Fluorine Compounds*, Reinhold, N. Y., 1958.

(10) I. L. Knunyants and A. V. Fokin, *Doklady Akad. Nauk S.S.S.R.*, **111**, 1035 (1956); *Chem. Abstr.*, **51**, 9472 (1957).

(11) J. M. Birchall *et al.*, *Proc. Chem. Soc.*, 367 (1960).

(12) C. E. Griffin and R. N. Haszeldine, *Proc. Chem. Soc.*, 369 (1960).

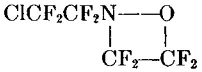
(13) W. E. Addison and R. M. Barrer, *J. Chem. Soc.*, 775 (1955).

(14) V. Thomas, *Compt. rend.*, **120**, 447 (1895); *Ann. chim. et phys.*, **7**, 13, 145 (1896).

(15) *Recent Aspects of the Inorganic Chemistry of Nitrogen*, Special publication No. 10, p. 12, The Chemical Society, London, 1957.

TABLE I

PRODUCTS OBTAINED FROM THE REACTION OF FLUOROOLEFINS $CF_2 = CX_2$ WITH NITRIC OXIDE AND FERRIC CHLORIDE

	Compound	Yield, %	From $CF_2 = CF_2$ B.P./630	n_D^t	d_4^t	Mol. Wt. Obs.	Calcd. C	Calcd. N	Calcd. Cl	Calcd. F	Found C	Found N	Found Cl	Found F
IV	$ClCF_2COF$	7	−22											
V	$ClCF_2CF_2ONO$	2	−16											
I	$ClCF_2CF_2NO$	71	−7			165								
VI	$ClCF_2CF_2Cl$	9.5	−1			169.5								
VII	$ClCF_2CF_2NO_2$	5.2	30.8	n_D^0 1.3236	d_4^0 1.5622	178								
VIII	$O_2NCF_2CF_2NO$	2.4	19.5–20.5	n_D^0 1.3354	d_4^0 1.5357	174.5	3.23		19.51	41.89	13.08		19.69	41.56
IX	$O_2NCF_2CF_2NO_2$	2.8	52	n_D^{25} 1.3501	d_4^{25} 1.5962	190	25.00	14.59		39.57	25.23	14.27		39.62
X	 $ClCF_2CF_2N—O$ / $CF_2—CF_2$	1.2	76			268	18.11	4.9	13.12	56.85	18.05	5.26	13.34	57.14
			From $CF_2 = CFCl$											
IV	$ClCF_2COF$	2	−22											
IX	$ClCF_2CFClONO$	2	16											
II	$ClCF_2CFClNO$	76	31.7	n_D^0 1.3455	d_4^0 1.5422	180								
XII	$ClCF_2CFCl_2$	7.3	41–42	n_D^{25} 1.3557	d_4^{25} 1.5629	188								
XIII	$O_2NCF_2CFClNO$	2	62	n_D^{25} 1.349	d_4^{25} 1.5494	186								
XIV	$O_2NCF_2CFCl_2$	7	70.5–71.5	n_D^{25} 1.3669	d_4^{25} 1.6199	199	12.12	7.07	35.86	28.78	12.44	6.97	35.67	28.5
XV	$O_2NCF_2CFClNO_2$	2	71.5 94.5	n_D^{25} 1.375	d_4^{25} 1.6704		11.48	13.39	16.98	27.22	11.69	13.07	17.12	27.42
			From $CF_2 = CCl_2$											
IV	$ClCF_2COF$													
III	$ClCF_2CCl_2NO$		72.5/630	n_D^{25} 1.3942	d_4^{25} 1.5859	195								
XVI	$ClCF_2CCl_3$		14–16/200 84/630 M.p. 35.5				11.76		69.51	18.72	11.91		69.47	18.62
XVII	$C_2F_2Cl_3NO_2$		74/200 110/630	n_D^{25} 1.4178	d_4^{25} 1.6599		11.16	6.51	49.77	17.67	10.90	6.24	49.96	17.48

