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Some Reactions of Zerovalent Metals with Aqueous Organometal(loid)s

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Aqueous solutions of bromoalkyltriphenylphosphonium bromides react with zerovalent metals, causing their dissolution. The reaction initially follows second-order kinetics, with the rate depending on both metal and bromide concentrations. Zerovalent metals similarly react with aqueous methylmercuric acetate and other dissolved organometals. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Ever since Sir Edward Frankland's preparation of diethylzinc,[1,2] the reaction between alkyl halides and zerovalent metals has been an important preparative method for organometallic compounds.[3,4] However, this reaction also has numerous nonsynthetic applications,[5] such as the use of zerovalent metals (especially iron) to remove chlorocarbons from contaminated groundwater.[6–8]

We have been investigating interactions between aqueous alkyl halides and metals as a potential cause of metal corrosion and dissolution into water.[9–14] Most haloalkyl compounds show low solubility in water (e.g. 0.09 M for methyl iodide,[14] and even less for most other alkyl halides), making accurate kinetic measurements virtually impossible. In an attempt to overcome this problem, we have been using water-soluble bromoalkyltriphenylphosphonium bromides as reagents. Also, since active metals such as iron or zinc are known to reduce dissolved aqueous inorganic ions of less active metals (e.g. mercury), we investigated whether this might also be true for corresponding organometal species. In this paper we report some of our findings.

EXPERIMENTAL

Metal foils and powders were purchased from Alfa/Aesar and used without further treatment. Iron and copper foils were 0.127 mm thick, while brass and zinc foils were 0.0254 and 0.254 mm thick respectively. National Institute of Standards and Technology Standard Reference Material (SRM) 365 consists of chips (16–35-mesh) with composition 99.90% Fe, 0.04% Ni and traces of other metals, given by Dr F. E. Brinckman. Methylmercuric acetate, trimethyllead acetate and tri-*N*-butyltin acetate were purchased from Alfa Chemical Company and used without further purification. Alkyl- and bromoalkyltriphenylphosphonium bromides were purchased from Aldrich Chemical Company and used as received. Solutions (0.1–5 mM) were prepared using aerated deionized water and used immediately.

Metal foils or powders (40–500 mg) were placed in screwtop vials containing 15–50 cm^3 of solution. Initial pH values, measured using pHydrion® paper, were usually 5.5–6.0 and did not vary during the course of the reaction. The vials were capped, shaken and placed in darkness for periods of up to ten days at temperatures of 22(±1)°C. Aliquots were removed periodically for testing.

Levels of copper were determined with a Hach DR-100 colorimeter, using the absorption of the copper-2,2′-bicinchonic acid complex at 565 nm.[13] Levels of zinc were also measured in a HachDR-100 colorimeter, using the absorption of a cyanozinc–cyclohexanone complex at 610 nm. Concentrations as low as 0.02 mg dm^{-3} (Cu) or 0.04 mg dm^{-3} (Zn), with uncertainties of 1–5%, could be measured. Concentrations of dissolved iron were measured similarly, using a Hach DR-100 colori-

