Kinetics of Oxidation of Uranium(IV) by Permanganate Ion in Aqueous Perchlorate Media

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The kinetics of oxidation of uranium(IV) by permanganate ion in 1.0 mol dm^{-3} perchloric acid solution has been investigated using a stopped-flow spectrophotometer. The reaction was found to be second order overall and first order in the concentrations of both reactants. The catalytic effect of the perchlorates of Hg^{2+}, Cu^{2+}, and Fe^{3+} on the reaction rate has been investigated. The activation parameters were evaluated and found to be $\Delta S^{\ddagger} = 30.52 \pm 1.22$ J K^{-1} mol^{-1}, $\Delta H^{\ddagger} = 62.89 \pm 1.87$ kJ mol^{-1}, and $\Delta G^{\ddagger} = 53.79 \pm 1.44$ kJ mol^{-1}. A tentative mechanism consistent with the kinetics is discussed.

Although much work has been done on the kinetics of uranium(IV) oxidation by one-[1-5] and two-equivalent[6,7] oxidants, there have been few reports of its oxidation by multi-equivalent oxidants. This is presumably because of the recognized complexity resulting from the hydrolysis of U^{IV} at low [H$^+$] and the protonation of MnO_4^- at high [H$^+$].

The present work has been undertaken as part of a series of investigations on the kinetics of oxidation of U^{IV} by one-[8,9] and two-equivalent[10] oxidants in perchlorate media. It is of interest to investigate the kinetic behaviour of MnO_4^- with a reduction system that provides the opportunity of a two-electron transfer.

Experimental

All materials were of AnalaR quality (BDH). Doubly distilled conductivity water was used in all preparations. The temperature was controlled within ± 0.1 °C.

A stock solution of potassium permanganate was prepared by dissolving the appropriate amount of the reagent in doubly distilled water and standardized against As_2O_3. The permanganate-ion concentration was determined spectrophotometrically at 526 nm, its absorption maximum, immediately prior to each run.

Uranium(IV) perchlorate solutions were prepared by electrolytic reduction of solutions of uranium(VI) perchlorate in perchloric acid and standardized spectrophotometrically as described earlier.[8]

The ionic strength of the reaction mixture was maintained constant at 1.0 mol dm^{-3} using sodium perchlorate as an inert electrolyte.

Kinetic Measurements.—The kinetics was conducted under pseudo-first-order conditions where permanganate ion was present initially in a large excess over the uranium(IV). All of the measurements were performed under a nitrogen atmosphere on a Durrum-Gibson stopped-flow apparatus with a fully thermostatted cell compartment. The absorbance change was monitored at 648 nm, the absorption maximum of uranium(IV) ion. It was verified that no interference due to other reagents or reduction products occurred at this wavelength. The absorption spectra of U^{IV} and MnO_4^- are shown in the Figure.

Results

Stoicheiometry.—The stoicheiometry of the overall reaction of MnO_4^- with excess of U^{IV} in 1.0 mol dm^{-3} HClO$_4$ and at unit ionic strength was determined spectrophotometrically. A ratio of [U^{IV}]$_{consumed}$/[MnO_4^-]$_0$ = 2.5 $\pm$ 0.1 was obtained for

Table 1. Pseudo-first-order rate constants at [U^{IV}] = 2.4 × 10^{-3}, [H$^+$] = 1.0, I = 1.0 mol dm^{-3} and 20 °C

10^2[MnO_4^-]/ mol dm^{-3}	$10^{-3}k_{obs.}$/s^{-1}	$10^{-3}k$/dm^3 mol^{-1} s^{-1}
1.52	0.11	1.43
2.61	0.18	1.38
3.52	0.25	1.42
4.41	0.31	1.41
5.42	0.38	1.39
		Average 1.41 $\pm$ 0.2
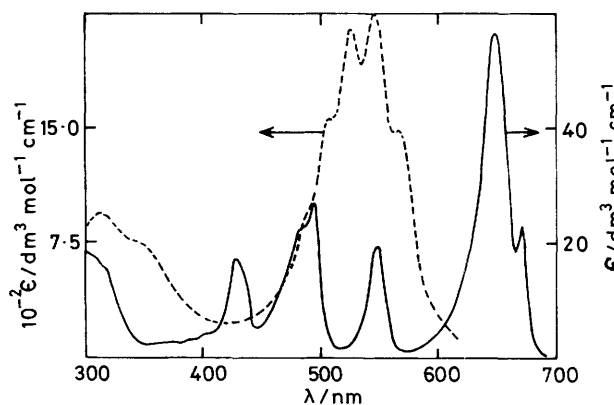
Figure 1. Absorption spectra of U^{IV} (——) and MnO_4^- (- - - -) in 1 mol dm^{-3} HClO$_4$ at 25 °C: [U^{IV}] = 1.1 × 10^{-2} and [MnO_4^-] = 2.7 × 10^{-4} mol dm^{-3}

several different initial concentrations of U^{IV}. This indicates that the stoicheiometry of the overall reaction conforms to equation (1).