$$\mathrm{FeCl_3 + NO \rightleftarrows FeCl_3NO}$$

$$\mathrm{FeCl_3NO + NO \longrightarrow FeCl_2NO + NOCl}$$

$$\mathrm{FeCl_3 + NOCl \longrightarrow FeCl_4NO}$$

$$\mathrm{FeCl_4NO + 2NO \longrightarrow FeCl_2NO + 2NOCl}$$

The formation with iron chlorides of such species as $\mathrm{FeCl_3NO}$ and $\mathrm{FeCl_2NO}$ is well established; the former is a red compound, whereas the latter is brown.[16] When nitric oxide reacts with the fluoroolefins tetrafluoroethylene, trifluorochloroethylene, 1,1-difluoro-2-dichloroethylene, in the presence of ferric chloride, the latter changes color from black to light brown as the reaction proceeds. This light brown material reacts with water with the evolution of nitric oxide; the iron in it is in the ferrous state. Very probably this brown material consist mostly of $\mathrm{FeCl_2NO}$. Appreciable quantities of the products and/or of starting materials were also absorbed by the packing of the reactor tube.

The mode of formation of nitrites, nitro, nitronitroso, and fully halogenated compounds which accompany the major product $\mathrm{ClCF_2CX_2NO}$ (where X is F or Cl) in these reactions is thought to follow the reaction path proposed in our previous paper.

The nitroso and nitro compounds reported in these studies have relatively high vapor pressures and indications are that they are extremely toxic. Even traces in the atmosphere cause a headanche after a short period of exposure; in larger concentrations they cause an instantaneous hyperanemic condition which is most noticeable at the ears. Compounds III, XIII, XV, and XVII are not thermally stable, and quickly decompose when distilled at normal pressure giving off nitrosyl chloride nitryl chloride as the case may be.

EXPERIMENTAL

Preparation of the reactor tube. A 90 cm. × 20 mm. pyrex glass tube wound with a heating wire was packed firmly with a 50-50 mixture of powdered anhydrous ferric chloride and 25-75 mesh powdered glass. (The function of the glass was to render the packing porous.) Each end of the tube was plugged with glass wool and with a rubber stopper provided with a 10 cm. × 8 mm. glass outlet. This reactor tube was then inserted in a glass jacket. A thermometer was placed between the jacket and the reactor. Plastic tubing was attached to each end of the reactor, one end leading to the product receiver and the other leading to a T-tube where the gaseous reactants were premixed. The product receiver was a trap immersed in a Dry Ice–butyl cellosolve bath.

Trifluorochloroethylene, nitric oxide, and ferric chloride. A ferric chloride reactor tube constructed in the manner described above was heated at 100° and flushed with dry nitrogen for 15 min. The temperature then was lowered to 45° and 117 g. (1 mole) of trifluorochloroethylene and nitric oxide in a ratio of approximately $\mathrm{2\ NO{:}1CF_2 = CFCL}$ by volume were passed through the tube during the course of 24 hr. The ratio and the rate of throughput of the reactants were roughly measured by means of two heavy mineral oil bubblers mounted between the T-tube and the reactant containers. The ratio of the two gases was so adjusted that a very slight excess of olefin was used; that is $\mathrm{2NO < CF_2{=}CFCl}$. The temperature of the tube was maintained at 45° throughout the reaction period. The product which was blue in color was collected in a trap immersed in a Dry Ice–butylcellosolve bath. During the course of the reaction a small quantity of a colorless gas that was not condensable at the Dry Ice bath temperature was continuously escaping from the product receiver. As the gaseous reactants were fed into the ferric chloride tube the color of the packing started changing from brown-black to light brown. This color change traveled slowly along the packing and just before all the olefin was used in the reaction the entire length of the packing had changed its color. At this point the color of the outcoming product also started changing from deep blue to blue-green to green. The crude product (147 g.) was fractionated in a 3-foot low-temperature distillation column which was previously flushed with nitrogen. During the first stages of fractionation a very slow stream of dry nitrogen was passed through the column in order to chase out any dissolved nitric oxide and also to prevent entrance into the system of atmospheric oxygen. Fractionation yielded the following: (a) 9 g. of a fraction, b.p. −30 to +20°/630 mm., which was green and consisted of three components (vapor phase chromatography); the starting olefin, 50%, the acid fluoride, $\mathrm{ClCF_2COF}$, and the nitrite, $\mathrm{ClCF_2CFCl\text{-}ONO}$, (b) 105 g. of $\mathrm{ClCF_2CFClNO}$, (c) 10 g. of $\mathrm{ClCF_2CFCl_2}$, (d) 3 g. of $\mathrm{O_2NCF_2CFClNO}$, (e) 10 g. of $\mathrm{O_2NCF_2CFCl_2}$, (f) 3 g. of $\mathrm{O_2NCF_2CFClNO_2}$, (g) 6 g. of higher boiling residue.

