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

Corrosion of Massive Magnesium by Organic Free Radical Ions Generated by Unipositive Magnesium

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Massive magnesium undergoes corrosion by organic free radical-ions generated from benzophenone and 4,4'-dimethylbenzophenone by means of unipositive magnesium. Evidence is presented to show that the corrosion process takes place by a chain reaction with ketyl radical-ions and +1 magnesium serving as chain carriers.

Previous communications from this Laboratory[1-3] dealing with the anodic oxidation of magnesium in sodium iodide–pyridine solutions in the presence of potential organic oxidants have shown that, in those cases where magnesium enters solution with an initial mean valence number (V_i) between one and two, "anodic reduction" products are found in quantity equivalent to oxidation of the metal from its initial mean valence state to the familiar dipositive state. From the nature of the "anodic reduction" products obtained when benzophenone[1] and 4,4'-dimethylbenzophenone[3] were employed as the organic oxidants, there appears to be little doubt that V_i values less than two can be explained in terms of the formation of unipositive magnesium as a primary electrode process. As a matter of fact, there is reason to believe that the sole primary anodic process is the production of +1 magnesium.[4,5]

It has been noted that an abnormally low (*i.e.*, <1) V_i value is found for magnesium when nitrobenzene is the organic oxidant present in the pyridine solution.[6] Since a V_i value no lower than 1 would be anticipated as a result of a strictly electrochemical process, it is clear that some reduction product(s) of nitrobenzene, unlike nitrobenzene itself, is able to corrode massive magnesium relatively rapidly. Even in those cases where the V_i values lie between 1 and 2 it is conceivable that the materials originally produced by interaction of +1 magnesium and organic additives are capable of attacking massive magnesium, and that V_i values in reality may be a measure of both electrochemical and non-electrochemical effects.

In this communication, major emphasis is given to the corrosion of massive magnesium by products formed by the "anodic reduction" of benzophenone and 4,4'-dimethylbenzophenone. Particularly valuable information could be obtained with these compounds because the products of "anodic reduction" in these cases do not attack the massive magnesium electrode during the course of electrolysis. However, corrosion begins to occur once the electrolytic process has been terminated.

Experimental[7]

Materials.—The 8-mm. magnesium rod from which all electrodes were cut was of 99.8% purity and was furnished by the Aluminum Company of America.[8] The sodium iodide employed as electrolyte was Merck and Co., Inc., reagent grade. Pyridine, Mallinckrodt analytical reagent, was dried over anhydrous barium oxide, distilled from sodium through a 45-cm. packed column, and stored over additional barium oxide until used. Benzophenone, m.p. 47–48°, and 4,4'-dimethylbenzophenone, m.p. 91–92°, were obtained from the Eastman Chemical Co.

Apparatus and Procedure.—The apparatus and procedure for carrying out electrolyses experiments have been described in a previous paper.[1] All electrolyses were made at a cell potential of 10–60 v., at a temperature of 40 ± 0.1°, and in an atmosphere of pure nitrogen. Initial mean valence numbers (V_i) were calculated as previously described.[1]

Products Resulting from Electrolysis Experiments.—Product isolation studies already have been carried out in those instances wherein magnesium is anodically oxidized in the presence of benzophenone and 4,4'-dimethylbenzophenone. Benzopinacol was obtained from benzophenone in 98% yield, based on the initial mean valence number and the quantity of magnesium entering solution.[1] In a similar fashion, tetra-*p*-tolylethylene glycol was formed from 4,4'-dimethylbenzophenone in 84% yield.[3] *In neither case was any other reduction product recovered from the anolyte.* With both additives, the major reduction product formed in the catholyte (after hydrolysis) was the appropriate benzhydrol; *no evidence for the formation of more than traces of pinacol was obtained.*

