AQUEOUS ELECTRON-TRANSFER REACTIONS. VANADIUM(IV) AS REDUCTANT COMPARED WITH IRON(II)

D. R. ROSSEINSKY

Department of Chemistry, The University, Exeter EX4 4QD, England

Received August 6, 1971 (Revised Manuscript Received November 15, 1971)

Contents

I. Introduction

Interest in electron-transfer reactions in solution has expanded enormously in the last 2 decades and, together with substitution reactions in solution, they form an important fraction of recent inorganic chemistry. There are a number of general reviews of the subject. For a background to the present article, particular reference might be made to those by Sykes,[1,2] Sutin,[3] and Newton and Baker.[4] Here our aim is frankly eclectic, to review in the light of current theories the reactions of just two reductants, the vanadium(IV) and iron(II) aquo ions, with a series of common oxidants. The oxidants, given in Table I, represent a notable diversity of reactant. Despite the hydrolytic changes necessarily accompanying electron transfer from VO^{2+} to form VO_2^+, in contrast with Fe^{2+} and Fe^{3+}, and notwithstanding the variety of oxidants, it can be stated immediately that there is a marked parallel between the Fe^{II} and V^{IV} reactions.[5] Specific minor deviations from this generalization can then legitimately be rationalized by mechanistic special pleading based on the structural peculiarities of the reductants. By way of introduction, theories for the mechanisms of electron transfer are outlined, in simplified but mildly novel form. The observed reaction patterns can be almost completely understood in the general terms of these theories.

Table I

Documented Oxidants of Both Vanadium(IV) and Iron(II)

Cationic	Mn^{III}	Fe^{III}	Co^{III}	Tl^{III}	
	V^{V}	V^{IV}	V^{III}	U^{V}	Ag^{II}
Other	Cl_2	Cl^{V}	Cr^{VI}	Cr^{V}	

Reductants of vanadium(V) and iron(III): Sn^{II}, I^-, $Fe(CN)_6^{4-}$

In passing, we feel pressed to comment that the electron-transfer literature suffers grievously from elaboration by footnote. Far from supplying an expository counterpoint, such insertions, frequently but irregularly repeated, make for needless verbal and logical interruption.

II. Theories of Electron Transfer

A. INTRODUCTION

Distinctions must be drawn firstly between *distant reaction* with reactants separated by many tens of ångströms, and *close reaction* involving separations of some few (less than 10, say) ångströms, and then between several possibilities of close reaction. While the former must necessarily be invoked for the electron transfer between reactants frozen at about 100-Å separations in acid glasses,[6] it is difficult to conceive of the

---

[1] A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967).

[2] A. G. Sykes, *Essays Chem.*, **1**, 25 (1970).

[3] N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

[4] T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, **No. 71**, 268 (1968).

[5] D. R. Rosseinsky, *J. Chem. Soc. A*, in press.

[6] (a) D. L. Baulch, F. S. Dainton, D. A. Ledward, and H. Sugier, *Trans. Faraday Soc.*, **62**, 2200 (1966); (b) A. C. Wahl, *J. Inorg. Nucl. Chem.*, **28**, 3069 (1966).

persistence of sufficient order in fluid phases for band conduction to occur in solution,[7] and unless further evidence persuades otherwise, this reviewer favors close-reaction mechanisms, as follows.

B. CLOSE REACTION

We initially formulate the mechanism of transfer of an electron between two oxidation states of the *same* element (hence termed here an *electron exchange* or *self exchange*), typically two hexaaquo ions M^{2+} and M^{3+}. The rate is measured either by the rate of transfer of isotopic labeling from one oxidation state to another in successive separations of oxidation state,[8] or from line broadening of resonance signals in those cases where electron transfer provides a relaxation mechanism.[9] In such reactions the chemical potentials of products and reactants are identical or virtually so. Thus the standard Gibbs-function change $\Delta F°_1$ is zero here; subscript "1" refers to the single element M. For redox reactions, below, "12" indicates the two elements reacting. In this case $\Delta F°_{12}$ can differ positively (*e.g.*, $Mn^{2+} + Fe^{3+} \rightarrow$) or negatively ($Mn^{3+} + Fe^{2+} \rightarrow$) from zero, sometimes greatly. $\Delta F°_{12}$ is obtained from chemical measurement of the equilibrium constant K_{12}, or from the standard electrode potentials $E°_1$ and $E°_2$ valid for the ionic-strength medium used for the reaction (commonly $NaClO_4 + HClO_4$ or $LiClO_4 + HClO_4$, at fixed total ionic strength). We proceed to consider some possibilities of nuclear configuration and electron distribution in the activated complex.

C. OUTER-SPHERE ADIABATIC MECHANISM

The ideas of Marcus,[10] Hush,[11] and Levich,[12] though not quoted exactly, are used here as bases for an outline[13] of the physical processes confronting the reacting particles. If for both reactants the ligands are observed in separate experiments to exchange with free ligand species in solution much more slowly than the rate of electron transfer, as in the reaction $Fe(CN)_6^{4-} + Fe(CN)_6^{3-}$, then the ligands clearly will remain coordinated during the electron transfer. The further inference is made that the coordination geometry persists, *i.e.*, that the coordination shells do not interpenetrate, in a consequently "outer-sphere" mechanism. Ford observes[14] that this is an extra assumption: transient labilization in the activated complex could allow one reactant normally *n*-coordinate to become $(n + 1)$-coordinate, so linking with a ligand of the other reactant to form a bridged activated complex. It is difficult, however, to envisage an empirical distinction between these possibilities, and here we shall follow the usual outer-sphere hypothesis.

The transfer of the electron is concomitantly assumed adiabatic, involving a smoothly incremental distribution over the oxidant transfer orbital, represented in the activated complex by the fractional extent of transfer α. For a symmetrical activated complex (to which the electron-exchange case will approximate), α should be just 0.5. Further simplifications ensue from the outer-sphere assumption, since, firstly, the reactant separation a, about 7–8 Å for aquo ions, allows neglect of dielectric saturation on juxtaposition. Hence the Coulomb energy, $u_{coul} = z_1z_2e^2/\epsilon a$, serves to predict the approach barrier, ϵ being the ordinary solvent permittivity. Then secondly, the interaction energy u_{res} for the putative one-electron bond formed by the transferring electron (a δ bond in transition metal ion reactions) will undoubtedly be small enough to be neglected, but may be assumed sufficient (say 0.02 eV) to give a tunneling probability κ of unity. If $u_{res} <$ 0.02 eV, say, then κ must be calculated from u_{res} by the Zener–Landau[15] formula, a complication commonly disregarded because of our ignorance of actual values of u_{res}.

Following the Franck–Condon principle, it is cheaper in energy for bond lengths of both reactants to become adjusted, before electron transfer, part way to their final values, rather than, in say $M^{3+} + {}^*M^{2+}$, to have unaccommodated electron transfer leaving an $M^{2+}\text{–}OH_2$ product with the bond length of its progenitor $M^{3+}\text{–}OH_2$, and its companion product ${}^*M^{3+}\text{–}OH_2$ with the ${}^*M^{2+}\text{–}OH_2$ bond length. This is illustrated in Figure 1. Simple potential functions for hydration bonds as in Figure 1, including the ligand fields, serve[11] to predict this reorganization energy u_{reorg}; the "roughness" arising from quantization of the vibrational excitation is ignored. u_{reorg} can be formulated alternatively in terms of the bond force constants.[10] For aquo ions the activated complex bond lengths $d^{\ddagger}$ will be close to the mean, $(d^{II} + d^{III})/2$ in our example; the separation a is then $2d^{\ddagger} + 2r_w$, where r_w is the H_2O radius commonly assumed to be 1.4 Å.

A further barrier arises from dielectric relaxation of the uncoordinated solvent, since, in the case of water, and generally, dipole relaxation time exceeds the charge fluctuation period within the activated complex.[11] Hence the ambient permittivity experienced by the transferred fraction α of charge is then only the electronic part n^2 (1.8 for water) in contrast with the total permittivity ϵ (78.5 for water), where n is the visible refractive index. The simplest continuum representation[13] of the adverse potential, which subjects the transferred charge αe [borne by a sphere of a diameter $2(d^{\ddagger} + r_w)$] to a dielectric relaxation barrier u_{diel}, yields for the latter

$$u_{diel} = \frac{(e/2)^2}{2(d^{\ddagger} + r_w)}\left\{\frac{1}{n^2} - \frac{1}{\epsilon}\right\} \qquad (1)$$

where α has been taken as $^1/_2$. This formula illustrates clearly the physical origin of the effect, which seems rather better described as a relaxation effect than a change in the Born hydration energy.[16] Marcus,[10] who first elaborated such a model, required preadjustment of the dielectric to minimize the barrier during the transfer. The work of preadjustment turns out to be exactly equal to u_{diel}. The marginal enhancement of u_{res} by the greater symmetry arising from preadjustment will not have much effect in the outer-sphere mechanism, in view of universal omission of u_{res} anyway on the grounds of its presumed smallness.

For a one-element electron exchange we sum the major terms for the potential employed in the Boltzmann exponent in collisional (Marcus[10]) or transition-state (Hush[11]) formulations.

---

(7) I. Ruff, *Quart. Rev., Chem. Soc.*, **22**, 199 (1968).

(8) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(9) C. R. Giuliano and H. M. McConnell, *J. Inorg. Nucl. Chem.*, **9**, 171 (1959).

(10) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964), and references quoted there.

(11) N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1961).

(12) V. I. Levich, *Advan. Electrochem. Electrochem. Eng.*, **4**, 249 (1966), and references quoted therein.

(13) D. R. Rosseinsky, *Chem. Rev.*, **65**, 467 (1965).

(14) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(15) (a) C. Zener, *Proc. Roy. Soc., Ser. A*, **140**, 660 (1933); (b) L. Landau, *Zh. Fiz. SSR*, **2**, 46 (1932).

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 464.

$$u = u_{\text{coul}} + u_{\text{reorg}} + u_{\text{diel}} + \begin{Bmatrix} u_{\text{trans}} \\ u_{\text{res}} \end{Bmatrix} \qquad (2)$$

u_{trans} is the tunneling barrier $-RT \ln \kappa$ mentioned earlier; the terms in braces are those commonly omitted, one in any event excluding the other.

Checks against experiment suffer some uncertainty from the choice of the preexponential factors for reactions in solution, but approximate agreement *is* found, and theoretical $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the aquo-ion reactions are quite impressive.[11] A huge but untypical disagreement[11] for $V^{2+} + V^{3+}$ (rate observed $\ll$ predicted) gives cause for concern.

