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Kinetics and Mechanism of Oxidation of Vanadium(IV) by Periodate in Aqueous Acidic Solutions

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The kinetics of oxidation of vanadium(IV) by I(VII) in aqueous acidic solutions follow the rate law

$$\frac{d[VO_2^+]}{2dt} = \frac{k_0[VO^{2+}]_T[I(VII)]_T}{[H^+]^2}$$

where $k_0 = 0.52 \pm 0.01$ M sec^{-1} at 25 °C and I = 1.0 M (NaClO$_4$). The rate law is consistent with a mechanism in which a deprotonated I(VII) species and monohydrolysed vanadium(IV), either prior to or concurrent with electron transfer, are the reactive species. A comparison with the rate of oxidation of Fe(II) by the same oxidant as well as the formation and decomposition of an intermediate suggest an inner-sphere mechanism.

Introduction

The kinetics and mechanism of oxidation of V(IV) by both complementary and non-complementary oxidants have been the subject of many investigations [1]. The oxidation of V(IV) – a one electron reductant – by non-complementary oxidants would necessarily form unstable oxidation states when the kinetics exhibit first order dependence on the reductant concentration. The evidence for one-electron transfer changes is often deduced either from the inhibition of the reaction by V(V) or by the disproportionation of the unstable oxidation state [2].

Reaction (1) between V(IV) and I(VII)

$$2VO^{2+} + I(VII) \xrightarrow{H^+,\, H_2O} 2VO_2^+ + I(V) + 3H^+ \quad (1)$$

is an example of a non-complementary reaction, V(IV) and I(VII) being the one-electron reductant and the two-electron oxidant respectively. The oxidation of V(IV) by I(V) is too slow to introduce any complications [3].

Rosseinsky has used the comparison between the rate constants of oxidation of V(IV) and Fe(II) by the same oxidant for the assignment of either an inner- or an outer-sphere mechanism [1].

Experimental

A stock solution of perchloric acid was prepared by dilution of concentrated perchloric acid (Hopkins and Williams, Analar) and standardised. Sodium perchlorate solution was prepared from (BDH) reagent grade and its concentration determined by cation-exchange method using Amberlite IR120(H) resin. Vanadium(IV) perchlorate was prepared as reported in the literature [4] and standardised spectrophotometrically at 760 nm (ϵ = 17.2). Vanadium(V) perchlorate was prepared by dissolving V_2O_5 in 2 *M* perchloric acid, and the solution standardised spectrophotometrically at 313 nm (ϵ = 389) [5]. The free acid in both vanadium(IV) and vanadium(V) solutions was determined using cation-exchange. The contributions of the cations VO^{2+} and VO_2^+ to the total $[H^+]$ was taken into consideration.

Periodate solutions were prepared by weight from $NaIO_4$ (BDH Analar). These were covered with Al foil to exclude light. Periodate solutions are reported to be decomposed by light [6].

The stoichiometry of the vanadium(IV)–periodate reaction was investigated under pseudo-first order conditions usually with periodate in excess in the hydrogen ion concentration range 0.10–1.0 *M* and I = 1.0 *M*. When vanadium(IV) was in excess, low $[H^+]$ concentration was used so as to suppress the VO^{2+}–IO_3^- reaction. The concentration of the species VO^{2+}, VO_2^+ and IO_4^- was determined from their absorbances and molar extinction coefficients using a Unicam SP500 spectrophotometer.

The kinetics of the vanadium(IV)–periodate reaction was studied by using a Durrum–Gibson stopped-flow spectrophotometer. The rate of the reaction was monitored at 313 nm, where the product VO_2^+ is the principal absorbing species. Constant temperature was maintained by circulating water from a constant-temperature bath through the reservoir containing the drive syringes. A Polaroid camera was used to photograph the output from the photomultiplier.

