Reactions of Solid Iron(III) Oxides with Aqueous Reducing Agents

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Summary One-electron reducing agents dissolve oxides containing Fe^{III} including 'insoluble' nickel ferrite; the mechanisms of such reactions can be interpreted by analogy with homogeneous electron-transfer reactions.

Oxide dissolution is of major importance in the extraction of metal from ores, and in the descaling of high temperature water-cooled plants. At present, strong acids or chelating agents are normally used in these processes. Many studies have been made of the mechanisms of dissolution, both experimental and theoretical.[1] The effects of added redox couples have been investigated.[2] Although it has long been known that iron metal can reduce Fe_2O_3 to give Fe^{2+} in solution,[3] only Zabin and Taube,[4] and recently Bradbury,[5] have considered the reaction of an aqueous reducing agent with a solid oxide as a redox process. We have found that many reducing agents dissolve iron(III) oxides, often many orders of magnitude more rapidly than conventional reagents, and we report here the results of a preliminary study of the kinetics and mechanisms of some of these reductive dissolution reactions.

α-Fe_2O_3, Fe_3O_4, and $NiFe_2O_4$ all contain Fe^{III} as the major metal ion. All are slow to dissolve even under conditions of very high thermodynamic solubility, indeed, nickel ferrite is generally regarded as insoluble on kinetic grounds.[6] However, the use of a suitable one-electron reducing agent leads to the rapid reduction of the Fe^{III} with resulting dissolution of the solid. Bradbury[5] showed that two-electron reductants react very slowly, if at all, whereas dithionite and thioglycollic acid react at an appreciable rate with Fe_2O_3. Drawing on the analogous reactions of Fe^{III} in solution, we have studied the reactions of these oxides with reagents based on Cr^{II}, V^{II}, V^{III}, and Fe^{II}.

Reactions were carried out by treating a weighed amount of finely powdered oxide with a large excess of reductant, and determining the amount of metal ions released as a function of time. A cubic rate law of the form in equation (1) was found where C and C_∞ refer to the concentrations of

$$(1 - C/C_\infty)^{1/3} = 1 - kt \qquad (1)$$

dissolved metal, and k is an observed rate constant. This law can be derived from the assumption that the rate is proportional to the instantaneous surface area and the approximation of uniform, spherical particles, k then includes terms in the oxide density and the mean radius, both of which are constant for a batch of oxide. Dividing by the reductant concentration yields an empirical second-order rate constant. Representative values are given in the Table, examples of reaction rates with acids and two-electron reductants are included for comparison. First-order dependence on reductant concentrations was observed in many reactions, but has not been verified in every case.

The order of reactivity is the same for each reductant, $Fe_2O_3 > Fe_3O_4 > NiFe_2O_4$, and for each oxide the order of reactivity of the reductants is also the same. In view of the variations in conditions, and the lack of complete rate laws in some cases, this constancy is probably only approximate.

The mechanisms of these reactions can be considered in detail. Thioglycollic acid reduces Fe^{3+}_{aq} *via* a co-ordinated intermediate.[7] A similar mechanism is possible here, with adsorption of the reductant at the oxide surface, and chemical bonding, such bonding has been observed with other chelate ligands.[8,9]

The reactions with Cr^{2+}_{aq} also have more than one possible mechanism. With all three oxides, the rate of reaction in dilute perchloric or sulphuric acid is very slow. A rate increase of four orders of magnitude, or greater, is obtained on the addition of chloride, and the rate law with Fe_2O_3 shows k proportional to $[H^+][Cl^-]$. The major Cr^{III} product is $CrCl^{2+}$. Zabin and Taube[4] pointed out that such results can be explained by participation of chloride *via* the reactive species $CrCl^+$. However, we feel that an inner-sphere mechanism is much more likely. Halide ions bind to the surface of similar oxides,[8] and such ions probably provide a facile pathway for inner-sphere electron transfer. The great difference in rates between chloride-free and chloride-assisted reactions seems more consistent with such a mechanism, since the addition of chloride to outer-sphere oxidants only leads to small changes in their reactivity to Cr^{2+}.[10] The analogy may be drawn between the reductive dissolutions of Fe^{III} oxides in chloride media and the well known dissolution of $CrCl_3$ by Cr^{2+}.

