$Et_2AlH{\cdot}NMe_3$ respectively, as outlined in the literature.[13] Alternatively, $Et_2AlH{\cdot}NMe_3$ was prepared by addition of NMe_3 to Et_2AlH, as described in the literature;[12] the routes gave products with identical ^1H NMR spectra.

Conclusions

The ^1H NMR data show strong evidence that both $EtAlH_2{\cdot}NMe_3$ and $Et_2AlH{\cdot}NMe_3$ are mixtures of all the species $Et_xAlH_{3-x}{\cdot}NMe_3$ in solutions of benzene or toluene.

The tendency for $EtAlH_2{\cdot}NMe_3$ to separate at −18 °C into a solid and a liquid which show different ratios of substituents on the metal is strongly suggestive that a fluxional mixture of species is also found for this compound in the pure liquid, and the vaporization behavior of both compounds further supports this hypothesis. For $Et_2AlH{\cdot}NMe_3$ the evaporation studies were performed under conditions similar to those in which the compound would be used in an MOCVD experiment: there was clear evidence that the composition of the vapor was different from that of the liquid, and after substantial exhaustion of the sample it was also clear that the compositions of both vapor and liquid were changing throughout the distillation. There was also evidence that the volatility of the compound progressively decreased during distillation.

In conclusion, although these compounds can be used as precursors for the MOCVD of aluminum-containing layers (this should be possible with virtually any mixture of aluminum alkyls and/or hydrides), there are very strong indications that the sources will not be well-behaved: the partial pressure of aluminum species they deliver into the reactor will be dependent upon their degree of exhaustion.

Registry No. $EtAlH_2{\cdot}NMe_3$, 19582-10-6; $Et_2AlH{\cdot}NMe_3$, 12079-02-6; $Et_3Al{\cdot}NMe_3$, 15318-08-8; $AlH_3{\cdot}NMe_3$, 16842-00-5.

Reactivity of Chromium Oxide in Aqueous Solutions. 1. Oxidative Dissolution

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Chromium(III) oxide, α-Cr_2O_3, is dissolved in aqueous media in the presence of Ce^{4+}, MnO_4^-, BrO_3^-, and $S_2O_8^-/Ag^+$ species in a process preceded by the formation of surface Cr–O–X complexes. The last cited reactant causes oxidation of Cr(III) by Ag^{2+} attack on the surface complex, whereas the other three additives promote dissolution by the formation of Cr(VI) through an internal redox process within the surface complex. Langmuir-type conditional constants for the formation of the surface complexes are presented and discussed, together with the rate constants that describe their evolution to dissolved Cr(VI). The analogy between these heterogeneous oxidations of α-Cr_2O_3 and oxidations of dissolved $Cr(H_2O)_6^{3+}$ is discussed.

Introduction

The general subject of metal oxide dissolution mechanisms poses interesting questions about the underlying chemistry. In particular, the relationship between the chemical interactions at the surface of a metal oxide with the known aqueous chemistry of the same metal ion has been the subject of several recent studies.[1-4]

Segall[5] et al. have proposed a classification of the dissolution reactions of metal oxides on the basis of the type of chemical bonding and electronic properties in the solid. According to this scheme, the most resistant to dissolution in aqueous media are covalent oxides, such as SiO_2, ZrO_2, etc. This classification of metal oxides in "ionic", "semiconductor", and "insulating covalent" is of course mainly operative, in the sense that it accounts for broad types of dissolution mechanisms. It is well-known that the true ionicity of metal oxides is still elusive,[6] and the distinction of semiconductors and covalent oxides is simply made on the basis of an arbitrary value of the bandgap.[7] Chromium(III) oxide is in itself a good example of a solid that can be described as either ionic or covalent: the ionicity from XPS data is calculated to be 2.6, whereas the use of a more sophisticated model leads to the value of 0.15.[6] Furthermore, it is possible to impart semiconducting properties to α-Cr_2O_3 by adequate thermal treatment in oxidizing or reducing atmospheres. In the classification of Segall et al., however, α-Cr_2O_3 falls clearly in the covalent class;[7] its thermodynamic solubility is high both in acids and in bases,[8] but the dissolution rates are higher in the basic media.[9] Indeed, the covalent Cr–O–Cr

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framework in α-Cr_2O_3 and in various hydrous Cr(III) oxides is responsible for the resistance to chemical attack and explains the passivity brought about by the oxidation of the surface of its alloys. The characteristics of the dissolution by acids and bases are essentially determined by the degree of cross-linking and hydration of hydrous oxides and will be described in a separate paper.

