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THE THERMAL STABILITY OF 8-HYDROXYQUINOLINE CHELATES IN HIGH-TEMPERATURE WATER

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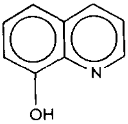
ABSTRACT

The effective thermal stabilities of metal derivatives of 8-hydroxyquinoline (oxine) in contact with liquid water are appreciably lower than those characteristic of the same compounds heated alone. Degradation in water occurs both by hydrolysis at the bonded metal atom (with liberation of unchanged 8-hydroxyquinoline) and by direct water attack at the organic portion of the molecule. The former mechanism tends to predominate at the lower temperatures. Volatilization of metal oxinates with steam (a scheme proposed for removing corrosion products from high-temperature steam systems) seems feasible for copper (and possibly iron) oxinates but does not appear promising for the corresponding alkaline earth chelates.

INTRODUCTION

Early work from this laboratory showed that a number of metal chelate derivatives of 8-hydroxyquinoline (**I**, "oxine") are sufficiently volatile to allow them to be sublimed in vacuo without significant thermal decomposition [1]. Subsequent studies confirmed and further defined the relatively high thermal stabilities of many of these chelates (when heated in the absence of other reactive chemical species) [2–6]. In 1972 Turner suggested that practical use might be made of the volatile and heat-stable characteristics of metal oxinates to remove deleterious metallic corrosion products (or their metal cation precursors) from steam boilers [7,8]. The process envisaged consisted of initial chemical reaction between dissolved oxine and corrosion products to form the corresponding metal oxinates followed by removal of oxinates by co-volatilization with steam. (The latter step is reminiscent of the steam distillation process commonly employed in organic chemical laboratories to

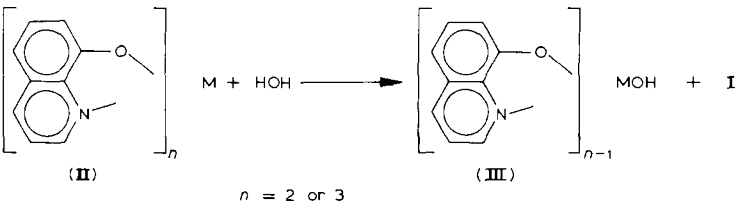


(I)

purify substances which would not distill at an appreciable rate in the absence of the additional driving force provided by the steam.)

The method suggested by Turner requires not only oxinate volatility but also adequate, effective, oxine and metal oxinate thermal stability *in water*. It cannot be assumed a priori (as implied by Turner) that the heat stability characteristics of these substances will be unaffected by the presence of water, which is known to hydrolyze many organic compounds and also to participate in numerous hydrolysis reactions with metal ions. While Turner [8] was able to demonstrate high effective heat stability for oxine, itself, in high-temperature water, corresponding experimental data for the metal oxinates seem not to be available.

At least two types of chemical reaction between metal oxinates and water appear relevant. The first involves partial hydrolysis of the oxinate without chemical alteration or disruption of the 8-hydroxyquinolate moiety, itself (reaction 1).



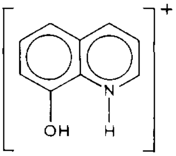
(1)

The consequences of reaction (1) to the process suggested by Turner would be dependent on the extent of hydrolysis and the relative volatility of the partially hydrolyzed chelate **III** compared to that of the parent oxinate **II**. It seems likely that the species **III** will be of lesser volatility due to the possibilities for intermolecular interaction inherent in the presence of the bonded hydroxyl group.

A second possible reaction would be by actual attack of water on the 8-hydroxyquinolate portion of the molecule, either by disruption of the heterocyclic or carbocyclic ring systems or by ring substitution. At least some of the reactions of this sort would be expected to result in nonvolatile metal-containing products.

Continuing interest in finding improved methods for removing corrosion products, or preventing their formation, in high-temperature steam systems has prompted us to obtain additional information on possible interactions between solid metal oxinates and liquid water at elevated temperatures. The experimental methods employed are based on our earlier techniques for studying the heat stabilities of oxinates when heated in the absence of other reactive chemical species [2–6]. While interest has centered here on the iron and copper oxinates, we have also included the alkaline earth oxinates in the present study, partially because of interest in magnesium and calcium corrosion products and partially as a further basis for comparison.