For redox reactions of elements "1" and "2", the free-energy change ΔF°_{12} accompanying the chemical transformation is of course governed by the potential energies of interaction of all particles in the system suitably averaged. The same interactions govern the formation of the activated complex and hence the activation free energy $\Delta F^{\ddagger}$. In particular, the fractional activated-state transfer of electron can be shown[11] to lead to a fractional contribution $\alpha\Delta F^{\circ}_{12}$ in $\Delta F^{\ddagger}$ and, with molecular potentials converted to molar free-energy terms and omitting terms included earlier in braces, we obtain

$$\Delta F^{\ddagger}_{12} = \Delta F_{\text{coul}} + \Delta F_{\text{reorg}} + \Delta F_{\text{diel}} + \alpha\Delta F^{\circ}_{12} \qquad (3)$$

If the "reorg" and "diel" terms are approximated by the averages for the exchange reactions 1 and 2, then

$$\Delta F^{\ddagger}_{12} = {}^{1}/_{2}(\Delta F^{\ddagger}_{1} + \Delta F^{\ddagger}_{2}) + \alpha\Delta F^{\circ}_{12} \qquad (4)$$

or, following Marcus' exposition[10]

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2} \qquad (5)$$

The k and K represent rate and equilibrium constant, respectively, and f is a factor partly taking account of departure of α from 0.5. Marcus[10] derives $\ln f$ as being

$$\ln f = (\ln K_{12})^2/4 \ln (k_1 k_2/Z^2) \qquad (6)$$

where Z is the assumed collision rate (*ca.* 10^{11} M^{-1} sec^{-1}) appearing in the preexponential of his rate-constant formulation.

Intuitive mechanistic prejudice dictates (independently of the derivation of f) that when ΔF°_{12} is very large and positive, the activation process *is* largely the formation of products, so here α should approach unity. It will not be precisely so since, for example, while ΔF_{reorg} will be largely included in $\alpha\Delta F^{\circ}_{12}$, ΔF_{diel} should be now markedly increased. On the other hand, if ΔF°_{12} is very negative we expect $\alpha \rightarrow 0$, from the microscopic reversibility principle for the previous case. Hush has illustrated but not exploited these contingencies.[11] That the extreme cases of ΔF°_{12} do not fall out immediately and obviously from the Marcus formulation seems to this reviewer to be a shortcoming of that theory. Nevertheless, the cross-reaction relation, eq 5 and eq 6, does hold for an ever-growing number of cases.[1-3] Failures can often be accounted for: $V^{III} + Cr^{II}$ (experimentally "too fast") proceeds by a bridged intermediate[17] precluding application of the theory, $Co^{III} + Fe^{II}$ (experimentally too slow)[18] involving a spin-state change in Co not accommodated by the theory. Failure with $Ce^{IV} + Fe^{II}$[19] (too slow) has not been entirely satisfactorily accounted for. A suggested[20] H-atom transfer (section II.E) does not explain inhibition of the in theory faster adiabatic path, and that one of the self-exchanges is bridged[16] (below) is a plausible but perhaps facile view. Invocation of preequilibria in Co^{III} reactions fails to salvage the outer-sphere cross-reaction model, and further thought is clearly called for in these few cases.

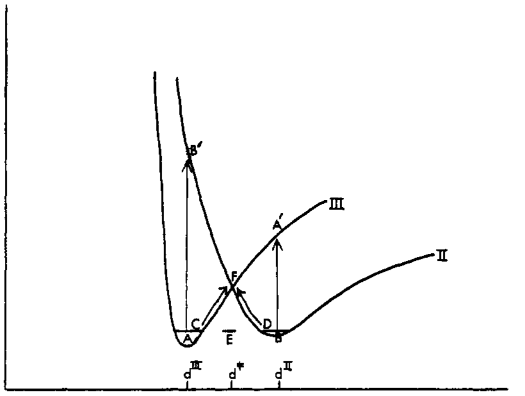

Figure 1. Ion–water potential energy *vs.* ion–water separation. Diagram contrasting an optical or "nonadiabatic" Franck–Condon transfer A, B → B′, A′ with an adiabatic transfer at F following reorganizations C–F and D–F. The energy u_{reorg} is *twice* the value EF (*two* ions reacting).

D. INNER-SPHERE ACTIVATED COMPLEX

Here a ligand X of one reactant becomes coordinated to the second reactant ion as well, forming a bridge. There is little

$$M^{III}X^{2+} + M^{2+} \rightleftharpoons \{M\text{-}X\text{-}M^{4+}\}^{\ddagger}$$

evidence that H_2O acts as a bridging ligand, but OH^- and O^{2-} as oxo ligands certainly may, and definite evidence of transfer of halides from inert oxidants[21] (such as Cr^{III} or many Co^{III} complexes) to inert products shows their bridging capacity. A typical example[22] is

$$(H_2O)_5Cr^{III}Cl^{2+} + {}^{*}Cr^{II}(OH_2)_6{}^{2+} \rightleftharpoons \{(H_2O)_5CrCl^{*}Cr(OH_2)_5{}^{4+}\}^{\ddagger} + H_2O$$

followed by decomposition to Cr^{II} and $(H_2O)_5{}^{*}CrCl^{2+}$. Labile reactants (Fe^{2+} and Fe^{3+}, for example) cannot be unequivocally demonstrated to bridge in the presence of halide ligands, and indirect or comparative arguments regarding mechanisms and efficacies of bridging have provided scope for extensive debate and experimentation. Thus, for some contrasting views on Fe^{2+}, see ref 23–25.

There are some correlations[24,26] supporting the view that a cross-reaction relation may be applicable also to bridged reactions. Before further discussion, we again outline for the whole process a breakdown into potential energy terms u, to analyze what is probably a smoothly concerted molecular event.

---

(17) A. Adin and A. G. Sykes, *J. Chem. Soc. A*, 351 (1968).

(18) L. E. Bennett and J. C. Sheppard, *J. Phys. Chem.*, **66**, 1275 (1962).

(19) M. G. Adamson, F. S. Dainton, and P. Glentworth, *Trans. Faraday Soc.*, **61**, 689 (1965).

(20) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(21) H. Taube, *Can. J. Chem.*, **37**, 129 (1959); *Pure Appl. Chem.*, **24**, 289 (1970); "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, London, 1970.

(22) D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80**, 1091 (1958).

(23) C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 504 (1970).

(24) R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, **90**, 6364 (1968).

(25) D. W. Carlyle and J. H. Espenson, *ibid.*, **90**, 2277 (1968).

(26) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

(i) Bridge formation can be viewed as involving two virtual terms: u_{dis} for displacement of M^{2+} ligand and u_{att} for the possibly minimal stabilization accruing from attachment of the bridge ligand X to the vacated site. Which reactant loses the ligand must be a question almost specific to each reaction, involving a balance of u_{dis} and u_{att} for the alternatives. (Often this is obvious.)

(ii) Concomitantly the juxtaposition of charged species involves a Coulombic *type* of interaction, but the relative smallness of separation *a* here precludes use of the macroscopic solvent permittivity. Probably account could be taken of dielectric saturation in u'_{coul} as by Laidler and Sacher's theory,[27] where close ionic approach is envisaged.

(iii) Thirdly, there will be a sum of terms for the charge transfer, associated with an "interaction" energy u_{tfr}. Electronic motion through the activated complex will be achieved by one of several possibilities:[28] stepwise redox involving X, direct overlap, superexchange or double exchange, with a u_{tfr} of in general problematical sign and magnitude. Endicott[24] remarks that the interaction energy here as for outer-sphere transfer could again be small. If appreciably *negative*, it would diminish the following associated barriers. Prior to transfer some minor bond-length adjustments, involving u_{reorg}, would mitigate Franck–Condon barriers as before. There would in some of the mechanisms listed be a dielectric relaxation barrier u_{diel}, appreciable but less than the outer-sphere value, if only because the distance traversed by the electron is smaller.

(iv) Finally, as for the outer-sphere mechanism, the extent of transfer and fraction of the overall ΔF°_{12} should again be of influence,[29] but contemplation of the previous terms suggests a more complex dependence here, in particular that α will be more closely related to the magnitudes of the accompanying u terms. Inclusion of αu^0_{12} serves to encompass such dependence.

The foregoing leads to the total potential

$$u^{\ddagger}_{12} = (u_{dis} + u_{att}) + u'_{coul} + (u_{tfr} + u_{reorg} + u_{diel}) + \alpha u^0_{12} \quad (7)$$

This expression (or more exactly, list), though not immediately evaluable, puts into perspective the complexity of bridging in contrast with outer-sphere transfers. It also illuminates the suggestion that many V^{2+} reactions are bridged, with rates that are substitution controlled,[3] being governed by the water exchange rate at V^{2+}. The redox rate constants and $\Delta H^{\ddagger}$ values do indeed often agree quite closely with the aquation rate values[30] for V^{2+}. Thus here $u_{dis} + u_{att}$ by inference predominate, u_{att} presumably being approximately constant, and probably small, for all incoming oxidant ligands. (V^{2+} redox reactions when faster than substitution are presumed outer sphere.) For other bridged reactions the assumption, underlying the cross-reaction relation, that all terms besides αu^0_{12} are the means of the appropriate electron-exchange values, is an eminently acceptable one, but no criteria have been formulated for anticipation of such presumably nonconforming cases as V^{2+}, where one group of terms is dominant in $u^{\ddagger}$.

A kinetic formulation illustrates the two kinds of reaction. We envisage three sequential steps, the first two of which are the penetration of the inner sphere, followed by the rearrangement of hydration molecules, and then possibly electron transfer. When penetration and its reverse, separation, occur many times before electron transfer occurs, then eq 7 applies, but if electron transfer occurs every time there is penetration the rate is controlled by the penetration process and approximates to the aquation value. Hence

$$\mathrm{ML} + \mathrm{M'} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{MLM'}$$

$$\mathrm{MLM'} \xrightarrow{k_3} \text{redox products}$$

and the rate equals $k_3k_1[\mathrm{ML}][\mathrm{M'}]/(k_2 + k_3)$.