$$2MnO_4^- + 5U^{4+} + 2H_2O \longrightarrow 2Mn^{2+} + 5UO_2^{2+} + 4H^+ \quad (1)$$
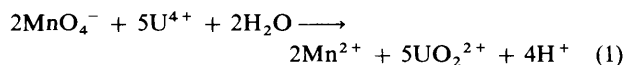
Dependence of the Reaction Rate on [MnO_4^-] *and* [U^{IV}].— Plots of $\ln(A_\infty - A_t)$ *versus* time, where A_t and A_∞ represent the absorbance at time t and infinite time, respectively, were linear for over three half-lives of the reaction at [H$^+$] = 1.0 mol dm^{-3}. This indicates that the reaction is first order with respect to [U^{IV}]. Pseudo-first-order rate constants, $k_{obs.}$, derived from

Table 2. Rate constants for the oxidation of U^{IV} by MnO_4^- at $[U^{IV}] = 2.4 \times 10^{-3}$, $[MnO_4^-] = 3.5 \times 10^{-2}$, $[H^+] = 1.0$, and $I = 1.0$ mol dm^{-3}

	10 °C	15 °C	20 °C	25 °C
$10^{-3}k_{obs.}/s^{-1}$	0.10	0.16	0.25	0.41
$10^{-3}k/dm^3\ mol^{-1}\ s^{-1}$	0.57	0.91	1.43	2.34

Table 3. Comparison of kinetic data for some uranium(IV) reactions

Oxidant	$E^{\ominus}/V$	$k_1/dm^3\ mol^{-1}\ s^{-1}$	$\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1}$	$\Delta H^{\ddagger}/kJ\ mol^{-1}$	$\Delta G^{\ddagger}/kJ\ mol^{-1}$	Ref.
NpO_2^+	0.74	8.0×10^{-6}	135.01	130.83	90.60	5
NpO_2^{2+}	1.14	2.2×10^1	30.93	76.08	66.86	4
PuO_2^{2+}	0.91	3.1	14.21	73.57	69.34	2
$HCrO_4^-$	1.20	6.3×10^4	33.02	55.59	45.75	21
VO_2^+	1.02	4.9×10^4	-41.80	35.65	52.42	22
MnO_4^-	1.52	9.2×10^3	30.52	62.89	53.79	This work

the gradients of these plots were obtained at a variety of MnO_4^- concentrations. The second-order rate constants, k, were obtained by dividing the appropriate values of $k_{obs.}$ by $[MnO_4^-]$ as shown in Table 1. The constancy of the values so obtained indicates that the reaction is also first order in $[MnO_4^-]$.

The excellent linearity of the first-order plots and the constancy of the second-order rate constants confirm that the reaction is second order overall. The rate laws are thus (2) in the presence of excess of MnO_4^- or (3) in general.

$$-d[U^{IV}]/dt = k_{obs.}[U^{IV}] \qquad (2)$$

$$-\frac{1}{5}\frac{d[U^{IV}]}{dt} = -\frac{1}{2}\frac{d[MnO_4^-]}{dt} = k[U^{IV}][MnO_4^-] \qquad (3)$$

Dependence of the Reaction Rate upon Added Salts.—Many investigators have postulated mechanisms for the oxidation of U^{IV} in which U^V is a reactive intermediate.[1,11] The main evidence in support of this is based on the catalytic effects of various cations and anions. This effect was studied here by adding the perchlorate salts of Fe^{III}, Hg^{II}, or Cu^{II} to the reaction mixtures. For example, a run at $[H^+] = 1.0$ mol dm^{-3} having $[Fe^{III}] = 0.01$, $[U^{IV}] = 2.4 \times 10^{-3}$, and $[MnO_4^-] = 3.5 \times 10^{-2}$ mol dm^{-3} at 25 °C gave $10^{-3}k = 9.3$ dm^3 mol^{-1} s^{-1}. The second-order rate constants for the catalysis of Hg^{II} and Cu^{II} were found to be 4.5×10^3 and 5.6×10^3 dm^3 mol^{-1} s^{-1}, respectively, under the same conditions.