Corrosion Experiments.—Electrolyses of varying duration were carried out between magnesium electrodes, the electrolytic solution consisting of a saturated (at 25°) sodium iodide–pyridine solution containing diaryl ketone in each compartment. Following electrolysis, the electrodes were removed, thoroughly cleaned with distilled water and 95% ethanol, dried and weighed. The initial mean valence number (V_i) with which the magnesium entered solution was then calculated. Freshly cleaned magnesium rods were weighed and placed in both anolyte and catholyte, the compartments of the cell being maintained under a nitrogen atmosphere. The rods were permitted to remain in contact with anolyte and catholyte solutions for long periods of time and were then removed, cleaned with 95% ethanol, dried and weighed. The magnesium rod which had been placed in the anolyte compartment always showed substantial loss in weight (Table I), whereas that in the catholyte was unattacked.

Product Isolation. A. With Benzophenone as Additive.—To the anolyte, after removal of the magnesium rod, was added 100 cc. of ice-cold 20% hydrochloric acid. The mixture was permitted to stand for 24 hr. and the red-brown precipitate which had formed was collected by filtration, washed with water and dried. The aqueous filtrate was extracted with several portions of ether (total volume 200 cc.) and the ether phase was employed to dissolve the red-brown precipitate. The resulting solution was washed with 50 cc. of 10% sodium carbonate solution and 50 cc. of 5% sodium bisulfite solution. The ethereal solution was then dried over anhydrous calcium chloride, filtered and the ether distilled. The solid residue was digested with 50 cc. of hot petroleum ether and the insoluble residue was dis-

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[1] M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **76**, 3622 (1954).

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

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

[4] D. J. Royer, A. W. Davidson and J. Kleinberg, *J. Inorg. and Nuclear Chem.* (in press).

[5] M. D. Rausch, W. E. McEwen and J. Kleinberg, *Chem. Revs.*, 417 (1957).

[6] M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **77**, 2093 (1955).

[7] All m.p.'s are corrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[8] The authors hereby express their appreciation for this courtesy.

TABLE I

CORROSION OF MASSIVE MAGNESIUM BY KETYL RADICAL IONS

Organic additive	Duration of electrolysis,[a] hr.	V_i	Loss of weight of anode during electrolysis, g.	Calcd. moles of ketyl radical-ion produced during electrolysis[b]	Duration of corrosion, hr.	Max. no. of g. atoms of Mg consumable by corrosion in accordance with mechanism a	Actual no. of g. atoms of Mg consumed by corrosion process
Benzophenone	12	1.52	0.2762	0.0054	100	0.0027	0.0075
	12.5	1.54	.3334	.0064	112.5	.0032	.0106
	19	1.54	.3894	.0074	122	.0037	.0084
	25	1.55	.3981	.0074	71	.0037	.0038
4,4'-Dimethylbenzophenone	19.5	1.52	.3411	.0067	143	.00335	.0086
	23	1.52	.3566	.0070	97	.0035	.0090
	24	1.52	.3883	.0077	144	.00385	.0097
	20	1.56	.4106	.0074	215	.0037	.0107

[a] All electrolyses were carried out between Mg electrodes at 40 ± 0.1°. The electrolyte consisted of a saturated NaI–pyridine solution. When benzophenone was used as additive, its concentration was 0.324 *m* and the current density was 0.020–0.015 amp. per sq. cm. When 4,4'-dimethylbenzophenone was employed as additive, its concentration was 0.5 *m* and the current density was 0.003–0.004 amp. per sq. cm. [b] As has been pointed out, the ketyl radical ion originally produced undoubtedly exists in equilibrium with its dimer, but the latter serves as a reservoir for reactive monomer.

solved in a minimum amount of chloroform. Addition of 95% ethanol to the chloroform solution caused the precipitation of a white solid which was identified as benzopinacol. Cooling of the petroleum ether solution yielded white crystals which were identified as benzhydrol. Fractional evaporation of the mother liquor gave several crops of crystals, one of which was shown to be dibenzhydryl ether, m.p. 109–110° (reported[9] m.p. 109–110°). Evaporation to dryness of the remaining solution gave a colorless residue which proved to be benzophenone.