E. FURTHER MECHANISTIC POSSIBILITIES

Hydrogen atom transfer has been favored by several workers as the reductive mechanism (summary, ref 1). In the most plausible of these suggestions hydrogen bonding between the hydration shells is supposed, and a rather cumbersome sequence of steps can depict the ferrying over of an electron by a proton, from say $Fe(OH_2)_6^{2+}$ to $Fe(OH_2)_6^{3+}$, concluding with the return of the "empty" proton to the Fe^{III} product. Distinguishing criteria are difficult to envisage. Something like this may indeed occur in a process quite properly treated by the outer-sphere theory, in which details of ligand structure are perhaps underemphasized. Since the frequency of charge fluctuation[11] is not incommensurate[13] with that of bond vibration, coupling of the two to attain a critical, reactive vibration could be termed H atom transfer. The question again remaining unresolved then is whether this detail of the transfer, differing from simple orbital overlap, is or is not of consequence in determining $u^{\ddagger}$.

Turning to a different aspect for aquo- and ammine-coordinated reactants, a very rough correlation between substitution and electron-exchange rates has been noted by Phillips and Williams[31] (*e.g.*, reactions involving Cr^{3+} are *all* slow). If electron exchange involves a bridge the relation arises from the term u_{dis}. But even for the outer-sphere mechanism some correlation is to be expected between the energy of a single-bond scission or stretch and the vibrational energy of the multibond breathing mode implied in u_{reorg}. We record these views because, in the absence of measurements, they do suggest that an order-of-magnitude guess for an electron-exchange rate might be based on substitution rates, if known. (The authors' caveat regarding big differences in $\Delta H^{\ddagger}$ for electron, compared with solvent, exchange is inapplicable, since substitution values are free of the *negative* ΔH contribution from Coulomb's law for juxtaposition of similar charges, the sign here not being widely appreciated. Nor is the authors' invocation of the Franck–Condon restriction quite in the spirit of the adiabatic theory; they imply that thermal reactions follow the process A, B → B', A' in Figure 1.)

III. The Reductants and Their Oxidized Forms

A. HEXAAQUOIRON(II)

This d^6 ion (^5D term) is a typical high-spin divalent ion of the first transition metal series, with an unremarkable ligand field

---

(27) E. Sacher and K. J. Laidler, *Trans. Faraday Soc.*, **59**, 396 (1963).

(28) J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, **29**, 32 (1960).

(29) I. A. W. Shimi and W. C. E. Higginson, *ibid.*, **29**, 123 (1960).

(30) M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

(31) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Oxford University Press, Oxford, 1966, p 446.

stabilization and six apparently (not necessarily) equivalent water ligands. The water exchange rate from the nmr line broadening[32] of the ^{17}O relaxation is 3×10^6 sec^{-1}. With allowance for mechanistic orders, most of its electron-transfer reactions are slower than this, so water removal in forming a bridge cannot in general be a rate determinant.

B. HEXAAQUOIRON(III)

Being d^5, a ^6S term, no ligand field stabilization arises. The water ligands are doubtless equivalent and are exchanged with rate constant[33] 3×10^2 sec^{-1} measured by ^{17}O nmr, a value also in excess of electron-transfer rates. (The conditions were[33] 25°, 0.375 *M* $Fe(ClO_4)_3$, 1.705 *M* $HClO_4$, and 0.73 *M* $NaClO_4$.)

C. VANADIUM(IV) ($(H_2O)_5VO^{2+}$)

1. *Differentiation of Coordination Sites*

While isolated V^{4+} is also represented by a D term, and the oxy ion has a 2+ charge and is hexacoordinate, the resemblance to iron(II) ends there. The V=O entity as coordination center has been reviewed recently.[34–36] In $(H_2O)_5VO(ClO_4)_2$ solid, and in solution, infrared is said[36] to show no complexing of ClO_4^-. In the solid $(H_2O)_5VOSO_4$, the V=O bond length is 1.67 Å, averaging in other complexes 1.62 ± 0.05 Å. Four equatorial waters have V–O lengths of 2.3 Å and the water trans to the oxygen is at 2.4 Å. Magnetic resonance investigations of VO^{2+} in solution have been interpreted in accordance with this structure, as in Figure 2. The equatorial water molecules, which (the O ligand being apex) form the base of a tetragonal pyramid, exchange slowly, with rate constant 500 sec^{-1}.[37–39] While there is disagreement about its precise lability, the axial H_2O is probably rapidly exchangeable. An estimate[39] of 10^{11} sec^{-1} was discounted as being the rate for second-sphere water exchange on the pyramidal faces, and a revised estimate was given, *ca.* 10^6 times the equatorial rate.[38] The vanadyl oxygen is relatively inert, with exchange rate constant[37] <20 sec^{-1}, possibly ≪20 sec^{-1}.

2. *Mechanistic Discrimination at Vanadium(IV)*

Because VO^{2+} is lower in symmetry than Fe^{2+}, it is to be expected that detailed changes in structure of V^{IV} activated complexes will have more pronounced effects than those in the Fe^{II} counterparts.

A detailed MO treatment has fortunately been carried out[40] for $(H_2O)_5VO^2$ which yields the result, crucial for V^{IV} electron transfer, that the unpaired electron is to be placed in the nonbinding b_2 (d_{xy}) orbital (Figure 3). Since this orbital, centered on the vanadium nucleus, is above the base of the tetragonal pyramid, *it will be accessible to oxidants approaching the pyramidal faces in an outer-sphere activated complex. Such a configuration* (in contrast with an inner-sphere one) *would be favored by cationic oxidants for which the more distant the attacking reactant the less the Coulomb repulsion of the vanadium core.* Cation proximity to the (negative) vanadyl oxygen would provide further aid.

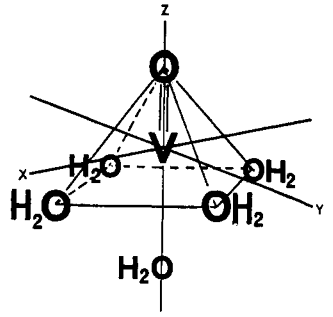

Figure 2. Structure of $(H_2O)_5VO^{2+}$ showing long bond to axial water and the situation of the vanadium nucleus above the base of the tetragonal pyramid having the vanadyl oxygen as apex.

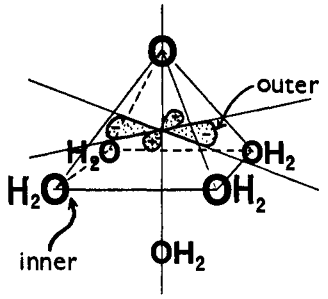

Figure 3. Access modes to V^{IV} b_2 orbital ($|\psi_{xy}|^2$ dotted) differentiated for inner-sphere and outer-sphere oxidants: equatorial attack or juxtaposition at pyramidal faces, respectively. (The vanadium nucleus is at the origin and the axes are as in Figure 2.)

By contrast *when the oxidant is anionic the Coulombic effect favors attainment of overlap with the b_2 orbital by inner-sphere attachment.* (This will shortly be seen to confer reactive advantage on V^{IV} relative to Fe^{II}.) However, the V^{IV} inner-sphere situation is not clear; it will be helpful to consider where the oxidant will be coordinated to the VO^{2+}, axially or equatorially. The thiocyanato and sulfato complexes of VO^{2+} have been studied kinetically, with overall complex-formation rates[41,42] of 160 and 10^4 M^{-1} sec^{-1}, respectively, the rate[42] for inner-sphere penetration by SO_4^{2-} being 1.5×10^3 sec^{-1}. This reviewer's opinion[42a] tended originally to axial coordination, being partly based on the explanation proposed for the enhanced sulfate association[43] with Cu^{2+}, that the two more distantly coordinated water molecules were the more readily replaceable. The parallel with V^{IV} is clear. However, this argument can be inverted: the weakness of water coordination could well, after complex formation, be inherited by an axial sulfate, and the electronic factors stabilizing the equatorial H_2O could equally there favor the SO_4^{2-}. Secondly, the tetrathiocyanato complex[34] is $OV(NCS)_4OH_2^{2-}$ with H_2O, not NCS^-, in the axial site. Thirdly, as pointed out by Connick,[33]

---

(32) T. E. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 302 (1962).

(33) R. E. Connick and M. R. Judkins, unpublished work. (I am indebted to Professor Connick for volunteering this result.)

(34) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

(35) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).

(36) R. J. H. Clark, "The Chemistry of Titanium and Vanadium," Elsevier, London, 1968, p 198.

(37) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **6**, 583 (1967).

(38) K. Wüthrich and R. E. Connick, *ibid.*, **7**, 1377 (1968).

(39) J. Reuben and D. Fiat, *ibid.*, **6**, 579 (1967).

(40) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(41) H. Strehlow and H. Wendt, *ibid.*, **2**, 6 (1963).

(42) P. Hurwitz and K. Kustin, *J. Phys. Chem.*, **71**, 324 (1967).

(42a) D. R. Rosseinsky, Chemical Society, Autumn Meeting, York, 1971, Abstract G8.

(43) P. G. M. Brown and J. E. Prue, *Proc. Roy. Soc., Ser. A*, **232**, 320 (1955).

the penetration rate of sulfate into the V^{IV} inner shell is close to the aquation rate for *equatorial*, not axial, water. Finally, Sykes, in discussion associated with ref 42a, has commented that in the bridged redox species, oxidant attached equatorially could overlap the b_2 transfer orbital better than one axially disposed. The arguments clearly point to a tentative conclusion on the side of equatorial rather than axial monoligand, and hence oxidant, attachment.

In order to estimate the strength of activated-complex bridging to vanadium(IV) relative to that possible with iron(II), we use as a pointer the relative values of the equilibrium constants K_{ass} for association with sulfate. The value for Fe^{2+} has been assessed[43a] as *ca.* 200 M^{-1}, while that for VO^{2+} is[41] 300 ± 50 M^{-1}; both are approximate estimates. But since we have presumed the availability at V^{IV} of only four attachment sites, the equatorial ones, there is implied a further 6/4-fold relative enhancement of association constant per site. The actual charge distribution within the $(H_2O)_5VO^{2+}$ entity must entail a core bearing a positive charge in marked excess of that on Fe^{2+}, and so retaining an anion the more strongly. (Compare the association in $[Co^{III}(NH_3)_5NO_2]^{2+}SO_4{}^{2-}$ for which K_{ass} is[44] larger than usual for $M^{2+}SO_4{}^{2-}$, doubtless because the Co^{III} charge, as seen by the $SO_4{}^{2-}$ from any angle but that screened by $NO_2{}^-$, is $>2+$.) Furthermore, in oxidations by $ClO_3{}^-$, a $VOClO_3{}^+$ intermediate is indicated by the kinetics,[45] the existence[46] of $VOBrO_3{}^+$ being unambiguously established in the bromate oxidation. Not only the strength of attachment of oxidant but also, in consequence, the interaction with the transfer orbital will be enhanced for V^{IV}, and this will diminish, relatively, the unfavorable *u* terms outlined in section II.D. Hence *rates for reaction of bridging oxidants should be greater than rates for outer-sphere oxidation by the same oxidants, by a factor larger for V^{IV} than for Fe^{II}.*

Starting with two other important factors, for completeness, we sum up the distinctions between the exemplar reductants as follows.