The vanadium(IV) and periodate concentrations were varied in the range 2.0–50.0 × 10^{-4} *M* and 5.0–50.0 × 10^{-3} *M* respectively. In most of the experiments performed the periodate concentration was always in large excess over that of vanadium(IV) to

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TABLE. Kinetic Data.[a]

Run No.	10^2[I(VII)] M	10^4[VO^{2+}] M	[H^+]$_o$ M	[H^+]$_{calc.}$ M	10^2k_{obs} sec^{-1}	k_2 M^{-1} sec^{-1}	k_o M sec^{-1}
1	2.00	5.0	1.00	0.981	1.06	0.530	0.509
2	3.00		1.00	0.972	1.725	0.575	0.546
3	3.80		1.00	0.963	2.318	0.610	0.565
4	4.58		1.00	0.955	2.83	0.618	0.564
5	0.50		0.30	0.296	3.05	6.10	0.534
6	1.00		0.30	0.291	6.39	6.39	0.541
7	2.00		0.30	0.282	12.0	6.00	0.477
8	3.00		0.30	0.272	23.7	7.90	0.580
9	3.40		0.30	0.267	28.56	8.40	0.598
10	5.00	3.0	0.30	0.253	46.5	9.30	0.600
11	5.00	2.0	0.30	0.253	46.5	9.30	0.600
12	0.0025	25.0	0.30	0.30	1.575	6.30	0.567
13	0.0025	50.0	0.30	0.30	3.25	6.50	0.585
14	2.00	5.0	0.90	0.882	1.36	0.68	0.529
15	2.00		0.80	0.782	1.68	0.84	0.514
16	2.00		0.70	0.682	2.24	1.12	0.521
17	2.00		0.60	0.582	3.02	1.51	0.511
18	5.00		0.60	0.555	8.05	1.61	0.498
19	2.00		0.50	0.482	4.06	2.03	0.472
20	2.00		0.40	0.381	7.46	3.73	0.544
21	2.00		0.20	0.181	28.8	14.40	0.472
22	1.50		0.20	0.186	22.5	15.00	0.519
23	2.00		0.10	0.082	164.0	82.0	0.551
24	1.50		0.10	0.086	105.2	70.1	0.518
25	1.00		0.10	0.091	67.4	67.4	0.541
26[b]	2.00		0.20	0.181	26.8	13.4	0.439
27[c]	2.00		0.20	0.181	27.4	13.7	0.449
28[d]	2.00		0.20	0.181	26.0	13.0	0.426

[a] T = 25 °C, I = 1.0 M($NaClO_4$). [b] [VO_2^+] = 5.0 × 10^{-4} M. [c] [VO_2^+] = 1.0 × 10^{-3} M. [d] [VO_2^+] = 1.5 × 10^{-3} M.

ensure pseudo-first order conditions. The dependence of the reaction rate on [H^+] was studied in the hydrogen ion concentration range 0.10–1.00 M. The effect of initially added vanadium(V) was studied in the range 5.0–15.0 × 10^{-4} M.

Results

Vanadium(IV) reacts with periodate, under all conditions investigated, by a 2.0:1.0 ratio in agreement with reaction (1).

The kinetics of the vanadium(IV)–periodate reaction, with either reactant in excess, in the [H^+] range 0.10–1.00 M, showed first order dependence on each reactant. Plots of log(A_∞ – A_t) as a function of time were linear up to at least 75% of reaction. Beyond this point deviations from linearity were observed whether periodate or vanadium(IV) is in exess. The pseudo-first order rate constant (k_{obs}) determined at various periodate and vanadium(IV) concentrations is shown in the Table. At fixed [H^+] the rate of the reaction is described by eq. 2

$$\frac{d[VO_2^+]}{2dt} = k_{obs}[VO^{2+}] \tag{2}$$

when periodate is in excess.