More important for practical purposes is the redox dissolution of chromium(III) oxides. Solubility of metal oxides is largely governed by the hydrolytic behavior of the metal ion;[7,8] the less soluble oxides are those formed by amphoteric metal ions that are neither strongly basic nor strongly acidic. Reduction of Cr(III) to Cr(II) leads to a substantial increase in basicity, while oxidation to Cr(VI) produces a large increase in acidity. As a result, both Cr(II) and Cr(VI) are more soluble in water: Cr(II) as $Cr(H_2O)_6^{2+}$, while Cr(VI) as anionic oxochromates(VI). This thermodynamic feature is illustrated by the Pourbaix diagram of chromium.[10] At pH 5 and 25 °C it is possible to dissolve α-Cr_2O_3 by reduction or by oxidation to produce undersaturated 0.01 mol dm^{-3} solutions.[11] Kinetically, the changes in rates of dissolution are also large: under comparable conditions of undersaturation, the breaking of the oxo bridges in α-Cr_2O_3 is many orders of magnitude slower than the equivalent processes in $Cr(OH)_2$ or CrO_3. In fact, when these species are created in the surface of α-Cr_2O_3, very fast phase transfer (dissolution) results.[7,11]

In practice, the dissolving power of oxidants has been well documented. For example, under hydrothermal conditions, stainless steels produce appreciable concentrations of chromate(VI) species when attacked by O_2. A well-established method for dissolving oxides grown on stainless steels uses an oxidative stage in which Cr_2O_3 is attacked by alkaline permanganate.[12] Dissolution by cerium(IV) has been described by Valverde and Wagner.[13] Very strong reductants are also effective,[14] but the practical uses of such additives are rather limited.

In this paper the kinetics of dissolution of α-Cr_2O_3 by a series of oxidants in acid media is described, and it is demonstrated that the chemical reactions involved bear a striking similarity to aqueous oxidation of Cr(III).

Materials and Methods

Two different oxides were used.

Oxide A was a commercial Cr_2O_3 (Puratronic), characterized by chemical analysis and X-ray diffraction, with a BET area of 1.73 m^2 g^{-1}.

Oxide B was obtained by calcination of a dried chromium (hydrous) oxide. The sample was prepared by a method described previously[15] with ^{51}Cr incorporated as radiotracer, then heated at a rate of 2 °C min^{-1}, and finally calcined for 1 h in air at 475 °C. This procedure converted the hydrous oxide to α-Cr_2O_3 while minimizing sintering and spalling of the particles. The powder X-ray diffractogram demonstrated the product to be α-Cr_2O_3; its BET area was 10.5 m^2 g^{-1}.

The dissolution of oxide A was evaluated in a magnetically stirred cylindrical beaker, provided with a jacket connected to a thermostat, the temperature of which was controlled at 65.0 ± 0.1 °C. In a typical experiment α-Cr_2O_3 (10 mg) was suspended in a solution of the appropriate acid concentration, and the reaction was initiated by adding variable amounts of the oxidant. Periodically, samples were removed with a syringe and filtered through a 0.22-μm Nuclepore membrane; the concentration of Cr(VI) in the filtrate was determined spectrophotometrically using diphenylcarbazide.[16] In some cases (including acid dissolution experiments), the total Cr content was measured by atomic absorption spectrometry with a Varian AARS instrument.

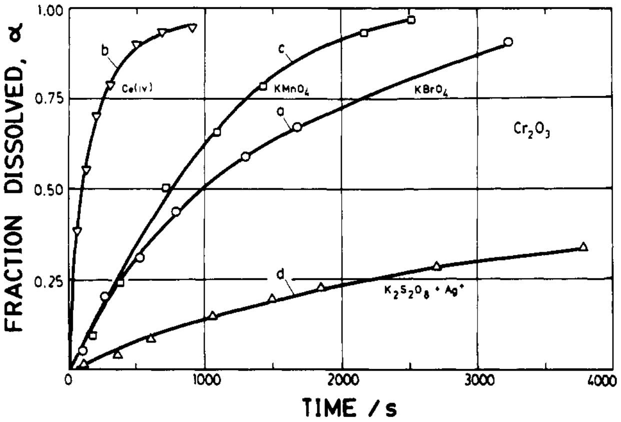

Figure 1. Fraction of the solid Cr_2O_3 (sample A), $\alpha = (w_0 - w)/w_0$ dissolved as a function of time: (a) in 0.4 mol dm^{-3} of $KBrO_3$ + 2.50 mol dm^{-3} of H_2SO_4 at 65 °C; (b) in 3×10^{-2} mol dm^{-3} of Ce(IV) + 1.0 mol dm^{-3} of HNO_3 at 25 °C; (c) in 0.08 mol dm^{-3} of $KMnO_4$ + 1.0 mol dm^{-3} of HNO_3 at 25 °C; (d) in 0.05 mol dm^{-3} of $K_2S_2O_8$ + 2.50 mol dm^{-3} of H_2SO_4 + 3.2×10^{-3} mol dm^{-3} of $AgNO_3$ at 65 °C.