(i) For outer-sphere reactions, the Marcus cross-reaction relation (section II.C) would predict, from the relative redox equilibrium constant for oxidations of ferrous and vanadyl ion, that if the self-exchange rates were comparable, then vanadium(IV) should in general be much more slowly oxidized than iron(II).

(ii) A complicating factor is the hydrolysis accompanying electron transfer from V^{IV}, but not from Fe^{II}. This will be dealt with in some detail in section III.E.

(iii) There must be a specificity of activated-complex geometries at V^{IV} much more marked than at Fe^{II}, as outlined in preceding paragraphs.

(iv) The enhanced association at V^{IV} implies that bridging here would result in concomitant rate enhancement relative to Fe^{II}.

These views, being both *post* and *propter*, will be largely borne out by the detailed review of reactions presented in section IV below.

D. AQUOVANADIUM(V)

Our knowledge of vanadium(IV) just outlined contrasts astonishingly with the scant attention given the equally important vanadium(V) ion. The empirical formula at acidity >0.2 *M* is $VO_2{}^+$, from analysis of the $[H^+]$ dependence of $V^{IV,V}$ electrode potentials.[47] It is supported by accordance[48] with the Bjerrum–Brønsted equation[49,50] for multi-ionic reactions, as a singly charged entity in the reaction[51] $V^V + I^- + 2H^+ \rightarrow$. This, however, appears to be the limit of our structural knowledge,[52] presumably circumscribed by the rather low solubility of *ca.* 0.2 *M* in molar concentrations of $HClO_4$, and the nonexistence of simple solid $VO_2{}^+$ salts. In the absence of certainty, informed speculation must serve, and I am indebted to Professor Michael T. Pope of Georgetown University for the following insights. The overall conversion[53] of tetrahedral vanadate ion $VO_4{}^{3-}$, in alkali, through meta- and (hexacoordinate) decavanadates, to $VO_2{}^+$ in acid, is sluggish, but the decavanadate $V_{10}O_{28}{}^{6-}$ to $VO_2{}^+$ conversion is rapid. This suggests hexacoordination for the latter, support being gleaned from Howarth and Richards' observation[54] of two lines in plots of V^{51} nmr shifts against average charge on V^V, attributable to two series of species with coordination numbers 4 and 6, respectively. The further observation[54] that nmr line widths indicate an unsymmetrical structure for $VO_2{}^+$, together with the common interpretation of the spectra of complexes[36] of V^VO_2 as involving a chromophore of C_{2v} symmetry, make compelling arguments for accepting cis locations for the oxygens. Contrast the apparently comparable actinides,[55] like aqueous $NpO_2{}^+$, which ir shows to be unarguably linear. So far as it is relevant, in the solid, KVO_3H_2O,[56] there are two short V–O bonds 1.66 and 1.68 Å at angle 105°, the other V–O being 1.91 and 2.01 Å. This observation is at least not in contradiction with a bent $VO_2{}^+$ formulation for the solid, though the V^V is pentacoordinate here.

E. PROTON TRANSFER IN THE VANADIUM(IV) TO -(V) TRANSFORMATION

Overall the half-reaction for oxidation of vanadium(IV) is

$$(H_2O)_5VO^{2+} = (H_2O)_4VO_2{}^+ + 2H^+ + e \qquad (8)$$

Particle numbers (nonelectronic) can be conserved by writing

$$(H_2O)_5VO^{2+} + 2H_2O = (H_2O)_4VO_2{}^+ + 2H_3O^+ + e \qquad (9)$$

The overall loss of two protons (dihydrolysis) is a feature of the vanadium oxidations absent from ferrous reactions. If in normal outer-sphere electron transfer from iron(II) the transition-state charge distribution is represented by an α of 0.5, such a value seems unlikely for vanadium(IV) unless the ionic structure undergoes a commensurate redistribution, to achieve a configuration intermediate between that of V^{IV} and V^V. Hence, concurrently with the electron transfer, or as a preequilibrium, just half the overall proton loss (monohydrolysis) would be expected to occur. Some experimental

---

(43a) K. B. Yatsimirskii, *Zh. Obshch. Khim.*, **24**, 1498 (1954).

(44) E. M. Hanna, A. D. Pethybridge, and J. E. Prue, *J. Phys. Chem.*, **75**, 291 (1971).

(45) C. W. Fuller and J. M. Ottaway, *Analyst*, **95**, 791 (1970).

(46) C. W. Fuller and J. M. Ottaway, *ibid.*, **94**, 32 (1969).

(47) M. J. La Salle and J. W. Cobble, *J. Phys. Chem.*, **59**, 519 (1955).

(48) D. R. Rosseinsky, *J. Inorg. Nucl. Chem.*, **33**, 3977 (1971).

(49) E. L. King, "Catalysis," Vol. II, P. H. Emmett, Ed., Reinhold, New York, N. Y., 1955, p 350.

(50) D. R. Rosseinsky, *J. Chem. Phys.*, **48**, 4806 (1968).

(51) J. B. Ramsey, E. L. Colichman, and L. C. Pack, *J. Amer. Chem. Soc.*, **68**, 1695 (1946).

(52) G. St. Nikolov and K. B. Yatsimirskii, *Proc. Symp. Coord. Chem., Jena, 1969, Sect. A*, 174 (1970).

(53) M. T. Pope and B. W. Dale, *Quart. Rev., Chem. Soc.*, **22**, 527 (1968).

(54) O. W. Howarth and R. E. Richards, *J. Chem. Soc.*, 864 (1965).

(55) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **21**, 542 (1953).

(56) C. L. Christ, J. R. Clark, and H. T. Evans, *J. Chem. Phys.*, **21**, 1114 (1953).

data support this idea,[57] but it remains largely intuitive, and some qualifications are noted in section IV.C.2. That part of the activation process involving V^{IV} alone, equivalent to that for Fe^{2+} alone, may then be envisaged as

$$H_2O + (H_2O)_5VO^{2+} \rightleftharpoons H_3O^+ + \{(H_2O)_4(HO)VO^{(1+\alpha)+} + \alpha e\}^{\ddagger} \quad (10)$$

If α is just smaller or just greater than 0.5, hydrolysis is probably as indicated, but $\alpha \rightarrow 0$ or $\alpha \rightarrow 1$ will presumably require nil or dihydrolysis, respectively, in the activated complex. If several extents of hydrolysis, *i.e.*, several kinetic hydrogen-ion dependencies, occur, then either several corresponding electronic α's are to be inferred, or only monohydrolysis occurs at V^{IV}, the remainder presumably arising elsewhere in the activated complex. The second view is somewhat arbitrarily taken in section IV.C.

The acidity constant for VO^{2+}, defined as $[VOOH^+][H^+]/[VO^{2+}]$, is 10^{-6} *M* in 3 *M* perchlorate media, and the dimerization constant[58] $[(VO)_2OH_2{}^{2+}][H^+]^2/[VO^{2+}]^2$ is 1.3×10^{-7} *M*. The former value is obtained from small imperfections in assuming the latter equilibrium to account completely for the V^{IV} equilibria in varying $[H^+]$ and must involve, therefore, some considerable uncertainty. It does accord in order of magnitude with other measurements in different conditions, and we shall thus return to it later. However, a precise estimate turns out to be not necessary for any kinetic or mechanistic purpose, since our premises hitherto implicit are firstly that the hydrolysis is to be viewed as essentially a constant process in all oxidations of VO^{2+}, and secondly can for the time being be considered part of the activation step, represented as a quasi-equilibrium, for example, in reaction with ferric ion

$$H_2O + Fe^{3+} + (H_2O)_5VO^{2+} \rightleftharpoons \{(H_2O)_4(OH)VOFe^{4+}\}^{\ddagger} + H_3O^+ \quad (11)$$

or more concisely and generally

$$\text{ox.}_{aq} + \text{red.}_{aq} - nH_{aq}{}^+ \rightleftharpoons \{\text{ox.}(OH)_n\text{red.}\}^{\ddagger} \quad (12)$$

We refer to Newton and Baker[4] for a nice exposition of such net activation processes.

To conclude with some obvious targets, a *caveat* is entered here against facile mechanistic interpretations derived from what are essentially just stoichiometries. Thus though chlorate, in the reaction[59] $V^{IV} + Cl^V$, oxidizes as $ClO_3^- + 2H^+ + e = ClO_2 + H_2O$, and V^{IV} reduces according to reaction 8, liberating two protons, any view that the same two protons enter in both half-reactions would be excessively presumptive. Furthermore, that an H^+ and an electron e are apparently concomitantly received by the Cl^V provides little basis for postulating H atom transfer. And finally, despite the conventional representation

$$VO^{2+} + ClO_3^- \longrightarrow VO_2^+ + ClO_2,$$

there is no strong justification for inferring O^- transfer to be the mechanism, though here it does represent the stoichiometry.

IV. Oxidations of Iron(II) and Vanadium(IV)

A. OBSERVED RATE CONSTANTS IN COMPARABLE CONDITIONS

We now plot the log of the experimental rate constant $k^V{}_{exptl}$ for oxidation of V^{IV}, against log $k^{Fe}{}_{exptl}$ for oxidation, by the same oxidant, of Fe^{II} (Figure 4). The conditions to which the rate constants refer were intended to be 1 *M* $HClO_4$, 1 *M* ionic strength, and 20°. These values are probably closest to the median of the not drastically diverse conditions actually employed, which range over 0.55 to 3 *M* in $HClO_4$ and ionic strength (for one reaction, down to 0.1 *M*), and 15 or 25°, in a number of cases. Where possible observed trends and activation energies have been used, for—let it be emphasized—*short* extrapolations to the required conditions. Where conditions differ somewhat from our chosen values, but are the same for the V^{IV} and Fe^{II} reactions, no effort has been made at adjustment. Only for $V^{IV} + Tl^{III}$ has an extensive extrapolation been necessary, from 80°, the experimental temperature chosen[60] because of the slowness of reaction. Use was made here (see below, section IV.C.2) of the relative energies of activation of V^{IV} and Fe^{II} reactions, the uncertainty from this assumption being only about a power of ten and so insufficient to invalidate this useful datum point.

