

Electron Transfer Reactions of Vanadium(IV) with Some Oxyanion Oxidants in Aqueous Perchloric Acid. Part I. Reaction with Chromium(VI) and Manganese(VII)

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The rate law $k[\text{Cr}^{\text{VI}}][\text{V}^{\text{IV}}]^2[\text{H}^+]^n/\text{V}^{\text{V}}$, with $n < 1$, is confirmed, and differences from the iron(II)–chromium(IV) result are explained. With proper interpretation the comparability of iron(II) with vanadium(IV) reactions is preserved. The reaction of vanadium(IV) with manganese(VIII) appears to be initially just of the second order, but non-stoichiometry and acceleration by product manganese(II) introduce later complications only qualitatively resolvable.

ELECTRON transfer reactions of vanadium(IV) are of interest, partly because of their unexpected parallelism with corresponding reactions of iron(II).¹ Here we report investigations of the reactions of vanadium(IV) with the anionic oxidants chromium(VI), manganese(VII), and (in the following paper) chlorine(V): none is en-

¹ D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. (A)*, 1968, 1022.

tirely simple kinetically. We can draw some useful conclusions from comparison of the chromium(VI) oxidation with the corresponding iron(II) reaction. The only other reaction of manganese(VII) with a metal cation reductant which has been analysed kinetically is the manganese(II)–(VII) reaction.² This obeys the

² D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, 1965, **61**, 2718.

simple rate law $k[\text{MnO}_4^-][\text{Mn}^{2+}]^2$. Kinetic spectrophotometry was used for both the V^{IV} reactions (Table 1).

TABLE 1

Molar absorptivities ϵ ($18^\circ \pm 3^\circ$)				
Ionic strength/(M)	[HClO ₄] (M)	Wave-length (nm.)	$10^{-3} \epsilon(\text{Cr}^{\text{VI}})$ (cm. ² mole ⁻¹)	$10^{-3} \epsilon(\text{V}^{\text{V}})$ (cm. ² mole ⁻¹)
1.0	1.0	350	1450	140
1.0	0.005	350	1554	141 ^a
2.0	0.5	375	972	33
2.0	1.0	375	942	33
2.0	2.0	375	878	33
1.0 and 2.0	1.0 and 2.0	525	$10^{-6} \epsilon(\text{Mn}^{\text{VII}}) = 2.45$	

^a From ref. 3.

RESULTS AND DISCUSSION

Vanadium(IV) with Chromium(VI).—We find that the rate law (1) established by Espenson³ is applicable in the conditions we employed. On integration we obtain equation (2), which is plotted in Figure 1, the

$$-d[\text{Cr}^{\text{VI}}]/dt = k[\text{VO}^{2+}]^2[\text{Cr}^{\text{VI}}]/[\text{VO}_2^+] \quad (1)$$

$$\begin{aligned} & (3[\text{Cr}^{\text{VI}}]_0 + [\text{V}^{\text{V}}]_0)([\text{V}^{\text{IV}}]_0 - 3[\text{Cr}^{\text{VI}}]_0) \ln([\text{V}^{\text{IV}}]/[\text{Cr}^{\text{VI}}]) \\ & - ([\text{V}^{\text{IV}}]_0 + [\text{V}^{\text{V}}]_0)/[\text{V}^{\text{IV}}] = \\ & k([\text{V}^{\text{IV}}]_0 - 3[\text{Cr}^{\text{VI}}]_0)t + \text{constant} \quad (2) \end{aligned}$$

linearity of which, together with a satisfactory constancy of k over 10–12-fold variation of vanadium-(IV) and -(V) concentrations (Table 2) confirms the rate law.