The aqueous layer remaining from the extraction with ether was made alkaline by addition of concentrated sodium hydroxide solution and extracted several times with ether, the total volume of extractant being 200 cc. The ether extract was taken to dryness, the residue dissolved in 30 cc. of 10% hydrochloric acid and filtered. The filtrate was made alkaline with 10% sodium hydroxide solution and the precipitate which formed was collected by filtration. This was recrystallized from ethanol–water, giving colorless crystals, m.p. 102–103°. There was no depression in melting point upon admixture with an authentic sample of α-pyridyldiphenylcarbinol, m.p. 104–105°.[10] Infrared spectra of the two samples in chloroform solution were identical.

For quantitative determination of the various products formed in the anolyte, during electrolysis and after corrosion, benzopinacol and α-pyridyldiphenylcarbinol were isolated as described above and weighed. The petroleum ether extract (see above) was cooled and the benzhydrol which precipitated was weighed. The mother liquor was evaporated to dryness and the residue dissolved in an amount of chloroform to give a concentration of 2.5 g. of solid per 100 cc. of solvent. An infrared method was used to determine the composition of the mixture. The percentage of benzhydrol in the chloroform solution was found by measurement of the absorption peak at 3590 cm.$^{-1}$ and comparison with a standard curve for the alcohol. The quantity of benzophenone was determined by measurement of the absorption peak at 1660 cm.$^{-1}$ and comparison with a standard for the ketone. The amount of dibenzhydryl ether in the ternary mixture was found by difference. The validity of this treatment was established by comparison of the spectrum of the unknown solution with that of a ternary mixture of benzhydrol, benzophenone and dibenzhydryl ether made up in the same proportions as found by the infrared method described above. The two spectra were virtually identical.

B. **With 4,4'-Dimethylbenzophenone as Additive.**—The anolyte, after removal of the magnesium rod, was added with cooling to 160 cc. of 21% phosphoric acid solution. After 15 min., 150 cc. of ice-cold 18% hydrochloric acid was added to the anolyte hydrolysate, and the resulting mixture was extracted with ether in a continuous extractor. The ether extract was washed with dilute sodium carbonate solution, dilute sodium thiosulfate solution, and then dried over anhydrous calcium sulfate. Distillation of the ether gave a pale yellow crystalline solid. The solid was dissolved in a low boiling petroleum ether–chloroform mixture (1:2 by volume) and an aliquot of the solution was subjected to chromatographic separation on an alumina column. Elution with petroleum ether–chloroform mixtures gave 4,4'-dimethylbenzophenone, tetra-*p*-tolylethylene glycol, 4,4'-dimethylbenzhydrol and a trace of a colorless solid, m.p. 116.5–117.5°.

Anal. Found: C, 81.24; H, 6.29.

The aqueous layer remaining from the ether extraction was made basic with sodium hydroxide solution and extracted with ether in a continuous extractor. The ether extract was taken to dryness, the residue dissolved in dilute hydrochloric acid and filtered. The filtrate was made alkaline with dilute sodium hydroxide solution and the solution permitted to stand for 12 hr. The precipitate which formed was filtered and recrystallized from ethanol–water (Norite), giving colorless crystals, m.p. 118.2–119.0°. There was no depression in melting point upon admixture with an authentic sample of α-pyridyl-di-*p*-tolylcarbinol, m.p. 119–121°.[11] Infrared spectra of the two samples in chloroform were identical.