The nitrites-1,2,2-trifluoro-1,2-dichloroethyl nitrite (XI) *and 1,1,2,2-tetrafluoro-2-chloroethyl nitrite* (V). These compounds are fuming light yellow-green liquids whose infrared spectra have strong bands at 5.5, 5.75, and 6.2 μ. V attacked the sodium chloride windows of the infrared cell leaving a permanent absorption band at about 7–7.2 μ in the cell. Both reacted vigorously with water giving strongly acid solutions which gave strong tests for fluoride ion, and for nitrous acid. A water solution of the first gave a voluminous precipitate with silver nitrate, that of the second did not. Both nitrites were converted to the ethyl ester of difluorochloroacetic acid when mixed with ethanol-sulfuric acid solution as follows:

In a 100-ml. three-neck flask provided with a stirrer, a fritted glass tubing and a reflux condenser, was placed 15 ml. of 95% ethanol. The flask was chilled to about 0° and 10 g. of concd. sulfuric acid was slowly added. While stirring and at 0°, 7 g. of V, b.p. −16°/630 mm., was vaporized into the ethanol–sulfuric acid solution through the fritted glass tubing. A small quantity of unchanged nitrite escaped from the solution during this process and collected in a Dry Ice cooled trap which was attached to the reflux condenser; this was reprocessed until all of it was absorbed. The reaction mixture was stirred for 1 hr. at 0°, then for 0.5 hr. at 50°. At the latter temperature some ethyl ether was produced. The reaction mixture was chilled and then mixed in a separatory funnel with 150 ml. of ice water. The organic layer (4.5 g.) which settled was drawn off and dried with a few granules of calcium chloride. The infrared spectrogram of this compound was superimposable on that of a known sample of difluorochloroethyl acetate.

Oxidation of 1,1,2,2-tetrafluoro-1-chloro-2-nitrosoethane (I) *to 1,1,2,2-tetrafluoro-1-chloro-2-nitroethane* (VII). Chromium trioxide, 30 g. (0.333 mole), 100 ml. of glacial acetic acid, and 50 ml. of concd. sulfuric acid were placed in a 250-ml. three neck flask provided with a stirrer, a condenser, and a fritted glass tubing. The flask was chilled to about 10° and kept at this temperature during the reaction. While stirring vigorously, 50 g. (0.3 mole) of I was allowed to vaporize into the oxidizing medium. Unchanged starting material escaping from the solution was collected in a Dry Ice-cooled trap which was attached to the reflux condenser; this was reprocessed through the reaction mixture several times until no more of its was absorbed. The flask was then brought to room temperature and stirring was continued for another hour. At the end of this period, air was bubbled through the

---

(16) P. C. L. Thorne and E. R. Roberts, *Inorganic Chemistry*, Interscience, 1954, p. 706.

reaction mixture to remove all volatile products which were then trapped in a Dry-Ice cooled receiver.

Fractionation of the liquid in the trap gave 29 g. of starting material I and 15 g. (65%) of VII, b.p. 30.8°/630 mm. n_D^0 1.3236, d_4^0 1.5622, lit.[16] n_D^{20} 1.3145.

The infrared spectrogram of this nitro compound was superimposable on that of the same compound obtained directly in the reaction of tetrafluoroethylene with nitric oxide.

