solvent. "$C_9H_{12}Fe_2(CO)_6$" is reported to form orange volatile crystals, m.p. 74°, soluble in hydrocarbon solvents. The infrared spectrum reported for "$C_9H_{12}Fe_2(CO)_6$" resembles very closely that of $C_8H_{10}Fe_2(CO)_6$. We feel that "$C_9H_{12}Fe_2(CO)_6$" is actually $C_8H_{10}Fe_2(CO)_6$ contaminated with sufficient $C_8H_{10}Fe(CO)_3$ and hydrocarbons to lower its melting point from 102° to 74° and to change the composition of the mixture to approximately $C_9H_{12}Fe_2(CO)_6$. Fischer, Palm, and Fritz[2] apparently did not use recrystallization from a hydrocarbon solvent as one of the steps in the purification of their product. Our observations suggest that a recrystallization step is essential to obtain pure $C_8H_{10}Fe_2(CO)_6$ since the chromatographic separation of $C_8H_{10}Fe_2(CO)_6$ and $C_8H_{10}Fe(CO)_3$ appears to be incomplete on columns of reasonable size.

The molybdenum complex $C_8H_{10}Mo(CO)_3$ is reported not to form cationic species such as $[C_8H_9Mo(CO)_3]^+$ or $[C_8H_8Mo(CO)_3]^{+2}$ by hydride ion abstraction with the triphenylmethyl carbonium ion $[(C_6H_5)_3C]^+$.[2] However, when the iron complex $C_8H_{10}Fe_2(CO)_6$ was treated with dichloromethane solutions of $[(C_6H_5)_3C][BF_4]$ or $[(C_6H_5)_3C][PF_6]$, orange crystalline precipitates were obtained. These precipitates, especially the tetrafluoroborate, were hygroscopic and the analytical data were not entirely satisfactory. Nevertheless, the analytical data were in definitely the best agreement with the formulation as salts of the cation $[C_8H_9Fe_2(CO)_6]^+$. A satisfactory n.m.r. spectrum of this cation could not be obtained. The salts were insoluble in dichloromethane, chloroform, or water. They appeared to be somewhat decomposed by more powerful solvents such as dimethyl sulfoxide to give paramagnetic material which broadened the resulting spectrum to an unmanageable extent.

The fact that the $[C_8H_9Fe_2(CO)_6]^+$ ion is obtained from triiron dodecacarbonyl in an over-all yield of only ~1% for the two steps has discouraged us from investigating this potentially interesting species in greater detail.

**Acknowledgment.**—The author is indebted to Mr. M. Bisnette for experimental assistance. Valuable gifts of the cycloöctatetraene required in large quantities for this work were obtained from Badische Anilin- und Sodafabrik, Ludwigshafen, Germany.

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Contribution from the Department of Chemistry,
University of Kansas, Lawrence, Kansas

# Anodic Dissolution of Calcium in N,N-Dimethylformamide[1]

By MAX L. RUMPEL, ARTHUR W. DAVIDSON, and JACOB KLEINBERG

*Received February 4, 1963*

The relationship between anodic dissolution and quantity of electricity was studied for electrolyses with a calcium anode in solutions of certain salts in N,N-dimethylformamide (DMF). For lithium chloride solutions, the weight loss of the anode was in accord with that calculated on the basis of primary oxidation to bipositive calcium ion. For sodium nitrate, lithium perchlorate, calcium perchlorate, potassium iodide, or lithium bromide solutions, the weight loss was greater than the value so calculated, even when direct chemical attack on the metal was taken into account. In each of these latter solutions, either reduction products of the electrolyte medium were produced at the anode during electrolysis, or else the anolyte, after electrolysis, was found to have reducing properties. These effects, although varying widely from one salt to another, were nearly independent of current density, concentration of salt in DMF, duration of electrolysis, or temperature in the range of conditions studied. All observations may be explained by the postulate of formation of unipositive calcium ion as the first step in anodic oxidation.

