A $Cp_4M_4X_4$ cluster with only two excess electrons already has 45–80% of the metal–metal bonding afforded by the *frontier* orbitals. It is therefore not surprising to find a large number of clusters with fewer than 12 excess electrons but with fairly short M–M bonds (Table VIII). Another consequence of the nearly nonbonding or weakly antibonding nature of the $1t_2$ orbital is that first-order Jahn–Teller distortions for partially filled $1t_2$ configurations are expected to be relatively weak. Thus, idealized T_d and D_{2d} geometries with differences in M–M distances ≤ 0.13 Å are seen for electron configurations t_2^2–t_2^5 (8–11 excess electrons, Table VIII). Small distortions from T_d symmetry also imply small splittings of the degenerate levels so that complex magnetic behavior for clusters with 8–11 excess electrons is anticipated.

Conclusions

The preponderance of experimental observations supports the Dahl model rather than the bonding scheme proposed by Bottomley and Grein. The qualitative Dahl model is also supported by an EHMO calculation with the "standard" Hoffmann parameterization. The major differences between this parameterization and the one used by BG seems to be that the H_{ii} value used by BG for the metal s orbitals places them at much lower energies. The frontier M–M orbitals would then contain more metal s character, and this might account for the high energy BG find for the 1a MO. The paramagnetism of $Cp_4Cr_4O_4$ is suggested to be caused by the small HOMO–LUMO separation. Professor F. Bottomley has recently informed us that $Cp_4Cr_4O_4$ is *diamagnetic* below 20 K. This low-temperature diamagnetism is predicted by the model presented here. We thank Professor Bottomley for this information.[65]

The most convenient synthesis of Mo–S cubane clusters of the type $Cp'_2Cp''_2Mo_4(\mu_3\text{-}S)_4$ seems to be the reaction of $Cp'_2Mo_2(CO)_4$ ($Mo{\equiv}Mo$) with either $Cp''_2Mo_2S_2(SH)_2$ or $Cp''_2Mo_2(SC_3H_6S)_2$. These clusters are readily oxidized by two reversible 1e processes in acetonitrile—no reductions are observed in this solvent.

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Appendix: Details of the Calculations

Extended Hückel molecular orbital (EHMO) calculations were performed with use of the programs ICON8 and FMO furnished by R. Hoffmann. We have employed noniterative calculations with the weighted H_{ij} formula.[33] Slater orbitals were used, and double-ζ expansions were employed for the metal d orbitals. Atomic parameters are collected in Table XI.[34] Molecular geometry was idealized to T_d symmetry for the M_4X_4 core (D_{2d} with the Cp rings). Atomic distances are listed in Table XII. These distances were chosen to closely match X-ray structural results when applicable.

Supplementary Material Available: Table III (thermal factors) and Table VIIS (complete list of bond angles) (4 pages); Table XIIIS (listing of F_o vs. F_c) (15 pages). Ordering information is given on any current masthead page.

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Contribution from the Institut de Chimie,
Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

Kinetics of Vanadium(III)–Chromium(II) Electron Transfer Revisited

François P. Rotzinger[1]

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The oxidation of Cr^{2+} by V^{3+} has been reinvestigated at higher acidities. This has led to the observation of the previously unknown outer-sphere electron-transfer pathway (k_{OS}). At $[H^+] = 0.56$–2.56 M, 25 °C, and $I = 3.0$ ($NaClO_4$) the known rate law $-d[V^{3+}]/dt = -d[Cr^{2+}]/dt = k_{obsd}[V^{3+}][Cr^{2+}]$ was confirmed, but a different acid dependence, $k_{obsd} = k_{OS} + k_{IS}K_a/[H^+]$, was found. The rate constant $k_{IS} = 370 \pm 20\ M^{-1}\ s^{-1}$ for OH^--mediated inner-sphere electron transfer is in agreement with the previous studies, while $k_{OS} = 0.20 \pm 0.03\ M^{-1}\ s^{-1}$ is of the order of magnitude of the value predicted by the Marcus theory (0.01–0.08 $M^{-1}\ s^{-1}$). The (acid catalyzed) decomposition of the binuclear intermediate $VOHCr^{4+}$ was not detected at high $[H^+]$. The V^{3+}–Cr^{2+} reaction represents a d_{σ^*}-donor–d_π-acceptor system. The intrinsic rate advantage for inner-sphere electron transfer, $\chi = k_{IS}(K_{IS} \rightarrow 1)/k_{OS}(K_{OS} \rightarrow 1) > 12\,000$, is large and comparable with values found for d_{σ^*}-donor–d_{σ^*}-acceptor systems.