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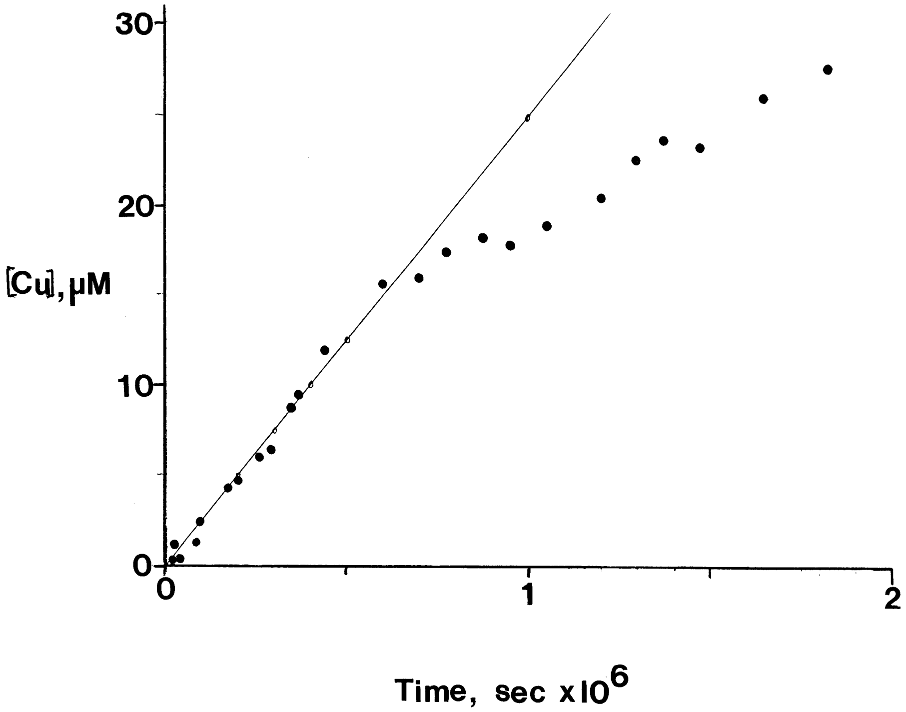


Figure 1 Dissolution of copper foil into water by **I**. Open circles are calculated points.

meter that measured the absorption of a 1,10-phenanthroline complex at 500 nm. Levels as low as 0.02 mg dm^{-3} could be measured with uncertainties of 1–5%. All analyses of mercury, tin and lead, plus selected analyses of copper and iron, were performed by Little Bear Laboratories, Inc. (LBL, Red Lodge, MT, USA) using ICP spectroscopy.

Calculations were performed on an Apple II® microcomputer, using a CURFIT® program to fit points to lines by the method of least squares. This program also enabled calculation of average uncertainties and coefficients of determination.

OBSERVATIONS

Dissolution patterns involving bromoalkylphosphonium bromides

Our earlier work suggested that copper dissolution followed a linear pattern over time.[13] More systematic investigation using 3-bromobutyltriphenylphosphonium bromide (**I**) on copper, zinc, iron and copper alloys generally showed an initially linear pattern of dissolution. Over long time periods, however, measured concentrations usually fell appreciably below those predicted from the initial linearity (Fig. 1). For copper and zinc, the period of linearity usually lasted approximately one week. Because of ready oxidation, hydrolysis and precipitation, the period of linearity for iron was usually less than one day. Most of our measurements have been made during this linear pattern.

Comparative studies using the series of phosphonium bromides $[(C_6H_5)_3P(CH_2)_nBr]^+Br^-$ (**II, III, IV;** $n = 1, 3, 4$) showed that rates of metal dissolution increased as the value of n increased (Table 1). Experiments with KBr or simple phosphonium bromides indicated that bromide ion, at least at our concentrations, $(1-5) \times 10^{-3}$M, showed no enhancement, and even repression, of copper dissolution relative to pure water. The two isomers **I** and **IV** differed markedly in their reactivity towards metals (Table 2), with **I** being considerably more active. As a result, **I** became the reagent of choice for most investigations. The salts **I–IV** showed no measurable tendency to hydrolyze over the experimental time periods (up to one week).