Dissolution experiments of oxide B were carried out by transferring 1–5 mg of the oxide of known γ activity into 100 cm^3 of a solution of desired composition in a polypropylene beaker with a Pyrex jacket through which water at 25.00 ± 0.05 °C was circulated. Aliquots of the reacting suspension, withdrawn at different times, were filtered through 0.22-μm pore size membranes and transferred to a counting tube, and their activity was measured in a Packard Auto-gamma 500 crystal scintillation counter. Proper corrections for background counts were made.

Results

Stoichiometry of Dissolution. Under the investigated experimental conditions, bromate, cerium(IV), and permanganate ions totally dissolved the indicated amount of α-Cr_2O_3 in less than 2 h (Figure 1a–c). The only chromium species detected in solution was $HCrO_4^-$, and the corresponding reactions are therefore given by

$$5Cr_2O_3 + 6BrO_3^- + 7H_2O \rightarrow 10HCrO_4^- + 3Br_2 + 4H^+ \quad (1)$$

$$Cr_2O_3 + 6CeOH^{3+} \rightarrow 2HCrO_4^- + 6Ce^{3+} + H_2O + 2H^+ \quad (2)$$

$$5Cr_2O_3 + 6MnO_4^- + 8H^+ + H_2O \rightarrow 10HCrO_4^- + 6Mn^{2+} \quad (3)$$

In eq 3, Mn^{2+} is the reaction product because of the highly acidic medium, which prevents the Mn^{2+}/Mn(VII) disproportionation.

Peroxodisulfate/Ag^+ does not bring about total dissolution (Figure 1d); the reaction stops when less than 40% of the solid has dissolved. Even though a high excess of peroxodisulfate was used, the final solutions did not contain any residual $S_2O_8^{2-}$. Thus, the main reaction involved in the disappearance of the oxidant is not the dissolution

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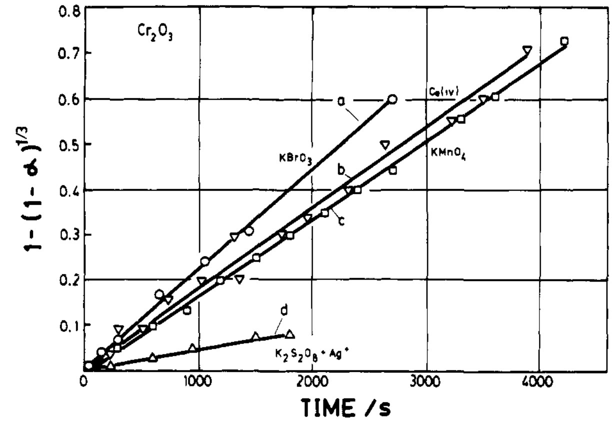

Figure 2. Plots of $1 - (1 - \alpha)^{1/3}$ as a function of time for the same systems as in Figure 1.

of Cr_2O_3 as $HCrO_4^-$ (eq 4) but the release of oxygen (eq 5), probably catalyzed by the oxide surface. The dissolution continues on further additions of $S_2O_8^{2-}$ to the partially reacted suspension:

$$Cr_2O_3 + 3S_2O_8^{2-} + 5H_2O \rightarrow 2HCrO_4^- + 6SO_4^{2-} + 8H^+ \quad (4)$$

$$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+ + \tfrac{1}{2}O_2 \quad (5)$$

The complications due to the consumption of $S_2O_8^{2-}$ did not affect the kinetic evaluation of the process, since in the interpretation of data only initial rates were considered. In the absence of Ag^+, no dissolution was observed.

In contrast to peroxodisulfate, ozone causes a release of Cr(III) and not Cr(VI) species. By analogy with the well-known solution chemistry of Cr(III), it can be postulated that the dissolution is mediated by peroxidic species (e.g., CrO_5) that form and decompose according to the stoichiometry given in eqs 6 and 7:

$$2Cr_2O_3(s) + 6O_3 \rightarrow 4CrO_5(aq) + 2O_2 \quad (6)$$

$$6H^+ + 2CrO_5(aq) \rightarrow 2Cr^{3+} + 3H_2O + \tfrac{7}{2}O_2 \quad (7)$$

Thus, the process may be described as the heterogeneous decomposition of ozone coupled with the acid dissolution of the oxide. The overall rates that could be achieved under the employed conditions were very low and did not warrant a detailed kinetic study.