For quantitative determination of the products formed in the anolyte, during electrolysis and after corrosion, the anolyte was hydrolyzed and extracted with ether as described above. The ether was evaporated and the residue dissolved in a low boiling petroleum ether–chloroform mixture (1:2 by volume). An aliquot of this solution was passed through an alumina column. By elution with petroleum ether–chloroform solutions containing gradually increasing proportions of the latter solvent, it was possible to isolate 4,4'-dimethylbenzophenone and 4,4'-dimethylbenzhydrol essentially quantitatively and in pure form. Only a fraction of tetra-*p*-tolylethylene glycol could be recovered pure by chromatography. Therefore, an independent determination of the latter compound was made by lead tetraacetate oxidation. An aliquot of the original extract from the anolyte was dissolved in glacial acetic acid and titrated with a solution of standardized lead tetraacetate (0.06 *N*) according to the method of Criegee, Buchner and Walther.[12] In control experiments it was possible by this method to determine tetra-*p*-tolylethylene glycol quantitatively in the presence of 4,4'-dimethylbenzophenone and 4,4'-dimethylbenzhydrol.

α-Pyridyl-di-*p*-tolylcarbinol was isolated as described above and weighed.

Results and Discussion

In previous communications[1,3] evidence has been presented that ketyl radical ions are formed by the reduction of benzophenone and 4,4'-dimethylbenzophenone by +1 magnesium anodically generated. These radical ions undoubtedly are in equilibrium with their appropriate pinacolate ions, and it is

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(9) E. Knoevenagel and W. Heckel, *Ber.*, **36**, 2827 (1903).

(10) B. Emmert and E. Asendorf, *ibid.*, **72**, 1188 (1939).

(11) F. J. McCarty, C. H. Tilford and M. G. Van Campen, Jr., THIS JOURNAL, **79**, 472 (1957).

(12) R. Criegee, E. Buchner and W. Walther, *Ber.*, **73**, 571 (1940).

TABLE II

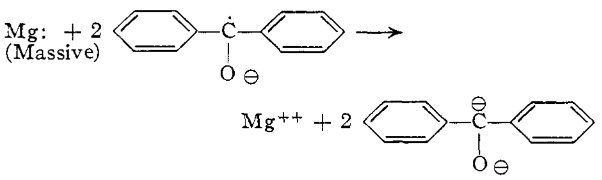
PRODUCT ISOLATION FOLLOWING CORROSION

Organic additive	Theoret. yield (g.) of pinacol based on V_1 and loss in wt. of Mg anode	Pinacol found after corrosion, g.	No. of g. atoms of Mg consumed by corrosion process	Benzhydrol isolated after corrosion, moles	2-Pyridyldiarylcarbinol isolated after corrosion, g.
Benzophenone	1.00	0.96	0.0075	0.0060[a]	0.40[b]
4,4'-Dimethylbenzophenone	1.41	1.35	.0086	.0080	0.17[c]

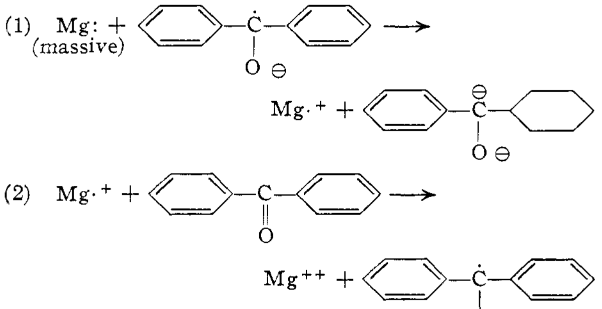
[a] Actually, 0.48 g. of benzhydrol and 0.57 g. of benzhydryl ether were isolated. [b] 0.0015 mole. [c] 0.006 mole.

likely that both the ketyl and pinacolate species are associated with dipositive magnesium ions. Inasmuch as only the pinacol is formed from each of the ketones during the electrolytic process and the benzhydrol is produced in the anolyte only during the corrosion process following electrolysis, it is evident that the magnesium anode is not attacked non-electrolytically during electrolysis.[13]

