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Anodic Reductions. III. Correlation between the Quantity of Unipositive Magnesium Produced Anodically and the Extent of Anodic Reduction

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Additional evidence is provided that, when magnesium is anodically oxidized in sodium iodide–pyridine solutions containing organic oxidants, initial mean valence numbers (V_i) less than 2 can always be accounted for by the presence of "anodic reduction" products in quantity equivalent to oxidation of the metal from its initial mean valence state to its common dipositive state. Specifically, it has been shown that 4,4′-dimethylbenzophenone, benzil and azoxybenzene are "anodically reduced" by unipositive magnesium, the products isolated after hydrolysis of the anolyte following electrolysis being tetra-*p*-tolylethylene glycol, benzoin and *trans*-azobenzene, respectively. The quantities of these reduction products can be correlated reasonably well with the amount of unipositive magnesium produced anodically.

Introduction

It has been demonstrated recently that in the anodic oxidation of magnesium in sodium iodide–pyridine solutions containing benzophenone the initial mean valence number (V_i) with which the anode enters solution can be correlated in a quantitative fashion with the extent of reduction of the ketone.[1] After hydrolysis of the anolyte, benzopinacol was isolated in 92–98% yield, the latter being based on the amount of product expected from the oxidation of the magnesium from its initial mean valence state (1.67–1.83) to the common dipositive form by the benzophenone. Up to the present communication, one other attempt to relate in a quantitative manner the extent of "anodic reduction" with V_i in pyridine solution had been made, namely, in the conversion of 2-methoxyphenyl mesityl ketone to 2,2′-dimesitoylbiphenyl by unipositive magnesium anodically generated.[2] In this case, the yield of the diketone amounted to only 36–40% of that expected from the quantity of +1 magnesium formed. However, in addition to 2,2′-dimesitoylbiphenyl a relatively large amount of unidentified polymeric material was isolated from the anolyte. It seemed highly probable that the polymeric material represented another reduction product and one very likely derived from the diketone, inasmuch as an apparently identical substance was obtained upon the "anodic reduction" of the diketone itself.

"Anodic reductions" have been observed also in aqueous media in electrolyses with active metals as anodes. Thus in the anodic oxidation of magnesium,[3] beryllium[4] and aluminum[5] in aqueous electrolytic solutions it was demonstrated qualitatively that a variety of inorganic oxidants, *e.g.*, MnO_4^-, ClO_3^-, Ag^+, were reduced in the anolyte by lower valent species of the active metals formed during the electrolytic process. In electrolyses carried out in non-oxidizing salt solutions with magnesium or beryllium as anode, the solvent itself was reduced to hydrogen by the unipositive form of the metal, and the volume of hydrogen liberated from the anolyte corresponded to that expected on the basis of the equation, *e.g.*

$$Mg^{+V_i} + (2 - V_i)H^+ = Mg^{++} + \frac{2 - V_i}{2} H_2$$

In view of the results in aqueous solution and that observed for the anodic oxidation of magnesium in sodium iodide–pyridine solutions containing benzophenone, it seemed essential to establish beyond doubt that the reducing power indicated by a V_i lower than two for magnesium can always be accounted for by the presence of "anodic reduction" products in quantity equivalent to oxidation of the metal from its initial mean valence state to its common +2 state.[6] The establishment of this generalization is particularly important since it has been shown that a number of active metals when anodically oxidized in pyridine solutions containing a variety of organic oxidants go into solution in initial mean valence states significantly lower than those corresponding to the number of valence electrons.[7]

In the present paper, three new cases are reported in which the extent of "anodic reduction" in pyridine solutions containing organic oxidants has been correlated in nearly quantitative fashion with the amount of unipositive magnesium generated anodically. The results of the experiments reported herein, together with the quantitative "anodic reductions" noted above, show conclusively that the initial mean valence number (V_i) represents a convenient measure of the extent of "anodic reduction" to be expected. All yields reported in the Experimental section were confirmed in repeat experiments.

It should be emphasized that in all three cases studied there was no non-electrolytic attack on massive magnesium by the various pyridine solutions employed.

Experimental[8]

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.[9] The sodium iodide employed as electrolyte was Merck reagent grade. Pyridine, Mallinckrodt analytical reagent, was dried over

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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] R. L. Petty, A. W. Davidson and J. Kleinberg, THIS JOURNAL, **76**, 363 (1954).