The only other large adjustment to an experimental value arises for oxidations by chromium(V), red. + Cr^V. This is preceded by a preequilibrium of red. + Cr^{VI}, the equilibrium constant *K* for which has been estimated approximately, for Fe^{II} as reductant, by Westheimer (see ref 70). The value of *K* for V^{IV} as reductant is then readily calculated from the standard-electrode-potential difference for $Fe^{III} + e = Fe^{II}$ and $V^V + e = V^{IV}$.[61] The precise value of *K* is not in fact of importance in that differing estimates would, in the plot contemplated, merely shift the $\{(Cr^V + V^{IV}), (Cr^V + Fe^{II})\}$ point up or down a line of exactly unit slope (Figure 4).

Rates of some oxidations by V^V and Fe^{III} can be used, with equilibrium constants from $E°$ values (Table II), to yield rate constants for the reverse reactions. This gives rates for the oxidations by V^{III} and by V^{IV}, in uncharacteristic roles here

Table II

$E°$ Values (Volts) and Equilibrium Constants[a]

In 1 *M* $HClO_4$: $Fe^{II} + V^V = Fe^{III} + V^{IV}$, $K = 6.7 \times 10^4$ (ref 65)
That is, for $Fe^{2+} + VO_2^+ + 2H^+ = Fe^{3+} + VO^{2+} + H_2O$, $K = 6.7 \times 10^4\ M^{-2}$

1 *M* $HClO_4$:	$V^{3+} + e = V^{2+}$	−0.267[66]
1 *M* $HClO_4$:	$Fe^{3+} + e = Fe^{2+}$	0.767[67]
0.5–1 *M* $HClO_4$:		0.741[68]
2 *M* $HClO_4$:		0.7375[67]
[Accepted here		0.748]
[Hence 1 *M* $HClO_4$:	$V^V + e = V^{IV}$	1.034]
1 *M* H_2SO_4:	$V^{IV} + e = V^{III}$	(0.34)[69]
"1 *M* H^+":	$Cr^{VI} + e = Cr^V$	⩽0.62[70]
1 *M* $HClO_4$:	$U^V + e = U^{IV}$	0.555[4]

[a] At 25°, perchloric acid solution; contrast ref 64.

---

(57) D. R. Rosseinsky and M. J. Nicol, *Electrochim. Acta*, **11**, 1069 (1966).

(58) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(59) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1200 (1970).

(60) W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, **29**, 49 (1960).

(61) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1196 (1970).

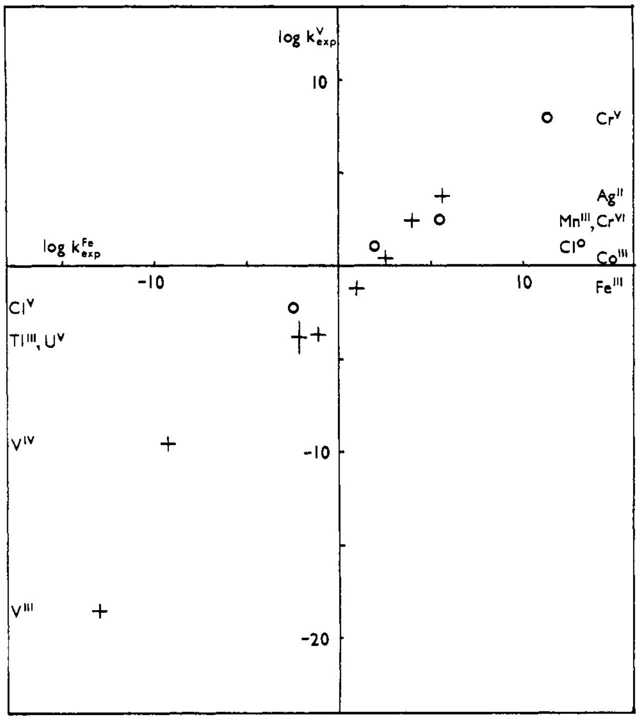

Figure 4. Experimental values of rate constants for Fe^{II} and V^{IV} reactions, plotted logarithmically. Symbols: +, cationic oxidants; O, noncationic oxidants.

as oxidants, because of course the opposite direction of reaction is the familiar one, particularly for V^{III}.

The plot in Figure 4 from the data of Table III shows a rough correlation of rate which might be expected for any pair of not too closely related reductants reacting with a variety of common oxidants. However, it is a close enough correlation to justify further examination of deviations from perfect linearity, in terms of the different electron-transfer mechanisms which are available to each system (section II) and the properties of the reductants (section III) and oxidants (section IV.B).

B. CATIONIC AND NONCATIONIC OXIDANTS

In Figure 4 rate constants for cationic oxidations are indicated differently from noncationic oxidations. Immediately some improvement of correlation ensues, but with exceptions. We presume the separation to arise from the duality of mechanism at vanadium(IV) suggested in section III.C.2, the cations juxtaposed at the pyramidal faces in outer-sphere reactions, noncations being coordinated in the equatorial position in inner-sphere oxidations.

This division of oxidants is somewhat unreliable since it is well known that particularly oxycations form demonstrable adducts in redox reactions, which establishes bridging.[62,63] So it is with VO^{2+} *as oxidant*, and in Table IV we list the oxidants together with *any* evidence of their acting as inner-sphere oxidants. All those for which such evidence exists (ClO_3^-, VO^{2+}, and Cl_2) deviate in the direction of favoring the oxidation of V^{IV} (Figure 4), which accords better with the precepts of section III.C.2.

Besides V^{III}, the remaining nonconformists are Cr^{VI} and Cr^V, which appear to fall with the outer-sphere oxidants while being certainly noncationic. The Cr^V deviation is undoubtedly due to the rapidity of the Cr^V electron-transfer reaction compared with the rate at which bridging at the equatorial V^{IV} site can occur; thus here outer-sphere electron transfer at V^{IV} is more rapid than coordination, with rate (section III.C.1) *ca.* 10^4 M^{-1} sec^{-1}. The Cr^{VI} point undoubtedly deviates because of neglect of acid dependence, since the graph implies that we may compare all the variety of acid-dependent paths, observed in 1 M $HClO_4$, for the one reductant, with all those for the other. This is not reasonable, and we examine particular $[H^+]$-dependent paths in the following section; only the Cr^{VI} and U^V points, in fact, are seriously shifted by this more detailed examination.

We can only attribute the downward deviation of the V^{III} oxidant to the condition $\alpha \rightarrow 1$ in consequence of the highly positive (though not uniquely so) $\Delta F°_{12}$ values +30 and +23 kcal mol^{-1}, respectively (section II.C). This is the least satisfactory, most *ad hoc*, argument adduced, but is still probably correct.

C. RATE CONSTANTS FOR SEPARATE HYDROGEN ION DEPENDENCES

1. *Basis of Comparison of Fe(II) and V(IV) Reactions*

Following the discussion of vanadium hydrolysis in section III.E, we compare rate constants for $VO^{2+} + \text{ox.} \rightleftharpoons \{VOH \cdot \text{ox.}\}^{\ddagger} + H^+$ (*i.e.*, k_{-1} values, in rate terms with $[H^+]^{-1}$) with those for $Fe^{2+} + \text{ox.} \rightleftharpoons \{Fe \cdot \text{ox.}\}^{\ddagger}$ (*i.e.*, k_0 values, in rate terms with $[H^+]^0$, the acid-independent terms). Furthermore, we generally compare k_{m-1} values for V^{IV} reactions with k_m values for Fe^{II} reactions, but now with less justification, because with $m \neq 0$ it is not exactly established how the electron-distribution parameter α, in Fe^{II} reactions particularly, varies with extent of proton loss.

The results are plotted in Figure 5, and all $[H^+]$ dependences and rates are collated in Table V.[77-81] The mechanistic conclusions of the preceding section remain unchanged, $HCrO_4^-$ and probably U^V now falling with bridging oxidants. Detailed consideration on each reaction follows.

---

(62) J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965).

(63) T. W. Newton and F. B. Baker, *ibid.*, **3**, 569 (1964).

(64) J. O. Hill, I. G. Worsley, and L. G. Hepler, *Chem. Rev.*, **71**, 127 (1971), who neglect the effects of ionic strength.

(65) J. Kentamäa, *Suom. Kemistilehti B*, **21**, 273 (1958).

(66) I. P. Alimarin, E. R. Nikolaeva, V. I. Tikhonova, and L. V. Bobrova, *Zh. Neorg. Khim.*, **7**, 298 (1962).

(67) A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66**, 1065 (1962).

(68) W. C. Schumb, M. S. Sherrill, and S. B. Sweetser, *J. Amer. Chem. Soc.*, **59**, 2360 (1937).

(69) G. Jones and J. H. Colvin, *ibid.*, **66**, 1563 (1944).

(70) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

(71) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557 (1966).

(72) R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966).

(73) T. J. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).

(74) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **70**, 1943 (1966).

(75) J. H. Espenson and L. A. Krug, *Inorg. Chem.*, **8**, 2633 (1969).

(76) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 722 (1967).

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

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

(79) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).

(80) G. Davies, *Inorg. Chem.*, **10**, 1155 (1971).

(81) D. H. Huchital, N. Sutin, and B. Warnqvist, *ibid.*, **6**, 838 (1967).