Introduction

The oxidation of Cr^{2+} by V^{3+} in acid aqueous solution was investigated and discussed by Espenson,[2] Sykes,[3] Haim,[4] and Adin and Sykes.[5] The presently accepted mechanism involves reactions 1–3 with $k_{IS}K_a = 0.624\ s^{-1}$ and $k_{-IS}/k_H = 0.108$ M.[2,6] The

$$V^{3+} + H_2O \rightleftarrows VOH^{2+} + H^+ \quad K_a \tag{1}$$

$$VOH^{2+} + Cr^{2+} \rightleftarrows VOHCr^{4+} \quad k_{IS}, k_{-IS} \tag{2}$$

$$VOHCr^{4+} + H^+ \rightarrow V^{2+} + Cr^{3+} + H_2O \quad k_H \tag{3}$$

$$V^{3+} + Cr^{2+} \rightarrow V^{2+} + Cr^{3+} \quad k_{OS} \tag{4}$$

relatively inert binuclear intermediate $VOHCr^{4+}$ with d^3-d^3 electron configuration is present at steady-state concentration. It is formed via inner-sphere electron transfer (reaction 2) and decays via acid catalysis (reaction 3). The outer-sphere reaction (4), however, was not detected under the experimental conditions ($[H^+] \leq 0.5$ M) used in earlier studies.[2,5] Therefore, the reaction was reinvestigated at higher acidity ($[H^+] = 0.56$–2.56 M, $I = 3.0$), where the concentration of the very reactive VOH^{2+} is lower. Then, the contribution of the outer-sphere reaction (4) became detectable.

The V^{3+}–Cr^{2+} reaction represents a d_{σ^*}-donor–d_π-acceptor electron-transfer system (d_{xy}, d_{xz}, and d_{yz} with π symmetry and $d_{x^2-y^2}$ and d_{z^2} with σ symmetry with respect to the metal–ligand bond axis). The intrinsic rate advantage for the inner-sphere pathway is of interest in comparison with the previously studied d_{σ^*}-donor–d_{σ^*}-acceptor systems.[7-9] In the d_{σ^*}–d_{σ^*} and d_{σ^*}–d_π systems, efficient donor–acceptor overlap is possible, since

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Table I. Experimental Rate Constants of the V^{3+}–Cr^{2+} Reaction at I = 3.0 ($NaClO_4$), 25 °C, and $[H^+]$ = 0.56–2.56 M

$[H^+]$, M	λ, nm	$10^2[V^{3+}]_0$, M	$10^2[Cr^{2+}]_0$, M	k_{obsd}, M^{-1} s^{-1}
0.56	570, 300	1.97	6.29	1.54, 1.58
0.56	300	2.26	5.76	1.62, 1.55
0.56	300	2.47	5.39	1.56, 1.60
0.56	300	4.44	1.80	1.62
0.66	300	1.97	6.29	1.39, 1.34
0.66	300	2.26	5.76	1.38
0.66	300	2.47	5.39	1.40
0.81	300	1.97	6.29	1.14, 1.16
0.81	300	2.26	5.76	1.22
0.81	300	2.47	5.39	1.20, 1.16
1.06	290	0.49	8.98	0.86
1.06	300	1.97	6.29	0.86, 0.88
1.06	570, 300	2.47	5.39	0.88, 0.86
1.56	570, 300	1.97	6.29	0.62, 0.65
1.56	570	2.47	5.39	0.66, 0.67
2.06	570, 290	1.97	6.29	0.55, 0.57
2.06	570	2.47	5.39	0.56, 0.57
2.56	570, 410, 300, 290	0.49	8.98	0.51, 0.52, 0.53, 0.53
2.56	570	1.97	6.29	0.53
2.56	570	2.47	5.39	0.52
2.56	570	2.96	4.49	0.50

$[VOHCr^{4+}]^\ddagger$ is expected to be bent.

