Table I. Spectroscopic Parameters

compd	$^{31}P\{^1H\}$ NMR spectra[a] δ	$^{31}P\{^1H\}$ NMR spectra[a] *J*, Hz	IR spectra[b] ν(CO), cm^{-1}
(dpmp)PdCl$_2$	18.8 (d)	57 (*J*(P–P))	. . .
	−40.7 (t)		
(dpmp)Mo(CO)$_4$	23.3 (d)	79 (*J*(P–P))	2010, 1923, 1900, 1885 sh
	−37.3 (t)		
Cl$_2$Pd(μ-dpmp)PdCl$_2$(NCCH$_3$)	22.4 (s)		
	5.6 (s)		
[Cl$_2$Pd(μ-dpmp)]$_2$Rh(CO)Cl	19.3 (s)		1986 sh, 1975
	9.3 (d)	128 (^{1}*J*(Rh–P))	
[Cl$_2$Pt(μ-dpmp)]$_2$Rh(CO)Cl	5.9 (d)	128 (^{1}*J*(Rh–P))	1980
	0.0 (s)	3525 (^{1}*J*(Pt–P))	
[(OC)$_4$Mo(μ-dpmp)]$_2$Rh(CO)Cl	23.8 (s)		2020, 1980, 1930 sh, 1900
	9.8 (d)	125 (^{1}*J*(Rh–P))	
dpmp	−33.0[c]	115 (*J*(P–P))	
	−22.5[c]		
	−33.8[d]		

[a] Recorded at 81 MHz with 85% H_3PO_4 external standard in dichloromethane solution at 25 °C. Abbreviations: s, singlet; d, doublet; t, triplet. [b] From Nujol mulls. [c] Second-order spectrum, chemical shift of terminal phosphorus atoms. [d] Chemical shift of internal phosphorus atom.

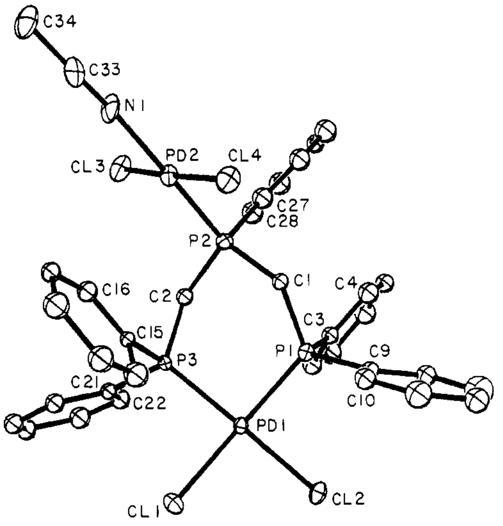

Figure 1. Perspective drawing of $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2\cdot CH_3CN$. Some selected bond distances (Å) and angles (deg) are as follows: Pd(1)–P(1), 2.239 (4); Pd(1)–P(3), 2.241 (4); Pd(1)–Cl(1), 2.324 (3); Pd(1)–Cl(2), 2.348 (4); Pd(2)–Cl(3), 2.300 (4); Pd(2)–Cl(4), 2.288 (4); Pd(2)–P(2), 2.230 (4); Pd(2)–N(1), 2.065 (14); Cl(1)–Pd(1)–Cl(2), 91.8 (1); P(1)–Pd(1)–P(3), 93.8 (1); Cl(3)–Pd(2)–Cl(4), 176.5 (2); Cl(3)–Pd(2)–N(1), 89.9 (4); Cl(4)–Pd(2)–N(1), 91.5 (4).

the yellow precipitate from acetonitrile. The structural results are shown in Figure 1.[12] The triphosphine ligand has assumed a skew-boat conformation, which allows the two palladium ions to be quite remote from one another (Pd···Pd = 5.854 Å).

The spectroscopic results in Table I suggest that phosphorus–phosphorus coupling in these complexes may be a useful indicator of structure. While the P–P coupling in the chelated complexes is less than in the free ligand, it is still substantial. In 1 and related species it it also sizable, generally ca. 50 Hz. However, in the last four examples in the table where chelated dpmp is acting as a bridge (probably with a skew-boat ring conformation), the P–P coupling is too small to be resolved and the natural line widths indicate that it must be less than 15 Hz.

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Registry No. 2, 84751-00-8; **3**, 86217-32-5; **4a**, 86217-34-7; **4b**, 86217-35-8; **5**, 86217-36-9; $Cl_2Pd(\mu\text{-dpmp})PdCl_2(NCCH_3)$, 86217-33-6; (dpmp)PtCl$_2$, 86217-37-0; BMo(CO)$_4$ (B = norbornadiene), 12146-37-1; (CO)$_4$Rh$_2$(μ-Cl)$_2$, 14523-22-9; (PhCN)$_2$PdCl$_2$, 14220-64-5.