Table III

Experimental Rate Constants for Oxidations of V^{IV} and Fe^{II}

Reaction (ref)	*Experimental*[a] *T (°C), [H$^+$], I (M)*	*Log (k/M^{-1} sec^{-1})*[b]	*Note*
$Fe^{III} + V^{IV}$ (82)	0–55.6, 0.05–1, 1.0	−1.32	
$Fe^{III} + V^{IV}$ (57)	0.3–25, 0.1–3, 3.0	−1.14 ($I = 3$ *M*)	
$Fe^{III} + Fe^{II}$ (8)	0–20, (0.02–0.55), (0.55)	1.00	
$Mn^{III} + V^{IV}$ (78)	5.5–19.6, 0.84–3, 3.04	2.36 ($I = 3.04$ *M*)	
$Mn^{III} + Fe^{II}$ (77)	(0.3–15), 0.54–3, 3.04	4.01 ($I = 3.04$ *M*)	
$Co^{III} + V^{IV}$ (79)	−2.1–20, 0.5–3, 3.0	0.32 ($I = 3.0$ *M*)	
$Co^{III} + Fe^{II}$ (80)	0–25, 0.25–3, 3.0	2.59 ($I = 3.0$ *M*)	
$V^{III} + V^{IV}$ (75)	16–35, 0.01–1, 1.0	−18.46	*c*
$V^{III} + Fe^{II}$ (76)	25, 0.25–1, 1.0	−13.05 (25°)	*c*
$Tl^{III} + V^{IV}$ (60)	(80), 1.8, 3.0	$-3.9 \pm 1 \begin{cases} 1.8\ M\ \mathrm{H^+} \\ I = 3\ M \end{cases}$	*d*
$Tl^{III} + Fe^{II}$ (89)	(25–45), 0.5–2, 3.0	−2.11 ($I = 3.0$ *M*)	*d*
$Cr^{V} + V^{IV}$ (94)	21.1, 1.0, 1.0	8.0 (21.1°)	*e*
$Cr^{V} + Fe^{II}$ (96)	20, (0.025–0.067), 1.0	11.34	*e*
$Cr^{VI} + V^{IV}$ (98)	25, 0.005–0.04, 1.0	2.26 (25°)	
$Cr^{VI} + Fe^{II}$ (97)	25, 0.01–0.08, ∼0.1	5.48 (25°)	
$Cl^{V} + V^{IV}$ (59)	21.1, 0.2–2.5, 0.5–4.5	−2.25 (21.1°)	
$Cl^{V} + Fe^{II}$ (99)	20, 0.11–1, 1	−2.48	
$Cl_2 + V^{IV}$ (104)	25, 0.1–1, 1.0	1.0 ± 0.3	
$Cl_2 + Fe^{II}$ (73)	25, 3.0, 3.0	1.90 (25°)	
$V^{IV} + V^{IV}$ (109)	0.2–34.2, 0.02–2, 2.0	−9.48 ($I = 2.0$ *M*)	*f*
$V^{IV} + Fe^{II}$ (108)	15–30, 0.55–2.5, 3.0	−9.25 ($I = 3.0$ *M*)	*f*
$U^{V} + V^{IV}$ (4)	25, 1.0, 1.0	−3.7 (25°)	
$U^{V} + Fe^{II}$ (4, 107)	25, 1.0, 1.0	−1.12 (25°)	
$Ag^{II} + V^{IV}$ (73)	25, 4.0, 4.0	3.7 (as cited)	
$Ag^{II} + Fe^{II}$ (73)	25, 4.0, 4.0	5.6 (as cited)	

[a] Parentheses indicate that the values enclosed were used in extrapolation. [b] Experimental values observed at or extrapolated to 20°, 1 *M* $HClO_4$, and $I = 1$ *M*, except where otherwise indicated. [c] From the reverse rates (of the V^{II} reactions), and equilibrium constants from Table II. [d] First step only. [e] Both values uncertain by identical amounts. [f] From the reverse rates (of the V^{III} reactions), and equilibrium constants from Table II.

Table IV

Evidence for Details of Mechanism of Oxidation for the Oxidants of Vanadium(IV) and Iron(II)

Oxidant	*Reaction*	*Mechanism*	*Evidence*
ClO_3^-	$V^{IV} + Cl^{V}$	Bridged	Kinetics show adduct[44]
	$Cr^{II} + Cl^{V}$	Bridged	Cl and *O coordinate to product Cr^{III} [71,72]
Cl_2	$Fe^{II} + Cl_2$	70% bridged	Excess $FeCl^{2+}$ absorbance[73]
VO^{2+}	$VO^{2+} + Cr^{2+}$	Bridged	$VOCr^{4+}$ adduct formed[62]
	$VO^{2+} + V^{2+}$	Bridged	VOV^{4+} adduct formed[63]
UO_2^+		Bridged?	Nil, but *cf.* VO^{2+} and[4,74] UO_2^{2+}
$HCrO_4^-$		Bridged?	Nil, but Coulomb interaction favorable
H_3CrO_4		Outer-sphere?	Electron-transfer rates putatively exceed substitution rate
V^{3+}		Outer-sphere	Reverse rates[75,76] exceed V^{II} substitution rate[30]
Tripositive oxidants, M^{3+}		Outer-sphere?	Coulomb repulsion minimal
Ag^{II}		Unknown	Nil

2. *The Tripositive Oxidants Fe^{3+}, Mn^{3+}, Co^{3+}, V^{3+}, and Tl^{III}*

The $Fe^{III} + Fe^{II}$ electron exchange[8] is probably the best studied electron transfer to date. The lowness of ionic strength employed (0.55 *M*) is without qualitative consequence, and the observed variation of rate with ionic strength I is used to make a small adjustment to $I = 1$ *M*. The main orders with respect to hydrogen ion are 0 and 1.

The reaction $Fe^{III} + V^{IV}$ has been studied directly by amperometry,[57] at $I = 3$ *M;* it is very rapidly terminated by the reverse reaction (also measured amperometrically[57]) because the equilibrium constant K is of course very small. The reverse reaction was studied at $I = 1$ *M* by spectrophotometry,[82] and the potentiometric K value[65] yields the rates for

---

(82) N. A. Dougherty and T. W. Newton, *J. Phys. Chem.*, **67**, 1099 (1963).

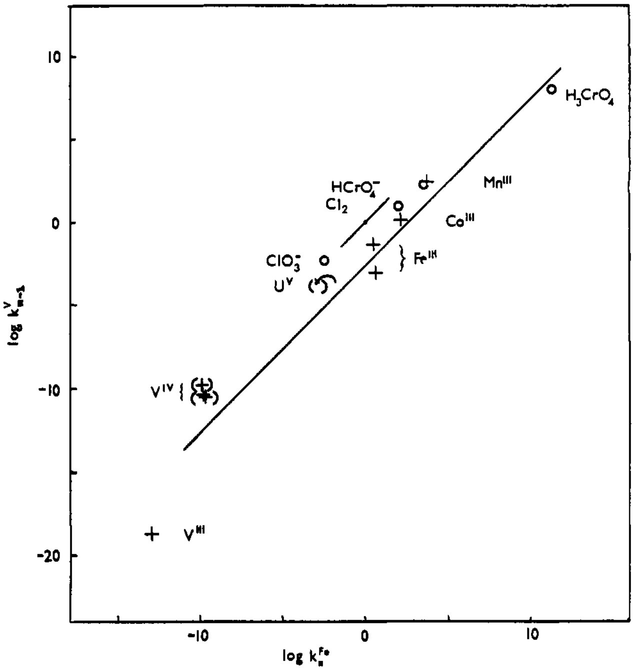

Figure 5. Log k_m for Fe^{II} reactions against log k_{m-1} for V^{IV} reactions. Symbols as in Figure 4 but parentheses indicate expected inner-sphere cationic oxidants. The longer line, of unit slope, has been drawn through points for putatively outer-sphere reactions, the shorter passes through the origin.

$Fe^{III} + V^{IV}$. The separate measurements are in general accord, but (Table V) the variation of $[H^+]$ dependences with change of conditions is notable, and undoubtedly real. The V^{IV} reactions have a greater number of $[H^+]$-dependent paths than do Fe^{II} reactions, doubtless because of the intrinsic protonic participation here with the consequently greater scope for variation. *A priori* prediction of such dependences would be an ambitious aim, even single-ion hydrolysis being not entirely understood in detail. There are two reaction pairs differing by unity in extents of deprotonation, and they straddle the correlation line for outer-sphere reactions rather than being parallel to it. This behavior also arises in the only other system providing more than one point, the oxidations *by* V^{IV}; see further comments in section IV.B.6.

The cobalt(III) reaction with Fe^{II} has been studied spectrophotometrically at $I = 1$ *M* by Bennett and Sheppard[18] and at $I = 3$ *M* by Davies,[80] with sufficient accord. A measurement on $Co^{III} + V^{IV}$ by Huchital, Sutin, and Warnqvist[81] agrees well with the extensive spectrophotometric study made earlier by Rosseinsky and Higginson.[83] (Sutin has frequently stated that our measurements agree with *his*.) The kinetic measurements[83] clearly indicate a hydrolysis constant K_h for Co^{III} of the order 10^{-8} *M* rather than[84] 10^{-1} *M;* the latter would require a different $[H^+]$-dependence analysis from that found[83] to fit.

The reaction $Mn^{III} + Fe^{II}$ has been studied amperometrically by Rosseinsky and Nicol,[77] with Diebler and Sutin's measurement[79] by spectrophotometry in accord. The reaction $Mn^{III} + V^{IV}$ has been examined spectrophotometrically by Rosseinsky and Nicol,[78] and, as with $Mn^{III} + Fe^{II}$, this system requires for Mn^{III} a K_h/M of the order unity in the interpretation of the $[H^+]$ dependence. The analysis implies