Oxidative dissolution can also be achieved by strongly oxidizing free radicals, such as $HO^\bullet$ or $BrO_2^\bullet$. These radicals can be adequately generated either by radiolysis of the solutions or chemically, for example, by Fenton-like reactions involving hydrogen peroxide and Fe(II). In both cases, $HCrO_4^-$ is the chromium species detected in solution. The operative mechanism is different and shall be described separately.[17]

Kinetics of Heterogeneous Dissolution. All data reported here could be fitted by the kinetic expression relating the fraction dissolved, α, to time t by

$$1 - (1 - \alpha)^{1/3} = kt \quad (8)$$

as shown in Figure 2.

In the case of peroxodisulfate eq 8 holds only for low degrees of dissolution ($\alpha < 0.25$). Although the data can be fitted well with eq 8, previous work[18] indicates that the values derived for k may be influenced by different factors, such as particle size distribution and morphology. Furthermore, a depletion of reagents, although important only in the case of peroxodisulfate, might introduce systematic errors in the rate derived from eq 8. These complications are avoided if all rates are expressed in terms of the measured initial slope, i.e., through the use of $k = (d\alpha/dt)_{t=0}$, which is identical to $3k$ in eq 8 (penetration rate, in s^{-1}). The following results with all oxidants are discussed in terms of k. The main purpose of this paper is to explore the influence of solution variables on the parameter k.

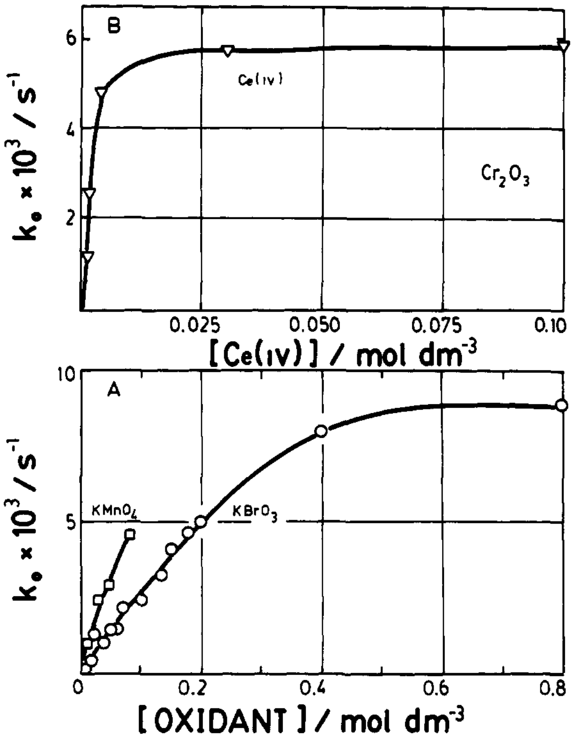

Figure 3. Dependence of the initial rate constant k on the concentration of the oxidant, at the same other conditions as in Figure 1.

Table I. Langmuir-Type Parameters Describing α-Cr_2O_3 Dissolution Rates by Various Oxidants

oxidant	k_{max}, s^{-1}	k'_{max}, s^{-1} g m^{-2}	K_s, dm^3 mol^{-1}	exptl conditions
Ce^{IV}	8×10^{-3}	5.7×10^{-4}	470	*a*
MnO_4^-	9.7×10^{-4}	9.2×10^{-5}	11	*a*
BrO_3^-	2.7×10^{-3}	1.5×10^{-3}	1.3	*b*
$S_2O_8^{2-}$	1.3×10^{-4}	7.2×10^{-5}	21	*c*
$S_2O_8^{2-}$	2.7×10^{-4}	1.5×10^{-4}	21	*d*

[a] Oxide B in HNO_3 (1 mol dm^{-3}), KNO_3 (1 mol dm^{-3}), t = 25 °C. [b] Oxide A in H_2SO_4 (2.5 mol dm^{-3}), t = 65 °C. [c] Oxide A in H_2SO_4 (2.5 mol dm^{-3}), $[Ag^+] = 1.6 \times 10^{-3}$ mol dm^{-3}, t = 65 °C. [d] Oxide A in H_2SO_4 (2.5 mol dm^{-3}), $[Ag^+] = 3.2 \times 10^{-3}$ mol dm^{-3}, t = 65 °C.

Dependence of *k* on Oxidant Concentration. Figure 3 shows that the rates of dissolution increase with increasing reagent concentration until a saturation value is reached. An analogous result had been found earlier by Segal and Williams for permanganate.[19] The curves in Figure 3 can be fitted with a two-parameter Langmuir-type equation, which yields straight lines:

$$k = \frac{k_{max}[ox]}{K_S^{-1} + [ox]} \quad (9)$$

The vaules of K_S and k_{max} that best fit the data are given in Table I.

