[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Anodic Reductions. IV. Reduction of Nitrobenzene, Nitrosobenzene, Azoxybenzene and Azobenzene[1]

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The reduction of nitrobenzene, nitrosobenzene, azoxybenzene and azobenzene by unipositive magnesium anodically generated has been investigated. Where conditions permitted, isolation of reduction products in amounts corresponding to those expected from oxidation of magnesium from its measured valence number to the dipositive state was achieved. Evidence is presented to show that in each case the intermediate product of "anodic reduction" is capable of corroding massive magnesium by a chain mechanism.

In previous communications from this Laboratory[2-4] evidence has been presented that in the anodic oxidation of magnesium in sodium iodide–pyridine solutions in the presence of potential organic oxidants, initial mean valence numbers (V_i) less than two frequently are obtained, and that when this is the situation, "anodic reduction" products can be isolated in quantities essentially equivalent to those expected from oxidation of the metal from the measured mean valence number to its familiar dipositive state. The nature of the reduction products and their quantities can reasonably be accounted for by the postulation that the active reducing agent in the anolyte is unipositive magnesium. As a matter of fact, there is reason to believe that the sole primary anodic process is the production of +1 magnesium, and that this species is in part oxidized by the organic oxidant and in part converted to the +2 state electrochemically.[5,6]

The impetus for the work described in the current communication arose from the observation that an abnormally low V_i value of 0.27 was found for the anodic dissolution of magnesium when nitrobenzene was the organic oxidant present in the pyridine solution.[7] Since a value no lower than one is to be expected for the valence number of magnesium as a result of a strictly electrochemical process, the abnormally low V_i value is indicative of non-electrolytic corrosion. However, solutions of nitrobenzene and inorganic electrolyte in pyridine attack massive magnesium only very slowly at the temperature of electrolysis; therefore the abnormally low V_i value must be attributed to the presence of some reduction product of nitrobenzene formed in the anolyte during electrolysis and capable of attacking the massive metal at a rather rapid rate. The formation of "anodic reduction" products which react readily with massive magnesium has been noted even with organic additives which

give rise to V_i values lying between one and two.[3] In the specific cases where benzophenone and 4,4'-dimethylbenzophenone were present in the anolyte, evidence was accumulated which showed that non-electrolytic corrosion of the magnesium anode following electrolysis proceeded by a chain reaction in which ketyl radical-ions and +1 magnesium function as chain carriers.[8]

The present paper describes in some detail the behavior of nitrobenzene and its stable reduction products, nitrosobenzene, azoxybenzene, azobenzene and hydrazobenzene, when used as additives in electrolyses carried out between magnesium electrodes in sodium iodide–pyridine solutions. Not only was a study made of products formed during electrolysis, but also of the corrosion of massive magnesium by these products.

Experimental

Materials.—The 8-mm. magnesium rod, from which all electrodes were cut, was of 99.8% purity and was obtained from the Aluminum Company of America.[9] The sodium iodide employed as electrolyte was Merck and Co., Inc., reagent grade and was dried at 110° before use. Pyridine, Fisher certified reagent, was dried over anhydrous barium oxide, distilled from sodium through a 3-ft. packed column, and stored over additional barium oxide. Nitrobenzene was fractionated through a 45-cm. column at atmospheric pressure. Azoxybenzene was obtained by reduction of nitrobenzene with arsenic(III) oxide in methanolic potassium hydroxide solution.[10] Phenylhydroxylamine was prepared before use by reduction of nitrobenzene with zinc dust in aqueous ammonium chloride, and nitrosobenzene was synthesized from phenylhydroxylamine by chromic acid oxidation.[11] Azobenzene was obtained by reduction of nitrobenzene with zinc dust in methanolic sodium hydroxide solution,[12] and hydrazobenzene by further reduction of azobenzene with aluminum powder in alkaline methanolic medium. 2-Hydroxypyridine of high purity was obtained from Eastman Kodak Co. and was recrystallized from ethanol and dried before use.