## Introduction

For a number of metals under appropriate conditions of anodic oxidation, values have been found for the initial mean valence, denoted by the symbol $V_i$ and defined as the number of faradays of electricity passed per gram-atom of metal electrolytically dissolved, which are less than the lowest familiar charge of a cation of the metal. These metals include aluminum,[2–7] titanium,[4–6] uranium,[4–6] magnesium,[4–6,8,9] beryllium,[4–6,10] zinc,[4–6,11] and cadmium.[11] The phenomenon of "abnormally" low oxidation states can plausibly be explained in terms of the hypothesis of primary anodic formation of an unstable unipositive ion which may then react with the solvent or the electrolyte to form a more stable product.

The previous observation in this Laboratory of $V_i$ values lower than two for beryllium and magnesium[8–10] suggested the desirability of an investigation of the anodic dissolution behavior of a third group IIA element, calcium. Since calcium metal is vigorously attacked by water, its electrolytic oxidation cannot be

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(1) Abstracted from part of a thesis submitted by Max L. Rumpel in partial fulfillment of the requirements for the degeee of Doctor of Philosophy, University of Kansas, 1962.

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studied in this medium. Calcium is not acted upon, however, by purified N,N-dimethylformamide (DMF), which was therefore chosen as the electrolytic medium for these studies. This solvent was also advantageous because of its relative inertness with respect to oxidation or reduction and its ability to dissolve a variety of salts to give electrically conducting solutions.

## Experimental

The N,N-dimethylformamide was distilled in a 1.2-m. fractionating column at atmospheric pressure under a current of purified nitrogen. The distillate, which boiled uniformly at 151° (lit.[12] 153°), was received in a glass container, and then stored in a controlled-atmosphere box which was continuously swept out with dry nitrogen.

Reagent quality salts to be used as electrolytic solutes were oven-dried at 150° and stored in glass-covered dishes in the controlled-atmosphere box. Preparation of solutions of the salts in DMF and filling of the electrolysis cell were carried out in the nitrogen atmosphere of the box.

The electrolysis vessel was a U-shaped cell constructed of 3-cm. Pyrex tubing, fitted with ground-glass stoppers in the form of caps; the outside width of the cell was 12 cm., the vertical distance from the bottom of the U to the ground-glass joints, 10 cm., and the length of the stoppers (including joints), 8 cm. A sintered glass disk in the center of the horizontal portion of the U separated the anode and cathode compartments, each of which held about 35 cm. of solution. In each leg of the U two side arms, one above the other, provided for the passage of inert gas into the compartment, either by bubbling through the electrolyte or by sweeping over the liquid surface, while effluent gas was vented through a third side arm in the stopper. The bottom of each compartment was equipped with a stopcock for drainage of the cell contents after electrolysis. A platinum wire serving both as a support and as an electrical lead was fused through each of the caps. To one of these leads the cathode, a platinum sheet of 4 cm.$^2$ total area, was permanently affixed. The other lead was hooked through a small hole in the anode when the latter was to be suspended in the cell. The assembled cell, when filled, was placed in an automatically regulated water bath which controlled the temperature to ±0.2° throughout the electrolysis. The temperature was held at 30° unless otherwise specified.

Calcium metal for the anodes was furnished by Bram Metallurgical Company in the form of rods machined to 1.3 cm. diameter. The surface was bright, and qualitative tests for common metallic contaminants were negative. Each rod was cut to 5 cm. in length and pierced at one end to admit a hook of platinum wire. The surface of the metal was cleaned in the controlled-atmosphere box before use by burnishing with a motor-driven wire brush. The anode was next placed in a glass capsule which was then removed from the box, evacuated, and weighed. The anode was then rapidly transferred to the prepared electrolysis cell and electrolysis was begun.

After electrolysis the anode was removed from the cell, washed under fresh DMF, rinsed in petroleum ether, and replaced in its capsule, where it was dried by rapid evacuation. The weight of the capsule and its contents was then again determined.

In every experiment, a separate calcium rod, of the same size and shape as the anode, was placed on the bottom of the anode compartment, beyond and out of contact with the anode, in order that any non-electrolytic corrosion effect might be detected. This corrosion control blank was handled in the same manner as was the anode.

The power source for the electrolyses was a full-wave mercury-tube rectifier with output continuously adjustable from zero to 760 volts. The total quantity of electricity passed through the cell was measured with a silver coulometer placed in series. Current density at the platinum cathode of the coulometer never exceeded 5 ma./cm.$^2$. Current and voltage for the electrolysis cell were monitored throughout the electrolysis by an ammeter and a voltmeter in the cell circuit. From the observed depth of immersion of the calcium rod, the anodic current density was estimated; its value never rose above 30 ma./cm.$^2$.

