

agreement with the values of 462 mm. at -36° and 480 mm. at -35° reported by Friedrichs.²⁰ For

(20) F. Friedrichs, *Z. anorg. allgem. Chem.*, **127**, 221 (1923).

the system semicarbazide-ammonia, the corresponding pressure is 640 mm. at -35.5° .

AUSTIN, TEXAS

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

The Anodic Oxidation of Some Active Metals in Pyridine

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The anodic oxidation of magnesium, aluminum, beryllium and cadmium in pyridine solutions containing a non-oxidizing inorganic electrolyte results in the conversion of the metals to their normal, stable oxidation states. However, when certain organic additives which are potential electron acceptors also are present in the anolyte, the metals enter solution with initial mean valence numbers significantly lower than their normal values. On the basis of valence number measurements, it has been possible to arrange the metals in an activity series, and also to construct an apparent electron affinity series for the organic additives. Indium and thallium are anodically oxidized in lithium chloride-pyridine solutions to species which are lower valent than that corresponding to removal of three valence electrons, the former element giving initial mean valence numbers in the neighborhood of 2.4, and thallium being converted essentially quantitatively to the unipositive state.

In a recent communication from this Laboratory¹ it was demonstrated that upon electrolysis of a solution of sodium iodide in pyridine between magnesium electrodes in a divided cell, magnesium is oxidized anodically to its familiar dipositive state. However, when benzophenone also is present in solution, the magnesium dissolves at the anode with an initial mean valence number (V_i) appreciably less than two. Although no lower state of this element is detectable in solution after electrolysis, hydrolysis of the anolyte yields benzopinacol, a reduction product of benzophenone, in quantity corresponding to the oxidation of the magnesium from its measured mean valence state to the common $+2$ state. It was noted further in the previous paper that initial mean valence numbers less than two also are obtained for magnesium when the metal is anodically oxidized in the presence of other organic compounds, *e.g.*, benzaldehyde, nitrobenzene and benzonitrile, which are susceptible to reduction.

The present report is concerned primarily with the anodic oxidation of the active metals magnesium, beryllium, cadmium and aluminum in electrolytic pyridine solutions, both in the presence and absence of organic substances potentially capable of undergoing reduction. Some observations on the behavior of indium and thallium in the absence of organic additives also are described. The initial mean valence number, V_i , of the cation formed has been employed to characterize the anodic behavior of the various metals, since it gives a measure of the extent of departure from normal current efficiency. This quantity has been calculated, as previously described,¹ by means of the equation

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

Experimental

Materials.—Magnesium and aluminum were obtained in rod form from the Aluminum Co. of America; the former metal had a purity of 99.8% and the latter of 99.99%. Beryllium, purchased from the Brush Beryllium Company was described as "of highest purity." Cadmium was J. T. Baker reagent grade. Indium, supplied by the Fairmount

Chemical Company, was of 99.9% purity, and thallium was obtained from the Fisher Scientific Company in the form of purified sticks. Cylindrical electrodes approximately 5.5 cm. long and 0.5 cm. in diameter were constructed from these metals. The sodium iodide and lithium chloride employed as electrolytes were of reagent grade and were dried at 110° before use. Pyridine was Mallinckrodt analytic reagent grade, and was dried over anhydrous barium oxide for several weeks, fractionally distilled through a 45-cm. packed column at atmospheric pressure, and stored over additional anhydrous barium oxide until used. The nitrobenzene, benzaldehyde, bromobenzene, benzonitrile and 1-heptyne were all originally of high purity and were dried and fractionally distilled before use. The benzophenone, *trans*-stilbene and ethyl benzoate, obtained from Eastman Kodak Co., were of White Label quality and were used without further purification.

Apparatus and Procedure.—The source of direct current was a full-wave mercury tube rectifier capable of supplying up to 1000 v. The quantity of electricity passed through the circuit was determined by means of a silver coulometer. The electrolyses were carried out in a divided cell similar to that described by Davidson and Jirik,² with compartments of a capacity of about 100 ml. each. The cell was immersed in a constant temperature bath maintained at $40 \pm 0.5^\circ$.