Dependence of the Reaction Rate upon $[H^+]$.—Unfortunately, the dependence of the rate of reaction on the hydrogen-ion concentration could not be tested over a wide range because of the danger of hydrolysis of U^{IV} at low $[H^+]$ ($K_h = 2.82 \times 10^{-2}$ mol dm^{-3} at 25 °C)[12] or the protonation of MnO_4^- at high $[H^+]$ ($K_a = 2.99 \times 10^{-3}$ dm^3 mol^{-1} at 25 °C).[13] In the range of $[H^+]$ used (0.8—1.0 mol dm^{-3}) no change in the reaction rate was observed.

Dependence of the Reaction Rate upon Temperature.—To determine the activation parameters, the reaction was carried out at four temperatures ranging from 10 to 25 °C at constant $[H^+]$ and ionic strength. The $k_{obs.}$ and k values at various temperatures are summarized in Table 2. A plot of the Eyring equation[14] gave a good straight line from whose slope and intercept the enthalpy and entropy of activation were determined,

respectively. The activation parameters were calculated using the least-squares method and are summarized in Table 3, along with results for other oxidants.

Discussion

A question of interest in connection with multi-equivalent oxidants in redox systems such as the present one is whether electron transfer proceeds through successive one-electron changes [equations (4) and (5)] or by two-electron transfer in a

$$MnO_4^- + U^{IV} \xrightarrow[slow]{k_1} MnO_4^{2-} + U^V \qquad (4)$$

$$MnO_4^{2-} + U^V \xrightarrow[fast]{k_2} MnO_4^{3-} + U^{VI} \qquad (5)$$

$$MnO_4^- + U^{IV} \xrightarrow{k_3} MnO_4^{3-} + U^{VI} \qquad (6)$$

single step [equation (6)]. The estimated value for the relevant U^V–U^{IV} couple[15] ($+0.58$ V) along with that for the Mn^{VII}–Mn^{VI} couple[15] ($+0.56$ V) indicate that one-electron transfer is unfavourable thermodynamically. However, the protonation of permanganate ion, $MnO_4^- + H^+ \rightleftharpoons HMnO_4$, shifts the $E^{\ominus}$ value of the Mn^{VII}–Mn^{VI} couple to more positive values ($+1.1$[16] or $+1.3$ V[17]). Although $HMnO_4$ is a stronger oxidizing agent than MnO_4^-, its amount is still small under the experimental conditions of $[H^+] = 1.0$ mol dm^{-3}.

In the alternative reaction mechanism which involves two-electron transfer in a single step, the estimated values of $E^{\ominus}$ for the couples U^{VI}–U^{IV} and Mn^{VII}–Mn^V are $+0.32$ and $+1.12$ V, respectively.[15] It appears that while the two-equivalent pathway is more favourable on energetic grounds, it is not prominent kinetically. This is because of the necessity of ligand exchange on the reductant.[18]

Comparison of the present reaction with those involving the oxidation of U^{IV} to other oxotype oxidants such as NpO_2^+,[5] NpO_2^{2+},[4] and PuO_2^{2+}[2] shows that the U^{IV}–MnO_4^- reaction is very much faster (Table 3). One possible explanation which may be considered is that this reaction may involve the transfer of oxygen from Mn^{VII} to U^{IV}. Published ^{18}O-exchange studies indicate the occurrence of such transfer.[19,20] A doubly bridged transition state undergoing a simultaneous transfer of two oxygen atoms was suggested for the reactions U^{IV}–$HCrO_4^-$[21] and U^{IV}–VO_2^+.[22] Therefore, an analogous transition state seems plausible. The configuration $O{\diagup}^{U}{\diagdown}O$ simulates the
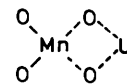
structures of both U^V and U^{VI} and has frequently been postulated in actinide reactions.[23]

