

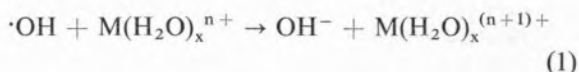


DO REACTIONS OF HYDROXYL RADICALS WITH METAL ION GO VIA OUTER SPHERE ELECTRON-TRANSFER (1)

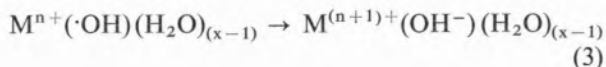
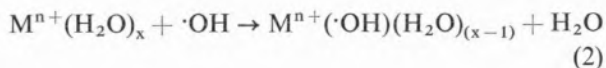
The logarithms of rate constants of reactions of hydroxyl radicals with metal ions in aqueous solution are plotted against experimental or theoretical one-electron oxidation potentials of the metal ions. Three types of behaviour become apparent. Certain ions show no relationship between log k and the E° value, which is interpreted in terms of rate determining ·OH radical addition or exchange. Rare earth and many transition metal ions show linear relationships between log k and E°. However, the line for the rare earths is not the same as that for the transition metals. Theoretical rates for electron-transfer reactions are calculated using Marcus theory, and it is suggested that the reaction of hydroxyl radicals with transition metal ions which cannot undergo rapid exchange of their water molecules probably proceeds via an outer sphere electron-transfer mechanism. With the rare earth ions the reaction may proceed via an inner sphere mechanism.

1 — INTRODUCTION

The reaction of the hydroxyl radical with metal ions in aqueous solution is probably the simplest example of oxidation of a charged species by a neutral molecule in the liquid phase, and a study of its mechanism may be expected to provide valuable information on the way oxidation occurs in more complex systems. Unfortunately, the mechanism of this reaction has not been unambiguously settled. The simplest possible mechanism involves direct electron-transfer [1], presumably *via* an outer sphere process [2] as in equation (1)



For electron-transfer reactions, correlations are frequently observed between the logarithm of the rate constant and the overall free energy change [3]. Such correlations have been treated theoretically by a number of workers [4]. Attempts to apply such a correlation to ·OH radical oxidation have so far had little success. Thus, while FARRAGGI and TENDLER [5] were able to demonstrate that the order of reactivity of ·OH with Sm (II), Yb (II) and Eu (II) follows the order of oxidation potentials of the divalent ions, BERDNIKOV [6] was unable to find any evidence for a correlation between the rate and overall free energy change for a rather wider range of hydroxyl radical oxidations of metal ions. This author, following an earlier suggestion by DAINTON *et al.* [7], has presented theoretical data to suggest that the reaction proceeds *via* a rate-limiting hydrogen abstraction by ·OH from a coordinated water molecule, followed by a rapid intramolecular electron transfer.



Abstraction of hydroxylic hydrogen atoms by alkoxy radicals has recently been observed by e. s. r. [8, 9]. The rate constant for this reaction,

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which may be expected to be of a similar order of magnitude to reaction (2), is $3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [8]. Whilst the coordination of water molecules to a positively charged metal ion may allow reaction (2) to be somewhat faster than this, hydrogen bonding in aqueous solutions will undoubtedly decrease the rate of hydrogen abstraction from the hydroxyl group [8], and it seems unlikely that reactions of hydroxyl radicals with metal ions which have rates of the order 10^9 – $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ proceed by this route.

Table 1

Oxidation potentials and rate constants for reactions of hydroxyl radicals with metal ions