Oxidation of 1-nitro-1,1,2,2-tetrafluoro-2-nitrosoethane (VIII) *to 1,1,2,2-tetrafluoro-1,2-dinitroethane* (IX). About 8.5 g. (0.85 mole) of chromium trioxide, 30 ml. of glacial acetic acid, and 10 ml. of concd. sulfuric acid were placed in a 250-ml. three-neck flask provided with a stirrer, a reflux condenser, and a dropping funnel. The flask and its contents were chilled to about 10° and while stirring 15 g. (0.85 mole) of VIII was added dropwise over a period of 15 min. The mixture was stirred at 10° for 1 hr., and at room temperature for another hour. At the end of this period the mixture was shaken with 200 ml. of ice water in a separatory funnel. The lower layer was drawn off and dried over calcium chloride. Distillation gave traces of starting material, and 10.2 g. (62.4%) of IX, b.p. 52°/630 mm. The infrared spectrogram of this dinitro compound was superimposable on that of the same substance obtained directly from the reaction of tetrafluoroethylene with nitric oxide.

BOULDER, COLO.

[CONTRIBUTION FROM RESEARCH LABORATORY OF UNION CARBIDE CONSUMER PRODUCTS CO., DIVISION OF UNION CARBIDE CORP.]

Electrochemical Synthesis. Reduction of Dinitro-, Iodoxynitro-, and Iodosonitrobenzenes to Azoxy Compounds

M. V. KING

Received January 3, 1961

The electrochemical reduction of some disubstituted nitro-, iodoxy-, and iodosobenzenes is investigated. The identity and yields of the major reduction products are given. It is also shown that, under the conditions used, there is always simultaneous attack of the aromatic ring and side groups.

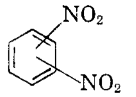
The electrochemical reduction of organic compounds has been studied extensively since 1900 and used where other synthetic methods either failed or proved less specific. The problems of variation of products with conditions such as *p*H, potential, cathode overvoltage, catalysts, and carriers have been extensively explored.[1,2]

One advantage in such reactions is the possibility to control the rate of reaction by controlling the current which is passed through the cell. Another advantage of electrochemical reactions lies in the fact that the product can easily be controlled by the availability of an additional variable, *i.e.*, the potential. Haber and others[3,4,5] have shown in the well known experiments on nitrobenzene that this compound is first reduced to nitrosobenzene, then hydroxylamine and finally to aniline, depending on the electrode potential used in the experiment. A great number of syntheses by either electrochemical reduction or oxidation is given in a review by Swann.[6]

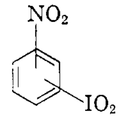
RESULTS AND DISCUSSION

The compounds chosen in this work are disubstituted benzenes which are good oxidizing agents and would, therefore, be expected to reduce fairly easily without complicating side reaction.

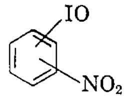
These compounds are given below



Dinitrobenzene



Iodoxynitrobenzene



Iodosonitrobenzene

The *ortho, meta,* and *para* isomers were compared to see if the structure would influence the type of product obtained.

The conditions used were a neutral magnesium bromide (1*M*) solution in water as electrolyte, a zinc plate anode, and a cathode consisting of a graphite cup containing the organic material mixed with acetylene black. The reaction rate was constant since the current was constant (0.5 amp.). The reaction was termed "complete" when the first few hydrogen bubbles became visible at the cathode.

The reduction data are given in Table I. In Table II are the initial open circuit potentials, E_{0_i}, of these compounds *versus* the hydrogen electrode, as well as the cell efficiencies. The efficiency is based on the number of coulometric equivalents passed through the cell divided by the number of theoretical equivalents assuming complete reduction of the substituent groups.

In a special instance, to see if the reaction could be stopped to reduce selectively, one of the two substituents, the reduction of *o*-, *m*-, and *p*-iodoxynitrobenzene up to 4 electrons per molecule was

---

(1) M. J. Allen, *Organic Electrode Processes*, Reinhold Publishing Corp., New York, N. Y., 1958.

(2) C. J. Brockman, *Electroorganic Chemistry*, John Wiley & Sons, New York, N. Y., 1926.

(3) F. Haber, *Z. Elektrochem.*, **4**, 506 (1898).

(4) F. Haber and C. Schmidt, *Z. Physikal. Chem.*, **32**, 271 (1900).

(5) L. Gattermann, *Ber.*, **29**, 3037, 3040 (1896).

(6) S. Swann, *Trans. Electrochem. Soc.*, **88**, 103 (1945).