Our specific experimental approach involves heating a sealed glass vial containing the two-phase system, solid oxinate plus water, at constant temperature. After cooling, the vial is broken open and the contents are leached either with pure water (for one series of experiments) or with aqueous hydrochloric acid (for the second series). The optical absorption of the leachate (suitably diluted) is then compared with that characteristic of the unheated oxinate. Hydrolysis or thermal decomposition of the oxinate results in either an increase or a decrease in optical absorbance depending on the products formed. Extraction with water is selective for detecting the formation of water-soluble oxine, such as that formed by hydrolysis reactions (1), since the oxinates, themselves, are essentially insoluble in water. By contrast, aqueous acid converts all unchanged oxinate, and also any free oxine present, to the oxinium ion **IV**. Thus, any change in measured optical absorbance for the acid solutions, as the result of heating an oxinate with water, indicates chemical alteration of the 8-hydroxyquinolate moiety, itself, irrespective of its initial chemical association with other species. The two approaches of extracting with water or with acid provide complementary information, as indicated in the discussion to follow.



(IV)

EXPERIMENTAL

The metal oxinates were prepared as described previously [1,4]. Thirty-mg samples of oxine or metal oxinate were weighed into 9 mm OD Pyrex tubes of the type previously described [1,4], and 1 ml of water was added. The ampules were evacuated while cooling in liquid nitrogen and were subsequently sealed with a torch. They were then heated for 10 h in a constant-temperature oven. To prevent excessive pressure buildup in the ampules at the higher temperatures each one was contained in outer stainless-steel jacket sealed at both ends by Swagelok fittings. A small amount of added water contained between the sealed glass ampule and the surrounding metal jacket served to minimize gas pressure differences across the glass membrane. Photographs of the type of glass ampule and metal protection tubes used here, plus further relevant experimental details, are given elsewhere [10b].

The heated ampules intended for acid extraction were cooled, broken open, extracted, and the resulting solutions filtered and diluted to volume as described previously [2]. Optical absorbance values for the diluted solutions were measured with a Cary Model 14 spectrophotometer (at 358 nm). One-cm path length quartz cells were used.

For the water-extraction runs each cooled ampule was wrapped in polyethylene film and crushed in a beaker. Distilled water (100 ml) was added and the mixture was stirred overnight at room temperature. The liquid was then filtered through filter paper and diluted to 250 ml. Optical absorbance (at 308 nm) of the resulting solution was measured as above.

RESULTS AND DISCUSSION

Water extractions

The results of extracting the contents of previously heated tubes which contain a metal oxinate plus water are plotted in Figs. 1 and 2. In each case the left-hand column of figures (Figs. 1A or 2A) refer to water extractions while the corresponding curves to the right (curves B) represent acid extractions of separately heated ampules. For all the curves the results are plotted in terms of the optical absorbance of diluted extracts vs. the furnace temperature used for the initial heating with water. Each point in the curves of Figs. 1 and 2 represents a separately prepared, heated, and leached reaction mixture.

For the water extraction curves one anticipates an optical absorbance value of zero for the unheated aqueous oxinate runs since the unchanged metal oxinates are essentially insoluble in water at room temperature. For heating temperatures where the hydrolysis reaction (1) becomes significant, however, non-zero values of absorbance should be observed due to the

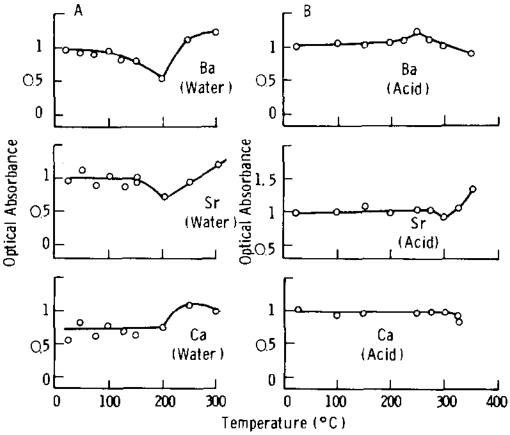


Fig. 1. Optical absorbance vs. furnace temperature for solid metal oxinates heated in contact with liquid water in sealed tubes. The tube contents were subsequently extracted with water or acid prior to absorbance measurements at room temperature.