To tie in our observations for these phosphonium

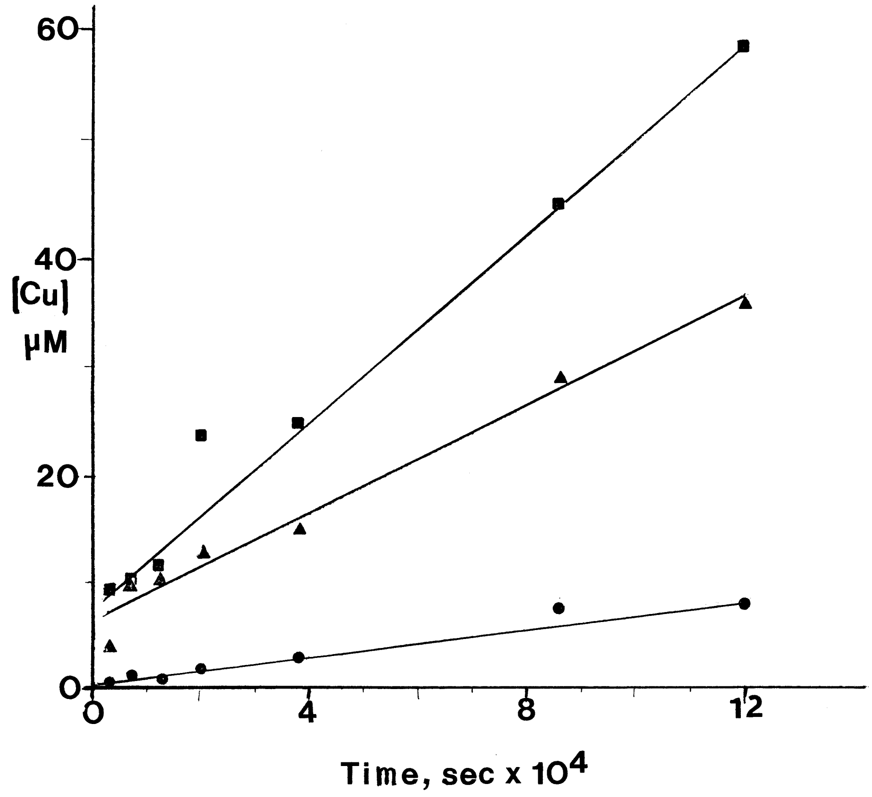


Figure 2 Dissolution of copper foil by (A) water; (B) aqueous **I**; (C) aqueous **V**.

bromides to earlier work using bromoalkanes, we did a comparative study of their dissolving ability on bronze powder (Table 3). Compound **I** showed an enhancement of dissolved copper comparable with 4-bromo-1-butene and markedly greater than bromobutane. In a comparative study on brass using **III** and the analogous *n*-propyltriphenylphosphonium bromide, **III** caused dissolution of both zinc and copper, whereas the other compound dissolved only zinc. Iron (SRM 365) dissolved more rapidly in the presence of **I** than **IV** (Table 4), although the difference was less than for copper.

In experiments to determine the effect of foil

Table 1 Comparative dissolution[a] of copper by alkyltriphenylphosphonium bromides

Compound	Time (min) 1050	2570	6915
Water	7.1	10	22.8
KBr	6.1	6.3	7.7
$[(C_6H_5)_3PCH_3]^+Br^-$	2.8	3.0	
$[(C_6H_5)_3PCH_2Br]^+Br^-$	3.8	5.0	
$[(C_6H_5)_3PC_3H_7]^+Br^-$	4.7	7.9	16.1
$[(C_6H_5)_3P(CH_2)_3Br^+]Br^-$	6.1	11	24.7
$[(C_6H_5)_3PC_4H_9]^+Br^-$	3.3	3.6	8.3
$[(C_6H_5)_3P(CH_2)_4Br]^+Br^-$	12	20	51.2

[a] Concentration units are µmol dm^{-3} (µM). Eight portions of copper foil (131.97 ± 1.02 mg) were treated with 0.100 dm^3 water or 3.68 × 10^{-3} M aqueous reagent.

Table 2 Comparative dissolution[a] of copper by three butyltriphenylphosphonium bromides

Compound	Time (min) 1100	2525	3985	5755
Water	4.5	5.3	6.3	7.9
$[(C_6H_5)_3PC_4H_9]^+Br^-$	3.5	3.8	6.9	7.5
$[(C_6H_5)_3P(CH_2)_4Br]^+Br^-$	9.4	12.0	19.0	27.0
$[(C_6H_5)_3PCH_2CH_2CHBrCH_3]^+Br^-$	37.0	64.0	99.0	117.0

[a] Concentration units are µmol dm^{-3} (µM). Four portions of copper foil (54.22 ± 0.10 mg) were treated with 0.150 dm^3 water or 3.18 × 10^{-3} M aqueous reagent.