## Results

Electrolysis of lithium chloride brought about no anomalous dissolution of the calcium anode. The average $V_i$ for four experiments in this medium was 1.94 with ±0.11 mean deviation.

Electrolysis of a DMF solution of sodium nitrate, however, did result in an anomalously high electrolytic weight loss of the calcium anode, as shown by a $V_i$ value of about 1.1. A gas (presumably a product of reduction of nitrate) was evolved at the anode as current was passed, and an appreciable amount of very firmly adherent light gray material was formed on the anode surface.

Electrolysis of calcium or lithium perchlorate also resulted in $V_i$ values less than two. Again, a gray deposit adhered to the anode. This substance whitened rapidly upon air exposure; the product, which dissolved readily in dilute hydrochloric acid, was found to contain about 35% calcium. A sample of the gray material placed in liquid ammonia produced traces of a blue color, suggesting that it had contained finely divided calcium metal; the bulk of the sample, however, turned white but did not dissolve. Although the original electrolyte solution had been free of chloride ion, the anode compartment was found to contain some chloride ion after electrolysis. Since the corrosion control blank in the anode compartment suffered no loss in weight during the experiment, the reduction of perchlorate to chloride cannot be attributed to non-electrolytic attack upon the metal.

With potassium iodide solutions in DMF, there was some evidence of non-electrolytic attack of the anolyte upon calcium metal; this effect, however, never exceeded 2% of the total weight loss of the anode during electrolysis. A small amount of a black solid which appeared on the anode could readily be removed before final weighing of the metal. The average $V_i$ for 24 runs was 1.06, with a mean deviation of only ±0.05. These experiments were performed under a wide range of conditions: concentrations from 2 to 10% by weight of potassium iodide in DMF, current densities at the anode from less than 2 up to 12 ma./cm.$^2$, and duration of electrolysis from 2 to 19.5 hr. The only significant variation in the $V_i$ was an increase with increased electrolyte concentration; the average value was 1.02 in 2 and 5% solutions and 1.12 in 10% solutions. However, since the anodic oxidation of a small quantity of iodide to free iodine in the 10% solutions was indicated by the temporary appearance of a red coloration near the anode, at least part of this apparent increase is illusory.

The anolyte solution at the end of the electrolysis was shown to reduce DMF solutions of silver nitrate, iodine, or mercury(II) chloride, appreciable amounts of silver

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metal, iodide ion, or a mixture of mercury(I) chloride and mercury metal being produced. In an attempt to identify the reducing agent (presumably a reduction product of DMF), in two instances the anolyte, after electrolysis, was distilled in an atmosphere of nitrogen, and the volatile fraction was subjected to chromatographic analysis. The chromatogram revealed no substances other than DMF and a trace of water; the DMF peak, however, tailed badly, so that small later peaks might easily have been masked. Attempts to determine the total quantity of reductant that had been produced in the anolyte were also unsuccessful, since no method could be devised for the accurate determination, in the presence of a high concentration of iodide, of such reductant.

Electrolysis of lithium bromide solutions with a calcium anode gave, for fourteen trials, an average $V_i$ of 1.48, with a mean deviation of ±0.05. In these experiments, temperatures of 25, 30, and 50° were used; anodic current densities varied from 3.7 to 29.6 ma./cm.$^2$, duration of electrolysis from 1 to 7 hr., and total quantity of electricity passed in individual runs from 400 to 1350 coulombs. No systematic trend of $V_i$ values with any of these variables was discerned. Non-electrolytic attack of the anolyte upon calcium, naturally greatest at 50°, was never more than 3% of the total anodic weight loss. During all of these electrolyses, a non-adherent black deposit, which fell to the bottom of the cell, formed on the anode, and a gas, identified as hydrogen, was evolved at the anode. (Very small amounts of gas appeared also at the surface of the corrosion control blank.) The deposit dissolved readily in dilute hydrochloric acid. Analysis of the entire contents of the anode compartment for two trials showed that about one-fourth of the calcium lost from the anode appeared in the black solid, the remainder being found in the solution.