Apparatus and Procedure.—The apparatus and procedure for carrying out electrolyses have been described in a previous communication.[2] All electrolyses were carried out at an applied potential of 35–50 v., the initial current density being approximately 0.004 amp. per sq. cm. Initial mean valence numbers (V_i) were calculated as previously described.[2]

Electrolyses with Azoxybenzene as Additive.—The results of electrolyses carried out at 40° have been reported earlier.[4] Contrary to a statement in our previous report,[4] azoxybenzene attacks massive magnesium non-electrolytically to a small extent.

(1) Abstracted from a portion of the dissertation by John Y. Yang in partial fulfillment of the requirements for the Ph. D. degree at the University of Kansas, 1957.

(2) M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, 76, 3622 (1954).

(3) M. D. Rausch, F. D. Popp, W. E. McEwen and J. Kleinberg, J. Org. Chem., 21, 212 (1956).

(4) W. E. McEwen, J. Kleinberg, D. L. Burdick, W. D. Hoffman and J. Y. Yang, THIS JOURNAL, 78, 4587 (1956).

(5) D. J. Royer, J. Kleinberg and A. W. Davidson, J. Inorg. and Nucl. Chem., 4, 115 (1957).

(6) M. D. Rausch, W. E. McEwen and J. Kleinberg, Chem. Revs., 57, 417 (1957).

(7) M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, 77, 2093 (1955).

(8) D. L. Burdick, A. V. Santoro, W. E. McEwen and J. Kleinberg, ibid., 79, 5467 (1957).

(9) The authors hereby express their appreciation for this courtesy.

(10) "Organic Syntheses," Coll. Vol. II, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 57.

(11) "Organic Syntheses," Coll. Vol. I, 1932, p. 445.

(12) "Organic Syntheses," Coll. Vol. III, 1955, p. 103.

Electrolyses with Azobenzene as Additive.—A series of electrolyses at 40° were carried out in which a sodium iodide–pyridine solution contained azobenzene (0.5 molal). Initial mean valence numbers (V_i), together with the duration of electrolyses, were: 1.61 (23 hr.), 1.58 (17 hr.), 1.57 (22 hr.) and 1.49 (24 hr.). For an electrolysis carried out at 15°, the value obtained was 1.30 and, at 50°, 1.31.

In the experiment in which the V_i value was 1.57, the anolyte, originally containing 4.1 g. of azobenzene, was hydrolyzed with an ice and water mixture. The precipitate was collected on a filter, washed with petroleum ether, and then extracted with cold methanol. Following the removal of the solvent from the methanol solution, there was obtained 1.33 g. of a white solid, m.p. 128°, and this substance was identified as hydrazobenzene by comparison of its infrared spectrum in 5% chloroform solution with that of authentic hydrazobenzene. An additional 0.14 g. of this reduction product was recovered from the petroleum ether washings, and 0.09 g. from the filtrate of the anolyte hydrolysate by continuous ether extraction. The yield for the "anodic reduction" of azobenzene was found to be 87% in terms of the V_i of magnesium.

The catholyte was hydrolyzed by the addition of 150 ml. of cold, deaerated 6 M hydrochloric acid. After the hydrolysate had been refrigerated for several hours, the mixture was filtered, the acid filtrate washed with ether and then neutralized with 6 M sodium hydroxide solution. The mixture was then extracted with ether in a continuous extractor. Distillation of the ether left 2.18 g. of a solid residue, m.p. 122–126°. The infrared spectra in chloroform solution of this material and authentic benzidine were identical. The current yield was 81%. (It proved to be more convenient to hydrolyze the catholyte with hydrochloric acid rather than with water. Obviously, the hydrazobenzene initially formed underwent the benzidine rearrangement.)