Ion	Number of ions in fig. 1	k_{obs} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) ^{a)}	E° for $M^{n+} M^{(n+1)+}$ couple ^{a)} (V)
Ag(I)	1	6.3×10^9 [13]	−1.93 [29]
Au(I)	2	4.7×10^9 [1]	−0.9 ^{b)}
Ce(III)	3	7.2×10^7 [1]	−1.44 [29]
Cr(II)	4	1.2×10^{10} [26]	+0.41 [29]
Cr(III)	5	3.2×10^8 [1]	−1.5 [14]
Cu(II)	6	3.5×10^8 [1]	−4.6 [31]
Eu(II)	7	9×10^8 [5]	+0.43 [5]
Fe(II)	8	2.3×10^8 [27]	−0.771 [29]
Fe(CN) ₆ ^{4−}	9	1.1×10^{10} [1]	−0.356 [29]
Mn(II)	10	1.4×10^8 [1]	−1.60 [29]
Mo(CN) ₈ ^{4−}	11	5.8×10^9 [28]	−0.73 [28]
Pr(III)	12	1.4×10^{10} ^{c)}	−2.86 [32]
Ru(CN) ₆ ^{4−}	13	5.7×10^9 [28]	−0.86 [28]
Sm(II)	14	6×10^9 [5]	+1.55 [5]
Sn(II)	15	2.5×10^9 [1]	−0.1 ^{b)}
Ti(III)	16	3.0×10^9 [26]	−0.20 [29]
Tl(I)	17	7.6×10^9 [1]	−2.22 [12]
VO ²⁺	18	6.4×10^8 [26]	−0.9994 [29]
Yb(II)	19	3×10^9 [5]	+1.15 [5]

a) Numbers in brackets refer to references.

b) Estimated from the plot of E° against ionization potential for ions of the same charge [30]

c) Weighted mean of the values in Ref. [32]

Other important mechanisms which must be considered involve hydrogen abstraction followed by a rate determining electron-transfer, and an inner sphere mechanism involving substitution of one of the water molecules by the hydroxyl radical followed by electron-transfer.

Earlier attempts at identifying the mechanism of the reaction of hydroxyl radicals with metal ions have been hampered by the lack of both reliable kinetic data, and standard electrode potentials for one-electron oxidations. Matters have been considerably improved recently by the publication of an important review of the kinetics of $\cdot\text{OH}$ radical reactions [1], and in the present study possible correlations between kinetic data and metal ion oxidation potentials have been examined, with the objective of understanding the mechanism of oxidation of metal ions by hydroxyl radicals.

2 — RESULTS AND DISCUSSION

Rate constants for hydroxyl radical reactions with metal ions, and either experimental or theoretical oxidation (E° values) of the metal ion $M^{n+} | M^{(n+1)+}$ couples are presented in Table 1. Using this data, values of the logarithm of the observed rate constant

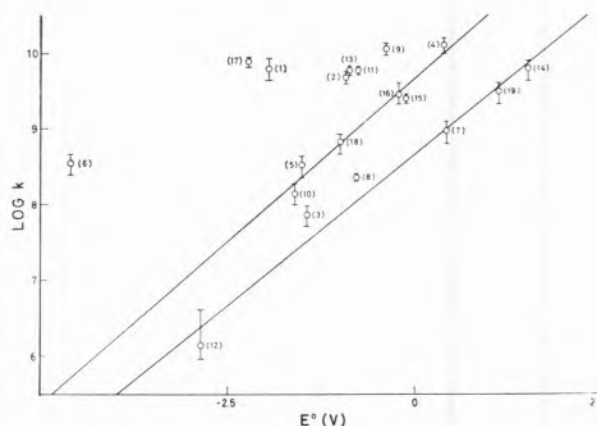


Fig. 1

Plot of $\log k_{\text{obs}}$ against standard oxidation potential for reaction of hydroxyl radical with metal ions. Numbers refer to number of ion in Table 1.

are plotted against the appropriate metal ion E° value (fig. 1). One potential problem in attempting a correlation such as this is that, because ligand rearrangement around the oxidized metal ion may follow electron-transfer, the equilibrium E° values measured by electrochemical techniques do not necessarily correspond to the same reaction which is studied kinetically. However, correcting the equilibrium E° values for ligand rearrangement is

only expected to alter them by at the most 0.2-0.3v, so that whilst this factor may alter the relative positions of some of the ions in the correlation plot, it is not expected to seriously affect its shape. From fig. 1 three clearly different types of behaviour are observed. For Cr (II), Ti (III), Sn (II), VO^{2+} , Cr (III) and Mn (II), a reasonable straight line is observed (least squares slope 0.85 ± 0.07). For the rare earth ions, a second, almost parallel line is observed (least squares slope 0.78 ± 0.07). With the other metal ions there is no correlation between the logarithm of the rate constant and the E° value. Strictly, we should correct the observed rate constants in the above plot for the diffusion of the reacting species [10]. However, this correction was found to make little difference to the general form of the graph, and as diffusion coefficients and sizes of the reacting species in solution are not known accurately, this correction was ignored for the correlation plot.

