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The effect of unsaturation on the reaction of aqueous alkyl bromides with brass foil

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Brass (a zinc/copper alloy) foil reacts with mixtures of water and alkyl bromides to give dissolution of zinc and copper. The relative rates of leaching depend on the bromide used: saturated bromides favor dissolution of zinc, whereas unsaturated bromides favor dissolution of copper. This difference is attributed to the formation of π-complexes between the unsaturated linkages and the copper atoms.

Keywords: Copper, zinc, direct reaction, alkyl bromide, corrosion, π-complexes

INTRODUCTION

In recent years, the potential roles of metal(loid)–carbon bonds in the movement of heavy elements into and out of aqueous media have received increasing attention. Biological methylation of mercury and other heavy metals by microorganisms makes an important contribution to their environmental circulation.[1] Reaction of methyl iodide (also found in the natural environment) with metal ores may provide another.[2-4]

Known since 1849, the direct reaction of alkyl halides with metals has been widely used to prepare water-sensitive organometallic reagents.[5] The presence of water does not prevent this reaction, although it destroys the metal–carbon bonds formed. Methyl iodide in water will react with tin and lead to form methylmetals.[6] Flow experiments on iron chips indicated that aqueous alkyl iodides markedly enhanced their dissolution.[4,7,8] These experiments also indicated that dissolution rates varied with the presence of alloying elements in the iron and/or carbon–carbon double bonds in the alkyl halides.[4,8]

To investigate this phenomenon more closely, we have used zinc, copper and brass foils as substrates and alkyl bromides (more reactive than the iodides) as reactants. This paper reports some of the findings.

EXPERIMENTAL

Brass foil (0.0254 mm thick; 70% Cu, 30% Zn), copper and zinc foils (0.254 mm; 99.9% purity) were purchased from Aesar Corp. Alkyl bromides were purchased from Aldrich Chemical Co. or Lancaster Chemical Co. and used without further purification. Brass surfaces were not cleaned or otherwise treated prior to reactions.

Pieces of metal foil (40–500 mg) placed in screwtop vials containing 15–35 cm^3 deionized water and 0.20–0.50 cm^3 alkyl bromide. The vials were capped, shaken and allowed to stand in darkness for periods up to ten days. Aliquots were removed at regular intervals to measure dissolved metal concentrations. Reactions were carried out at 22 (±1) °C. Water was not deaerated.

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.[9] Levels of zinc were measured also on a HACH DR-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.

Calculations were performed on an Apple IIe® microcomputer. Points could be fitted to lines using a CURFIT® program and the methods of least squares. This program also enabled calculations of average uncertainties and coefficients of determination.

OBSERVATIONS

Earlier qualitative results suggested that the presence of unsaturated carbon–carbon linkages in alkyl halides altered the rate of dissolution of metals with which they reacted.[8] To test this in a systematic manner, we used some ω-bromo-1-alkenes, $Br(CH_2)_nCH{=}CH_2$ ($n = 2$–4), along with their saturated counterparts. Table 1 gives a typical set of results.

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Table 1 Comparative leaching effects of some alkyl bromides on brass

Alkyl bromide	[Zn] (mg dm^{-3})	[Cu] (mg dm^{-3})	[Zn]/[Cu]
None (control)	1.20	1.00	1.20
$CH_3CH_2(CH_2)_2Br$	7.60	0.74	10.3
$CH_2{=}CH(CH_2)_2Br$	7.00	6.10	1.15
$CH_3CH_2(CH_2)_3Br$	4.00	1.00	4.00
$CH_2{=}CH(CH_2)_3Br$	9.80	3.40	2.88
$CH_3CH_2(CH_2)_4Br$	4.20	0.20	21.0
$CH_2{=}CH(CH_2)_4Br$	3.80	2.70	1.41

Brass strips (43.67 ± 0.36 mg) were added to mixtures of 25 cm^3 water and 0.200 cm^3 alkyl bromide in vials. The measurements were taken after nine days. The solution pH remained constant at 5.5.