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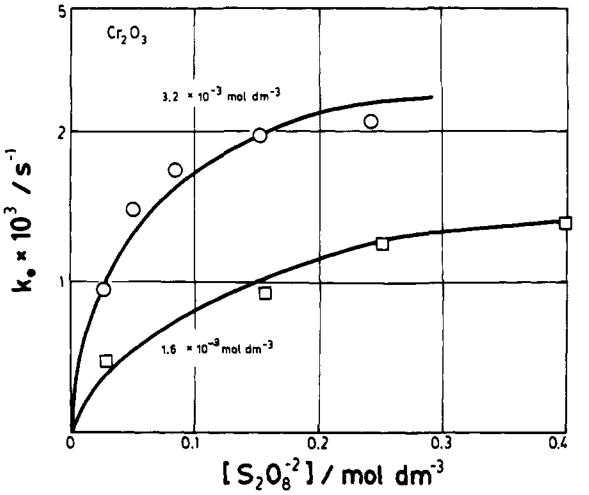

Figure 4. Plots of k as a function of $[S_2O_8^{2-}]$ at 65 °C in the presence of 2.50 mol dm^{-3} of H_2SO_4 and $AgNO_3$: (a) 3.2×10^{-3}; (b) 1.6×10^{-3} mol dm^{-3}.

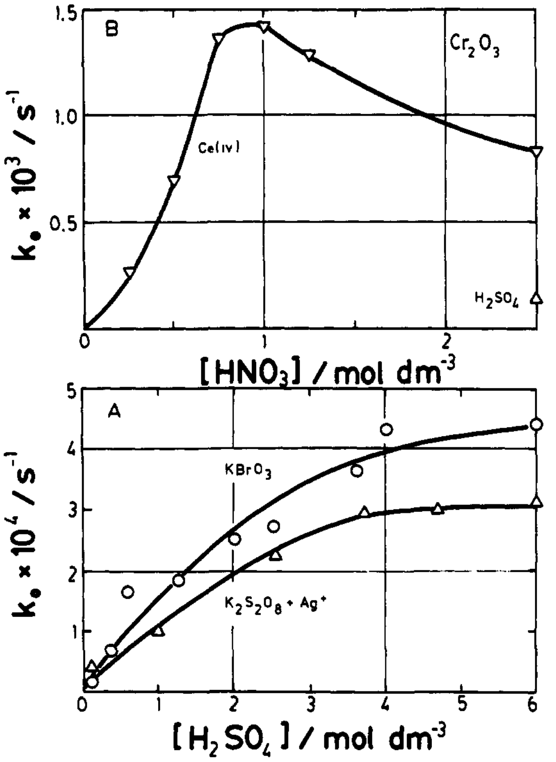

Figure 5. Dependence of k on the acid concentration at the constant oxidant concentrations and temperatures: (A) 0.1 mol dm^{-3} of $KBrO_3$, 65 °C, and 0.085 mol dm^{-3} $K_2S_2O_4$ + 3.2×10^{-3} mol dm^{-3} $AgNO_3$, 65 °C; (B) 4×10^{-3} mol dm^{-3} Ce(IV), 25 °C.

In the case of peroxodisulfate, Figure 4 shows that k is proportional to Ag^+ at $[S_2O_8^{2-}]$ = 0.16 M. The application of eq 9 to these data demonstrates that k_{max} increases with increasing $[Ag^+]$, while K_S remains constant.

The values of k as a function of the sulfuric acid concentration in the presence of two different oxidizing agents is presented in Figure 5A; plots of log k vs log $[H^+]$ yield orders changing from 1.0 to 0.46 for BrO_3^- and from 1.2 to 0.6 for $S_2O_8^{2-}$. The effects of both H_2SO_4 and HNO_3 were studied in experiments with Ce(IV) as oxidant. Figure 5B shows that the dissolution of the oxide A proceeds faster with increasing $[HNO_3]$ until a maximum is reached at $[HNO_3] \sim 1$ mol dm^{-3}; at still higher acidity the rate decreases somewhat. The measurements with oxide B (not shown) are in reasonable agreement, once the data are corrected for the difference in the surface area.

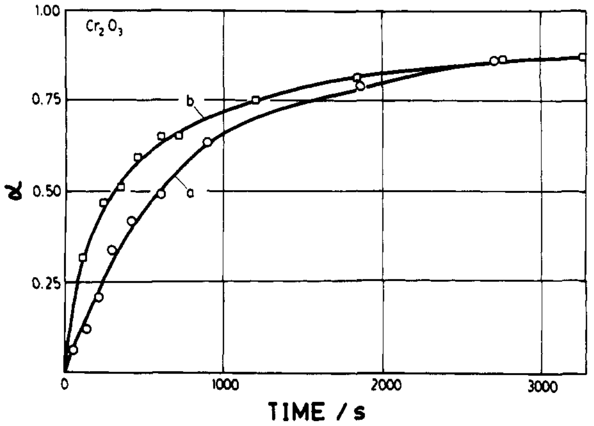

Figure 6. Fraction of solid dissolved as a function of time in 4×10^{-3} mol dm^{-3} of Ce(IV) + 1 mol dm^{-3} of HNO_3 at 25 °C: (a) oxide A; (b) oxide B.