The fact that corrosion of massive magnesium occurs following electrolysis and the additional observation that the product of corrosion is a benzhydrol could conceivably be explained on the basis of either of two mechanisms: (a) reaction of two ketyl radical-ions with massive magnesium to produce two dinegative benzhydrol anions plus dipositive magnesium, *e.g.*



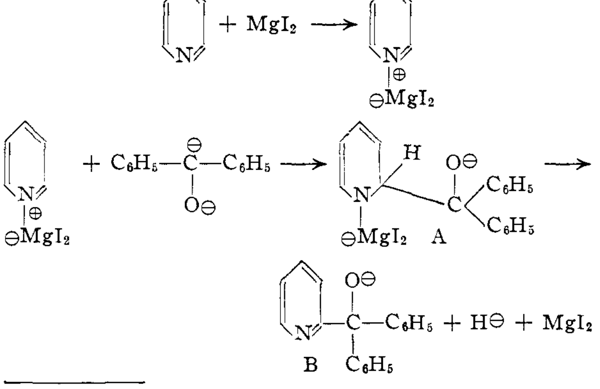
(b) a chain reaction in which unipositive magnesium and ketyl radical ions function as chain carriers and massive magnesium and ketone serve as sources of the chain carriers, *e.g.*



Of course, with either possible mechanism, hydrolysis of the dinegative benzhydrol anion affords the corresponding benzhydrol.

In order for mechanism a to be operative, the quantity of magnesium consumed during the corrosion process would be limited by the amount of ketyl radical ion formed during electrolysis. Furthermore, with this mechanism, the quantity of ketyl radical ion would steadily diminish as the corrosion process progressed. Actually, neither of these conditions was realized during corrosion. As a matter of fact, as shown by the data of Tables I and II, the quantity of massive magnesium brought into solution during the corrosion process was considerably greater than the amount permitted by mechanism a, whereas the amount of pinacol (formed from ketyl) remained relatively constant. These experimental facts eliminate mechanism a, and are consistent with the chain mechanism b.[14]

On the basis of chain mechanism b, the number of g. atoms of magnesium consumed in the corrosion process should equal the number of moles of the benzhydrol (or its derivatives) isolable from the hydrolysate of the corrosion mixture. As is seen in Table II, the yield of the benzhydrol ranges from 80 to 93% of that expected. However, if it is permissible to include in the total yield of the benzhydrol the quantity of 2-pyridyldiarylcarbinol found, the expected yield of the benzhydrol is realized. The origin of the 2-pyridyldiarylcarbinol poses a question. A number of alternative routes for its formation need to be considered. It would not appear likely that the compound arises by attack of the ketyl radical ion on the solvent, because the carbinol has never been isolated following a normal electrolysis. The only other species present in the corrosion mixture which could conceivably attack pyridine is the dinegative benzhydrol anion. However, the 2-pyridyldiarylcarbinol is never found in the catholyte after electrolysis and the dinegative benzhydrol anion is a major reduction product in this compartment of the electrolytic cell.[1] Since a major difference in the composition of anolyte and catholyte is the presence of dipositive magnesium ion in the former, it seems reasonable to suppose that this cation plays a role in formation of the 2-pyridyldiarylcarbinol, namely, that of an acid catalyst for a condensation reaction between the solvent and the dinegative benzhydrol anion, *e. g.*



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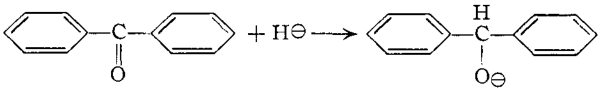
[13] In two out of approximately forty experiments with 4,4'-dimethylbenzophenone as additive an unusually low initial mean valence number (V_i = *ca.* 1.2) was obtained for magnesium (ordinarily, the values were 1.52 ± 0.03). Only when these abnormal V_i values were found was any 4,4'-dimethylbenzhydrol isolated from the anolyte hydrolysate following electrolysis.