Table 2 Unit dissolution rates of zinc and copper in aerated water

Metal substrate	No. of runs	Average rate[a] (μg metal s^{-1} s^{-1} m^{-2} foil)	Range[a] (μg metal s^{-1} m^{-2} foil)
Zinc foil	8	7.0 (2.6)	10.4–4.4
Copper foil	9	1.0 (0.3)	2.0–0.7
Brass foil			
Zinc	10	6.8 (2.5)	12.0–3.5
Copper		1.2 (0.4)	2.0–0.6

[a] Concentrations were measured 18–22 h after initiation of reaction. Figures in parentheses are standard deviations.

As part of a more quantitative approach, we determined the unit rates of dissolution over the first 24 h. These are listed in Table 2. The rate of dissolution of copper in aerated water is slightly lower than the reported literature value[10] of 1.7 ± 0.3 μg m^{-2} s^{-1} (i.e. per square meter of metal foil). Interestingly, these rates were virtually identical for pure metal and the corresponding metal in brass. Experimental rates for the metals in the presence of alkyl bromides (Table 3) indicate that ω-bromo-1-alkenes sharply increase the rate of dissolution for copper and slightly increase the rate for zinc.

Table 3 Unit dissolution rates of zinc and copper from brass foil in aerated water and alkyl bromide mixtures

Alkyl bromide	No. of runs	Zinc[a] (μg s^{-1} m^{-2} foil)	Copper[a] (μg s^{-1} m^{-2} foil)
$CH_3CH_2(CH_2)_2Br$	12	7.2 (3.6)	2.1 (1.4)
$CH_2{=}CH(CH_2)_2Br$	8	11 (6)	10 (6)
$CH_3CH_2(CH_2)_3Br$	3	4.7 (1.5)	1.4 (0.3)
$CH_2{=}CH(CH_2)_3Br$	3	7.2 (3.8)	6.8 (3.4)
$CH_3CH_3(CH_2)_4Br$	3	4.7 (0.8)	0.9 (1.2)
$CH_2{=}CH(CH_2)_4Br$	3	8.9 (5.0)	8.3 (5.7)

[a] Concentrations were measured 18–22 h after initiation of reaction. Figures in parentheses represent standard deviations.

Plots of dissolved metal versus time usually gave a linear relationship, as shown in Fig. 1. For the reaction of brass with water or with water and saturated alkyl bromides, [Zn] levels rose more rapidly than [Cu]; however, for reactions involving brass and ω-bromo-1-alkenes, the linear slopes for both metals were very similar, with that for [Cu] occasionally exceeding that for [Zn]. Numerical values for two separate experiments appear in Table 4.

As a further test, mixtures of 1-bromoheptane and 7-bromoheptanenitrile were prepared (keeping the total number of moles constant) and reacted with brass foil in water. The levels of dissolved metals, especially copper, increased as the mole fraction of 7-bromoheptanenitrile increased (Fig. 2).

Table 4 Growth of dissolved-metal concentrations with time[a]

Alkyl bromide	Slope (mg dm^{-3} min^{-1})	Intercept (mg dm^{-3})	Coefficient of determination
C_4 series			
Control			
Zn	1.07×10^{-4}	0.145	0.984
Cu	7.16×10^{-6}	0.0286	0.984
1-Bromobutane			
Zn	1.18×10^{-4}	0.148	0.986
Cu	6.90×10^{-6}	0.0192	0.980
4-Bromo-1-butene			
Zn	1.21×10^{-4}	0.101	0.984
Cu	1.42×10^{-4}	0.0286	0.987
C_7 series			
Control			
Zn	9.54×10^{-5}	0.739	0.999
Cu	2.80×10^{-5}	0.0304	0.995
1-Bromoheptane			
Zn	9.27×10^{-5}	0.937	0.994
Cu	8.35×10^{-6}	0.0107	0.999
7-Bromoheptane nitrile			
Zn	1.65×10^{-4}	0.800	0.947
Cu	1.59×10^{-4}	0.189	0.950

[a] Pieces of brass foil (66.8 ± 0.2 mg for C_4 series; 56.2 ± 0.4 mg for C_7 series) were treated with mixtures of 25 cm^3 water and 0.10 cm^3 RBr for eight days. Six measurements were made during that period.