All electrodes were thoroughly cleaned, washed, dried and weighed before use; the magnesium, beryllium, cadmium, thallium and indium electrodes were cleaned by treatment with dilute nitric acid solution, the aluminum electrodes with dilute sodium hydroxide solution. The sodium iodide-pyridine solutions (0.5 *m*) and lithium chloride-pyridine solutions (2.0 *m*) were prepared with a minimum exposure to air and moisture. When an electrolysis was performed in the presence of an organic additive, the anolyte and catholyte contained equivalent quantities of this substance. In each electrolysis experiment the metal used as anode was also employed as cathode. Dry oxygen-free nitrogen was passed over the surface of both anolyte and catholyte during electrolysis and the current density was maintained between 0.004 and 0.007 amp. per sq. cm., corresponding to an applied potential of 20 to 35 v. for the sodium iodide-pyridine solutions and 130–190 v. for the lithium chloride-pyridine solutions. The time of electrolysis varied from 10 minutes to 2 hours; the variation had little effect on the initial mean valence numbers obtained.

Some remarks regarding choice of electrolyte are pertinent at this point. Sodium iodide, although not so soluble as lithium chloride, appears to be a better conductor in pyridine. With sodium iodide, however, there exists the considerably greater possibility that the oxidation of the anion may compete with the dissolution of metal as the anode reaction. On the other hand, when lithium chloride is employed as electrolyte there is the definite possibility that at current densities sufficiently high to obtain a reasonable rate of dissolution of the anode, sparking may occur, and

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

(2) A. W. Davidson and F. Jirik, *ibid.*, **72**, 1700 (1950); Fig. 1.

the dissolving process may not proceed smoothly. With magnesium as anode and in the current density range mentioned above, lithium chloride proved to be an unsuitable electrolyte because of the sparking phenomenon, whereas dissolution of the magnesium occurred smoothly in sodium iodide solutions, no oxidation of iodide ion being observed. It should be noted, however, that with lithium chloride and a current density of 0.001 amp. per sq. cm. (applied potential of 40–60 volts) no sparking occurred at the anode, and initial mean valence numbers similar to those found in sodium iodide solutions were obtained for magnesium. With beryllium as electrodes, sodium iodide was not suitable as electrolyte, iodide ion being oxidized at the anode; with lithium chloride, no sparking occurred at the anode. Either electrolyte could be employed with aluminum and cadmium electrodes. Lithium chloride was satisfactory for use with indium and thallium.

On completion of electrolysis, the electrodes were thoroughly cleaned with distilled water and acetone, wiped gently with a soft cloth, dried and weighed. In many electrolyses one or both of the electrodes became coated with material which in most instances could be satisfactorily removed by the washing and wiping process. With beryllium and indium, however, wiping appeared to remove some of the surface metal, and these electrodes were washed only. After electrolysis the thallium anode was coated with a substance which could not be completely removed by water, organic solvents or wiping. Initial mean valence numbers obtained for this metal must, therefore, be considered to be slightly high.

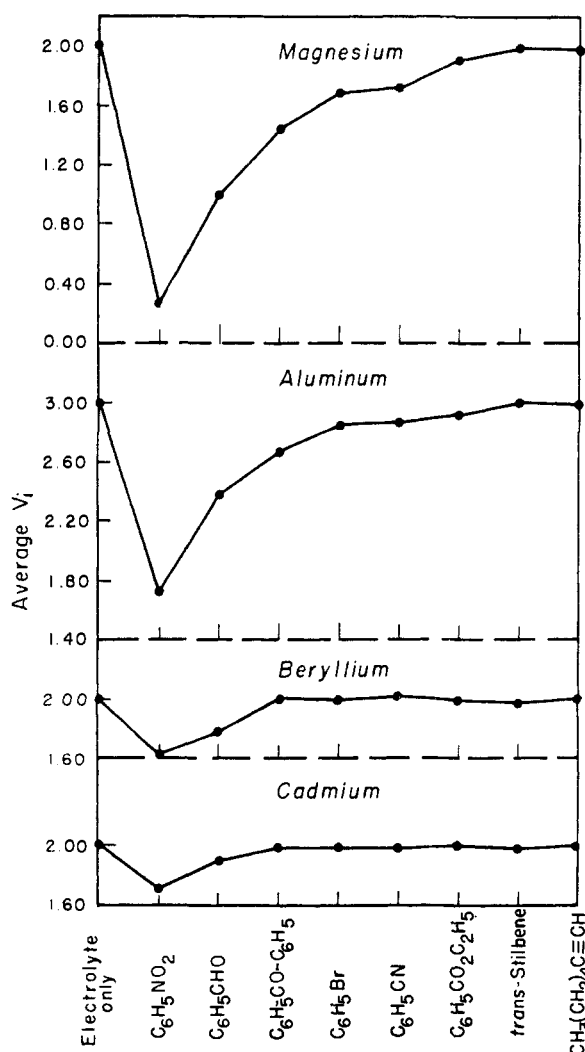


Fig. 1.—Anodic behavior of some active metals in the presence of potential electron acceptors.