In three runs at 25° and three at 50°, the volume of evolved hydrogen was measured by collection over mercury in a buret. If it is assumed that in these experiments chemical (non-electrolytic) oxidation of both calcium metal and any lower valent cation to calcium(II) is accompanied by production of hydrogen gas, the equation

$$V_i = \frac{2Q}{Q + \frac{v}{11200} - \frac{m}{20.04}}$$

may be derived from stoichiometric considerations. Here $v$ is the volume in milliliters of evolved hydrogen converted to standard conditions, $Q$ is the number of faradays passed, and $m$ is the non-electrolytic weight loss of the calcium metal. A comparison of the $V_i$ values obtained directly from the electrolytic weight loss, $w$, of the anode (*i.e.*, $V_i = 40.08Q/w$) with those calculated from the volume of hydrogen evolved is shown in Table I.

Although the generally excellent agreement between the $V_i$ values obtained for each individual electrolysis by two independent methods does not prove the validity of our assumptions as to mechanism, it does show these assumptions to be consistent with all the experimental data.

Table I

Comparison of $V_i$ Values Determined by Two Different Methods

| Temp., °C. | $Q$, faradays × 10$^3$ | $w$, g. | $m$, g. × 10$^3$ | $v$, ml. at STP | $V_i$, from wt. loss | $V_i$, from evolved $H_2$ |
|---|---|---|---|---|---|---|
| 25 | 7.03 | 0.1881 | 1.2 | 26.9 | 1.50 | 1.50 |
| 25 | 7.24 | .2029 | 0 | 32.5 | 1.43 | 1.43 |
| 25 | 11.36 | .2970 | 0 | 38.7 | 1.53 | 1.53 |
| 50 | 9.03 | .2435 | 3.6 | 39.4 | 1.49 | 1.46 |
| 50 | 10.98 | .2852 | 6.4 | 38.5 | 1.54 | 1.56 |
| 50 | 8.61 | .2344 | 6.8 | 40.6 | 1.47 | 1.45 |

## Discussion

The fact that $V_i$ values less than 2 but greater than unity were obtained in the electrolytic dissolution of calcium in some DMF solutions can be best explained by postulating the electrolytic formation of unipositive calcium ion. In the presence of an oxidizing agent, this ion is oxidized to the familiar bipositive ion, while the oxidizing agent is itself reduced. The presence of chloride in the anolyte after electrolysis with a perchlorate is readily accounted for in terms of this hypothesis.

When no oxidizing agent is present in the anode compartment, the unipositive calcium ion may return to the anode to be oxidized electrolytically, as appears to be the case with lithium chloride as electrolyte; it may react with the solvent, as it seems to do in potassium iodide solutions; it may disproportionate to the metal and bipositive calcium ion; or two or more of these reactions may occur simultaneously.

A possible reaction scheme which explains all the observations in the dissolution of calcium in the presence of lithium bromide is

$$Ca = Ca^+ + e^- \text{ (electrolytic)} \qquad \text{(a)}$$

$$Ca + x\text{DMF} = Ca^{2+} + H_2 + \text{(reduction products)} \qquad \text{(b)}^{13}$$

$$Ca^+ = Ca^{2+} + e^- \text{ (electrolytic)} \qquad \text{(c)}$$

$$2Ca^+ = Ca + Ca^{2+} \qquad \text{(d)}$$

Since a $V_i$ value of 1.5 indicates that equal amounts of calcium(I) and calcium(II) are formed as a result of electrolytic action, reaction (c) accounts for about 50% of the bivalent calcium produced. The remainder of the calcium(I) disproportionates in the immediate vicinity of the anode, producing finely divided calcium metal and bipositive calcium ion. It is to be noted that according to this mechanism one-fourth of the metal which was initially oxidized anodically is converted back to the metal—now, however, in a highly reactive condition. Reaction (b), which at the surface of the bulk calcium is insignificant, should occur rapidly for the metal produced by reaction (d). If it is assumed that the bivalent calcium produced by reaction (b) remains, along with a trace of finely divided calcium

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(13) Because of the impossibility of excluding water entirely from the system, the hydrogen evolution might conceivably have been due to water present as an impurity. This hypothesis, however, does not explain the extremely low rate of gas evolution from the corrosion control sample.

metal (which would account for the black color), in the solid formed at the anode (from whose surface the hydrogen gas was evolved), then one-fourth of the calcium lost from the anode would indeed be expected to appear in this material at the end of the electrolysis.