[4] B. D. Laughlin, J. Kleinberg and A. W. Davidson, *ibid.*, **78**, 559 (1956).

[5] E. Raijola and A. W. Davidson, *ibid.*, **78**, 556 (1956).

[6] It should be emphasized that the low V_i values found for the active metals cited (Mg, Be, Al) imply the existence of lower oxidation states not found in stable compounds of these elements.

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

[8] All melting points are corrected.

[9] The authors hereby express their appreciation for this courtesy

anhydrous barium oxide, distilled from sodium through a 45-cm. packed column, and stored over additional barium oxide until used. 4,4′-Dimethylbenzophenone, m.p. 91–92°, was obtained from the Eastman Chemical Co. Benzil was prepared from benzoin by the method described in reference 10. Azoxybenzene was obtained by reduction of nitrobenzene with arsenic(III) oxide in methanolic potassium hydroxide solution.[11]

Apparatus and Procedure.—The apparatus and procedure for carrying out the various electrolyses have been described in a previous communication.[1] All electrolyses were made at a cell potential of 10–60 v., the current density being between 0.003 and 0.007 amp. per sq. cm.

Electrolyses with 4,4′-Dimethylbenzophenone as Additive.—A series of electrolyses were carried out in which a sodium iodide–pyridine solution contained 4,4′-dimethylbenzophenone (0.5 molal). Initial mean valence numbers (V_i) with which the magnesium anode entered solution were calculated by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 24.32}{107.88 \times \text{wt. of Mg lost from anode}}$$

The values obtained, together with the duration of the electrolyses, were as follows: 1.56 (26 hr.), 1.53 (27 hr.), 1.49 (30 hr.), 1.54 (29 hr.), 1.52 (29 hr.).

In the experiment in which the V_i value equalled 1.54, the anolyte, originally containing 4.63 g. of 4,4′-dimethylbenzophenone, was added with cooling to 125 ml. of 21% phosphoric acid solution. A solid which precipitated was collected by filtration and amounted to 4.47 g. Continuous ether extraction of the filtrate afforded an additional 0.08 g. of solid material. Analysis by infrared absorption (see below) showed that the original precipitate was a binary mixture of 29% by weight of the pinacol, tetra-*p*-tolylethylene glycol, and 71% of the original ketone. The solid obtained from the ether extract was found to contain 80.4% of the pinacol and 19.6% of the starting ketone. The total quantity of pinacol (1.365 g.) corresponded to an 84% yield based on the amount of product expected from the oxidation of the magnesium from its initial mean valence (1.54) to the dipositive form by the ketone.

The infrared spectra of known synthetic mixtures of 4,4′-dimethylbenzophenone and tetra-*p*-tolylethylene glycol were taken in chloroform solution in a 0.05-mm. cell. (The solutions contained 6.25% by weight of solute.) A calibration curve was made by plotting the percentage by weight of the pinacol in the various mixtures against the difference in the heights of the absorption peaks at 1612 cm.$^{-1}$ (characteristic of original ketone) and 1518 cm.$^{-1}$ (characteristic of the pinacol). Infrared spectra of the solid materials isolated from the anolyte showed them to contain only the ketone and pinacol, and the quantities of each present were obtained by use of the calibration curve.

In another electrolysis, the solid which precipitated on acidification of the anolyte was subjected to fractional crystallization from ethanol–chloroform mixture and from the more soluble fractions a colorless solid, m.p. 169–172° dec., was obtained. The melting point of an authentic sample of tetra-*p*-tolylethylene glycol, prepared by the method of Gomberg and Bachmann,[12] was not depressed upon admixture with this colorless solid. The infrared spectra (in chloroform solution) of the two samples were identical.