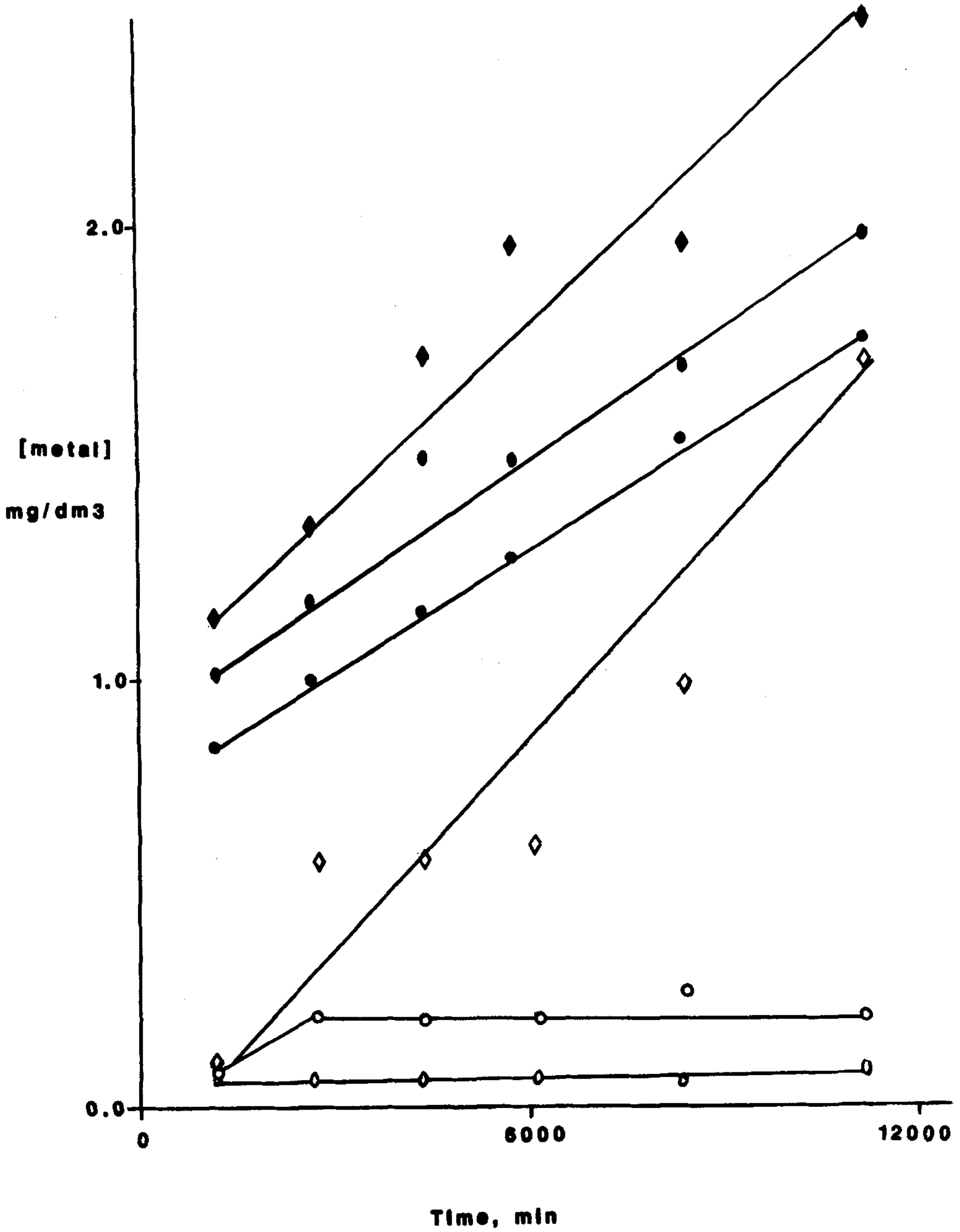

Figure 1 Dissolution of zinc (solid symbols) and copper (open symbols) from brass by alkyl halides: ●, ○, control; ●, ○, 1-BrC$_6$H$_{13}$; ♦, ◊, Br(CH$_2$)$_6$CN.

DISCUSSION

Best of dissolution

When a two-component alloy undergoes corrosion, the more active metal leaches out preferentially;[11,12] for brass, this is termed 'dezincification'. Our observations indicate that dezincification occurs readily in aerated water and is enhanced only slightly by the presence of alkyl bromides. The efflux of zinc is high during the first 24 h, with subsequent dissolution occurring more slowly. By contrast, very little copper dissolves in the presence of water only, or water with saturated alkyl bromides. Reaction of brass with ω-bromo-1-alkenes or the analogous 7-