Electrolyses with Hydrazobenzene as Additive.—Two electrolyses in which a sodium iodide–pyridine solution contained hydrazobenzene (0.5 m) gave initial mean valence numbers for magnesium of 1.89 (23 hr.) and 1.98 (23 hr.) at 40°. Gas evolution, presumably of hydrogen, was observed at both anode and cathode. After the hydrolysis, small amounts of azobenzene were isolated from the anolyte. When sodium iodide, after having been weighed, was redried at 110° and used with minimum exposure to air and moisture, gas evolution was not observed. Initial mean valence numbers for the anodic dissolution of magnesium, together with the duration of the electrolyses, were: 2.27 (22 hr.), 2.36 (22 hr.) at 40°, and 2.10 (20 hr.), 2.17 (43 hr.), 2.22 (44 hr.) and 2.21 (48 hr.) at 30°.

The entire contents of the anode compartment from a run in which the V_i value of magnesium was 2.27 were added to an ice and water mixture. The hydrolysate was refrigerated, the precipitate collected on a filter, and organic material extracted by washing with cold ether. Crystallization from petroleum ether of the residue obtained by removal of the ether gave 0.35 g. of trans-azobenzene. The calculated yield of this compound, based on the V_i of magnesium, was 0.29 g. In other typical experiments, the amount of azobenzene isolated from the anolyte was consistently higher than the calculated yield by 0.04–0.06 g. This slightly higher yield can be explained by the assumption that some air oxidation of hydrazobenzene occurred during the treatment of the reaction mixture following electrolysis.

Electrolyses with Phenylhydroxylamine as Additive.—With 0.5 m phenylhydroxylamine as additive, V_i values of 1.58 (7 hr.) and 1.49 (22 hr.) at 30° were found for the dissolution of the magnesium anode. Although the electrolyte, sodium iodide, had been dried carefully, gas evolution was observed. trans-Azobenzene together with a large amount of tar were obtained from both anolyte and catholyte following hydrolysis with ice-water. The decomposition of phenylhydroxylamine on standing precluded calculation of a current yield.

Electrolyses with Nitrosobenzene as Additive.—Electrolyses at 30° in which nitrosobenzene (0.5 m) was the organic oxidant gave initial mean valence numbers (V_i) for magnesium of 0.85 (20 hr.), 0.57 (20 hr.), 0.24 (19 hr.), 0.25 (18 hr.), 0.98 (45 hr.), 0.76 (4 hr.), 0.81 (3 hr.), 1.04 (47 hr.), 1.00 (29 hr.) and 0.55 (23 hr.). During the electrolyses in which V_i values of magnesium were approximately one, the cathode in each experiment was repeatedly

replaced in order to maintain the current density near its initial value of 0.004 amp. per sq. cm.

In the experiment in which the V_i value was 0.98, the entire contents of the anolyte were added to 250 ml. of ice-water and the resulting hydrolysate neutralized with cold 6 M hydrochloric acid. The mixture was then extracted with low boiling petroleum ether in a continuous extractor, and from the petroleum ether solution there was obtained a reddish-black solid. Extraction of this solid material with ligroin, followed by removal of the solvent, gave a red residue. Sublimation of the latter at 65° and 1 mm. pressure gave 1.48 g. of a red sublimate, m.p. 62–63°, whose infrared absorption spectrum in 3% chloroform solution was found to be identical with the spectrum of a synthetic binary mixture of 87% trans-azobenzene and 13% azoxybenzene. The residue from the sublimation contained only tar. From the data given above it can be calculated that azobenzene and azoxybenzene were obtained from the anolyte hydrolysate in 93% yield on the basis of the V_i value. The catholyte hydrolysate was found to contain a large amount of tar and was not investigated further.

The anolyte from a run in which the V_i value was 1.04 was hydrolyzed and worked up in the same manner as described above. Following sublimation, 1.33 g. of a red sublimate was obtained. Infrared analysis indicated that this material consisted of a binary mixture of 84% trans-azobenzene and 16% azoxybenzene. Chromatographic separation was carried out by adsorbing on alumina a petroleum ether solution containing 0.62 g. of this red substance. On elution with petroleum ether (b.p. 35°), there was obtained 0.46 g. of an orange colored solid, m.p. 68–69°, further identified as azobenzene by its infrared spectrum in 3% chloroform solution. Further elution with a chloroform–petroleum ether mixture containing 10% by weight of the former yielded 0.16 g. of azoxybenzene, m.p. 36–37°. The combined yield was 94%.