Following a typical electrolysis, the catholyte was added with cooling to 140 ml. of 18% hydrochloric acid. A viscous yellow oil separated from the aqueous layer. The oil was taken up with ether and the aqueous layer was extracted continuously with the same solvent. The combined ether extract was washed with dilute sodium carbonate solution, dilute sodium thiosulfate solution, and then dried over anhydrous calcium sulfate. The residue from the ether extract was distilled at 1 mm. pressure, the bulk of the material coming over as a colorless liquid at 150–152° and solidifying on cooling. The solid material was dissolved in low boiling petroleum ether and subjected to chromatographic separation on an alumina column. The only substances obtained on elution with chloroform–petroleum ether mixtures were 4,4′-dimethylbenzophenone and 4,4′-dimethylbenzhydrol, the latter being more firmly adsorbed. The benzhydrol, crystallized from ligroin, exhibited a m.p. of 67.5–68.5°, reported 69°.[13] An authentic sample of 4,4′-dimethylbenzhydrol was prepared by reduction of 4,4′-dimethylbenzophenone with sodium borohydride and infrared spectra in chloroform solution of the two samples were identical.

Electrolyses with Benzil as Additive.—Electrolyses in which benzil (0.5 *m*) was organic additive gave initial valence numbers (V_i) for magnesium of 1.48 (33 hr.), 1.47 (32 hr.) and 1.48 (24 hr.). At the end of the electrolysis in which the V_i value was 1.48 (33 hr.) the dark red contents of each compartment of the cell were hydrolyzed by addition to 150 ml. of 18% hydrochloric acid. After the anolyte hydrolysate had been refrigerated for 24 hr. the mixture was filtered and 4.87 g. of solid material collected. A continuous ether extraction of the acidic filtrate yielded an additional 0.75 g. of solid product, giving a total recovery of 5.63 g. of solid material from an original 6.25 g. of benzil. Extraction of a portion of the solid product with low boiling petroleum ether in a Soxhlet extractor for a period of 11 hr. left a residue of pure benzoin, m.p. 135–136°. The melting point of an authentic sample of benzoin was not depressed on admixture with this residue.

The infrared spectra of known synthetic mixtures of benzil and benzoin were taken in chloroform solution in a 0.05-mm. cell. (The solutions contained 5.3% by weight of solute.) A calibration curve was made by plotting the percentage by weight of benzoin in the various mixtures against the difference in the heights of the absorption peaks at 880 cm.$^{-1}$ (characteristic of benzil) and 980 cm.$^{-1}$ (characteristic of benzoin). The spectra of the solid material obtained from the anolyte showed it to contain only benzoin and benzil, the former being present to the extent of 24.4%. This corresponds to 1.37 g. of benzoin, a 92% yield in terms of the V_i of the magnesium.

Infrared analysis of the solid material obtained from the catholyte hydrolysate also showed only benzoin and benzil to be present, the former in quantitative current yield.

Electrolyses with Azoxybenzene as Additive.—With this organic additive (0.5 *m*) as oxidant, V_i values for magnesium of 1.03 (40 hr.), 1.05 (39 hr.), 1.13 (26 hr.) and 1.05 (20 hr.) were found.

In the experiment in which the V_i value was 1.05, the anolyte, originally containing 4.50 g. of azoxybenzene, was added to 150 ml. of freshly boiled 18% hydrochloric acid. The resulting mixture was extracted with low boiling petroleum ether in a continuous extractor and from the ether solution there was obtained 3.92 g. of a red solid. Sublimation of 0.06038 g. of this solid at 60° and 1 mm. pressure yielded 0.03112 g. of sublimate, m.p. 62°. Recrystallization of the sublimate from ligroin gave pure *trans*-azobenzene, m.p. 68–69°, reported 68°. The infrared spectra in chloroform solution of this material and authentic *trans*-azobenzene were identical. It can be estimated from the melting point data for mixtures of *trans*-azobenzene and azoxybenzene[14] that the original sublimate (m.p. 62°) consisted of a binary mixture of *trans*-azobenzene and azoxybenzene containing 91% of the former. From the weight data given above it can be calculated that *trans*-azobenzene was present in the red solid obtained from the anolyte hydrolysate in 94% yield based on the V_i of the magnesium. Confirmation of this yield was obtained by the complete identity of the infrared absorption spectrum of the original red solid in 3% chloroform solution with the spectrum of a synthetic mixture of *trans*-azobenzene and azoxybenzene made up to correspond to the ratio of the two compounds found to be present in the red solid by the sublimation technique. It should be emphasized that in the sublimation all of the *trans*-azobenzene present in the red solid had been sublimed; only azoxybenzene could be recovered from the sublimation residue.