Experimental Section

Physical Measurements. UV–vis spectra and the kinetic runs were recorded on a Kontron Uvikon 810 spectrophotometer thermostated to 25.0 ± 0.2 °C.

Reagents. Stock solutions of $Cr(ClO_4)_3$ (0.198 M, 0.12 M $HClO_4$) and $VO(ClO_4)_2$ (0.118 M, 0.36 M $HClO_4$) were prepared as described.[2,10] VO^{2+} and Cr^{3+} (as CrO_4^{2-})[10] were analyzed spectrophotometrically (VO^{2+}, ϵ_{760} = 17.0 M^{-1} cm^{-1};[11] CrO_4^{2-}, ϵ_{374} = 4830 M^{-1} cm^{-1} [12]). Cr^{2+} and V^{2+} were prepared by quantitative reduction of Cr^{3+} and VO^{2+} with amalgamated zinc (Cr^{2+}, ϵ_{713} = 4.83 M^{-1} cm^{-1}; V^{2+}, ϵ_{559} = 4.34 M^{-1} cm^{-1}). The solutions of Cr^{2+}, V^{2+}, and V^{3+} (prepared freshly every day) were handled under nitrogen, which was deoxygenated by passage through two Cr^{2+} solutions (0.5 M). The solutions of Cr^{3+} and VO^{2+} were already deoxygenated prior to reduction in order to prevent any formation of oligomers by air oxidation. V^{3+} (0.109 M, 0.12 M $HClO_4$) was prepared by mixing V^{2+} and VO^{2+} in the ratio 27:23, leaving an excess (8%) of V^{2+} in order to avoid any oxidation of Cr^{2+} by VO^{2+}. The reactant solutions were prepared by mixing the V^{3+} or Cr^{2+} solutions in a 1:1 ratio with 1–5 M $HClO_4$ at I = 5.0 ($NaClO_4$), giving reactant solutions with I = 3.0 and identical $[H^+]$.

Kinetics. Various ratios of Cr^{2+} and V^{3+} solutions with identical $[H^+]$ and I = 3.0 ($NaClO_4$) (prepared as described above) were mixed in a serum-capped 2-cm quartz cell at 25 °C. The optical density was monitored spectrophotometrically as a function of time at various wavelengths (Table I). The values of k_{obsd} and $\Delta\epsilon$ were determined by nonlinear least-squares procedures. The function $\sum(\Delta D_{obsd} - \Delta D_{calcd})^2$ was minimized (e.g. $\Delta D_{calcd} = D_\infty - D(t) = \Delta\epsilon([Cr^{2+}]_0 - [V^{3+}]_0)/(([Cr^{2+}]_0/[V^{3+}]_0) \exp\{([Cr^{2+}]_0 - [V^{3+}]_0)k_{obsd}t\} - 1)$ for $[Cr^{2+}]_0 > [V^{3+}]_0$). The values of k_{obsd} obtained at constant $[H^+]$ showed no variation with the wavelength of study or with the concentration of the reactant in excess (Cr^{2+} or V^{3+}). Measurements made under pseudo-first-order conditions produced the same rates (Table I). The reactions in 0.1–0.4 M H^+ ($NaClO_4$) and 0.5 M H^+ ($LiClO_4$) were measured on a HP 8450 A spectrophotometer in a 1-cm cell. The preparation of the Cr^{2+} and V^{3+} solutions was modified as follows: the Cr^{3+} and VO^{2+} solutions were reduced directly in the $NaClO_4/HClO_4$ or $LiClO_4/HClO_4$ media in order to yield Cr^{2+} or V^{3+} solutions at I = 3.0.