Also included in Figure 5B is the rate at 2.5 mol dm^{-3} H_2SO_4, which is appreciably slower (by a factor >300) than in HNO_3 under otherwise identical conditions.

The rate of dissolution by MnO_4^- is not very sensitive to acidity[19] in the range 0.25–2.50 mol dm^{-3}.

Comparison of the Behavior of the Different Oxide Samples. The reaction with Ce(IV) was used to explore the difference in reactivities of oxides A and B. Figure 6 compares the α–t relationship for the two samples in 4×10^{-3} mol dm^{-3} Ce(IV) and 1 mol dm^{-3} HNO_3, which yield $k = 1.42 \times 10^{-3}$ s^{-1}, or $k' = 8.17 \times 10^{-4}$ g m^{-2} s^{-1} for A and $k = 4.0 \times 10^{-3}$ s^{-1}, or $k' = 3.83 \times 10^{-4}$ g m^{-2} s^{-1} for B. The rates calculated per unit area differ only by a factor of ~2, despite the very different history of both solids.

Discussion

The above data can be interpreted on the basis of the known behavior of the used oxidants in homogeneous solutions, the chemistry of Cr(III), and the well-established patterns of anion and cation adsorption onto metal oxides.

The mechanism of oxidation of aqueous Cr(III) by oxoanions and Ce(IV) will be discussed first. The hydrated species, $Cr(H_2O)_6^{3+}$, is inert toward substitution because of its d^3 electronic configuration. Typical half-lives for water exchange in $HClO_4$ media vary from 30 to 80 h at 27 °C;[22] oligomers formed by hydrolyzed Cr(III) are not less stable toward substitution than $Cr(H_2O)_6^{3+}$. Furthermore, on oxolation, the breaking of oxo bridges becomes even more difficult unless proton attacks restore the hydroxo bridge.

Because of these features, the substitution at surface Cr(III) centers is not particularly fast and, more importantly, it does not bring about noticeable enhancement of the rate of oxo bond breakage.

Oxidants are known to substantially increase the rate of water exchange in $Cr(H_2O)_6^{3+}$.[20] This effect is very important in the case of Ce(IV) and less so for Cr(VI), which is certainly related to the mechanism of oxidation.

In general, mechanisms of oxidation by oxo anions involve a previous formation of M–O–X bridges ("esterification"). In view of the inertness of M = Cr(III) toward substitution, such esters are formed through the breakage of O–X bonds within the oxoanion. It is well established that in such cases the rates of oxidation follow the same trends as the rates of substitution on X.[21]

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The kinetics of oxidation of $Cr(H_2O)_6^{3+}$ by the oxidants used in this work has been the subject of several reports. The best discussed case is that of Ce(IV),[22] for which the following mechanism has been postulated:

$$\mathrm{Ce^{IV} + Cr^{III} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ce^{III} + Cr^{IV}} \tag{10}$$

$$\mathrm{Ce^{IV} + Cr^{IV} \xrightarrow{k_3} Ce^{III} + Cr^{V}} \tag{11}$$

$$\mathrm{Ce^{IV} + Cr^{V} \xrightarrow{fast} Ce^{III} + Cr^{VI}} \tag{12}$$

Although the detailed nature of the equilibrium 10 is not discussed, it is noted that it is also responsible for the enhancement of the water exchange in $Cr(H_2O)_6^{3+}$. It seems likely, therefore, that reaction 10 includes the formation of a binuclear ion that may be atacked by another Ce^{IV} to yield Cr^{V} without the need to involve Cr^{IV} as an intermediate:

$$\mathrm{Ce^{IV} + Cr(H_2O)_6^{3+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ce^{IV}{-}O{-}Cr^{III}(H_2O)_5} \tag{13}$$

$$\mathrm{Ce^{IV} + Ce^{IV}{-}O{-}Cr^{III}(H_2O)_5 \xrightarrow{k_3} 2Ce^{III} + Cr^{V}} \tag{14}$$

The information in the literature about the oxidation of aqueous Cr^{3+} by MnO_4^-, BrO_3^-, and $S_2O_8^{2-}$ (Ag^+) is more scanty. Except for the last species it seems, however, reasonable to accept that the mechanism involves substitution on the central atom of the oxidant, assisted by preceding protonation, and further formation of a dinuclear complex with highly reactive intermediate oxidation state ions. For example, the mechanism of the oxidation of the Fe^{2+} by MnO_4^- is given by[23] (rds = rate-determining step):

$$\mathrm{MnO_4^- + Fe^{2+} \rightleftarrows O_3MnOFe^+} \tag{15}$$

$$\mathrm{O_3MnOFe^+ \xrightarrow{rds} Fe(III) + Mn(VI)} \tag{16}$$

The former equilibrium involves the substitution of one H_2O in the Fe(II) coordination sphere by MnO_4^-; in the similar oxidation reaction of Cl^-, this ion substitutes OH^- in the coordination sphere of Mn(VIII).[24] Although outer-sphere oxidations by MnO_4^- have also been postulated (e.g., of SO_3^{2-}),[25] these processes seem less important in heterogeneous systems.