TABLE 2

Rate constants for the $\text{V}^{\text{IV}}\text{--Cr}^{\text{VI}}$ reaction at 1M-hydrogen-ion concentration

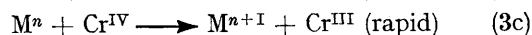
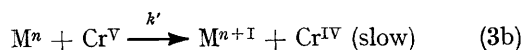
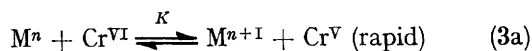
Temp.	Ionic strength 2.00M			
	$10^4[\text{V}^{\text{IV}}]$ (M)	$10^4[\text{Cr}^{\text{VI}}]$ (M)	$10^3[\text{V}^{\text{V}}]$ (M)	k (l. mole ⁻¹ min. ⁻¹)
21.1°	10.4	1.53	4.54	323
21.1	19.8	1.40	4.33	251
21.1	19.8	1.42	8.66	268
Average: 281 ± 28				
15.0	5.95	1.08	1.29	225
15.0	5.95	1.08	1.27	241
15.0	5.95	1.08	1.25	230
Average: 232 ± 6				
Temp.	Ionic strength 1.00M			
	$10^4[\text{V}^{\text{IV}}]$ (M)	$10^4[\text{Cr}^{\text{VI}}]$ (M)	$10^3[\text{V}^{\text{V}}]$ (M)	k (l. mole ⁻¹ min. ⁻¹)
16.0	5.90	1.42	0	204
16.0	5.90	1.42	0	292
16.0	3.90	1.42	0	283
16.0	5.90	1.42	0	220
Average: 250 ± 37				
21.1	4.50	1.48	4.4	282

Espenson's findings³ appeared at the completion of our own survey, which we present to complement his work: ours has led us to some conclusions additional to those adduced by Espenson. The rate law appears³ to be closely akin to that^{4,5} for reaction of iron(II) with chromium(VI). We denote reductant of oxidation state n by M^n ; then at constant acidity the mechanism

³ J. Espenson, *J. Amer. Chem. Soc.*, 1964, **86**, 1883, 5101.

⁴ D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. (A)*, 1969, 2887.

indicated is as in reactions (3). Hence $k = k'K$ or,



distinguishing the systems, $k_{\text{Fe}} = k'_{\text{Fe}}K_{\text{Fe}}$ and $k_{\text{V}} = k'_{\text{V}}K_{\text{V}}$. In the vanadium(IV) reaction conditions (*i.e.*, low Cr^{VI}) the chromium oxidant is predominantly monomeric, as HCrO_4^- and some H_2CrO_4 . Now our k_{V} value of 282 l. mole⁻¹ min.⁻¹ in 1M-HClO₄, though higher than the value³ 37 l. mole⁻¹ min.⁻¹ for 0.005M-HClO₄, indicates a dependence of k on $[\text{H}^+]$ of power less than unity. On the other hand, k_{Fe} for the iron(II)

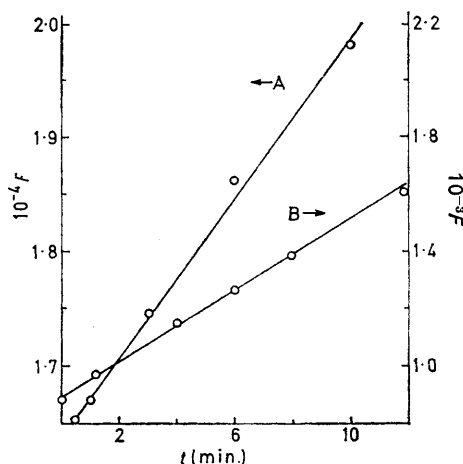
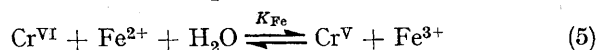
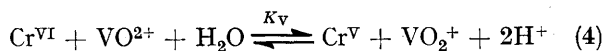