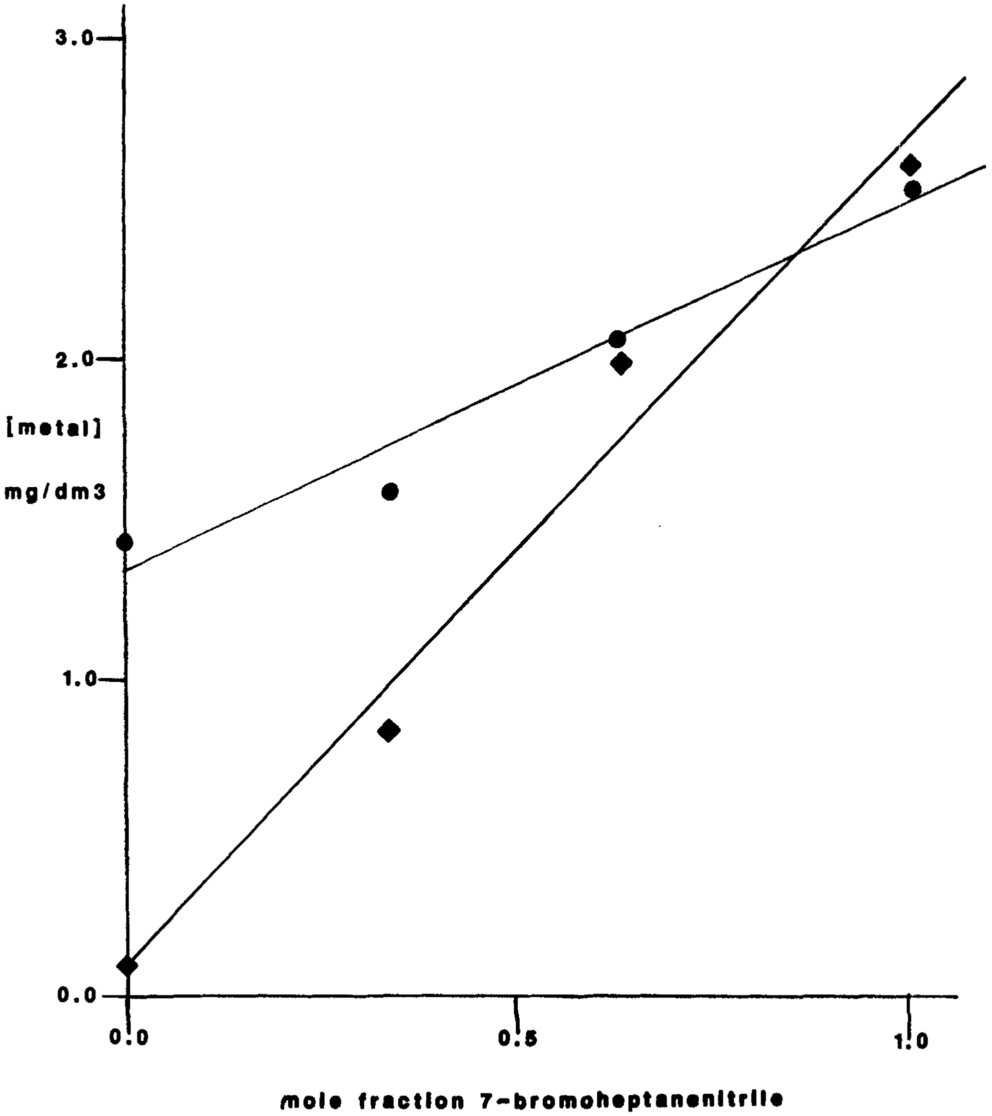

Figure 2 Dissolution of zinc (●) and copper (◆) from brass by mixtures of 1-bromoheptane and 7-Bromoheptane nitrile over 186 h.

bromoheptanenitrile, Br$(CH_2)_6$CN, causes a great enhancement of dissolution rates, often 20-fold or more.

Experiments were carried out using allyl bromide and related molecules (e.g. 3–bromocyclohexene). Whilst these leached out copper quite readily, they also hydrolyzed rapidly; the pH of the reaction system usually fell from an initial value of 6.0 to 1.0 within the first 24 h. Copper dissolves readily in acid solution in the presence of air.[13] By contrast, the ω-bromo-1-alkene reaction caused no appreciable change in pH for periods up to eight days.

Mechanism of reaction

The direct reaction is heterogeneous, involving solid metals and liquid alkyl halides. Its most common example, the Grignard reaction, has received various mechanistic investigations.[14,15] The rate-determining step in this reaction requires reaction of organic halide at the magnesium surface.[14] It is not unreasonable to assume that this would apply to other metals. Various studies on the adsorption of alkyl halide vapors onto metal surfaces indicate that they bind through the halogen atom.[16]

Elsewhere we have proposed the following mechanism for the dissolution of metals by aqueous alkyl halides (Eqn [1a–c]):[4,7]

$$\mathrm{R{—}X_{(aq)} + M_{(s)} \rightarrow M \cdot X{—}R_{(s)}} \quad [1a]$$

$$\mathrm{M \cdot X{—}R_{(s)}\ RMX_{(s)} \rightarrow RMX_{(aq)}} \quad [1b]$$

$$\mathrm{RMX_{(aq)} + H_2O \rightarrow RH + MX(OH)} \quad [1c]$$