Results and Discussion

The present reinvestigation of the V^{3+}–Cr^{2+} reaction was carried out at $[H^+]$ = 0.56–2.56 M, 25 °C, and I = 3.0 ($NaClO_4$). The known[2,5] rate law $-d[V^{3+}]/dt = -d[Cr^{2+}]/dt = k_{obsd}[V^{3+}][Cr^{2+}]$ was confirmed. Furthermore, at a given $[H^+]$, k_{obsd} was independent of the wavelength, $[V^{3+}]_0$, and $[Cr^{2+}]_0$. The reproducibility was good (Table I).

Table II. Observed and Calculated Rate Constants of the V^{3+}–Cr^{2+} Reaction

$[H^+]$, M	k_{obsd}, M^{-1} s^{-1} [a]	k_{calcd}, M^{-1} s^{-1} (rate law II)[b]
0.56	1.58 ± 0.03 (7)	1.53
0.66	1.38 ± 0.03 (4)	1.33
0.81	1.18 ± 0.03 (5)	1.12
1.06	0.87 ± 0.01 (5)	0.90
1.56	0.65 ± 0.02 (4)	0.68
2.06	0.56 ± 0.01 (4)	0.56
2.56	0.52 ± 0.01 (7)	0.49

[a] Errors are standard deviations. Numbers of determinations are given in parentheses. [b] k_{OS} = 0.20 M^{-1} s^{-1}; $k_{IS}K_a$ = 0.74 s^{-1}.

Table III. Acid Dissociation Constants, Formal Potentials, and Self-Exchange Rates

ion	pK_a	E_f, V	k_{exch}, M^{-1} s^{-1} [a]	ref
V^{3+}	2.7	−0.242	1.0×10^{-2}	18–20
Cr^{3+}	4.29	−0.41	$\lesssim 2 \times 10^{-5}$	10, 21, 22
			$\simeq 10^{-4}$–10^{-3}	8

[a] For $M^{2+/3+}$.

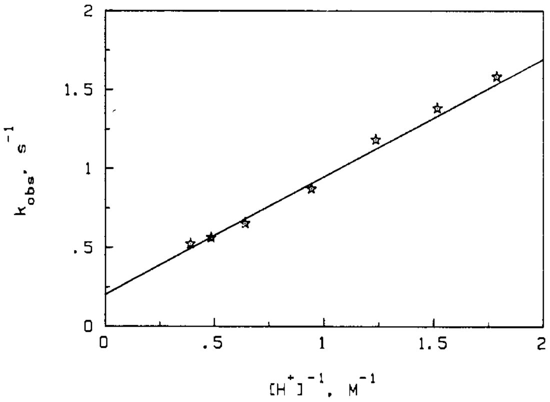

Figure 1. Plot of k_{obsd} vs. $[H^+]^{-1}$ (linearized expression of rate law II). The solid line shows the least-squares fit.

From reactions 1–4, assuming $VOHCr^{4+}$ at steady-state concentration and $K_a << [H^+]$, rate law I was derived. In this rate

$$k_{obsd} = k_{OS} + k_{IS}K_a/(k_{-IS}/k_H + [H^+]) \qquad (I)$$

law, the term k_{OS} has been added to the previously observed[2,5] expression $k_{obsd} = k_{IS}K_a/(k_{-IS}/k_H + [H^+])$. The ratio k_{-IS}/k_H is predicted to decrease with increasing ionic strength, since k_H increases. Thus, at high acidity ($[H^+] \geq 0.5$ M) and high ionic strength (I = 3.0), the ratio k_{-IS}/k_H becomes negligible compared to $[H^+]$, and rate law I reduces to II,[13] which has been observed for other electron-transfer reactions involving metal aqua ions and their conjugate bases.[14]