The relative rates of the oxidation of U^{IV} by $HCrO_4^-$, VO_2^+, and MnO_4^- are in the expected order $[k(HCrO_4^-)^{21} > k(VO_2^+)^{22} > k(MnO_4^-)]$. The plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ for these reactions was linear, but the slope was very much less than that of 0.5 as required by Marcus theory.[24] This indicates that at least some of the reactions proceed *via* an ion-pairing mechanism. Under the experimental conditions of $[H^+] = 1.0$ mol dm^{-3}, uranium(IV) exists as U^{4+} which could participate in an ion-pair mechanism,* equation (7) where $k_{11}K_{11} = k$. It

$$U^{4+} + MnO_4^- \xrightarrow{K_{11}} U^{4+}MnO_4^- \xrightarrow{k_{11}} product \qquad (7)$$
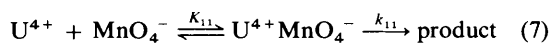
$$k_{obs.}' = \frac{k_{11}K_{11}[MnO_4^-]_T}{1 + K_{11}[MnO_4^-]_T} \qquad (8)$$

* As suggested by a referee.

Table 4. Activation parameters for some permanganate reactions

Reagent	$\Delta S^{\ddagger}/J\ K^{-1}$ mol^{-1}	$\Delta H^{\ddagger}/kJ$ mol^{-1}	$\Delta G^{\ddagger}/kJ$ mol^{-1}	Remarks
U^{IV}	+30.52	62.89	53.79	This work
$W(CN)_8^{4-}$	+25.92	54.76	47.04	Outer sphere[28]
$Fe(phen)_3^{2+}$	+68.13	64.79	44.49	Outer sphere[16]
$Fe(CN)_6^{4-}$	+152.57	89.87	44.40	Outer sphere[a]
$Mo(CN)_8^{4-}$	-23.41	45.14	52.12	Outer sphere[b]

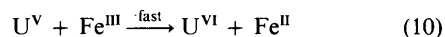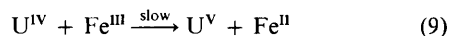[a] M. A. Rowoof and J. R. Sutter, J. Phys. Chem., 1967, 71, 2767.
[b] L. Thomas and K. W. Hicks, Inorg. Chem., 1974, 13, 749.

is expected that the ion pair would be more appreciable at the higher reagent concentrations. The rate equation can be expressed as in (8) where $[MnO_4^-]_T$ denotes the total concentration of permanganate ion ($[MnO_4^-] + [U^{4+}MnO_4^-]$).

Furthermore, the thermodynamic parameters observed for a series of common reactions may be considered as good evidence in support of the reaction mechanism.[25,26] The kinetic parameters observed for the reactions of some inorganic substrates with MnO_4^- are summarized in Table 4. It has been shown that the $\Delta S^{\ddagger}$ values for a group of outer-sphere reactions involving MnO_4^- tend to be more positive (-23 to $+153$ J K^{-1} mol^{-1})[27,28] than $\Delta S^{\ddagger}$ for a set of inner-sphere reactions (-54 to -113 J K^{-1} mol^{-1}).[29] The entropy of activation of the present reaction falls within the range observed for the outer-sphere mechanism. Such a similarity, while not in itself indicative of an outer-sphere mechanism as is the case of the reactions of $W(CN)_8^{4-}$, $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline), $Fe(CN)_6^{4-}$, and $Mo(CN)_8^{4-}$ with MnO_4^-, approximates the ion pairing mechanism owing to the overall charge of the reductant.

In view of the pronounced catalytic effect on the reaction rate, the oxidation of U^{IV} has frequently been reported to be affected by various ionic species.[6,11] Owing to the fairly moderate reaction between U^{IV} and Fe^{III},[1] these measurements were carried out with iron(III) mixed with MnO_4^- in one syringe reservoir of the stopped-flow apparatus and the U^{IV} in the other. The U^{IV}–Fe^{III} reaction was slow enough to be unimportant during the time required for complete reduction of MnO_4^-.