The rate of oxidation of $Cr(H_2O)_6^{3+}$ by $S_2O_8^{2-} + Ag^+$ is known to be first order in Ag^+ and zero order in Cr(III); the order in $S_2O_8^{2-}$ is fractional.[26-28] The mechanism involves the generation of some very reactive intermediate(s) of Ag^+, without participation of Cr(III).

The general trends in the adsorption of oxoanions and hydrolyzable cations onto metal oxides will be considered next.

Any of the current models of the metal oxide/water interface can be used to describe the experimental results. Without entering into the detailed structure of the double layer, the approach of Dzombak and Morel[29] will be used.

Chemisorption of anions of the XO_n^{m-} type is taken as a process of substitution for OH^- in the first coordination sphere of surface metal ions. In view of the noted inertness of Cr(III), it is again inferred that one X–O bond is broken according to

$$\mathrm{{\equiv}Cr{-}OH + HO{-}XO_{\mathit{n}-1} \rightleftarrows {\equiv}CR{-}O{-}XO_{\mathit{n}-1} + H_2O} \tag{17}$$

In eq 17 charges are left unspecified. A buildup of the charge at the interface severely limits the extent of surface complexation, unless the process involves enough H^+ ions to establish electroneutrality. Thus, a very steep rise in affinity is noted as the pH is lowered to values determined by the pK of the acid oxidant and of the surface, respectively.

Chemisorption of hydrolyzable cations follows the same principle. Here, however, the requirement of electrical neutrality defines a steep increase in affinity when pH *increases* beyond a certain threshold value, again defined by the hydrolysis constants of the cations and the pK_a value of the surface OH groups. The interpretation of Ce(IV) adsorption is more involved because the polymerization equilibria must be taken into account. In the studied acidity range, Ce(IV) forms a suite of polymeric cations such as $Ce_2(OH)_2^{6+}$, $Ce_2(OH)_3^{5+}$, $Ce_2(OH)_4^{4+}$, and $Ce_6(OH)_{12}^{12+}$, and speciation changes appreciably when pH changes.[8] It is well-known[30] that polymerization brings about a large increase in adsorption affinity, and the adsorption of Ce(IV) is therefore expected to increase strongly as the acidity decreases in the range $1 > [H^+] > 0.1$.

The dependence of the rates of dissolution on ligand concentration follows the trend expected for the chemisorption equilibrium. The values of k_{max} and K_S given in Table I are related to the rate at the total coverage and to the equilibrium adsorption constant in the Langmuir-type adsorption isotherm. The dissolution of chromium(III) oxide takes place under rather different conditions in the presence of Ce(IV) and MnO_4^- (25 °C suffices for a rather fast dissolution), as compared to BrO_3^- and $S_2O_8^{2-}$ (Ag^+) (65 °C is required). The K_S values are in principle less sensitive to the temperature and the previous history of the oxide, yet the dependence on the pH is important. The order of the complexation constant K_S is given by $Ce(IV) \gg S_2O_8^{2-} > MnO_4^- > BrO_3^-$, the hydrolyzable cation Ce(IV) being as expected more strongly adsorbed. The dependence on HNO_3 of the rate of dissolution by Ce(IV) (Figure 5B) shows a bell shape, resulting from an increasing adsorption affinity (K_S) combined with a decreased rate of reaction (k_{max}) as the acidity decreases. The drastic decrease of the rate in sulfuric acid (Figure 5B) can be attributed to the complexation of Ce(IV) by sulfate to $CeSO_4^{2+}$ and concurrent desorption. It was indicated previously that maxima in the k vs pH plots correlate with the dependence of the adsorption affinity of anions onto iron oxides.[2,29,31] All constants are low for the studied oxoanions, which is characteristic of anions of strong acids; the somewhat larger affinity of $S_2O_8^{2-}$ is due to its charge and size. The constancy of K_S for the system $S_2O_8^{2-} + Ag^+$ at two different $[Ag^+]$ concentrations demonstrates that the chemisorption equilibrium does not involve Ag^+.