Table V

Rate Constants for Particular [H⁺] Dependences

Reaction (ref)	*Observed orders in $[H^+]$, n*	*Log ($k_n/M^{-(n+1)}$ sec^{-1}) 20°, I = 1 M*
$Fe^{III} + V^{IV}$ (82)	$\{-1, -2(-3)\}$	k_{-1} −1.33, k_{-2} −3.12
$Fe^{III} + V^{IV}$ (57)	0, −1, −2	(I = 3.0 *M*)
$Fe^{III} + Fe^{II}$ (8)	0, −1	k_0 0.52, k_{-1} 0.59 (I = 0.55 *M*)
$Mn^{III} + V^{IV}$ (78)	0, −1	k_0 1.96, k_{-1} 2.52 (I = 3.04 *M*)
$Mn^{III} + Fe^{II}$ (77)	0, −1	k_0 3.71, k_{-1} 4.17 (I = 3.04 *M*)
$Co^{III} + V^{IV}$ (83)	0, −1	k_0 −0.3, k_{-1} 0.17
$Co^{III} + Fe^{II}$ (80)	0, −1	k_0 2.12, k_{-1} 2.39
$V^{III} + V^{IV}$ (75)	$\{-2, -1\}$	k_{-1} −18.72, k_{-2} −18.80 (25°)
$V^{III} + Fe^{II}$ (76)	$\{0\}$	k_0 −13.05 (25°)
$Tl^{III} + V^{IV}$ (60)	−1?	
$Tl^{III} + Fe^{II}$ (89)	0,[60] −1, −2?	
$H_3CrO_4 + V^{IV}$ (94)	0[92]	k_0 8.0[70,94]
$H_3CrO_4 + Fe^{II}$ (96)	+1[92]	k_1 11.34[70,96]
$HCrO_4^- + V^{IV}$ (98)	0	k_0 2.26
$HCrO_4^- + Fe^{II}$ (97)	(+1), +2	k_1 3.64, k_2 5.48 (I = 0.1 *M*) ($k_1 < 3.64$ at I = 1 *M*)
$ClO_3^- + V^{IV}$ (59)	0 (+1)	k_0 −2.25 (21.1°)
$ClO_3^- + Fe^{II}$ (99)	+1	k_1 −2.48
$Cl_2 + V^{IV}$ (104)	−1	k_1 1.0 ± 0.3 (25°)
$Cl_2 + Fe^{II}$ (73)	?	$k_{0?}$ 1.9 (25°)
$V^{IV} + V^{IV}$ (109)	$\{+1, 0, -1 (-2)\}$	k_{-1} −10.26, k_0 −10.42, k_{-1} −9.66 k_{-2} −11.25 (I = 2.01 *M*)
$V^{IV} + Fe^{II}$ (108)	$\{+2, +1, 0\}$	k_2 −9.82, k_1 −9.62, k_0 −9.87 (I = 3.0 *M*)
$V^V + V^{IV}$ (4)	+3	k_3 −3.7
$U^V + Fe^{II}$ (4)	(+4?), +2	(k_4 say −3?) k_2 −1.1
$Ag^{II} + V^{IV}$ (73)	?	
$Ag^{II} + Fe^{II}$ (73)	?	

$$Mn^{3+} + H_2O \overset{K_h}{\rightleftharpoons} MnOH^{2+} + H_3O^+$$

with

$$Mn^{3+} + \text{red.}^{2+} \xrightarrow{k} Mn^{2+} + \text{ox.} \ldots \tag{13}$$

and the activation process *either*

$$MnOH^{2+} + \text{red.}^{2+} \rightleftharpoons \{MnOH\ \text{red.}^{4+}\}^{\ddagger} \tag{14}$$

or

$$H_2O + Mn^{3+} + \text{red.}^{2+} \rightleftharpoons \{MnOH\ \text{red.}^{4+}\}^{\ddagger} + H_3O^+ \tag{15}$$

The kinetically unresolvable option of the last two representations is always open when inverse hydrogen-ion concentration dependences arise. While (15) which incorporates (14) must always be correct, there is *implied* in the form of (14) that MOH^{2+} is the sole reactant in the corresponding elementary reaction, which is an unnecessary and unproven restriction. The emphasis given to this point here accompanies the simplifying thesis of section III.E that, throughout, it is the vanadyl part of the activated complex that undergoes proton loss. This view can be tested by an examination of the points for the Mn^{III} and Co^{III} oxidations, where we recall that

---

(83) D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, 31, (1960).

(84) B. Warnqvist, *Inorg. Chem.*, **9**, 682 (1970).

$M^{3+} + Fe^{2+}$ is compared with $M^{3+} + VO^{2+} - H^+$. In the V^{IV} reactions, Mn^{III} oxidizes relatively rather faster than Co^{III} (the Mn^{III} point being displaced upward on the graph, Figure 5), but the relative rate-constant increment (say tenfold) is by no means equal to the enhanced hydrolyzability of Mn^{III} alone, *ca.* a 100-fold, as it would be were this hydrolysis simply transferred to the Mn^{III} center in the V^{IV}-containing activated complex. Thus the occurrence must be inferred of one or both of the remaining possibilities, that an OH^- bridge is formed between Mn^{III} and V^{IV}, or that only V^{IV} hydrolysis occurs in the activated complex enhanced by the presence, albeit outer sphere, of the more acidic Mn^{III}. If bridging occurs, however, the question arises as to why the acidic Mn^{III} should benefit more from it than the less acidic Co^{III}, and the question must be left open. Cerium(IV) studies should be useful here, if extreme care is taken with acid dependences as in ref 19.

In order to treat the Mn^{III} oxidations equivalently with the other M^{III}, the rate constant for reaction 15 has been calculated by multiplying the rate constant obtained[78] as for reaction 14 by the K_h value employed.[78] (The mean of the two[78] calculations is taken here, Table V.)

The sequence of rates $Mn^{III} > Co^{III} > Fe^{III}$ holds for both reductants; according to electrode potentials, and, more rigorously, the cross-reaction relation, Co^{III}, the strongest oxidant, is out of place. (This displacement persists with other classes of substrate as well.[85]) Presumably this deviation arises from the spin-state change in $Co^{III} \rightarrow Co^{II}$ (section III.C) for which no quantitative theory exists.

The reaction rates for oxidations by V^{3+} are from the equilibrium constants and the observed rates for[75,76] $V^{II} + V^{V}$ and $V^{II} + Fe^{III}$. These latter reactions are deemed outer sphere because the rates are faster than the $V^{II} - OH_2$ substitution-exchange rate.[80] The observed rate constants are 1 M $HClO_4$, 25°, for[76] $V^{II} + Fe^{III}$, $k = 1.8 \times 10^4\ M^{-1}\ sec^{-1}$ and[75] 1 M $HClO_4$, 25°, for $V^{II} + V^{V}$, $k = 4.74 \times 10^3\ M^{-1}\ sec^{-1}$. It is notable that the V^V oxidation has a rate somewhat *less* than the Fe^{III} oxidation despite the enhanced equilibrium constant for the former (greater by 6.7×10^4 fold). However, our chosen brief being to examine V^{IV} and Fe^{II} reactions, we are obliged to note the downward deviation of the point in Figures 4 and 5 for the oxidations by V^{III}, by microscopic-reversibility arguments also outer sphere. This is explained in section IV.B as being a consequence of the presumptive condition $\alpha \rightarrow 1$. In other words, it is only a little more difficult to achieve the charge distribution for the activated complex than it is for the products, in which the extent of transfer "α_{prod}" is unity. Use of the equilibrium constants to calculate rates in the desired direction then introduces a difference between them of a factor *amounting to* approximately the $Fe^{II} + V^V$ equilibrium constant. The conclusion $\alpha \rightarrow 1$ is thus merely the converse, rather cumbersomely introduced, of what is virtually the observation that $\alpha \rightarrow 0$ for V^{II} + ox. There is here an implication regarding the self-exchange rates which will be taken up in section IV.F; they appear to be comparable, from the closeness of the observed k values quoted earlier in this paragraph. (Following section III.E, for the V^{IV} reaction since $\alpha \rightarrow 1$ we might consider k_{-2} not k_{-1}, but they are nearly identical. However, k_{-2} introduces intractable dimensional problems.)

Further examples of Fe^{II} and V^{IV} reactions with such extremely positive $\Delta F°_{12}$ values are not available. $Fe^{III} + Cr^{II} \rightleftarrows Fe^{II} + Cr^{III}$ can be invoked,[86] but its counterpart, the $V^V + Cr^{II}$ reaction, involves a very rapidly formed adduct in a complicated and hitherto unresolved mechanism.[87,88]

The oxidations by M^{3+} are among the few for which activation parameters are available (Table VI). Two features call for comment. Firstly the k_{-1} activation energies are remarkably similar for a common oxidant. We cannot simply explain this by facile invocation of a common process while at the same time retaining our comparison of k_0 for Fe^{II} with k_{-1} for V^{IV}, and we record this underlining of the tentativeness of the comparison, and the need to check future activation measurements for the comparability noted.

Table VI

Activation Energies for Experimental Rate Constants (k_{exptl})[a] and for Independent Paths (k_n)[b]

Reaction (ref)	*I, M*	*$RT^2(d \ln k/dT)$, kcal mol^{-1}*
$Fe^{III} + V^{IV}$ (57)	3.0	k_{exptl} 21.3, k_0 21.0, k_{-1} 20.6, k_{-2} 25
$Fe^{III} + Fe^{II}$ (8)	0.55	k_{exptl} 16.5, k_0 8.0, k_{-1} 19.9
$Mn^{III} + V^{IV}$ (78)	3.04	k_{exptl} 12.3, k_0 11.7, k_{-1} 16 ± 1
$Mn^{III} + Fe^{II}$ (77)	3.04	k_{exptl} 12.2, k_0 11.2, k_{-1} 17.3 ± 1.5
$Co^{III} + V^{IV}$ (79)	3.0	k_{exptl} 21.2, k_0 22.4, k_{-1} 16.5
$Co^{III} + Fe^{II}$ (18)	1.0	k_{exptl} 15.5, k_0 9.9, k_{-1} 17.9
$Tl^{III} + V^{IV}$ (60)	3.0	k_{exptl} 24.6? (by inference; see text)
$Tl^{III} + Fe^{II}$ (89)	3.0	k_{exptl} 21.1

[a] k_{exptl} values are for 1 M $HClO_4$ solutions (although no marked differences in activation quantities were discerned for acidities 0.5 to 3 M). [b] Subscript n refers to order in $[H^+]$.

Secondly, V^{IV} activation energies are always greater than Fe^{II} values by on average 3.5 kcal mol^{-1}. This observation has been used to make an estimate for the $Tl^{III} + V^{IV}$ rate at 20°; the observed rate at 80° roughly equals the $Tl^{III} + Fe^{II}$ rate observed at 20°, and the adjustment seems a reasonable one. The error in the estimated rate is unlikely to exceed an order of magnitude.

There have been several studies[89–91] of the reaction $Tl^{III} + Fe^{II}$, of which one path is $[H^+]$ independent.[60] For both this and the corresponding V^{IV} reaction, the participation of Tl^{II} as intermediate leads to the full mechanism[91,60]

$$Tl^{III} + M^{\overline{N}} \rightleftarrows Tl^{II} + M^{\overline{N+1}}$$

$$Tl^{II} + M^{\overline{N}} \longrightarrow Tl^{I} + M^{\overline{N+1}}$$

The data do not allow a comparison of rates for the second step, but it is interesting that once again the same kinetic mechanism holds for both Fe^{II} and V^{IV}.

The activation quantities indicate that a large, say 50°, change in temperature, as the standard at which to compare rates, is unlikely to qualitatively affect the conclusions arrived at in this review.

---

(85) A. McAuley, *Coord. Chem. Rev.*, **5**, 245 (1970).

(86) G. Dulz and N. Sutin, *J. Amer. Chem. Soc.*, **86**, 829 (1964).

(87) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

(88) J. H. Espenson, private communication.