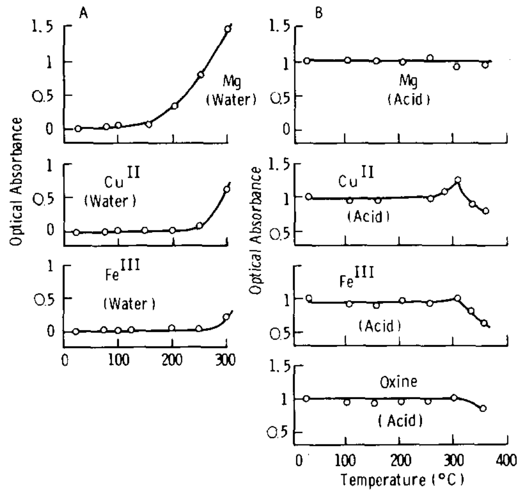


Fig. 2. Optical absorbance vs. furnace temperature for oxine or metal oxinates heated in contact with liquid water in sealed tubes. The tube contents were subsequently extracted with water or acid prior to absorbance measurements.

liberation of water-soluble oxine (reaction 1). These predictions are consistent with the experimental results (Fig. 2) obtained for the Mg, Cu^{II}, and Fe^{III} oxinates which show significant departures of optical absorbance values from zero for temperatures above 170, 250 and 250°C, respectively.

Surprisingly, the water extracts from Ca, Sr and Ba oxinates heated with water show appreciable optical absorbance values at the lowest temperatures employed, including room temperature (Fig. 1A). The most likely explanation for this behavior is that significant hydrolysis by reaction (1) has occurred over the several day storage periods (at room temperature) between the preparation of the sealed capsules and heating them in the furnace *.

An additional distinct region of optical absorbance increase occurs for the Ca, Sr and Ba oxinates, beginning at about 200°C. Possibly, this may be associated with a second stage of hydrolysis, shown in reaction (2).

$$\mathbf{III} + H_2O \rightarrow M(OH)_2 + \mathbf{I} \qquad (2)$$

Acid extractions

The results from a second series of sealed vial runs in which, however, the cooled reaction mixtures have been extracted with acid are shown in Figs. 1B and 2B. One expects here the curves to consist of straight lines parallel to the

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* The varying period of storage would also account for the lower-temperature scatter of points for the Ca and Sr curves of Fig. 1.

temperature axis, with initial non-zero ordinate values, over those temperature regions where chemical alteration of the 8-hydroxyquinolate moiety has not taken place. This will be true even when metal hydrolysis reactions, such as (1) or (2), occur. Departure of the curves of Figs. 1B and 2B from the initial horizontal is then an indication of chemical attack directly at the organic portion of the oxinate ring system. Possible changes in the oxinate entity include disruption of the heterocyclic or carbocyclic ring system, ring substitution, or polymerization reactions which incorporate oxinate units into high molecular weight, acid-resistant products.

Examination of the curves of Fig. 2B shows oxine itself to be stable in water to at least 300°C *, while Cu^{II} and Fe^{III} oxinates begin to decompose at about 250°C **. For these two compounds oxinate chemical attack and hydrolysis (Fig. 2A) seem to occur more-or-less simultaneously. A visible deposit of copper metal (identity confirmed by X-ray diffraction analysis of the isolated solid) formed in the tubes containing Cu^{II} oxinate and water, when these were heated above 250°C. Thus, decomposition probably occurs here by an internal oxidation–reduction reaction involving oxidation of bound oxinate to unknown organic products. A similar mechanism can be suggested for the decomposition of Fe^{III} oxinate, the iron being reduced in this case to Fe^{II}. Similar oxidation–reduction mechanisms have been proposed for the decomposition of Cu^{II} and Fe^{III} EDTA complexes in high-temperature water [10]. It is significant to note that Cu^{II} and Fe^{III} oxinates decompose at appreciably higher temperatures when heated in the absence of water [4,6]. Thus, water must play some role (possibly catalytic) in the oxidation–reduction reactions observed here.