[14] Evidence for corrosion of magnesium by a chain mechanism also has been obtained when azoxybenzene, azobenzene and benzil were used as additives in the anolyte (unpublished observations of J. Y. Yang and W. H. Hoffman).

It has not been established at which point the dihydropyridine derivative A is converted to the completely aromatic species B. If the hydride ion is lost to the pyridine solution before hydrolysis, as shown above, it is likely that it will add to diarylketone present to give the conjugate base of the benzhydrol, *e.g.*



As a matter of fact, in a control experiment, carried out in a pyridine solution containing sodium iodide and magnesium iodide, it has been found that hydride ion (from sodium hydride) adds quantitatively to benzophenone at 40°. If indeed the hydride ion is lost before hydrolysis, then the amount of the 2-pyridyldiarylcarbinol cannot be included in the total yield of the benzhydrol formed by corrosion.

Finally, with regard to the corrosion process (mechanism b), the following observation should be made. Although the attack of the ketyl radical ion on the massive metal is depicted to show the formation of unipositive magnesium, the question can be raised as to whether the latter actually is formed in the free state. It is entirely conceivable that as the ketyl radical ion abstracts an electron from one magnesium atom on the surface of the metal, a molecule of ketone accepts an electron from the metal at another point on the surface to form a new ketyl radical ion. In any event, unless these two processes are synchronous, the active form of the metal is still essentially +1 magnesium.

Miscellaneous Observations

A number of miscellaneous observations are worth noting. It has been suggested to us by a number of people that the low V_i values found for magnesium when anodically oxidized in the presence of various additives could be explained in terms of local cell action due to the presence of trace amounts of metallic impurities. Two strong arguments against this interpretation exist. One, when benzophenone or 4,4′-dimethylbenzophenone is used as additive, there is a remarkable consistency in V_i values (Table I) which would hardly be expected if local cell action occurred. In the second place, only pinacol is obtained on hydrolysis of the anolyte after electrolysis, and certainly dissolution of the anode by local cell action during the electrolytic process would give rise to the dinegative benzhydrol anion, inasmuch as the ketyl radical-ion is the most reactive species present in the anolyte.

It also has been suggested that the low V_i values possibly can be attributed to disintegration of the anode at its surface to form the colloidal metal. The consistency of the V_i values also argues against this hypothesis. Moreover, it is unlikely that colloidal metal would be produced at the relatively low voltages employed in the electrolyses.

The possibility that the formation of pinacolate in the anolyte occurs by means of the Gomberg–Bachmann reaction,[15] *i.e.*, by reaction of the binary mixture $Mg–MgI_2$[16] on the ketone additive has been considered and rejected. In a control experiment, massive magnesium was permitted to stand for about 24 hr. in contact with a pyridine solution containing benzophenone, magnesium iodide and sodium iodide. No characteristic blue color of the ketyl radical ion (in pyridine) was developed and the magnesium metal suffered no loss in weight.

The possible role of dipositive magnesium in the formation of the 2-pyridyldiarylcarbinol in the anolyte during the corrosion process has been noted. An interesting metal ion effect also has been observed in catholyte during electrolysis. With sodium iodide as electrolyte and diaryl ketone as additive, the major reduction product of the latter is the benzhydrol. However, from electrolyses in which the catholyte contained magnesium(II) iodide and ketone, substantial amounts of pinacol, as well as benzhydrol, were isolated. Two possible routes for the production of pinacol can be suggested: (1) an acid-catalyzed (*i.e.*, by Mg^{++} ion) addition of the dinegative benzhydrol anion to the benzophenone; and (2) the direct formation of pinacolate by acceptance of electrons at the cathode by a Mg^{++} ion–benzophenone complex.

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[15] M. Gomberg and W. E. Bachmann, THIS JOURNAL, **49**, 236 (1927).

[16] During electrolysis some dipositive magnesium is formed in the anolyte, which contains sodium iodide as electrolyte.