Possible explanations for the behaviour displayed on the graph can be given from a consideration of theoretical and literature data. Considering first the ions which show no correlation between $\log k$ and E° , Ag (I), Tl (I) and Au (I) (having a completed d shell) and Cu^{2+} undergo very rapid exchange of the coordinated water molecules [11], and it appears likely that the $\cdot\text{OH}$ radical will replace water at a similar rate (*ca* 10^9 - $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), so that the reaction with these ions probably occurs *via* substitution of water by the hydroxyl radical, followed by intramolecular electron-transfer. Experimental support for this comes from pulse radiolysis studies of aqueous solutions of thallium (I) [12], silver (I) and copper (II) [13]. BERDNIKOV [6] has suggested on kinetic grounds that in the reaction of hydroxyl radical with Cu (II) a complex is formed between these two species with no overall electron-transfer. This certainly seems likely on thermodynamic grounds if the theoretical potential (-4.6 V , 30) of the $\text{Cu}^{2+}|\text{Cu}^{3+}$ couple is correct. However, ROSSEINSKY [14] has suggested that the E° value for this couple should be considerably lower than this, so that copper (III) formation cannot be ruled out. With the three cyano complexes substitution is not possible, and it is possible that the reaction goes *via* outer sphere electron-transfer. On the other hand many other inorganic anions, including cyanide [15] and thiocyanate [16] react with

hydroxyl radical by addition, followed in the latter case by electron-transfer, and it is quite possible that such a mechanism is operative here too.

With both the rare earth and transition metal ions reasonable correlations are observed, suggesting the possibility of simple outer sphere electron-transfer. However, the ions fall on two different lines, implying different mechanisms for the two groups of metal ions. To obtain further information on the mechanism, theoretical estimates of the rate of outer sphere electron-transfer have been made using the theory of MARCUS [4, 10]. According to this theory the free energy of activation (ΔG^*) of an electron-transfer reaction can be related to the overall free energy change of the reaction (ΔG°) by the equation.

$$\Delta G^* = W + \lambda/4 + \Delta G^\circ/2 + (\Delta G^\circ)^2/4\lambda$$

where W is the difference between the work of bringing together reactants and separating products. This is small compared with the other terms, and is ignored in the present treatment. λ is a solvent rearrangement parameter, given by

$$\lambda = (1/2a_1 + 1/2a_2 - 1/a_{12})(D_{\text{op}}^{-1} - D_s^{-1})(\Delta Z)^2 e^2$$

where a_1 , a_2 and a_{12} are the effective radii of reactants and transition state, D_{op} and D_s are optical and static dielectric constants of the medium, ΔZ is the number of electrons transferred, and e is the electronic charge. From these, the activation-energy controlled rate constant (k_{act}) can be determined

$$k_{\text{act}} = Z \exp(-\Delta G^*/RT)$$

where Z is the collision number in solution, taken as $10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In the present calculations radii of the metal ions in solution were taken [14] as the crystal ionic radius plus 1.38 \AA (the contribution of the hydration sphere to the radius [17]. With VO^{2+} , the radius is assumed to be that of the VO^{2+} ion (1.93 \AA , [18]). The hydrated radius of the hydroxyl radical was assumed to be the gas phase $\cdot\text{OH}$ radical radius (from Ref. [19]) plus 1.38 \AA . The effective radius of the transition state (a_{12}) was considered to be the sum of a_1 and a_2 . An E° value of -1.9 V was taken for the $\text{OH}^-/\cdot\text{OH}$ couple [6, 20].

Values of the theoretical activation-energy-controlled rate constants for transition metal and rare earth ions are compared with experimental values in Table 2. The agreement between theoretical and experimental values is disappointing. This must be due in part to the large number of assumptions which have to be made for both reaction radii and E° values. However, the theoretical rates for the transition metal ions are of a similar order of magnitude to the experimental values, whilst those for the rare earth ions Sm^{2+} and Yb^{2+} are clearly not. These results support the idea that reaction between hydroxyl radicals and transition metal ions which do not have labile water ligands probably proceeds *via* outer sphere electron-transfer.