Examination of the acid-extraction curves (Figs. 1B and 2B) shows the organic portions of the magnesium and calcium oxinates to be stable in water to at least 350 and 300°C, respectively. Since these two chelates appear to be largely hydrolyzed at these temperatures (Figs. 1A and 2A), the acid extraction results may actually reflect the high, observed stability of free oxine (bottom curve in Fig. 2B). The strontium and barium oxinates are also considerably hydrolyzed at the higher temperatures in water, but here the acid extraction curves show attack at the 8-hydroxyquinolate moiety to occur at lower temperatures (280 and 240°C, respectively) than is characteristic of the magnesium and calcium compounds. It seems likely that here one is observing a destructive interaction between free oxine (produced by reactions (1) and (2)) and high concentrations of hydroxyl ion resulting from (2).

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* Turner [8], using different experimental conditions, found oxine to be stable in water to at least 400°C. The apparent drop in optical absorbance for oxine (Fig. 1B) at 350°C, if real, may indicate chemical interaction between oxine and the glass walls of the containing ampule.

** Fe^{II} oxinate was not included in the present study since this chelate is reported to be stable only in the presence of strong reducing agents [9].

It is interesting to note that the decreasing order of thermal stability of the 8-hydroxyquinolate entity in the alkaline earth chelates exposed to water is Mg > Ca > Sr > Ba (Figs. 1B and 2B). This order parallels the increasing solubilities of the respective hydroxides produced by reaction (2). Published values of solubility for Mg, Ca, Sr and Ba hydroxides at 100°C are, respectively, 0.004, 0.08, 21.8, and 94.8 g/100 ml of water [11]. These data show that the hydroxyl content of solutions resulting from reaction (2) will be very much higher for the Ba and Sr oxinates than those characteristic of the corresponding Mg and Ca chelates.

Implications to oxinate volatility in steam

Listed in Table 1 are the maximum usable temperatures for oxine and the metal oxinates as estimated from Figs. 1 and 2. These temperatures are taken to be the values below which hydrolysis is not important as inferred from the measured optical absorbance values. Since the period of heating used here (10 h) may be unrealistically long in terms of oxinate exposure time in actual high-temperature steam systems, we have also considered temperatures 50°C higher, on the assumption that the curves of Figs. 1 and 2 might be shifted to the right to this extent, provided temperature exposure times were sufficiently short. The latter set of temperatures is listed in column 4 of Table 1.

Columns 3 and 5 of Table 1 list the observed degrees of volatilization of the oxinates (as determined by thermogravimetric analysis in vacuo [1]) at the two sets of temperatures. The results show that Cu^{II} oxinate is significantly volatile at both temperatures while appreciable Fe^{III} oxinate evaporates only at the higher of the two. The alkaline earth oxinates are essentially non-volatile at both temperatures. These results indicate that Cu^{II} oxinate (and possibly the analogous Fe^{III} chelate) may be suitable for the steam volatilization scheme suggested by Turner [7,8]. The alkaline earth oxinates, however, appear to be insufficiently volatile at temperatures where metal ion hydrolysis and/or other types of oxinate decomposition are not serious.

TABLE 1

Volatility of oxinates at their maximum usable temperature (10 h heating)

Oxinate	Max. usable temp. (°C)	% Volatilized at max. usable temp.	Max. usable temp. + 50 (°C)	% Volatilized at max. usable temp. + 50°C
Oxine	300	100	350	100
Cu^{II}	250	52	300	100
Fe^{III}	250	0	300	13
Mg	150	0	200	0
Ca	< 25	0	< 75	0
Sr	< 25	0	< 75	0
Ba	< 25	0	< 75	0

Finally, we note that there are many known derivatives of oxine which contain one or more organic substituents in the oxinate ring system [12]. Conceivably, some of these compounds may give metal chelates which are substantially more volatile than the unsubstituted metal oxinates, without compromising effective thermal stability in water. In particular, by analogy with volatility results reported for metal β-diketonate chelates [13], the use of oxine substituted with fluorine atoms or with bulky alkyl groups may be advantageous in obtaining increased volatility. Alkyl groups (e.g., *t*-butyl) are presumably effective in this regard as the result of decreasing metal–metal interactions in neighboring molecules by increasing metal–metal interatomic distances.

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