FIGURE 1 Rate plots for $\text{V}^{\text{IV}}\text{--Cr}^{\text{VI}}$ reaction, of $10^{-4}F$ against time. F is the left-hand side of equation (2) divided by $[\text{V}^{\text{IV}}]_0 - 3[\text{Cr}^{\text{VI}}]_0$. (a) $5.9 \times 10^{-4}\text{M-V}^{\text{IV}}$, $1.42 \times 10^{-4}\text{M-Cr}^{\text{VI}}$, 1.0M-HClO₄; 16° C. (b) [Divide abscissa numerals by 4]. $5.95 \times 10^{-4}\text{M-V}^{\text{IV}}$, $1.27 \times 10^{-4}\text{M-V}^{\text{V}}$, $1.08 \times 10^{-4}\text{M-Cr}^{\text{VI}}$, 1.0M-HClO₄, 1.0M-NaClO₄; 15° C

oxidation is proportional to $[\text{H}^+]^3$. We can explain the difference as being largely a consequence of the differing extents of hydrolysis of the first-step products vanadium(V) and iron(III) respectively. Thus, compare reactions (4) and (5).



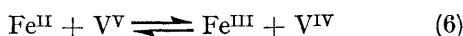
Clearly $[\text{Cr}^{\text{V}}]$ in (4) is *ceteris paribus* inversely proportional to $[\text{H}^+]$ of a power higher by two than that in (5), and this dependence is reflected in the kinetic result. Alternatively, if the reacting Cr^{V} species in (4) and (5) themselves differ in protonation, the observations must be attributed to larger difference of the $[\text{H}^+]$ dependence in the k' steps. For economy of hypothesis, we prefer the former explanation.

The slowness of the second step involving $\text{Cr}^{\text{V}} \longrightarrow \text{Cr}^{\text{IV}}$ in both the iron(II) and vanadium(IV) reactions

⁵ J. Espenson and E. L. King, *J. Amer. Chem. Soc.*, 1963, **85**, 3328.

is deemed^{3,5} to be associated with a change in the Cr co-ordination number from 4 to 6.

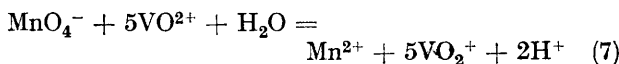
The rate constant for the main iron(II)-chromium(VI) pathway for 1M-perchloric acid, is 4.7×10^8 l. mole⁻¹ min.⁻¹, the [H⁺]-dependence being omitted from the dimensionality. This is the fastest oxidation in the sequence of oxidants for iron(II), $\text{Ti}^{\text{III}} < \text{Fe}^{\text{III}} < \text{Co}^{\text{III}} < \text{Mn}^{\text{III}} < \text{V}^{\text{V}} < \text{Cr}^{\text{VI}}$. Apart from Cr^{VI}, the rates of oxidation of vanadium(IV) in 1M-HClO₄ have been found to follow just this sequence.^{1,6} The present result, however, appears to interrupt this notable comparability, V^{IV}-Cr^{IV} now apparently falling (at 282 l. mole⁻¹ min.⁻¹) between oxidations by Co^{III} and Mn^{III}. However, equilibria (4) and (5) with equilibrium constants K_V and K_{Fe} precede the rate-determining reactions (rate constants k'_V and k'_{Fe}) with Cr^V. In order to compare k' values we need to multiply k_V by K_{Fe}/K_V which is simply K_6 for reaction (6) in 1M-HClO₄ (ca.



2×10^5).⁷ Then we have $k_{\text{Fe}} = k'_{\text{Fe}}K_{\text{Fe}}$ and $k_V K_6 = k'_V K_{\text{Fe}}$. Expressed differently, $k'_{\text{Fe}} \propto k_{\text{Fe}}$ and $k'_V \propto k_V K_6$, the proportionality constant being $1/K_{\text{Fe}}$ (and thus $\gg 1$). Hence $k_V K_6 = 5.6 \times 10^7$ l. mole⁻¹ min.⁻¹; with $k_{\text{Fe}} = 7 \times 10^8$ l. mole⁻¹ min.⁻¹, k' values for Cr oxidations are thus shown to be the highest for V^{IV} as well as for Fe^{II}, and both the comparability of Fe^{II} and V^{IV} reactions, and the sequence V^{IV} rate < Fe^{II} rate,^{1,6} are preserved.