Table 3 Metal content of bronze powder after treatment with aqueous bromoalkyl compounds[a]

System	Cu (mg g^{-1})	Sn (mg g^{-1})	Sn (mg g^{-1} Cu)
Blank	894	81	90.6
	873	91	104
Water	965	81	83.9
Water/$CH_3CH_2CH_2CH_2Br$	999	85	85.1
Water/$CH_2 = CHCH_2CH_2Br$	909	85	93.5
Water/**I**	859	83	96.6

[a] 130 mg of bronze powder was treated with 0.150 dm^3 water or aqueous mixture for one week. The solids were then analyzed by Little Bear Laboratories. Duplicate measurements were made for the blank (untreated powder).

Table 4 Dissolution of iron[a] from SRM 365

	Concentration		
Time (min)	Water	**IV**	**I**
50	1.65	1.65	5.37
97	1.45	4.48	8.6
135	3.94	10.4	16.5
179	5.19	14.0	16.8
237	5.35	23.1	25.6
287	6.45	30.5	33.1
19,980 333	10.6	39.6	40.7

[a] Concentration units are μmol dm^{-3} (μM). Portions of 205.72 ± 0.04 mg SRM 365 were treated with 0.050 dm^3 water or 2.42×10^{-3} M aqueous reagent.

substrate size on the extent of dissolution, we found that there was only a slight increase in extent of dissolution with increasing mass of foil (Table 5). Often (but not always consistently) at any given sampling time, the concentration of dissolved metal increased linearly with the mass of foil substrate (Table 6).

Dissolution by aqueous organometals

When iron or copper metal substrates were treated with aqueous methylmercuric acetate (**V**), trimethyllead acetate (**VI**) or tri(*n*-butyl)tin acetate (**VII**), the metal substrate showed substantial dissolution, often at rates comparable with or exceeding the phosphonium salts (Fig. 2). For **V** and **VI,** reactions were first-order with respect to the dissolved organometal; for **VII,** low solubility, combined with opalescence in solution, made accurate readings very difficult to obtain; nonetheless, substantial dissolution occurred. Treatment of a solution of **V** with various metals resulted in decreased concentration (Table 7).

DISCUSSION

The carbon-bromine bond in the series **I–IV** can react with zerovalent metals, causing them to be oxidized and dissolve in water. We have previously proposed a mechanism involving adsorption of halides onto metal surfaces, followed by reaction to give dissolution.[11,13] A similar mechanism has been proposed for the dechlorination of chlorocarbons by metals.[7] Organic halides are known to bond to metals through the halogen atom,[5] and unsaturated alkyl bromides may also bond through the carbon–carbon multiple bond.[13] The presence of a triphenylphosphonium cation must affect the attachment of the bromoalkyl group to a metal surface, but there is at present insufficient evidence to indicate how this might occur.

Kinetic data for chlorocarbon–iron systems indicate that the rate of reaction is first-order with respect to the concentration of chlorocarbon and also apparently first-order with respect to the quantity of metal available for reduction.[7] Our observations are similar: the formation of product (dissolved metal) obeys first-order kinetics, and there appears to be first-order dependence on

Table 5 Effect of mass upon metal dissolution from foils reacting with 3-bromobutyltriphenylphosphonium bromide

			Mass of foil		[Metal]	
Metal foil	Reaction time (s)	**I** (M)	Range (mg)	High/low	Range (M)	High/low
Copper	4.33×10^5	2.64×10^{-3}	118.93–36.17	3.29	$(1.25–1.08) \times 10^{-4}$	1.16
	5.17×10^5	1.15×10^{-3}	38.10–3.26	11.7	$(3.15–1.86) \times 10^{-5}$	1.69
	7.75×10^5	1.30×10^{-3}	360.14–94.20	3.82	$(5.81–4.67) \times 10^{-5}$	1.24
Zinc	9.28×10^4	3.93×10^{-4}	204.41–20.76	9.85	$(10.5–2.13) \times 10^{-5}$	4.93
Lead	8.40×10^4	1.02×10^{-3}	296.14–15.92	18.6	$(4.63–1.88) \times 10^{-6}$	2.46
Brass	2.42×10^{-5}	1.02×10^{-3}	329.04–26.14	12.6	$(7.95–2.68) \times 10^{-5}$	2.97