An interesting gradation in $V_i$ values is observed for solutions containing chloride, bromide, and iodide ions. As implied earlier, this variation appears to be related to a change in mechanism, although the reason for the dependence of the mechanism on the presence of a particular halide is not apparent.

**Acknowledgment.**—M. L. R. takes this opportunity to thank the National Science Foundation for fellowships received while this work was in progress. The research was financed in part by the General Research Fund of the University of Kansas.

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CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM AND HAAS COMPANY,
REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

# A Simple Preparation of Substituted Chlorophosphonium Salts; the Salt $FPCl_3SbCl_6$[1]

BY JOHN K. RUFF

*Received March 21, 1963*

The reaction of tertiary phosphines with excess antimony pentachloride produced phosphonium salts. Phosphines of the types $RPCl_2$, $R_2PCl$, and $R_3P$ were employed. Reaction of $FPCl_2$ with antimony pentachloride in the presence of chlorine was found to yield the salt $FPCl_3SbCl_6$. The constitution of these materials is discussed.

The recognition that phosphorus pentachloride possessed an ionic constitution, both in the solid state[2] and in polar solvents,[3] supported the belief that alkyl or aryl halophosphoranes of the types $RPX_4$, $R_2PX_3$, and $R_3PX_2$ were also partially ionized, and that adducts formed between these phosphoranes or phosphorus pentachloride and metal halides capable of forming polyhalo metal anions were actually phosphonium salts.

$$C_6H_{11}PBr_4 + SbBr_3 \longrightarrow C_6H_{11}PBr_3SbBr_4{}^4$$

$$(C_6H_5)_3PCl_2 + SbCl_5 \longrightarrow (C_6H_5)_3PClSbCl_6{}^5$$

$$PCl_5 + MCl_n \longrightarrow PCl_4MCl_{n+1}{}^6$$

Evidence for the ionic constitution of these adducts was based upon their electrical conductivity in solution and in a few cases on transport measurements. Phosphoranes of the types $(RO)_{4-n}PX_{n+1}$ and $(R_2N)_{4-n}PX_{n+1}$ were also found to be ionic although the exact nature of the ions involved is not known.[7,8] Adduct formation of this type of phosphorane with metal halides is not necessarily indicative of an ionic constitution since for example the complex $R_2NPCl_4 \cdot FCl_5$[9] could also have the covalent structure $Cl_5P \leftarrow N(R_2)\text{-}PCl_4$.

As noted above, the general method used for the preparation of the adducts was based on the reaction of a halo-substituted phosphorane with a halide ion acceptor.[4-6] The requisite halophosphoranes were obtained from halogenation of the corresponding phosphines and in some cases were found to be unstable and difficult to purify. A simple method of preparation of a number of substituted chlorophosphonium hexachloroantimonate salts has been developed in which isolation of these intermediates was not necessary.

## Results and Discussion

Tertiary phosphines were found to react with antimony pentachloride to produce substituted chlorophosphonium salts according to the stoichiometry

$$R_3P + 2SbCl_5 \longrightarrow R_3PClSbCl_6 + SbCl_3$$

Although the over-all reaction might formally be considered as consisting of two consecutive reactions (chlorination followed by chloride ion abstraction), it was not possible to isolate the intermediate chlorophosphorane ($R_3PCl_2$), even when an excess of the phosphine was employed. The reaction was found to proceed readily with a number of differently substituted phosphines. The compounds that were prepared are listed in Table I. In general the phosphonium salts precipitated as they formed.

Recrystallization of the initial precipitates was not necessary as they were obtained analytically pure. The antimony trichloride remained in solution and could be isolated in moderate yield. Several of the products were prepared by reaction of equimolar mixtures of antimony pentachloride and the chlorophosphorane. The products obtained by both methods were identical. It was not possible to prepare the trichlorothiophenoxyphosphonium salt ($C_6H_5SPCl_3SbCl_6$) by either method. Chlorination of the sulfur–phosphorus bond occurred and benzenesulfenyl chloride was apparently formed.

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[1] This work was performed under Contract Number DA-01-021 ORD 11878.

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