Electrolyses with Nitrobenzene as Additive.—With 0.5 m nitrobenzene as the potential organic oxidant, a series of electrolyses was carried out at 30°, while the current density was maintained at about 0.004 amp. per sq. cm. by repeated replacement of the magnesium cathode. Initial mean valence numbers for the anodic dissolution of magnesium were 0.42 (27 hr.), 0.39 (22 hr.), 0.50 (28 hr.), 0.48 (33 hr.) and 0.42 (20 hr.).

In the experiment in which the initial mean valence number of magnesium was 0.42, the anolyte, consisting of a brown solid suspended in a dark brown solution, was added to 250 ml. of an ice and water mixture, neutralized with 6 M hydrochloric acid and then subjected to extraction with low boiling petroleum ether in a continuous extractor. The residue resulting from evaporation of the solvent from the petroleum ether solution was steam distilled. Subsequent sublimation of the steam distillation residue at 65° and 1 mm. pressure yielded 0.47 g. of a red solid, m.p. 60–62°. The infrared spectra of this material in 3% chloroform solution and a synthetic binary mixture of 83% trans-azobenzene and 17% azoxybenzene were identical. Results obtained from infrared analysis were confirmed by actual isolation of trans-azobenzene and azoxybenzene from the red sublimate. Thus, 0.35 g. of the former compound and 0.10 g. of the latter were obtained by eluting, successively with petroleum ether and chloroform–petroleum ether mixtures, an alumina column on which the red sublimate had been adsorbed. Based on the assumption that the reduction of nitrobenzene by unipositive magnesium gave a binary mixture of azobenzene and azoxybenzene of the same composition as that isolated, the yield from the anolyte was 38%. Another typical experiment in which the V_i value was 0.385 gave a yield of 55% for the "anodic reduction" of nitrobenzene. In each case only tar was obtained from the catholyte following hydrolysis.

Condensation of Nitrosobenzene with Phenylhydroxylamine in Pyridine.—Equimolar amounts of nitrosobenzene and phenylhydroxylamine were found to condense readily and completely in pyridine to give azoxybenzene. The conjugate base of phenylhydroxylamine, which is the actual species to be expected from "anodic reduction" of nitrosobenzene, should condense with the latter compound even more readily under similar conditions.

Corrosion Experiments.—With hydrazobenzene as additive, where V_i values greater than 2 were obtained when the sodium iodide electrolyte was thoroughly dried, there was no non-electrolytic corrosion of massive magnesium following

electrolysis. With nitrobenzene and nitrosobenzene as additives, no quantitive corrosion studies were carried out inasmuch as the abnormally low V_i values obtained indicated that corrosion of the massive magnesium anode was actually occurring during electrolysis. It was demonstrated qualitatively, however, that massive magnesium was attacked non-electrolytically by products formed in the anolyte when these substances were used as additives.

Following an electrolysis at 40° of 4-hr. duration in which azoxybenzene was the additive and the V_i value was 1.04, a freshly cleaned magnesium rod was placed in the anolyte and permitted to stand for 44 hr. Whereas the magnesium anode lost 152 mg. during electrolysis, non-electrolytic corrosion of the fresh rod amounted to 232 mg.

In a 6-hr. electrolytic run at 40° in which azobenzene was the additive, the magnesium anode lost 184 mg. and the V_i value was found to be 1.34. A fresh magnesium rod placed in the anolyte after electrolysis and allowed to stand for 46 hr. lost 178 mg. It is interesting and significant that the only reduction product isolated from the hydrolysate of the mixture following corrosion was identical with that produced on "anodic reduction," namely, hydrazobenzene.