Results and Discussion

The Anodic Behavior of Magnesium, Beryllium, Cadmium and Aluminum.—Although there is convincing evidence available to show that reduction of certain solutes (or of the solvent, *e.g.*, water) can be effected in the anode compartment of an electrolytic cell by the use of an active metal, such as magnesium,^{1,3} as a sacrificial anode, there remains some question as to the mechanism of reduction. It has been proposed that reduction occurs as a secondary process taking place in the anolyte and brought about by unipositive magnesium, which is produced together with stable, normal dipositive magnesium in the primary anodic process. The V_i values observed for magnesium anodes in experiments where anodic reduction of certain solutes, or of the solvent, has been demonstrated have always been less than 2, an observation consistent with the postulate of the formation of a substantial fraction of unipositive magnesium in the primary anodic process. Yet one apparently general experimental observation, based on only a very small number of experiments, however, has not been explained previously; *viz.*, a lowering of V_i occurs *only* when an oxidant is present in the anolyte (or when the solvent itself is reduced), even though control experiments show that the oxidant alone in the absence of an electrical current does not attack massive magnesium. In order to obtain more information on this behavior, a number of active metals, magnesium, aluminum, beryllium and cadmium, have been used as anodes in electrolysis experiments with anhydrous pyridine as solvent; in these experiments a series of potential electron-acceptor molecules, nitrobenzene, benzaldehyde, benzophenone, bromobenzene, benzonitrile, ethyl benzoate, *trans*-stilbene and 1-heptyne, have been used as solutes, together with a suitable inorganic electrolyte. The results are summarized in Table I and Fig. 1.

With each metal, control experiments, conducted under the same conditions of temperature, electrolyte and organic additive concentration, and time as the electrolyses, showed that direct non-electrolytic reaction between metal and electrolyte was negligible. Furthermore, no significant loss in weight of the cathode occurred in most of the electrolyses.⁴ In the absence of potential electron-acceptor molecules as solutes, all four metals gave V_i values corresponding to anodic dissolution to the normal, stable oxidation states of the metals. Therefore it now appears to be a perfectly general rule that a lowering of V_i for these metals is observed only when the anolyte contains an electron-acceptor molecule as solute (or when the anolyte solvent itself is readily subject to reduction). It should be emphasized, however, that not all potential electron-acceptor molecules cause a lowering of V_i values.

When nitrobenzene was present as solute the V_i values for magnesium were all well below 1.00, a

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

(4) There was some loss in weight of aluminum cathodes when benzonitrile and bromobenzene were the organic additives. Since the anolytes in each of these experiments did not attack aluminum after electrolysis, it would appear that different reduction products were formed in the anolyte and catholyte.

TABLE I
 ANODIC OXIDATION OF ACTIVE METALS IN PYRIDINE SOLUTIONS^a

Organic additive	Mg		Al		Be		Cd	
	No. of expts.	V_i	No. of expts.	V_i	No. of expts.	V_i	No. of expts.	V_i
None	5	2.01 ± 0.03	5	3.01 ± 0.05	5	2.01 ± 0.04	4	2.01 ± 0.04
Nitrobenzene ^b	6	0.27 ± .16	5	1.73 ± .23	5	1.63 ± .21	5	1.71 ± .14
Benzaldehyde ^b	5	1.00 ± .12	5	2.38 ± .14	5	1.78 ± .07	4	1.90 ± .03
Benzophenone ^c	6	1.45 ± .19	5	2.68 ± .14	5	2.01 ± .05	5	1.99 ± .02
Bromobenzene ^b	5	1.68 ± .16	5	2.86 ± .08	3	1.99 ± .05	4	2.00 ± .05
Benzonitrile ^b	5	1.72 ± .16	4	2.87 ± .11	4	2.02 ± .04	3	1.99 ± .02
Ethyl benzoate ^b	4	1.90 ± .05	3	2.92 ± .02	3	1.99 ± .01	3	2.01 ± .03
<i>trans</i> -Stilbene ^d	4	1.99 ± .02	4	2.99 ± .03	4	1.99 ± .02	3	1.99 ± .02
1-Heptyne ^b	4	1.98 ± .03	4	2.99 ± .03	4	2.02 ± .02	3	2.01 ± .03

^a For electrolyses with Mg and Cd electrodes the electrolyte consisted of 130 cc. of 0.5 *m* NaI in pyridine; for experiments with Be and Al electrodes 2.0 *m* LiCl was the electrolyte. In each case, half the volume of electrolyte was added to the anolyte and half to the catholyte. ^b 5 cc. added to each the anolyte and catholyte. ^c 5 g. added to each the anolyte and catholyte. ^d 1.5 g. added to each the anolyte and catholyte.

fact which obviously requires some additional comment, since a value no lower than 1.00 would be anticipated even if all of the magnesium went into solution in the unipositive state in an uncomplicated electrolysis reaction. The explanation for this anomalous behavior lies in the fact that the anolyte following electrolysis, in contrast to the behavior of a control mixture, attacked massive magnesium readily. Evidently some reduction product of nitrobenzene, unlike nitrobenzene itself, is able to react with massive magnesium in an oxidation-reduction reaction and bring some of it into solution, presumably as dipositive magnesium ions.