If apart from the acidity-dependence the vanadium(IV) result is accepted as showing an identity of mechanism with iron(II), then first, participation of a suggested⁸ iron(IV) intermediate is strongly contraindicated, the corresponding vanadium analogue, V^{VI}, being virtually non-existent in condensed matter. Secondly, as in the case⁴ of iron(II), a pathway of the first order in vanadium(IV) is to be expected at very low V^{IV}.

Vanadium(IV) with Manganese(VII).—The reaction (7)



has long been used in the volumetric estimation of vanadium. The stoichiometry of 5 only holds when the acidity is low, however, and certainly in kinetic runs where MnO₄⁻ is in excess our experiments (Table 3) show stoichiometries falling as low as 2.8. The values of (V^{IV} consumed)/(MnO₄⁻ consumed) were obtained by measuring the final [MnO₄⁻] spectrophotometrically, and the total final concentration of oxidising species, assumed to be V^V + MnO₄⁻, by amperometric titration with standard iron(II) solution. Since (see p. 1199) some small amount of the final oxidant is actually Mn^{III}, the tabulated stoichiometries are upper limits. The non-stoichiometry, varying somewhat with concentration, can only be attributed to reaction with water of a high oxidation state (VI or V?) of Mn, which must arise albeit transiently in the overall process (7).

⁶ D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, 1968, **64**, 2410.

TABLE 3

Stoichiometries in the V^{IV}-Mn^{VII} reaction at ionic strength 3.00M at ca. 20°

(Each entry except that for H₂SO₄ is based on 4 or 5 measurements)

Initial 10 ⁴ [Mn ^{VII}] (M)	Initial 10 ⁴ [V ^{IV}] (M)	Other species	[V ^{IV}] reacted / [Mn ^{VII}] reacted
0.35—0.85	4.33—4.56	3M-H ⁺	4.7—4.4
0.694—0.702	0.74—2.30	3M-H ⁺	2.8—4.0
(0.807)	2.30	3M-H ₂ SO ₄	3.9
0.687	1.04—2.60	1M-H ⁺	3.6—4.3
0.698	1.04—2.60	0.4M-H ⁺	4.1—4.4
0.698	1.56	(0.5—5) × 10 ⁻⁴ M-Mn ^{II} , 1M-H ⁺	3.2—3.4

The simple second-order rate law for a stoichiometry of 5 would be (8) but there are two complications, the

$$([\text{V}^{\text{IV}}]_0 - 5[\text{Mn}^{\text{VII}}]_0)^{-1} \times$$

$$\ln \left\{ \frac{[\text{Mn}^{\text{VII}}]_0}{[\text{V}^{\text{IV}}]_0} \cdot \frac{[\text{V}^{\text{IV}}]_0 - 5([\text{Mn}^{\text{VII}}]_0 - [\text{Mn}^{\text{VII}}])}{[\text{Mn}^{\text{VII}}]} \right\} = kt \quad (8)$$

effect of manganese(II) and the departures from stoichiometry. It is shown below that the addition

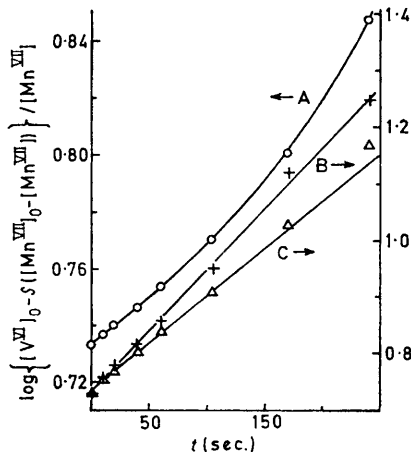


FIGURE 2 Second-order rate plots for V^{IV} + Mn^{VII}, with assumed stoichiometries S of A, 5; B, 3; and C, 2.27; 5.39×10^{-6} M-Mn^{VII}, 2.9×10^{-4} M-V^{IV}, ca. 7×10^{-6} M-Mn^{II}, 1.0M-HClO₄, ionic strength 3.0M; 10.5°C