Results and Discussion

It is noteworthy that with nitrobenzene, nitrosobenzene, azoxybenzene and azobenzene as additives, V_i values for magnesium significantly less than two were obtained. However, with hydrazobenzene as organic additive and thoroughly dried sodium iodide as electrolyte, the V_i values were appreciably greater than two. This fact indicated that an anodic reaction competing with the dissolution of magnesium was occurring and, indeed, an oxidation product of hydrazobenzene, namely, trans-azobenzene, was isolated from the anolyte following hydrolysis in quantity in reasonably good agreement with that expected on the basis of the V_i value and the amount of current which had flowed through the solution.

In line with other studies[2,4] in which the quantities of "anodic reduction" products were in excellent agreement with those expected from amounts of $+1$ magnesium anodically generated, a similar situation was found to hold with most of the organic additives employed in the current investigation. Thus, with azobenzene as additive, hydrazobenzene was obtained as the only reduction product from the anolyte hydrolysate in 87% yield; with azoxybenzene, a quantitative yield of trans-azobenzene was found, a figure in substantial agreement with that reported previously[4]; with nitrosobenzene, the anolyte hydrolysate afforded a mixture of trans-azobenzene and azoxybenzene in a combined yield of 93%. It is significant that with nitrosobenzene as additive no starting material could be recovered after electrolysis, even though insufficient unipositive magnesium was produced to effect complete reduction. In addition to the reduction products, appreciable tarry material was found in the anolyte. By way of comparison, unreacted azobenzene and azoxybenzene could be recovered after electrolysis. It was only with nitrobenzene as additive that relatively low yields of reduction products (38–55% of mixtures of trans-azobenzene and azoxybenzene) were found. It seems reasonable to suppose that the relatively large quantities of tar also obtained arose from nitrosobenzene, another reduction product and the precursor of the two products isolated.

It is a striking fact that, whereas hydrazobenzene is obtained from reduction of azobenzene,
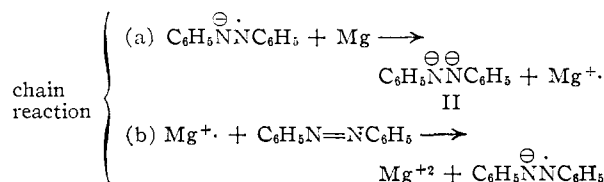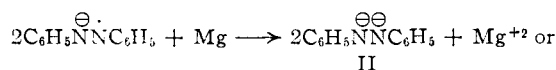
only trans-azobenzene results from reduction of azoxybenzene, and a mixture of trans-azobenzene and azoxybenzene from nitrobenzene and nitrosobenzene. The explanation for this became apparent after studies had been carried out to determine the point at which oxygen was lost from nitrobenzene, nitrosobenzene and azoxybenzene, respectively. After an electrolysis in which nitrobenzene was employed as additive, a precipitate which had formed in the anolyte was collected by filtration and washed free of pyridine with successive portions of anhydrous chloroform and ether. Addition of the solid to water gave a gelatinous precipitate of magnesium hydroxide and a solution which was basic to litmus and gave tests for sodium and iodide ions. *These observations definitely show that oxide ion was formed during the electrolytic process.* Identical results were obtained with nitrosobenzene as additive. However, when azoxybenzene was present in the electrolytic solution, the solid which had formed in the anolyte was completely soluble in water and the resulting solution gave no test for hydroxide ion. Furthermore, no 2-hydroxypyridine could be obtained from the pyridine mother liquor, although control experiments showed that small amounts of the hydroxypyridine could have been detected. *It is therefore clear that in the conversion of azoxybenzene to azobenzene by "anodic reduction" an oxide ion is lost during the hydrolysis process.* Since nitrobenzene and nitrosobenzene give azoxybenzene on reduction and since no *free* azobenzene is formed in the anolyte during electrolyses with the azoxybenzene as additive, it is evident that no further reduction of any of these additives to the conjugate base of hydrazobenzene could have been expected.