Table 2

Experimental and theoretical rate constants for reaction of hydroxyl radicals with metal ions

Ion	Ionic radius ^{a)} (Å)	Rate constants ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	
		Calculated	Observed
Cr(II)	0.89 [33]	1.10×10^{10}	1.2×10^{10}
Ti(III)	0.76 [18]	9.88×10^{10}	3.0×10^9
Sn(II)	0.93 [18]	9.13×10^{10}	2.5×10^9
VO^{2+}	1.93 [18]	8.10×10^8	6.4×10^8
Cr(III)	0.63 [18]	2.21×10^6	3.2×10^8
Mn(II)	0.80 [18]	1.02×10^6	1.4×10^8
Sm(II)	1.30 [33]	$< 10^4$	6×10^9
Yb(II)	1.22 [33]	1.87×10^5	3×10^9
Eu(II)	1.29 [33]	2.70×10^9	9×10^8
Fe(II)	0.74 [18]	1.13×10^{10}	2.3×10^8
Ce(III)	1.07 [18]	2.86×10^7	7.2×10^7

a) Numbers in brackets refer to references.

Further Marcus theory calculations were carried out on the reaction between hydroxyl radicals and rare earth ions. Rough agreement between theoretical and experimental rates was obtained if rare earth ion radii were assumed to be just the crystal ionic radii. Theoretical values obtained using this assumption were: Sm^{2+} , $k = 3.7 \times 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$; Yb^{2+} , $k = 6.0 \times 10^{10} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$; Eu^{2+} , $k = 8.4 \times 10^{10} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$. These calculations predict that the reaction of $\cdot\text{OH}$ radicals with Yb^{2+}

and Eu^{2+} should be controlled by diffusion ($k_{\text{diff}} = 1.1 \times 10^{10} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ calculated from the Debye equation [21] assuming diffusion coefficients of $2.3 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the hydroxyl radical [1], and $0.7 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the metal ions [22]), whereas in fact the rates are somewhat slower than that of the reaction of $\cdot\text{OH}$ and Sm^{2+} . It is not unreasonable that in these cases rough agreement between theory and experiment is observed by using the unhydrated crystal radius, as although rare earth ions are coordinated to a large number of water molecules in aqueous solution ($N = 12$ or 13 [23]), these are not bound very tightly and ligand exchange is rapid. Trivalent rare earth ions have rates 10^7 - $10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ for exchange of their water molecules [24], and the rates for the divalent ions would be expected to be even faster, so that the mechanism could possibly involve ligand exchange followed by rate limiting electron-transfer in a water-bridged complex between the metal ion and the hydroxyl radical. The mechanism in this case is probably best considered as inner sphere electron-transfer, and theoretical rates should be modified to allow for both diffusion and exchange processes. Inner sphere mechanisms have previously been reported for certain oxidations of Eu (II) [25].

3 — CONCLUSIONS

Both empirical correlation plots, and theoretical calculations suggest that a variety of mechanisms are responsible for the oxidation of metal ions by hydroxyl radicals. With transition metal ions which can undergo rapid exchange of coordinated water molecules reaction probably occurs by substitution followed by intramolecular electron-transfer. With rare earth ions, substitution to give a water-bridged metal ion-hydroxyl radical species, followed by rate limiting electron-transfer is suggested as a possibility. The reaction between hydroxyl radicals and transition metal ions which cannot undergo rapid exchange of their water molecules probably occurs *via* an outer sphere electron-transfer mechanism.

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RESUMO

O estudo da variação das constantes cinéticas das reacções entre iões metálicos e o radical hidróxilo em soluções aquosas com o potencial de oxidação dos mesmos iões para a transferência de um electrão revela três comportamentos distintos. Com alguns iões não se verifica qualquer correlação entre $\log k$ e E° o que parece ser devido ao facto de a velocidade das reacções estar controlada pelo passo cinético da adição ou da troca do radical $\cdot\text{OH}$. Com os iões das terras raras e com muitos iões dos metais de transição há uma correlação linear entre $\log k$ e E° , sendo todavia a recta de correlação para as terras raras distinta da dos metais de transição. Cálculos das constantes cinéticas pela teoria de Marcus sugerem que a reacção entre os iões dos metais de transição e $\cdot\text{OH}$ seguem um mecanismo de transferência de electrão via a esfera externa de hidratação enquanto com os iões das terras raras a reacção parece ter lugar através da esfera interna de hidratação.