From the catholyte, hydrolyzed and worked up in the same manner as described for the anolyte, there was obtained *trans*-azobenzene, azoxybenzene and a large amount of tar. The presence of the latter precluded calculation of current yield.

Discussion

In terms of the product isolated from anolyte it

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[10] "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 87.

[11] "Organic Syntheses," Coll. Vol. II, 1943, p. 57.

[12] M. Gomberg and W. E. Bachmann, This Journal, **49**, 236 (1927).

[13] J. Wieler, *Ber.*, **7**, 1181 (1874).

[14] H. Hartley and J. M. Stuart, *J. Chem. Soc.*, **105**, 309 (1914).

appears that "anodic reduction" of 4,4′-dimethylbenzophenone proceeds in the same manner as in the case of benzophenone previously reported.[1] It may be assumed that unipositive magnesium anodically generated gives up an electron to the ketone to form the corresponding ketyl radical-ion, which then dimerizes to yield the magnesium pinacolate. Subsequent acid hydrolysis affords the pinacol, tetra-*p*-tolylethylene glycol. Whereas the yield of benzopinacol actually isolated after anodic reduction of benzophenone amounted to 92–98%, in terms of the quantity of +1 magnesium produced, the yield of tetra-*p*-tolylethylene glycol, determined by infrared analysis, equalled 84%. It is felt that this yield is indicative of quantitative conversion, inasmuch as all the solid originally added to the anolyte was not recovered and the method of analysis employed is probably accurate to within only 5%. The experiments with 4,4′-dimethylbenzophenone represent the first stage of a larger investigation in which an attempt will be made to correlate the extent of "anodic reduction" with the electronic effects of *meta* and *para* substituents in the benzophenone series.

Although no attempt was made to effect a quantitative separation of products formed in the catholyte, 4,4′-dimethylbenzhydrol appeared to be the major product, again in analogy with the benzophenone case. A small amount of 4,4′-dipyridyl was also isolated and probably resulted from hydrolysis and air oxidation of the conjugate base of tetrahydro-4,4′-dipyridyl, formed by cathodic reduction of the solvent.

It is interesting that both "anodic" and cathodic reduction of benzil gave practically quantitative yields of benzoin (upon hydrolysis following electrolysis). It is evident that benzil is reduced by an *over-all* two-electron process in each compartment, but it is not known whether the electrons were accepted in a stepwise fashion or simultaneously by the benzil molecule. In view of the fact that unipositive magnesium is a one-electron reductant, it seems probable that reduction in the anolyte occurs in a stepwise manner. Experiments are presently underway to elucidate the reduction mechanism(s). In addition, a series of "anodic reductions" of compounds of the type $C_6H_5CO(CH_2)_nCOC_6H_5$ are being conducted in an attempt to correlate V_i values with the magnitude of n and also to determine whether cyclic pinacols will result in favorable cases.

Recently it was observed in our laboratory[7] that a V_i value of about 0.3 was obtained for magnesium in pyridine solutions containing nitrobenzene as additive. Since the anode was not corroded non-electrolytically by the original solutions, this extremely low value could only have resulted from a combination of normal electrolytic dissolution of the magnesium and attack by some very reactive species formed during electrolysis. In the current investigation azoxybenzene was employed as additive inasmuch as it represents a conveniently accessible compound which may be one of the intermediate products in the "anodic reduction" of nitrobenzene. In future studies other accessible intermediate reduction products will be employed as additives in order to provide evidence as to the detailed course of the nitrobenzene reduction. Although the V_i value for magnesium in the presence of azoxybenzene was 1.03–1.13, conceivably reasonable values even in the absence of competing non-electrolytic corrosion, it was nevertheless found that the solution following electrolysis attacked massive magnesium. Since the original solutions containing azoxybenzene did not corrode magnesium, it can be concluded that some reduction product of the additive is sufficiently reactive to attack the metal. Moreover, *trans*-azobenzene obtained in quantitative yield from the anolyte does not itself in sodium iodide–pyridine solutions attack massive magnesium. Hence, the only possible conclusion is that a reactive free radical or radical-ion derived from azoxybenzene is responsible for the non-electrolytic corrosion. This does not preclude the possibility that other intermediates between azoxybenzene and nitrobenzene may also corrode massive magnesium.

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