The corrosion of massive magnesium brought about by the initial product of the "anodic reduction" of azobenzene (see Corrosion Experiments, Experimental section) has provided information pertinent to the mechanisms of both the "anodic reduction" and corrosion processes. It should be kept in mind that neither azobenzene nor hydrazobenzene attack massive magnesium non-electrolytically; however, the anolyte solution following electrolysis of azobenzene corrodes the metal readily. In keeping with the mechanism of "anodic reduction" proposed in previous papers,[2–4,6] it is thought that $+1$ magnesium anodically generated is the effective reducing agent for the organic additive. It can be calculated from the V_i value of 1.34 and the amount of magnesium (184 mg.) entering solution that the apparent quantity of Mg^+ produced was 0.0050 g. ion. The loss in weight of magnesium on corrosion (178 mg.) corresponded to 0.0073 g. atom. Furthermore, only a single product, hydrazobenzene, was found in the hydrolysate either after electrolysis alone or after electrolysis followed by corrosion. Only one species derived by reduction of azobenzene by $+1$ magnesium capable of corroding massive magnesium with formation of the conjugate base of hydrazobenzene can be visualized, namely, the radical-ion I.[13]

$$Mg^+ \cdot + C_6H_5N{=}NC_6H_5 \longrightarrow Mg^{+2} + C_6H_5\overset{\cdot \cdot}{N}NC_6H_5$$

<div align="center">I</div>
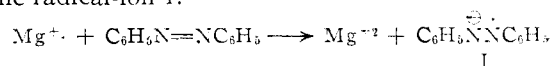
(13) Radical-ion I has been isolated in the form of its lithium salt by

Corrosion of magnesium by I to produce the conjugate base of hydrazobenzene II and $+2$ magnesium could conceivably occur by either of the two routes

$$2C_6H_5\overset{\ominus}{N}\overset{\cdot}{N}C_6H_5 + Mg \longrightarrow 2C_6H_5\overset{\ominus\ominus}{N}NC_6H_5 + Mg^{+2}\text{ or}$$
$$\text{II}$$

chain reaction $\begin{cases} \text{(a) } C_6H_5\overset{\ominus}{N}\overset{\cdot}{N}C_6H_5 + Mg \longrightarrow \\ \qquad\qquad C_6H_5\overset{\ominus}{N}\overset{\ominus}{N}C_6H_5 + Mg^+\cdot \\ \qquad\qquad\qquad\text{II} \\ \text{(b) } Mg^+\cdot + C_6H_5N{=}NC_6H_5 \longrightarrow \\ \qquad\qquad Mg^{+2} + C_6H_5\overset{\ominus}{N}\overset{\cdot}{N}C_6H_5 \end{cases}$
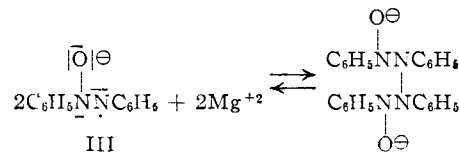
The quantitative data cited above exclude the first of these routes, inasmuch as the amount of magnesium brought into solution was approximately three times as great as the 0.0025 g. atom required by this route.

The formation of hydrazobenzene from the radical-ion I produced in the anolyte during electrolysis undoubtedly resulted from disproportionation of the conjugate acid of I (or its dimer) produced on hydrolysis. It is unlikely that the radical-ion I underwent any significant degree of disproportionation to produce azobenzene and the conjugate base of hydrazobenzene prior to hydrolysis since such a reaction would leave the solution depleted of the only species capable of attacking magnesium metal. Finally, it should be pointed out that some corrosion of the magnesium anode during electrolysis to produce the conjugate base of hydrazobenzene has not been excluded.
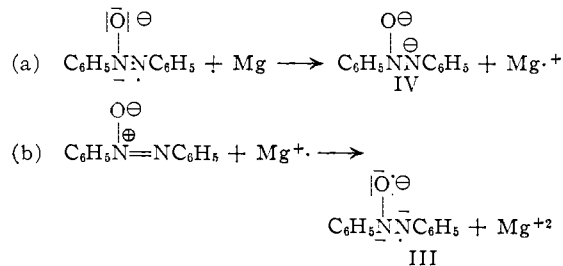
Evidence that the product initially formed on "anodic reduction" of azoxybenzene is capable of corroding massive magnesium by a free radical chain reaction also has been obtained. Thus in an electrolysis in which the V_i value was 1.04 and the calculated quantity of $+1$ magnesium consumed in reaction with azoxybenzene amounted to 0.006 g. atom, corrosion (44 hr.) following electrolysis brought 0.0096 g. atom of magnesium into solution. The "anodic reduction" and corrosion reactions may be visualized to occur as