Supplementary Material Available: Listings of atomic fractional coordinates, thermal parameters, and bond lengths and distances for $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2\cdot CH_3CN$ (5 pages). Ordering information is given on any current masthead page.

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[12] Orange crystals of $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2\cdot CH_3CN$ were obtained from gradual cooling of a saturated acetonitrile solution of the complex. Crystal data and details of refinement: space group $P2_12_12_1$ (No. 19); $T = 140$ K; $a = 12.302$ (4), $b = 12.483$ (3), $c = 24.316$ (5) Å; $Z = 4$; Mo Kα, $\lambda = 0.71069$ Å; P2 diffractometer; ω scans; 2θ(max) 50°; blocked-cascade least squares; $R = 0.069$; 3193 reflections, $I > 3\sigma(I)$; 234 parameters.

Heterogeneous Electron Transfer as a Pathway in the Dissolution of Magnetite in Oxalic Acid Solutions

Sir:

The dissolution of metal oxides is a process of importance in several fields such as hydrometallurgy, passivity of metals, and cleaning of boilers and metal surfaces in general. The basic ideas concerning the process of dissolution of metal oxides were put forward by Engell,[1] Wagner and Valverde,[2,3] and Vermilyea,[4] and the subject was reviewed by Diggle[5] some years ago. For the specific case of dissolution of iron oxides by acidic solutions containing complexing agents, our recent review[6] and references therein may be consulted. In the case

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of iron(III) oxides, it has been shown[7,8] that reduction of Fe(III) to Fe(II) brings about a large increase in the rate of dissolution. The origin of this increase is the greater lability of Fe(II)–O bonds as compared to Fe(III)–O bonds; it is thus a phenomenon similar to the observed increase in dissolution of metal oxides in the presence of Cr(II) and the catalysis by the latter of the homogeneous substitution reactions of Cr(III).[9,10]

Oxalic acid is one of the most effective reagents for dissolution of magnetite under mild acid conditions. Magnetite is the oxide that confers passivity to steel surfaces.[11] In the present communication we discuss the more salient features of the mechanism of dissolution of magnetite by oxalic acid solutions, with special focus on the role played by ferrous ions in the process.

Reagents were of analytical purity or better and were used as provided. Magnetite was prepared by oxidation with potassium nitrate of a slurry of ferrous oxide hydrate in the presence of hydrazine.[12] The specific surface area of magnetite was measured on a Micromeritics surface analyzer by nitrogen adsorption and BET procedure. The value obtained was 9.7 $m^2\ g^{-1}$. Powder X-ray diffraction, scanning electron microscopy, Mössbauer spectroscopy, and analytical determinations showed the material to be highly crystalline, high-purity stoichiometric magnetite.

Kinetic experiments were carried out in a cylindrical beaker provided with a water jacket and a magnetic stirrer. A suspension containing 40 mg of magnetite in 150 cm^3 of an oxalic acid solution of adequate pH and concentration and containing also the desired amount of Fe(II) in the form of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was equilibrated for 24 h; the usual pH employed in this preconditioning stage was 7.6, under which condition no dissolution takes place. Dissolution was started by lowering the pH to 4.1. To avoid oxidation of Fe(II), nitrogen was continuously bubbled through the solution during the conditioning period and during dissolution. Periodically, samples of the well-stirred suspension were taken with a syringe and poured into a large volume of water containing thioglycolic acid and ammonia in excess. The resulting suspension was filtered through a Nuclepore membrane (pore size 0.45 μm), and the absorbance of the red complex at 530 nm was measured in a Shimadzu UV-210A spectrophotometer.[13,14] The amount of dissolved iron was calculated by using an extinction coefficient $\epsilon = (3.96 \pm 0.01) \times 10^2\ m^2\ mol^{-1}$.[15]

In the dissolution of metal oxides by noncomplexing agents, the transfer of both metal and oxide ions from the solid to solution must be considered, both being possible rate-determining steps.[4,5] In acidic complexing solutions, surface oxide or hydroxide ions are easily replaced by complexing ions.[16-18] Thus, the rate of dissolution is controlled by the rate of phase transfer of complexed metal cations. In order for this mechanism to be operative, it is essential as a first requirement that the reagent be strongly adsorbed on metal ions of the solid. The adsorption process of oxalic acid on magnetite has been characterized by measuring the electrokinetic mobility of magnetite particles in oxalic acid solutions. The results are shown in Figure 1; mobilities in indifferent electrolyte (KNO_3) taken from ref 19 are also shown for comparison. The large decrease (with sign inversion) of the mobility in the acidic range indicates the replacement of $Fe{-}OH_2^+$ by $Fe{-}(OOC^-)_2$ as the charge-bearing species on the interface.[19]