The data given are in accord with the rate expression (3)

$$\frac{d[VO_2^+]}{2dt} = \frac{k_o[VO^{2+}][I(VII)]}{[H^+]^2} \tag{3}$$

as shown by the constancy of the quantity k_o given in the last column of the Table. The average value of k_o at 25 °C and I = 1.0 M is 0.52 ± 0.01 M sec^{-1}.

It is perhaps worth mentioning that the rapid equilibrium (4) between periodate and hydrogen ions

$$H^+ + HL^- \rightleftharpoons H_2L/K_1 \tag{4}$$

(HL^- = [IO_4^-] + [$H_4IO_6^-$] = total periodate concentration), was considered as this would deplete the initial [H^+]$_0$. The thermodynamic value of K_1 is reported [7] as 200 M^{-1} at 25 °C. K_1 was determined as 150 ± 10 Mn^1 at ionic strength 1.0 M at 25 °C. This value was used in the calculation of free [H^+] (shown in the Table as [H^+]$_{cal}$) for each run. The results indicate that >90% of periodate ions are protonated in the acid range investigated.

Discussion

The rate law shows an activated complex containing one V(IV), one I(VII), and two protons less than do the dominant forms of V(IV) and I(VII) being dealt with. Two mechanisms, kinetically indistinguishable, consistent with the rate law are shown by eqs. 5–7.

$$VO(OH_2)^{2+} + I(VII) \underset{}{\overset{K_2}{\rightleftharpoons}} [VO(OH)I(VII)]^{\ddagger} + H_3O^+ \quad (5)$$

$$[VO(OH)I(VII)] \xrightarrow{k_3} VO_2^+ + I(VI) \quad (6)$$

$$VO(OH_2)^{2+} + I(VI) \xrightarrow{fast} VO_2^+ + I(V) \quad (7)$$

and eqs. 8–11

$$VO(OH_2)^{2+} + H_2O \rightleftharpoons VO(OH)^+ + H_3O^+ \; K_3 = 10^{-6} \mathit{M} \quad (8)$$

$$VO(OH)^+ + I(VII) \overset{K_4}{\rightleftharpoons} [VO(OH)I(VII)]^{\ddagger} \quad (9)$$

$$[VO(OH)I(VII)]^{\ddagger} \xrightarrow{k_3} VO_2^+ + I(VI) \quad (10)$$

$$VO(OH_2) + I(VI) \xrightarrow{fast} VO_2^+ + I(V) \quad (11)$$

The rate laws (12) and (13) are derived from the two mechanisms shown by eqs. 5–7 and 8–11 respectively assuming that K_2 and K_4 are small:

$$\frac{d[VO_2^+]}{2dt} = \frac{k_3K_2[VO^{2+}]_T[I(VII)]_T}{[H^+] + K_1[H^+]^2} \quad (12)$$

$$\frac{d[VO_2^+]}{2dt} = \frac{k_3K_4[VO^{2+}]_T[I(VII)]_T}{1 + (K_1 + 1/K_3)[H^+] + (K_1/K_3)[H^+]^2} \quad (13)$$

Both rate laws (12) and (13) would take the experimental form for the limiting conditions $K_1[H^+]^2 >> [H^+]$ (eq. 12) and $(K_1/K_3)[H^+]^2 >> (1 + K_1 + 1/K_3)[H^+]$ (eq. 13).

The reduction of I(VII) to I(V) seem to proceed via one-electron transfer steps. Such a process has been reported for the Fe(II)–I(VII) reaction where the formation of free-radicals was ascertained [6].