anodic reduction

$$2Mg^+ + 2C_6H_5\overset{O\ominus}{\overset{|\oplus}{N}}{=}NC_6H_5 \longrightarrow$$

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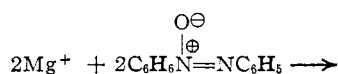
treatment of N,N′-dilithiohydrazobenzene with an equivalent quantity of azobenzene (G. Wittig and O. Stichnoth, *Ber.*, **68**, 928 (1935)). Polarographic evidence for the existence of the radical-ion also has been obtained (see, *e.g.*, A. Volpi, *Gazz. chim. ital.*, **77**, 473 (1947)).

$$2C_6H_5\overset{|\overline{O}|\ominus}{N}\overset{\cdot}{N}C_6H_5 + 2Mg^{+2} \rightleftharpoons \begin{array}{c} C_6H_5NNC_6H_5 \\ \overset{O\ominus}{|} \\ C_6H_5NNC_6H_5 \\ \overset{|}{O\ominus} \end{array}$$
$$\text{III}$$

corrosion

(a) $\quad C_6H_5\overset{|\overline{O}|\ominus}{N}\overset{\cdot}{N}C_6H_5 + Mg \longrightarrow C_6H_5\overset{O\ominus}{\overset{|\ominus}{N}}NC_6H_5 + Mg\cdot^+$
$$\qquad\qquad\qquad\qquad\qquad\qquad\text{IV}$$

(b) $\quad C_6H_5\overset{O\ominus}{\overset{|\oplus}{N}}{=}NC_6H_5 + Mg^+\cdot \longrightarrow$
$$\qquad\qquad C_6H_5\overset{|\overline{O}\cdot\ominus}{N}\overset{-}{N}C_6H_5 + Mg^{+2}$$
$$\qquad\qquad\qquad\text{III}$$

It should be pointed out that azoxybenzene itself can corrode massive magnesium. However, control experiments indicated that less than one-third of the quantity of magnesium brought into solution in the corrosion experiment cited above could be attributed to attack by azoxybenzene.

Additional support for the free radical chain mechanism of corrosion was gained by examination of the effect of pyrrole, a substance known to be capable of capturing free radicals,[14] as an inhibitor of corrosion following electrolysis. The addition of this substance to the anolyte mixture after electrolysis decreased markedly the extent of corrosion, the degree of inhibition being roughly proportional to the quantity of pyrrole added.[15]

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(14) J. B. Conant and B. F. Chow, THIS JOURNAL, **55**, 3475 (1933).

(15) Whereas 75 mg. was lost from a magnesium rod during a corrosion period of 19 hr. in the absence of pyrrole, 53 mg. was lost in a similar period when 1.5 g. of the inhibitor had been added to the anolyte following electrolysis, and the loss in weight amounted to only 28 mg. when 4.5 g. of pyrrole had been added. In each case the conditions of electrolysis were substantially identical. It is of interest that a magnesium rod placed in the catholyte also underwent corrosion after electrolysis had been stopped. In three experiments in which no pyrrole, 1.5 g. and 4.5 g., respectively, were added to the catholyte after electrolysis, the loss in weight of the metal amounted to 66, 5 and 5 mg.