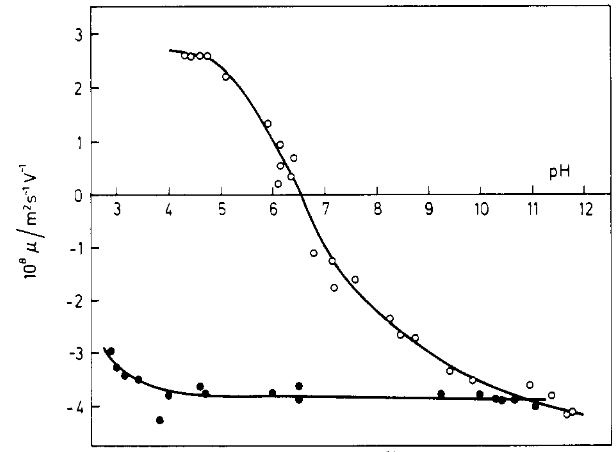

Figure 1. Electrokinetic mobilities μ as a function of pH of magnetite suspended in oxalic acid solutions (●) ([oxalic acid] = 2.4×10^{-3} mol dm^{-3}, ionic strength 2.8×10^{-2} mol dm^{-3}) and suspended in indifferent electrolyte solutions (○) (ionic strength 0.1 mol dm^{-3}). All experiments were performed at T = 30 °C.

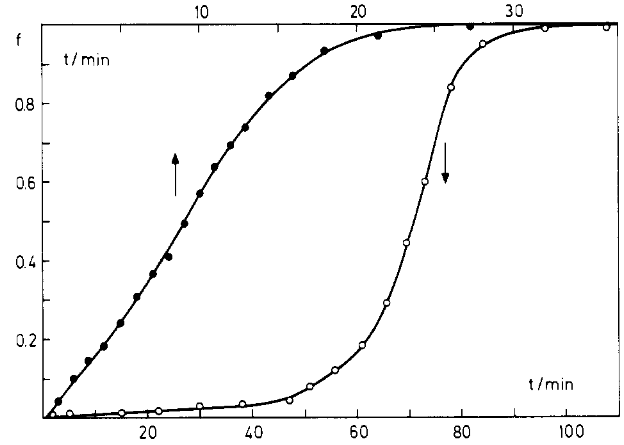

Figure 2. Dissolution of magnetite by oxalic acid (0.1 mol dm^{-3}), expressed as dissolved iron fraction (f) vs. time, with (●) and without (○) added Fe(II) (6×10^{-4} mol dm^{-3}). Both experiments were performed at pH 4.1 and T = 30 °C.

In the acidic pH range, ad~~sorption is followed by~~ dissolution, in a process that is characterized by rather well-defined induction periods. In the conditions of our experiments, i.e. 30 °C, 0.1 mol dm^{-3} oxalic acid, pH 4.1, this induction period is ca. 60 min. After the induction period, dissolution is very fast, being complete in around 20 min (see Figure 2, open circles).

The shape of the dissolution profile, expressed as a fraction f of solid dissolved as a function of time (Figure 2), is typical of an autocatalytic process, which may be due to several factors. The first possibility is that the surface of the solid needs to be conditioned; i.e., rather slow surface equilibration

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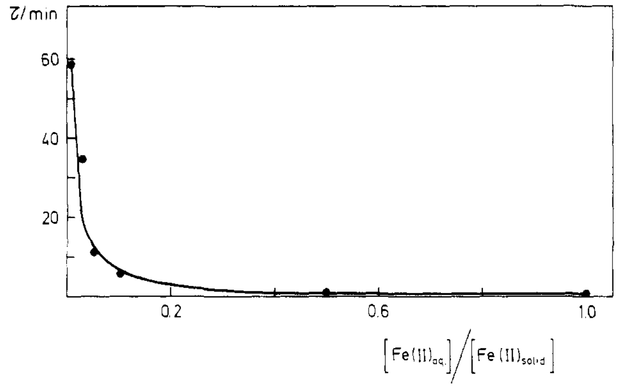

Figure 3. Induction period τ as a function of Fe^{II}(aq) concentration, expressed as its ratio respective to the concentration of Fe(II) originated by total dissolution of the solid. All experiments were performed at pH 4.1 and T = 30 °C.

processes may account for the induction period. This possibility was explored by preconditioning the solid in oxalate solutions at pH 8 for up to 7 days. The reaction profiles obtained were quite similar to the one shown in Figure 2 with an induction period corresponding to zero time of preconditioning. Furthermore, in another experiment, a partially reacted slurry was filtered off and the solid thoroughly rinsed. Upon resuspension of the solid in a solution of the same composition as the original, the induction time was observed again.