initially of manganese(II) results in an enhancement of initial rate. In qualitative conformity with this, owing presumably to manganese(II) as product, we find an increase of rate in excess of the second-order rate law for stoichiometry 5, as runs proceed (see Figure 2). It has not been possible, below, to reconcile the initial with the later manganese(II) effect. This is partly due to the non-stoichiometry noted above. If the stoichiometry is actually <5, curvature will be introduced into a second-order plot for which stoichiometry 5 has been erroneously taken.

In order to simplify the otherwise intractable kinetics we have chosen to include the effect of manganese(II)

⁷ D. R. Rosseinsky and M. J. Nicol, *Electrochim. Acta.*, 1966, **11**, 1069.

⁸ C. Wagner and H. Preiss, *Z. anorg. Chem.*, 1928, **168**, 1928.

on the rate plot in with the stoichiometry, selecting an apparent stoichiometry S which best fits the rate law (9).

$$([\text{V}^{\text{IV}}] - S[\text{Mn}^{\text{VII}}])^{-1} \times \ln \left\{ \frac{[\text{Mn}^{\text{VII}}]_0}{[\text{V}^{\text{IV}}]_0} \cdot \frac{[\text{V}^{\text{IV}}]_0 - S([\text{Mn}^{\text{VII}}]_0 - [\text{Mn}^{\text{VII}}])}{[\text{Mn}^{\text{VII}}]} \right\} = kt \quad (9)$$

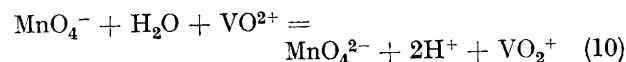
As expected from the dual burden they bear, these values mostly lying between 2 and 3.5 are rather lower than the direct stoichiometry measurements, 2.8 to 4.7. The numerical consequence of this procedure is only a general lowering of the rate constants by 20–30%, the precise value of S finally taken not appreciably affecting the final rate constant. To exemplify, in one run (Figure 2) with $S = 5$, $k(5)$ is 38.2 l. mole⁻¹ sec.⁻¹ from the initial slope, while $k(3)$ is 29.9 and the final $k(2.2)$ is 28.8 l. mole⁻¹ sec.⁻¹. The fitted k values (Table 4) are indeed satisfactorily constant, and though