The reduction of Fe^{III} by U^V should the latter be formed is necessarily a rapid reaction.[1] Newton and Baker[30] estimated the second-order rate constant for this reaction to be ca. 10^5 dm^3 mol^{-1} s^{-1} at 25 °C and $[H^+] = 1.0$ mol dm^{-3}. The second-order rate constant for the oxidation of Fe^{II} by MnO_4^- under the same conditions was found to be $\leqslant 10^4$ dm^3 mol^{-1} s^{-1}.[31] Accordingly, the catalytic effect can be simply explained in terms of reactions (9) and (10). The effect of Cu^{II} and Hg^{II} on the

$$U^{IV} + Fe^{III} \xrightarrow{slow} U^V + Fe^{II} \qquad (9)$$

$$U^V + Fe^{III} \xrightarrow{fast} U^{VI} + Fe^{II} \qquad (10)$$

reaction rate may be explained in a similar manner [equations (11) and (12)]. In this context, it should be noted that there

$$U^V + Cu^{II} \xrightarrow{fast} U^{VI} + Cu^I \qquad (11)$$

$$U^V + Hg^{II} \xrightarrow{fast} U^{VI} + Hg^I \qquad (12)$$
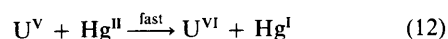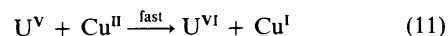
does not appear to be any experimental confirmation of an ion-pair or outer-sphere two-electron transfer process.[32]

References

1 R. H. Bates, Can. J. Chem., 1955, 33, 1780.
2 T. W. Newton, J. Phys. Chem., 1958, 62, 943.
3 T. W. Newton, J. Phys. Chem., 1954, 63, 1493.
4 J. C. Sullivan, A. J. Zeilen, and J. C. Hindman, J. Am. Chem. Soc., 1960, 82, 5288.
5 N. K. Shastri, E. S. Amis, and J. O. Wear, J. Inorg. Nucl. Chem., 1965, 27, 2413.
6 A. C. Harkness and J. Halpern, J. Am. Chem. Soc., 1959, 81, 3526.
7 R. A. Silverman and G. Gordon, Inorg. Chem., 1976, 15, 35.
8 R. M. Hassan, T. Kojima, and H. Fukutomi, Bull. Res. Lab. Nucl. React., Jpn., 1980, 5, 41.
9 R. M. Hassan, T. Kojima, and H. Fukutomi, Bull. Res. Lab. Nucl. React., Jpn., 1981, 6, 35.
10 R. M. Hassan, T. Kojima, and H. Fukutomi, VI International Symposium on Solute-Solute-Solvent Interactions, Japan, 1982, p. 113.
11 F. B. Baker, and T. W. Newton, J. Phys. Chem., 1961, 65, 1897.
12 R. H. Betts, Can. J. Chem., 1955, 33, 1755; R. L. Lawerence, J. Am. Chem. Soc., 1934, 56, 776.
13 A. Carrington and M. C. R. Symons, Chem. Rev., 1963, 63, 443; N. Baily, A. Carrington, N. A. K. Lott, and M. C. R. Symons, J. Chem. Soc., 1960, 290.
14 S. Glasstone, K. J. Laidler, and H. Eyring, 'The Theory of Rate Processes,' McGraw-Hill, New York, 1941, p. 417.
15 W. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey, 1952.
16 K. W. Hicks and J. K. Sutter, J. Phys. Chem., 1971, 75, 1107.
17 F. M. Moore, M.Sc. Thesis, Eastern Michigan Unversity, 1975.
18 M. C. Ondrus and G. Gordon, Inorg. Chem., 1972, 11, 985.
19 G. Gordon and H. Taube, Inorg. Chem., 1962, 1, 69.
20 G. Gordon and A. Andrews, Inorg. Chem., 1974, 13, 1733.
21 J. H. Espenson and R. T. Wang, Inorg. Chem., 1972, 11, 955.
22 A. Ekstrom, Inorg. Chem., 1977, 16, 845.
23 T. W. Newton and F. B. Baker, Acc. Chem. Res., 1967, 71, 268.
24 R. W. Marcus, J. Phys. Chem., 1963, 67, 853.
25 N. Sutin, Acc. Chem. Res., 1958, 1, 225.
26 K. W. Hicks, D. L. Toppen, and R. G. Linck, Inorg. Chem., 1972, 11, 310.
27 F. M. Moore, and K. W. Hicks, Inorg. Chem., 1975, 14, 413.
28 K. W. Hicks, J. Inorg. Nucl. Chem., 1976, 38, 1381.
29 F. Freeman, J. Am. Chem. Soc., 1981, 103, 1154.
30 T. W. Newton and F. B. Baker, J. Phys. Chem., 1966, 70, 1943.
31 B. M. Gordon, L. L. Williams, and N. Sutin, J. Am. Chem. Soc., 1961, 83, 2061.
32 G. Gordon, Proc. Int. Conf., Coord. Chem., 1970 12, 11.