Table 6 Dissolution of zinc[a] as a function of zinc foil mass

	Reaction time (min)			
Mass of foil (mg)	38	121	350	1547
20.76	7.5	11.0	12.0	21.3
33.59	7.3	11.0	13.0	36.1
50.20	8.4	13.0	17.0	38.2
80.27	8.7	13.0	18.5	47.6
131.09	9.8	16.0	22.9	86.8
204.41	11	17.1	30.9	105

[a] Concentration units are µM (µmol dm^{-3}). Portions of 0.254 mm zinc foil were treated with 0.020 dm^3 portions of a 3.93×10^{-4} M solution of **I**. Each set of concentrations showed a linear relationship between foil mass and dissolved [Zn].

Table 7 Lowering of dissolved methylmercuric acetate levels by treatment with zerovalent metals

	Hg concentration		
Metal	(mg dm^{-3})	M × 10^5	Lowering (%)
Control	3.6	1.8	—
Sn	3.2	1.6	11
Cu	2.3	1.15	36
Pb	2.1	1.05	42
Zn	0.80	0.40	78
Fe	0.33	0.165	91

[a] 0.035 dm^3 portions of 1.79×10^{-5} M $CH_3HgC_2H_3O_2$ [77.56% Hg] solution were treated with 1.145 ± 0.014 µmol metal powder at ambient temperatures for 90.4 h (= 3.254×10^5 s). Analyses were done by Little Bear Laboratories.

reaction rate for the quantity of metal substrate as well. The more active zinc and iron dissolve faster than copper, as would be expected, and alloys of copper show more rapid loss of the more active component, again as expected.[13] The enhanced activity of **I** relative to **IV** apparently arises from the secondary carbon atom of **I.** Other effects may also contribute to the marked variation in reaction rates observed for different bromoalkyltriphenylphosphonium salts. These systems are currently being investigated in more detail.

The dissolution of copper by **V,** or the dissolution of iron by **V, VI** or **VII,** may occur through oxidation of the substrate metal. Copper foil treated with **V** showed a light-gray sheen and analysis (LBL) indicated the presence of metallic mercury. The alkylmetal species may be adsorbed onto the surface of the metal, with transfer of an alkyl group and/or electron. Treatment of natural or waste waters with metals such as iron could provide a useful means for removing toxic organometal species as well as chlorocarbons.[8]

CONCLUSIONS

The use of water-soluble organometal(loid)s as reagents for reaction with zerovalent metals in water may well provide a model for investigating corresponding interactions of haloalkyl species and metals. Since these can form solutions of accurately known concentrations, and since a variety of both

$[(C_6H_5)_3PCH_2CH_2CH(Br)CH_3]^+Br^-$

I

$[(C_6H_5)_3PCH_2Br]^+Br^-$

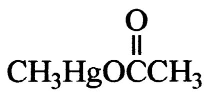
II

$[(C_6H_5)_3PCH_2CH_2CH_2Br]^+Br^-$

III

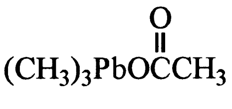
$[(C_6H_5)_3PCH_2CH_2CH_2CH_2Br]^+Br^-$

IV



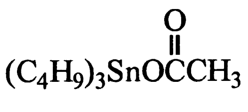
$CH_3HgO\overset{\overset{O}{\|}}{C}CH_3$

V



$(CH_3)_3PbO\overset{\overset{O}{\|}}{C}CH_3$

VI



$(C_4H_9)_3SnO\overset{\overset{O}{\|}}{C}CH_3$

VII

metal substrates and reagents may be employed, a large number of combinations become possible, with a corresponding expansion of knowledge. Similar considerations apply to the interactions between dissolved toxic organometals and zerovalent metals. We are currently actively investigating these various systems.

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