When brass reacts with aqueous saturated alkyl bromides, these compounds will attach by the bromine atom, probably preferentially to the more active zinc. Inclusion of an unsaturated linkage in the hydrocarbon chain provides an additional source of binding, viz. formation of a bond between the π-electrons and a metal atom. Since zinc does not form such bonds, the unsaturated bromide will bind preferentially to the copper. Consequently, the copper might undergo oxidative addition and dissolve rapidly when such linkages are present. This also results in a secondary enhancement of zinc release.

Since these reactions were carried out under aerobic conditions, the role of atmospheric oxygen must also be considered. The high values for the intercepts (Table 4; Fig. 1) (calculated [Zn] at $t = 0$) indicate a large rapid initial efflux of zinc, with subsequent dissolution occurring more slowly. These data suggest that release of zinc from brass arises primarily from corrosion by oxygen and water. For copper, aerobic corrosion is very slow, and is not enhanced much by saturated alkyl bromides. The great enhancement by unsaturted bromides suggests that this is the primary process in these systems.

CONCLUSIONS

The two metals present in brass dissolve at different rates. Saturated alkyl bromides preferentially enhance the dissolution of zinc, whilst corresponding unsaturated bromides favor the dissolution of copper, probably through formation of π-complexes to that metal. Investigations into these and related systems are continuing.

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