$$k_{obsd} = k_{OS} + k_{IS}K_a/[H^+] \qquad (II)$$

In fact, a least-squares fit of the experimental data (Table II) to rate law I leads to an insignificant and negative value for k_{-IS}/k_H. However, for the reasons discussed above, this does not argue against the existence of the intermediate $VOHCr^{4+}$. At high acidity, $VOHCr^{4+}$ may still be present but escapes detection in the kinetics. The minimized function was $\sum_i w_i(k_{obsd,i} - k_{calcd,i})^2$ with $w_i = 1/\sigma_i^2$. A good fit was also obtained for rate law II (Table II, Figure 1), and the parameters k_{OS} = 0.20 ● 0.03 M^{-1} s^{-1} and $k_{IS}K_a$ = 0.74 ± 0.04 s^{-1} were found. With use of $pK_a(V^{3+})$ = 2.7 (I = 3.0 ($NaClO_4$), 25 °C)[18] the rate constant for inner-sphere electron transfer k_{IS} = 370 ± 20 M^{-1} s^{-1} was obtained.

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Table IV. Experimental Rate Constants of the V^{3+}–Cr^{2+} Reaction at I = 3.0 ($NaClO_4$), 25 °C, λ = 570 nm, and $[H^+]$ = 0.1–0.4 M

$[H^+]$, M	$10^2[V^{3+}]_0$, M	$10^2[Cr^{2+}]_0$, M	k_{obsd}, $M^{-1}\ s^{-1}$
0.10	1.67	1.67	4.92, 5.38
	2.5	2.5	4.92, 5.16, 5.32, 5.20
	5.0	5.0	5.06, 4.72, 5.44
			5.1 ± 0.3 (av)
0.30	2.83	4.65	2.49
	2.65	4.97	2.55
	2.47	5.30	2.59
			2.54 ± 0.05 (av)
0.40	3.00	4.32	2.00
	2.65	4.97	2.05
	2.33	5.56	2.11
			2.05 ± 0.06 (av)

At lower acidity (viz. $[H^+] \leqslant 0.5$ M at the experimental $[V^{3+}]_0$), traces of the dimer VOV^{4+} [15] (or $V_2(OH)_2{}^{4+}$), formed by dimerization of VOH^{2+}, perturbed the visible spectrum of V^{3+} due to the strong absorbance of VOV^{4+} at 410 nm (ϵ = 6800 $M^{-1}\ cm^{-1}$).[15] At this wavelength, the kinetics became $[V^{3+}]_0$-dependent and biphasic at higher $[V^{3+}]_0$ ($[V^{3+}]_0 \geqslant 0.02$ M) and lower $[H^+]$ ($\leqslant$0.5 M). The first reaction phase involved a decrease of absorbance, presumably due to the reduction of VOV^{4+}. The absorbance then increased in the second phase due to the slower reduction of V^{3+} and VOH^{2+}. In earlier work[2,5] the reactions were monitored at 570 nm. In the present study, it was confirmed that the kinetics at 570 nm are uniphasic and only very slightly $[V^{3+}]_0$ dependent, if at all (Table IV). Obviously, the hydrolytic dimer does not interfere when the reaction is followed at 570 nm. Even under second-order conditions, the rate constants obtained at $[H^+]$ = 0.1–0.4 M (Table IV), were less accurate than those at higher acidity. In this low-acidity range, mixing of the reactants became relatively slow compared to the rate of the reaction and, furthermore, the point at zero time is subject to some systematic error. Nevertheless, the kinetic data were consistent with rate law I as expected ($k_{OS} = 0.18 \pm 0.04\ M^{-1}\ s^{-1}$, $k_{IS}K_a = 0.81 \pm 0.07\ s^{-1}$ and $k_{-IS}/k_H = 0.048 \pm 0.026$ M).