The influence of Fe(II) and Fe(III) concentration in solution was then explored. In the same Figure 2 we compare the kinetics of two similar runs, in one of which a ferrous salt had been added beforehand (solid circles); it can be seen that the induction period practically disappears. The same situation, with the induction period decreasing in a rather erratic fashion, is observed when ferric salt is added and the system is kept for some time in the light, in which case Fe(II) species are generated by photolysis of $Fe(C_2O_4)_3^{3-}$,[20] while if light is rigorously excluded, the induction period is not suppressed by addition of Fe(III). This indicates that the species involved in the autoacceleration of the dissolution reaction is the Fe(II) ion transfered from the solid to the solution.

Figure 3 shows the dependence of the induction period on Fe^{II}(aq) concentration; the plot shows that an initial ratio $Fe^{II}(aq)/Fe^{II}(s) = 0.2$ is enough to reduce the induction period to practically zero.

On the basis of all this evidence we propose the following mechanism for the dissolution of magnetite by oxalic acid solutions. As already mentioned, the first step must be the replacement of surface –OH groups by oxalate (eq 1; $-Fe^{III}-R$ indicates that this species is part of the solid).

$$-Fe^{III}-OH + {}^{-}OOC-COOH \rightleftharpoons -Fe^{III}(C_2O_4) + H_2O \quad (1)$$

An analogous equilibrium can in principle be written for Fe(II) of the solid; however, because of the relative strengths of Fe–O bonds, Fe(II) is expected to be released quickly as compared to Fe(III), and the dissolution rate is probably governed by Fe(III) phase transfer. During the induction period, Fe(III) complexed by oxalate must be dissolved according to eq 2. This must be a slow process, and this accounts for the induction period.

$$-Fe^{III}(C_2O_4) \rightleftharpoons Fe(C_2O_4)^{+}(\text{adsorbed}) \rightleftharpoons Fe(C_2O_4)^{+}(\text{bulk}) \quad (2)$$

During the induction period, when (2) is rate determining, Fe(II) builds slowly into solution. However, once a critical amount is reached, a new pathway gives rise to fast dissolution. This is the reductive dissolution through reactions 3 and 4.

$$Fe^{II}(C_2O_4)(\text{adsorbed}) + -Fe^{III}(C_2O_4) \rightleftharpoons Fe^{III}(C_2O_4)^{+}(\text{adsorbed}) + -Fe^{II}(C_2O_4) \quad (3)$$

$$-Fe^{II}(C_2O_4) \rightleftharpoons Fe(C_2O_4)(\text{adsorbed}) \rightleftharpoons Fe(C_2O_4)(\text{bulk}) \quad (4)$$

Either (3) or (4) may be rate determining. The reductive process may take place if the Fe(III) complex is stabilized in relation to the Fe(II) complex. Thus, ligands that stabilize Fe(II) are not effective in bringing about dissolution; this has been demonstrated with $Fe^{II}-CN^{-}$ complexes.[21]

In the presence of added Fe(II), the induction period disappears because reaction 3 takes place directly; a certain minimum amount of Fe(II) is required because competition for adsorbed oxalate must take place between $Fe^{II,III}(s)$, H^+, and added Fe(II).

Oxalate plays an unique role among complexing carboxylic ligands in the dissolution of magnetite; it not only facilitates the electron-transfer reaction (3) but also mediates in a relatively fast dissolution during the initial induction period (the induction period is much shorter than in the case of the dissolution of magnetite by ethylenediaminetetraacetic[22a] or nitrilotriacetic acid.[22b] This unique role has been used in the development of a very efficient scale removal formulation used in the decontamination of nuclear power plants.[23]

No direct evidence is provided by the present study as to whether (3) is an outer-sphere or inner-sphere electron transfer. Oxalate is known to be a very efficient bridging ligand in electron-exchange reactions involving Cr(III)/Cr(II),[24] Co(III)/Cr(II),[25,26] and Co(III)/Fe(II)[27,28] couples, and the activated state in the electron-transfer reaction (3) probably involves Fe(III) as the solid, Fe(II) in solution, and a bridging oxalate ion. It should be noted however that oxalic acid is in large excess in our system, and an outer-sphere transfer from $Fe(C_2O_4)_2^{2-}$(aq) to a surface $-Fe^{III}(C_2O_4)$ group cannot be ruled out.

Registry No. Magnetite, 1309-38-2; iron oxide (Fe_3O_4), 1317-61-9; iron, 7439-89-6; oxalic acid, 144-62-7.

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[PtCl(PEt$_3$)(CH(PPh$_2$S)$_2$)], a Novel C,S-Bonded Chelate with Dynamic Stereochemistry Controlled by a Metal–Ligand Pivot

Sir:

The monoanions (**1**) derived from acetylacetone and its dithio analogue have been extensively studied as ligands in inorganic chemistry. By contrast the analogous phosphorus-containing species (**2**) have been essentially ignored,[1] even

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