TABLE 4

Rate constants (l. mole ⁻¹ sec. ⁻¹) for reaction of V ^{IV} with Mn ^{VII} at 10.7° (ionic strength 3.00M)				
Other initial concns. and rate constants k				
Initial concentrations (fixed)	10 ⁴ [Mn ^{VII}] (M)	k	10 ⁴ [Mn ^{VII}] (M)	k
1.00M-H ⁺	0.346	24.8	0.538	26.7
2.9 × 10 ⁻⁴ M-V ^{IV}	0.460	26.8	0.647	29.8*
ca. 7 × 10 ⁻⁶ M-Mn ^{II}	0.497	27.9	0.733	25.9
(* only: 6.5 × 10 ⁻⁵ M-V ^V)	Average: 27.0 ± 1.2			
	10 ⁴ [V ^{IV}] (M)	k	10 ⁴ [V ^{IV}] (M)	k
1.00M-H ⁺	1.74	26.9	3.48	30.1
ca. 0.53 × 10 ⁻⁴ M-Mn ^{VII}	2.32	27.5	4.06	28.5
ca. 7 × 10 ⁻⁶ M-Mn ^{II}	2.90	28.8	5.80	28.4 †
(† only: 8.76 × 10 ⁻⁵ M-Mn ^{VII})	Average: 28.4 ± 0.8			
	10 ⁴ [Mn ^{VII}] (M)	k	10 ⁴ [V ^{IV}] (M)	k
2.00M-H ⁺	0.325	2.42	41.1	
ca. 6 × 10 ⁻⁶ M-Mn ^{II}	0.600	2.97	46.2	
(‡ only: 8.3 × 10 ⁻⁴ M-Mn ^{II})	0.864	3.98	45.8	
	0.973	3.21	48.8	
	0.601	2.97	93.4 ‡	
	10 ⁴ [Mn ^{II}] (M)	k	10 ⁴ [Mn ^{II}] (M)	k
1.00M-H ⁺	ca. 0.06	27.2	2.31	52.6
58 × 10 ⁻⁴ M-V ^{IV}	0.29	33.5	4.58	59.2
(0.84–0.90) × 10 ⁻⁴ Mn ^{VII}	0.96	43.0	4.58	59.6 §
(§ only: 3.48 × 10 ⁻⁴ M-V ^{IV} and 0.43 × 10 ⁻⁴ M-Mn ^{VII})			6.86	62.3
Rate constants at 21.1°				
	10 ⁴ [Mn ^{VII}] (M)	k	10 ⁴ [Mn ^{VII}] (M)	k
1.00M-H ⁺	0.20	66.6	0.456	54.1
2.9 × 10 ⁻⁴ M-V ^{IV}	0.236	65.5	0.581	64.3
ca. 4 × 10 ⁻⁶ M-Mn ^{II}	0.326	74.8	0.679	67.9
	0.422	56.9	Average: 65.7 ± 3.9	

there remains the complication of the manganese(II) effect dealt with below, the evidence is strongly in favour of the simple second-order reaction of V^{IV} with Mn^{VII} as the rate-determining step.

The dependence of rate on [H⁺] (Table 4) indicates an order about or just less than unity in hydrogen ion. Since V^{IV} loses two protons from its hydration shell in forming V^V, we infer that MnO₄⁻ is protonated before or during electron transfer. Certainly the Mn product of the first step is likely to be HMnO₄⁻ (acidity constant K_a ca. 10⁻¹⁰ mole l.⁻¹)⁹ rather than MnO₄²⁻. This follows from the electrode potentials¹⁰ which yield for the process (10) an equilibrium constant of ca. 10⁻⁷ mole² l.⁻².



Such an adverse value would require an appreciable reverse reaction, with retardation by V^V which (Table

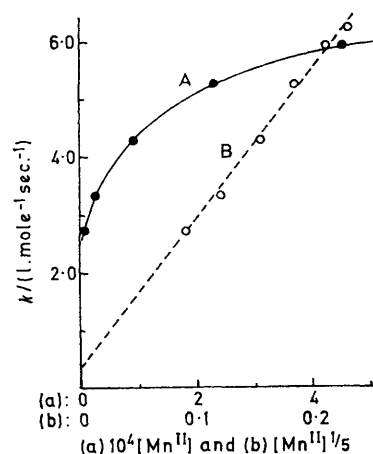


FIGURE 3 Dependence of fitted second-order rate constants for V^{VI} + Mn^{VII} on initial manganese(II) concentration (to first or one-fifth power)

4) is not observed. The K_a value for HMnO₄⁻ as immediate product accords with the kinetic data.