The rate constant for OH^--mediated inner-sphere electron transfer, $k_{IS}K_a = 0.74 \pm 0.04\ s^{-1}$, is in good agreement with $k_{IS}K_a = 0.624\ s^{-1}$ (25 °C and I = 0.6–0.8) from the literature.[2]

The Marcus theory[16,17] predicts $k_{OS} \simeq 0.01$–$0.08\ M^{-1}\ s^{-1}$ (self-exchange rates, potentials, and acid dissociation constants are given in Table III). It is known[23,24] that medium effects may arise from the replacement of H^+ by Na^+ at constant ionic strength. These medium effects are smaller when Li^+ is used as supporting electrolyte instead of Na^+ due to the similar activities of Li^+ and H^+.[25] At $[H^+]$ = 0.50 M the rate constant was found to be $1.93 \pm 0.06\ M^{-1}\ s^{-1}$ when $LiClO_4$ was used as supporting electrolyte. The solutions at $[H^+]$ = 2.56 M ($k_{obsd} = 0.52 \pm 0.01\ M^{-1}\ s^{-1}$) did not contain any $NaClO_4$. On the basis of the observed rates at these two $[H^+]$, the rate constants in $LiClO_4$ are estimated as $k_{IS}K_a \simeq 0.88\ s^{-1}$ and $k_{OS} \simeq 0.18\ M^{-1}\ s^{-1}$. Obviously, the k_{OS} term is not due to medium effects, although they certainly contribute to k_{OS} to some extent. The value of k_{OS} is also in agreement with predictions of the Marcus theory.

Conclusions

In addition to the known[5,6] (inner-sphere) reaction mechanism of the oxidation of Cr^{2+} by V^{3+} (reactions 1–3) the outer-sphere pathway (4) has been detected at higher acidities, where the concentration of VOH^{2+} was lower.

In earlier studies of inner- and outer-sphere electron transfer[7–9] the intrinsic rate advantage for the inner-sphere pathway over the outer-sphere one was defined as $\chi = k_{IS}(K_{IS} \rightarrow 1)/k_{OS}(K_{OS} \rightarrow 1)$. In this example, K_{OS} and K_{IS} refer to the equilibrium constants of reactions 4 and 5. Reaction 5 is a two-step process involving

$$VOH^{2+} + Cr^{2+} \rightleftarrows V^{2+} + CrOH^{2+} \quad K_{IS} \qquad (5)$$

the intermediate $VOHCr^{4+}$ [5,6] at a steady-state concentration. Since this intermediate has a very short lifetime, it is reasonable to assume that its energy is higher than that of $V^{2+} + CrOH^{2+}$. With use of the approximation of the Marcus theory $k_{12} \simeq (k_{11}k_{22}K_{12})^{1/2}$ for the outer-sphere as well as the inner-sphere pathway, χ may be estimated on the basis of the corresponding rate and equilibrium constants: $\chi \simeq k_{IS}(K_{OS}/K_{IS})^{1/2}/k_{OS} = k_{IS}\{K_a(V^{3+})/K_a(Cr^{3+})\}^{1/2}/k_{OS} = 1.2 \times 10^4$. Since reaction 5 proceeds in two steps via the intermediate $VOHCr^{4+}$, which is less stable than $V^{2+} + CrOH^{2+}$, the effective K_{IS} is even smaller and therefore $\chi > 1.2 \times 10^4$.

The intrinsic rate advantage for d_{σ^*}-donor–d_{σ^*}-acceptor systems ranges typically between $\simeq 10^3$ and $\simeq 10^7$ depending on the number of electrons involved in the M_1–X–M_2 bond.[7–9]

For the d_{σ^*}-donor–d_{π}-acceptor system Cr^{2+}–V^{3+}, the intrinsic rate advantage for the inner-sphere pathway, $\chi > 1.2 \times 10^4$, is comparable to the d_{σ^*}-donor–d_{σ^*}-acceptor systems, presumably because efficient donor–acceptor overlap is also possible in *bent* d_{σ^*}-donor–d_{π}-acceptor systems.

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Registry No. Cr^{2+}, 22541-79-3; V^{3+}, 22541-77-1.

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