The mechanism of oxidation of vanadium(IV) by periodate most probably proceeds by an inner-sphere mechanism. Both vanadium(IV) and periodate ions are labile, and substitution into their inner co-ordination spheres is likely [8, 9]. The assignment of an inner-sphere mechanism to this reaction seems to be supported by the following observations: (i) Rosseinsky has observed that the rates of oxidation of vanadium(IV) are invariably smaller than those of Fe(II), and for outer-sphere reactions can be up to several hundredfold slower. When the evidence suggests an inner-sphere oxidant the rates become relatively less small [1]. Thus a comparison of the rate constants for the $[H^+]$ dependences ($[H^+]^{-2}$ for V(IV) and $[H^+]^{-1}$ for Fe(II)), where the rate constants are 0.52 M sec^{-1} and 16.0 sec^{-1} at 25 °C and I = 1.0 M for the oxidation of V(IV) and Fe(II) [10] respectively, would indicate an inner-sphere mechanism for the oxidation of vanadium(IV) by periodate ions. In fact a plot of log k_o^V against k_o^{Fe} would place a point in the inner-sphere region of Fig. 6 of ref. (1). (ii) The second support for an inner-sphere mechanism could be derived from the stopped-flow traces which indicate the rapid formation of an intermediate and its slow decomposition as shown in the Figure. (iii) The observation [11] that periodate ion fails to oxidise $Fe(phen)_3^{2+}$ which is inert and has no effective bridging atom is in keeping with substitution as a prerequisite for oxidation by periodate [12].

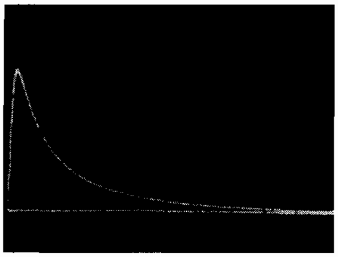

Figure. Stopped-flow trace of transmittance at 313nm of V(IV)–periodate reaction as a function of time; $[VO^{2+}]$ = 5.0 × 10^{-4} M, [Periodate] = 1.0 × 10^{-2} M, $[H^+]_o$ = 0.10M, I = 1.0M ($NaClO_4$), T = 25 °C. The ordinate scale is 5% transmittance per major division and the abscissa scale is 0.50 sec per major division. The lower trace corresponds to transmittance at infinite time.

The periodate ion species which is involved in the oxidation of vanadium(IV) has not been specified. The two species IO_4^- and $H_4IO_6^-$ are known to exist in equilibrium in aqueous solutions. It is tempting to view IO_4^- as the reactive species because of its smaller size compared to $H_4IO_6^-$ when substitution is viewed as occurring on vanadium(IV). It may also be possible for the substitution to occur on I(VII) with the vanadium(IV) oxygen acting as the bridging atom.

The deviation from linearity of the first order plots observed beyond 75% reaction probably results from the disproportionation of I(VI) to give I(VII) and I(V). The disproportionation of I(VI) is not unlikely in view of instability of +6 oxidation as observed in the flash photolysis of I(V) where IO_3 and IO_4^{2-} are produced [13].

References

1 D. R. Rosseinsky, *Chem. Rev., 72,* 215 (1972) and refrs. therein.

2 Adeleye Adegite, *J. Chem. Soc. Dalton,* 1199 (1975)

3 C. W. Fuller and J. M. Ottaway, *Analyst, 95,* 791 (1970).
4 Richard R. Thompson, *Inorg. Chem., 10,* 1892 (1971).
5 K. M. Davies and J. H. Espenson, *J. Am. Chem. Soc., 92,* 1884 (1970).
6 M. C. R. Symons, *J. Chem. Soc.,* 2794 (1955).
7 L. G. Sillen, "Stability Constants, Special Publication No. 17".
8 K. Wüthrich and R. E. Connick, *Inorg. Chem., 6,* 583 (1967).
9 I. Pecht and Z. Luz, *J. Am. Chem. Soc., 87,* 4068 (1965).
10 Fouad R. Al-Eziry and Yousif Sulfab, to be published.
11 Yousif Sulfab, unpublished results.
12 See for example E. Chaffee and J. O. Edwards, "Progress in Inorganic Chemistry", editor J. O. Edwards, V. 13, p. 205, Wiley, 1970.
13 F. Barat, L. Giles, B. Hickel and B. Lesigne, *J. Phys. Chem., 76,* 302 (1972).