Manganese(II) added initially results in acceleration, as shown in Table 4. The fitted S values, average 2.3, are no different from the preceding ones. The variation of k with [Mn^{II}] is shown in Figure 3. Clearly manganese(II) reacts with manganese(VII) to form an intermediate which reacts with vanadium(IV) more rapidly than does manganese(VII). The identity of the intermediate might be established by a full kinetic analysis involving the simultaneous observation of manganese(VII) disappearance, vanadium(V) appearance, and possibly the occurrence of manganese(III) in the system; facilities are not available to do this. However, the rate constant for reaction of vanadium(IV) with manganese(III) is known⁶ to be 100 l. mole⁻¹ sec.⁻¹, that is, only about 5 times that for reaction with permanganate. Thus manganese(III) would be expected to accumulate to some extent. If excess of manganese(VII) is used,

⁹ L. Sillen and A. Martell, 'Stability Constants,' The Chemical Society, London, 1961.

¹⁰ W. M. Latimer, 'Oxidation Potentials,' Prentice-Hall, Englewood Cliffs, New Jersey, 4th edn.

and the absorbance of this excess subtracted, the spectrum of the final solution does indeed show a new maximum in the region of the manganese(III) peak, 460 nm. (Table 5). [From a study of the reaction of

TABLE 5

Spectrum of final reaction solution: Absorbances

Solution 1: $7.0 \times 10^{-5}\text{M-Mn}^{\text{VII}}$, 1.00M-HClO₄.
 Solution 2: $7.0 \times 10^{-5}\text{M-Mn}^{\text{VII}}$, $1.30 \times 10^{-4}\text{M-V}^{\text{IV}}$, 1.00M-HClO₄
 (studied 30 min. after mixing).

Wavelength (nm.)	Solution 1	Solution 2	Solution 2	Solution 2
	(Mn ^{VII})	(Mn ^{VII} + Products)	(Mn ^{VII} only)	(Products)
420	0.019	0.029	0.015	0.014
440	0.030	0.036	0.015	0.021
460	0.085	0.062	0.040	0.022
480	0.205	0.118	0.100	0.018
500	0.400	0.212	0.198	0.014
520	0.590	0.276	0.280	(-0.004)
530	0.675	0.342	0.342	0.000
550	0.645	0.330	0.320	0.010

(Column 4 values calculated from the 530 nm. absorbance and the column 3 values)

manganese(II) with permanganate,² the amount of manganese(III) expected from such direct reaction is small.]

While the enhancement of rate constant by the presence of manganese(II) added initially can be accommodated (Figure 3, B) by the inclusion of a factor $[\text{Mn}^{\text{II}}]^{\ddagger}$ in the rate, now apparently $k''[\text{V}^{\text{IV}}][\text{Mn}^{\text{VII}}] - [\text{Mn}^{\text{II}}]^{\ddagger}$, no simple mechanism can account directly for this empirical rate law. Our preceding analysis is based on the behaviour given by Figure 3, curve A for low-Mn^{II} conditions.

Apart from the acidity effect, the reaction is thus superficially comparable with $\text{V}^{\text{IV}} + \text{ClO}_3^-$ (following paper), being predominantly of the second order, participation of product species introducing kinetic complexity in both. The mechanistic difference from the $\text{V}^{\text{IV}}-\text{Cr}^{\text{VI}}$ reaction arises from the smallness of the equilibrium constant for the first step of the latter reaction.

EXPERIMENTAL

Vanadium-(IV) and -(V) solutions in perchloric acid, and the NaClO₄ solutions for the ionic-strength maintenance, were made from AnalaR reagents and standardised by established methods.⁷ AnalaR potassium dichromate was used for the chromium(VI). Runs were started by the addition of vanadium(IV) to chromium(VI) solutions. Chromium(VI) concentration changes were followed spectrophotometrically in a thermostatted optical cell in a Zeiss PM4Q(11) spectrophotometer, at 350 or 365 nm. Molar absorptivities are in Table 1.

Potassium permanganate solutions were prepared from the AnalaR reagent, and boiled and filtered. They were standardised amperometrically with iron(II) solution. The reactions with permanganate were again studied in thermostatted optical cells, by following the manganese(VII) absorption at 525 nm. At this wavelength absorption due to other species were negligible (Table 1).

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