Although there is no other obviously abnormal V_i value listed in Table I, the organic additives on the basis of their behavior could nevertheless be grouped into four distinctly different categories: (1) Two of the additives, *trans*-stilbene and 1-heptyne, caused no lowering of V_i values for any of the metals. (2) Four of the additives, benzophenone, bromobenzene, benzonitrile and ethyl benzoate, caused a lowering of the V_i values for magnesium and aluminum, but not for beryllium or cadmium. (3) Nitrobenzene caused a lowering in the V_i values for beryllium and cadmium, whereas benzaldehyde caused a lowering in the V_i values for aluminum, beryllium and cadmium, but the solutions following electrolysis did not in any instance attack the metals. (4) Nitrobenzene caused a lowering in the V_i values for magnesium and aluminum, whereas benzaldehyde caused a lowering in the V_i value for magnesium, but in these cases the solution following electrolysis did attack the massive metals.

Although it is clear that no simple and single explanation can accommodate all of the observations listed above, there is one theory that deserves consideration. Eyring,⁵ when presented with some of the observations uncovered in this Laboratory, suggested that any active metal capable of forming ions of more than one oxidation state probably goes into solution in all of the possible states when used as a sacrificial anode. In the absence of additives potentially capable of undergoing reduction, unstable ions such as Mg^+ and Al^+ return to the anode, give up the remaining valence electrons and revert to the stable ions. In the presence of molecules which can function as electron acceptors, however, the unstable ions in lower valence states can

give up their remaining valence electrons to the acceptor molecules and thereby become oxidized to the normal, stable states. The acceptor molecule is, of course, reduced in the process. Therefore a lowering in the value of V_i for a given metal becomes apparent only when there are present molecules capable of accepting electrons and undergoing reduction.

These ideas and the results summarized in Table I permit the construction of an apparent reactivity series in pyridine solution of the various organic additives employed in these studies. Since the magnitude of the lowering of V_i values for the various metals may be considered to depend upon the electron-acceptor properties of the additives, the following list can be termed an order of decreasing electron affinities for the additives: nitrobenzene > benzaldehyde > benzophenone > bromobenzene > benzonitrile > ethyl benzoate > *trans*-stilbene \cong 1-heptyne.

It also is possible to construct an apparent order of reactivity of metals for this series of experiments. The reactivity of the metal evidently depends on the operation of at least two effects: (1) the ease with which the metal forms a lower valent ion, and (2) the readiness with which these lower valent ions give up their remaining valence electrons. Although it is not possible to sort out the individual effects, the results indicate the following over-all activities of the metals as reducing agents when used as anodes in electrolyses carried out in pyridine solution: magnesium > aluminum > beryllium > cadmium.

The results, taken as a whole, also clearly demonstrate that the effects are specific electrochemical effects and not vaguely defined corrosion effects. First of all, examination of Fig. 1 reveals a definite parallelism in the behavior of the four metals and of the eight organic additives potentially capable of undergoing reduction. Such a parallelism would be anticipated in an orderly process such as electrolytic dissolution of sacrificial anodes followed by secondary processes occurring in the anolyte, but would not be anticipated in disorderly surface corrosion phenomena. Secondly, the concept of the formation of unstable unipositive magnesium as a primary electrode process, followed by reduction of an organic additive, has been demonstrated convincingly in the case of benzophenone.¹ Benzopina-

(5) H. Eyring, private communication.

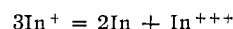
col was produced and isolated in nearly theoretical current yield. This actual demonstration of a reduction occurring in the anode compartment of an electrolytic cell and its quantitative correlation with a lowering in the V_i value for magnesium lends credence to the postulate that an observed lowering in the V_i value for any of the active metal anodes considered in these studies always indicates that reduction of some species in the anolyte has taken place. In short, the V_i value has true chemical significance and represents a convenient measure of the extent of anodic reduction.