Only limited conclusions can be extracted by comparing k_{max} values, which are expressed for unit area as k'_{max} in Table I. For $S_2O_8^{2-}$ the latter parameter is proportional

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to Ag^+ and the dissolution probably involves a slow attack of Ag(II), generated in solution, on the surface $\equiv Cr—S_2O_8^{2-}$ complexes.

The value of k'_{max} is in fact a composite number:

$$k'_{max} = k^{int}_{max}\Gamma_{sat} \tag{18}$$

The variations observed in Table I may arise from different surface densities at saturation (Γ_{sat}) or from inherent different reactivities (k^{int}_{max}). The most important conclusion is that the order of k'_{max} values does not reflect the actual ability of different reagents to dissolve chromium oxide. For instance, the highest tabulated value, which is for BrO_3^-, is in fact an extrapolated figure, not achievable in practice, whereas the maximum rate is easily obtained with Ce(IV) (Figure 3).

For the set of reagents that react by similar mechanisms (except for $S_2O_8^{2-} + Ag^+$), the aggressiveness toward Cr_2O_3 is related more to K_S than to k_{max}. The precursor formation seems to be as important on the surface of the oxide as in homogeneous solutions.

The acid dependence of the dissolution rate (Figure 5) results from the acid influence of K_S and k_{max}. A detailed analysis would require the measurement of this dependence at various oxidant concentrations, especially where saturation rates cannot be achieved. Only in the case of Ce(IV) can the effects of acidity on K_S and k_{max} be solved. As stated, K_S is expected to decrease with increasing acid concentration, and the right branch in Figure 5B is due to this effect. The descending branch in alkaline media must be attributed to the requirement of protons to bring about dissolution, i.e., the influence on k_{max}. The latter data can be fitted, within the error margins, by either first- or second-order rate laws on $[H^+]$. In the standard surface complexation approach,[3] this dependency is explained by identifying a peculiar surface complex, among the many that may form, as the reactive species. Thus, the sensitivity of k_{max} to pH is explained not as the change in the rate of dissolution but as the change in surface speciation; it is then further assumed that the reactive species dissolves at a rate that is pH independent. Following this line of reasoning, the effect of pH on K_S suffices to explain all our experimental results. There are other well-documented examples, in which the reactivity of surface complexes seems to be pH independent; there is no evidence, however, that this is a general feature and, furthermore, the surface density of anions at the "maximum" coverage usually is a function of the pH.[32,33] A pH dependence of k^{int}_{max} and/or Γ_{sat} may be embodied in the results.

In the redox chemistry of aqueous Cr(III) → Cr(VI) species, the barriers are seemingly associated with the kinetic stage Cr(IV) $\rightleftarrows$ Cr(V), at which a change in the coordination number takes place; it is tempting to conclude that the same stage controls the dissolution behavior.

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Registry No. Cr_2O_3, 1308-38-9; Ce, 16065-90-0; MnO_4^-, 14333-13-2; BrO_3^-, 15541-45-4; $S_2O_8^{2-}$, 15092-81-6; Ag^+, 14701-21-4.

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Preparation, Characterization, and Pyrolysis of $[-B_{10}H_{12}\cdot diamine]-_n$ Polymers: A New Route to Boron Nitride

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Polymers of type $[-B_{10}H_{12}\cdot diamine]-_n$ have been prepared by reaction of decaborane(14) with various diamines, including $H_2NCH_2CH_2NH_2$, $Me_2NCH_2CH_2NMe_2$, $HN(CH_2CH_2)_2NH$, and $N(CH_2CH_2)_3N$ in diethyl ether solution. The polymers, all white solids, were characterized by elemental, thermogravimetric, and thermomechanical analysis and molecular weight determinations. The synthesis and characterization of copolymers and end-capped oligomers are also described. Pyrolysis of such polymers in a stream of argon to 1000 °C gave boron carbonitride in high yield. Pyrolysis in a stream of ammonia gave almost carbon-free boron nitride. Heating of these amorphous ceramics to 1500 °C gave a crystalline material. The pyrolysis mechanism involves early conversion of the covalent polymer, by proton transfer from boron to nitrogen, to a nonvolatile diammonium salt of the $[B_{10}H_{10}]^{2-}$ anion. These polymers serve as low-loss binders for ceramic powders and as precursors for ceramic monoliths. Short (5 cm) fibers could be drawn from syrups of such polymers in DMF; subsequent pyrolysis gave ceramic fibers.

Introduction

There is much current interest in boron-containing ceramics: boron nitride, boron carbide, and metal borides. In particular, recent efforts have been focused on boron nitride.[1] A variety of methods exists for the preparation of hexagonal boron nitride powder, and this material is an article of commerce.[1] A new direction in ceramics processing, the pyrolysis of processable (i.e., soluble or fusible) polymers ("preceramic polymers"[2]), which has been applied

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