The reductions with trisbipyridylchromium(II) [$Cr(bipy)_3^{2+}$] and trispicolinatovanadium(II) [$V(pic)_3^-$] are outer-sphere. Both complexes are strongly bound,[11] and co-ordinatively saturated. The complex $V(pic)_3^-$ is a strong reductant, with $E^\circ = -0{\cdot}41$ V, based on the stability constants of V^{II} and V^{III},[12] and reduces very rapidly such species as $Co(NH_3)_6^{3+}$ and $Co(ethylenediamine)_3^{3+}$.[13] The rate laws of some of the reactions of these reductants have been studied in detail. The reaction between Fe_2O_3 and $Cr(bipy)_3^{2+}$ is first order in Cr^{II}, and has an activation enthalpy of 7·2 kcal mol^{-1}† (pH 6·2, 0·1 M cacodylate). The rate increases by a factor of three between pH 7 and 5·5. The reduction of $NiFe_2O_4$ by $V(pic)_3^-$ has been fully investigated, and will be published in detail elsewhere.[13] A brief summary of the major results of this study is given here. The activation enthalpy is 15 kcal mol^{-1} (pH 4·4, 0·1 M acetate), and the pH dependence shows a ten-fold increase in rate between pH 6 and 3. The pH effect can, in both cases, be assigned to

Table. Empirical second-order rate constants for oxide dissolution.[a]

Reductant	pH	$T/^\circ C$	$k_2(Fe_2O_3)$	$k_2(Fe_3O_4)$	$k_2(NiFe_2O_4)$
H_2SO_4 (2M)	>0	60	$6{\cdot}5 \times 10^{-4}$	—	$3{\cdot}9 \times 10^{-7}$
HCl (1M)	0	60	$4{\cdot}2 \times 10^{-3}$	1×10^{-3}	$1{\cdot}3 \times 10^{-6}$
Oxalate	5	60	$2{\cdot}8 \times 10^{-5}$	—	$\leqslant 5 \times 10^{-6}$
Catechol	3	80	$\leqslant 10^{-3}$	—	—
TGA[b]	3·5	80	0·13	—	0·001
Cr^{2+}/Cl^-[c]	1	40	1·1	0·10	0·011
$Cr(bipy)_3^{2+}$	5·4	60	26	—	0·036
V^{2+}	1	25	50	8·3	0·040
$V(pic)_3^-$[d]	4·4	80	>100	$\geqslant 80$	2·2

[a] Units are $l\ mol^{-1}\ min^{-1}$, $k_{obs}/[H^+]$ or $k_{obs}/[red]$. [b] Thioglycollic acid. [c] 0·1 M Cl^- (see text). [d] pic = picolinate = pyridine-2-carboxylate. Some reactions have also been investigated with V_{aq}^{3+}, V^{III} (citrate), $V(pic)_3$, and Fe^{II} (ethylenediaminetetra-acetate), all of which reduce Fe_2O_3 at measurable rates.

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† 1 cal = 4·184 J

the protonation of surface oxygen ions, making the Fe^{III} ions more readily reducible. The fact that both reactions show the same trend implies that the effect is not simply due to electrostatic interactions. With all reductants used the reduction of Fe^{III} ions in $NiFe_2O_4$ is accompanied by the parallel dissolution of Ni^{2+}.

The reaction of Fe_2O_3 with $V(pic)_3^-$ is too rapid to be measured by sampling methods. It has been suggested that these rates are approaching the diffusion-controlled limit for solid–solute reactions.[14]

We also assign an outer-sphere mechanism to the reductions by V^{2+}_{aq}; the apparent inability of Cr^{2+} to utilise surface-bound water or other oxygen atoms at the interface in a rapid inner-sphere reaction suggests that such a pathway is not available for V^{2+} either. Outer-sphere correlations obtained in solution are not applicable here; for example, $Cr(bipy)_3^{2+}$ usually reacts much faster than V^{2+} in solution reactions.[15]

The question of one- or two-electron reactions arises both with V^{II} and with Cr^{II} reductants. The stoicheiometry found with Fe_2O_3 is 1 : 1 Fe^{III}: Cr^{II} and 2 : 1 Fe^{III}: V^{II}, both for aquo and chelated reductants in the presence of excess of oxide. The absence of dimeric Cr^{III} products implies that one-electron transfer is the major route in the chloride-assisted reaction. Simultaneous, two-electron transfers are generally considered unlikely in outer-sphere reactions, and we have found that both V^{3+} and $V(pic)_3$ react quite rapidly with Fe_2O_3, and so successive one-electron reactions seem probable with the V^{II} reductants.

Thus we conclude that heterogeneous electron-transfer reactions involving solid oxidants and aqueous reductants can be analysed by drawing on the analogies of similar, homogeneous solution reactions. However, a detailed mechanistic assignment cannot always be made as easily as in homogeneous cases, and interfacial phenomena, such as adsorption of reagents, can introduce new considerations.

This work was performed in part under a contract with the Electric Power Research Institute, and is published by permission of the Central Electricity Generating Board. We thank Drs. D. Bradbury, T. Swan, and C. J. Wood for their advice and encouragement.

(*Received, 5th August* 1980; *Com.* 863.)

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