The Anodic Behavior of Indium and Thallium.—Except for the recent preparation of aluminum(I) iodide,⁶ the chemistry of the active metals whose anodic behavior has just been discussed is characterized by a notable lack of solid compounds in which the elements exhibit any oxidation state other than that corresponding to their number of valence electrons. In contrast to this, indium and thallium form well-defined compounds containing these metals in lower valence states. Thus for indium, mono- and dihalides have long been known, and compounds of unipositive thallium are generally more stable than those of the tripositive element.

The behavior of indium and thallium as anodes in pyridine solutions is consistent with the relative stability of lower oxidation states of these elements.

(6) W. C. Schumb and H. H. Rogers, *THIS JOURNAL*, **73**, 5806 (1951).

When indium was oxidized anodically in pyridine containing lithium chloride *alone* as electrolyte, a V_i value of 2.41 ± 0.17 (for five experiments) was obtained, and a residue of metallic indium invariably formed in the anolyte. The metal is considered to result from a disproportionation of a lower valent indium species.



A similar disproportionation has been reported for lower valent indium in aqueous, acetic acid² and liquid ammonia solutions.⁷ The electrolytic oxidation of a thallium anode in lithium chloride-pyridine solutions gave a V_i value of 1.05 ± 0.07 (for five experiments). Neither the indium nor the thallium electrode was attacked non-electrolytically by the lithium chloride-pyridine solution, but there was some loss in weight of the thallium cathode during electrolysis. In view of the low V_i values obtained for these metals in the presence of a non-oxidizing inorganic electrolyte, no experiments with organic potential electron-acceptors were performed.

Acknowledgment.—The authors are indebted to the Office of Ordnance Research, U. S. Army, for a research grant which made this investigation possible.

(7) A. D. McElroy, J. Kleinberg and A. W. Davidson, *ibid.*, **74**, 736 (1952).

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[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Carbon Compounds Produced by Pile Neutron Irradiation of Crystalline Ammonium Sulfate: Target Dissolved in Water

BY PETER E. YANKWICH AND W. R. CORMAN, JR.

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The radiocarbon activities produced when pile neutron-irradiated ammonium sulfate crystals are dissolved in water or 1 *M* sodium hydroxide have been subjected to chemical fractionation. Carbon dioxide is formed in greatest amount (40% of the total activity); other radio compounds formed are methylamine (16%), formic acid (16%), formaldehyde (13%), urea (7%), cyanide (6%), and carbon monoxide, methanol and methane (each less than 3%). Comparison of these yields with those obtained from irradiated ammonium bromide demonstrates clearly the role of oxygen in the crystals as a scavenger for highly reduced combinations including the nascent carbon, but does not permit a clear decision in any particular case as to whether or not the radio compound is formed as such in the sulfate crystals.

When samples of neutron-irradiated ammonium bromide are dissolved in water, numerous one-carbon compounds containing C^{14} can be identified among the products. Of the total radiocarbon in such a sample, about 11% is in the form of oxygen-containing compounds (carbon monoxide and dioxide, formic acid, formaldehyde, methanol, and urea), while the remainder consists of small amounts of methane and cyanide and a very large amount of methylamine.¹ While some of the oxygen-combined activity may be due to reactions of nascent carbon with water, air or other impurities in the crystals irradiated, it may be due also to combination with the solvent water of carbon-containing groups of atoms trapped under strain in the irradiated solid. In an effort to learn more concerning the fate of the recoil carbon in the nuclear reaction

(1) P. E. Yankwich and J. D. Vaughan, *THIS JOURNAL*, in press.

$\text{N}^{14}(\text{n,p})\text{C}^{14}$, we have subjected a sample of ammonium sulfate to pile-neutron irradiation and have performed chemical fractionations of the radiocarbon compounds which result when samples of this target material are dissolved in water and in 1 *M* sodium hydroxide.

Experimental

Sample Preparation and Irradiation.—Twenty grams of reagent grade ammonium sulfate was dried at 110° for two hours then placed in a quartz tube which was stoppered with a perforated cork (to permit escape of hydrogen or other gaseous evolve during the course of the irradiation), and the whole enveloped in Parafilm to exclude air. (The crystals occupied about two-thirds of the tube volume. A stream of dry helium was used to displace included air before the tube was sealed.) The pile irradiation was carried out at the Argonne National Laboratory, whose staff kindly recorded the following: irradiation time, 1172 hours; sample temperature, 36° ; X-ray and γ -ray flux, 530 R. min.⁻¹; neutron flux, approximately 10^{12} cm.⁻² sec.⁻¹. The sample was allowed to cool off for six months following