(89) C. E. Johnson, *J. Amer. Chem. Soc.*, **74**, 959 (1952).

(90) O. L. Forcheimer and R. P. Epple, *ibid.*, **74**, 512 (1952).

(91) K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 3044 (1953).

3. *Chromium(V) and -(VI)*

These reactions have been reviewed recently by Espenson.[92] While some differences in interpretation of the minor kinetic paths have been noted, rates for the main mechanisms, though obtained for somewhat differing conditions, are in fair enough accord, for both iron(II)[93,94] and vanadium(IV).[95,96] The paths predominating are $[Fe^{II}]^2[HCrO_4^-][Fe^{III}]^{-1}$ and $[V^{IV}]^2 \cdot [HCrO_4^-][V^V]^{-1}$, which imply preequilibria of reductant with chromium(VI) followed by further reaction of reductant with the chromium(V) from the preequilibrium.

The chromium(V) oxidant is, from a consideration of kinetic hydrogen-ion dependences of a variety of reactions,[92] probably H_3CrO_4. It is not at first sight clear why a bridge mechanism does not operate, since Cr^V is not cationic, and cationicity has been one criterion, *ceteris paribus*, for our outer-sphere classification. Following section III.C.1, the reason strongly indicated is that the rate of coordination at V^{IV} probably has a ceiling at *ca.* 10^4 M^{-1} sec^{-1} (the SO_4^{2-} complex-formation rate) which consequently is also the maximum rate for bridge formation. Any electron transfer proceeding faster, as with Cr^V, must then do so by an outer-sphere mechanism. Labilization by the transition-state hydrolysis we have imputed to V^{IV} is unlikely to suffice for bridging.

Espenson, in some penetrating experiments,[92,97,98] has separated out rates of the direct reaction of $HCrO_4^-$ with V^{IV} and with Fe^{II}. The appropriate $[H^+]$ order (unity) for Fe^{II}, to be compared with the only observed order (zero) for V^{IV}, places this reaction properly in the bridged group. The ionic strength for the Fe^{II} reaction was only *ca.* 0.1 *M*, and at the higher ionic strengths used for V^{IV}, the former rate would be slower still,[48,49] shifting the plotted point more firmly to within the area for bridged reactions.

4. *Chlorine(V) and -(0)*

The oxidation of V^{IV} by ClO_3^- has evoked recent interest.[45,59,99,100] In the simplest interpretation unit orders in V^{IV} and Cl^V were proposed,[59] but there are a variety of complications largely involving Cl^- and ClO_3^- adducts[45,100] to V^{IV}. Thus, Ottaway and Fuller's[45] interpretation of a drift of second-order rates with $[ClO_3^-]$ as implying a V^{IV}–ClO_3^- intermediate supports (and indeed in part prompted) our differentiation of bridging in V^{IV} and Fe^{II} reactions. Now ClO_3^- when oxidizing Cr^{II} undoubtedly is bridged since both Cl and O fragments become demonstrably[71,72] infixed with the product Cr^{III}, and we presume an inner-sphere mechanism with V^{IV} (and, less effectively, with Fe^{II}). Only brief and piecemeal data on the Fe^{II} reaction with chlorate have been published,[99] but the form of the rate law $k[H^+][ClO_3^-][Fe^{2+}]$, and approximate value of *k*, seem secure.[100] Once again major paths for V^{IV} and Fe^{II} differ in reactants by one proton, in accord with the views of section IV.B.1.

Ottaway and Fuller's result,[45] for the V^V–Cl^V preassociation constant multiplied by rate constant for adduct decomposition, agrees well with both Rosseinsky and Nicol's value[59] for the bimolecular rate constant, and with Shakhashiri and Gordon's.[99] (The stoichiometric factor 6 is properly included in the rate-constant definition in ref 59.)

A feature of the chlorate oxidations is their slowness, prompting the query "why?". Regarding the structures,[101] in the solids $NaClO_3$ and $KClO_3$ the Cl–O distance is 1.46 Å, and bond angle 108°, in a trigonal-pyramidal configuration, and in ClO_2 the values are respectively 1.49 Å and 116°. While ClO_3^- sheds an oxygen on reduction (section III.E), the loss may be more apparent than real[59] if $ClO_2(aq)$ is hydrated in solution; otherwise the bond lengths and angles suffer no drastic modification on reaction and no obvious conclusions are to be drawn. However, the measurements on exchange of O between H_2O solvent and both[72,102] ClO_3^- and ClO_2 show an extreme sluggishness, the enriched oxygen fraction of ClO_3^- surviving recrystallization,[72] and virtually nil exchange with ClO_2 being observable in days. Thus simply the bond strength, or the steepness of variation of bond potential energy with distance, serves to inhibit ligand exchange, and, following the views in the conclusion of section II.E, presumably to slow down electron transfer as well. A very slow rate for self-exchange in $Cl^V + Cl^{IV}$ can be confidently predicted, from both this conjecture regarding O exchange and the slowness of the redox reactions; a test (1 hr) experiment gives partial confirmation.[103]

Chlorine itself as oxidant of Fe^{II} has been studied by Conocchioli, Hamilton, and Sutin[73] who observed more than 70% $FeCl^{2+}$ as product (an excess over the equilibrium amount, exemplifying the product-analysis technique exploited to advantage by Sutin in establishing inner-sphere mechanisms). The reaction was studied at only one acidity. The kinetic mechanism of the reaction with V^{IV} appears complicated,[104–106] especially when extra Cl^- is added initially, but the $[H^+]^{-1}$ order is clear. If summarily treated as first order in V^{IV} and Cl_2, then the range of *k* obtained is that shown (Tables IV and V). [I am grateful to Dr. M. H. Ford-Smith for so kindly divulging these unpublished data.] The location of the Cl_2 point with the bridged (*i.e.*, faster) V^{IV} reactions is satisfactory.

5. *Silver(II) and Uranium(V)*

The silver(II) results,[81] for reaction with both Fe^{II} and V^{IV}, were obtained at 4 *M* $HClO_4$ only. The extent of hydrolysis (Ag^{2+} or $AgOH^+$?) is unknown.

Uranium(V), UO_2^+, has limited stability to disproportionation, and the rates of[107] $Fe^{III} + U^{IV}$ and[4] $V^V + U^{IV}$ were actually used, together with Table II equilibrium constants, to get its rate of reaction. The rate for $U^V + Fe^{II}$ then shows a +2.2 power dependence on $[H^+]$, which is presumably predominantly +2 with a small higher order contribution. For V^{IV} the main dependence is $[H^+]^3$ which, consonantly with our views regarding protonic orders for the two reductants in section IV.B.1, requires comparison with an $[H^+]^4$

---

(92) J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

(93) J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963).

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

(95) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 1883, 5101 (1964).

(96) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1196 (1970).

(97) J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1880 (1970).

(98) K. M. Davies and J. H. Espenson, *ibid.*, **92**, 1889 (1970).

(99) B. Z. Shakhashiri and G. Gordon, *ibid.*, **91**, 1103 (1969).

(100) G. Gordon, private communication.

(101) L. Pauling, "Nature of the Chemical Bond," Oxford and IBH Publishing Co., Calcutta, Indian Edition, 1967, pp 324, 356.

(102) R. K. Murmann and R. C. Thompson, *J. Inorg. Nucl. Chem.*, **32**, 1404 (1970).

(103) H. Taube and H. W. Dodgen, *J. Amer. Chem. Soc.*, **71**, 2501, 3330 (1949).

(104) M. H. Ford-Smith, private communication.

(105) A. Adegite, Ph.D. Thesis, University of Sussex, 1969.

(106) M. H. Ford-Smith and A. Adegite, to be published.

(107) R. H. Betts, *Can. J. Chem.*, **33**, 1780 (1955).

path in Fe^{II}. We assume the higher order path experimentally indicated to be this fourth-order path, and in Figure 5 denote this assumption with an arrow. If this shift is valid, U^{V} falls with the bridging oxidants, like the other oxycationic oxidant VO^{2+}.

6. *Vanadium(IV), -(III), and -(V)*

Vanadium(III) as oxidant has been dealt with in section IV.C.2, but some further aspects of its redox reactions need to be considered below.

For V^{IV} as oxidant of Fe^{II} the observations of Higginson and Sykes[108] on $Fe^{III} + V^{III}$, and the equilibrium constant from $E°$ values (Table II) are used, as with $V^{V} + V^{III} \rightleftarrows 2V^{IV}$ investigated by Daugherty and Newton.[109] There are three separate $[H^+]$ dependences for comparison here. They are, for each reductant, closely similar in rate, inescapably, in view of the necessarily narrow $[H^+]$ range used; otherwise all three paths would not have been observable. It is slightly disappointing that the three points fall just across rather than along the direction of the correlation (Figure 5), but *inter alia* medium effects, and possibly values of α not exactly 0.5, will become relatively important in attempts at such finenesses of discrimination. The evidence from other reactions (Table IV) indicates V^{IV} to be a bridging *oxidant*, and so it appears to act here, all points falling within the inner-sphere group.

Neglecting Fe^{II} briefly to comment on an aspect of the vanadium interreactions, it is a curious feature of the[75] $V^{V} + V^{II}$ and[109] $V^{V} + V^{III}$ reactions that the values of $S^{\ddagger}$, the standard entropy of the activated complex, are both anomalously negative. The anomalies have been tentatively ascribed to medium effects, but it is not clear why the common reactant V^{V} should be so singled out. It seems possible that the standard entropy of V^{V} may be in error. However, variations with solution composition of some few per cent in the equilibrium constant[57] for $Fe^{II} + V^{V}$ are presumably also medium effects. The conclusion compelled is that in general small differences in activation quantities for concentrated media are not to be given undue significance. But equally, it is the kineticist's basic tenet that gross differences are not medium effects but valid mechanistic data.

The $Fe^{II} + V^{V}$ reaction, discussed in section IV.C.2, must be considered again here with the vanadium self-exchange, V^{V} now serving an oxidant of Fe^{II} and V^{IV}. The exchange reaction, V^{IV} with V^{V}, has been studied by nmr line broadening,[9] but regrettably in high chloride concentrations in order to dissolve sufficient V^{V}. One measurement without Cl^- was said to indicate only that "exchange is rapid . . . in a path not involving chloride." In the presence of chloride it was found that rate $\propto [V^{IV}][V^{V}]^2[H^+][Cl^-]^?$, there being no information regarding the order with respect to Cl^- or the orders for the chloride-free reaction.

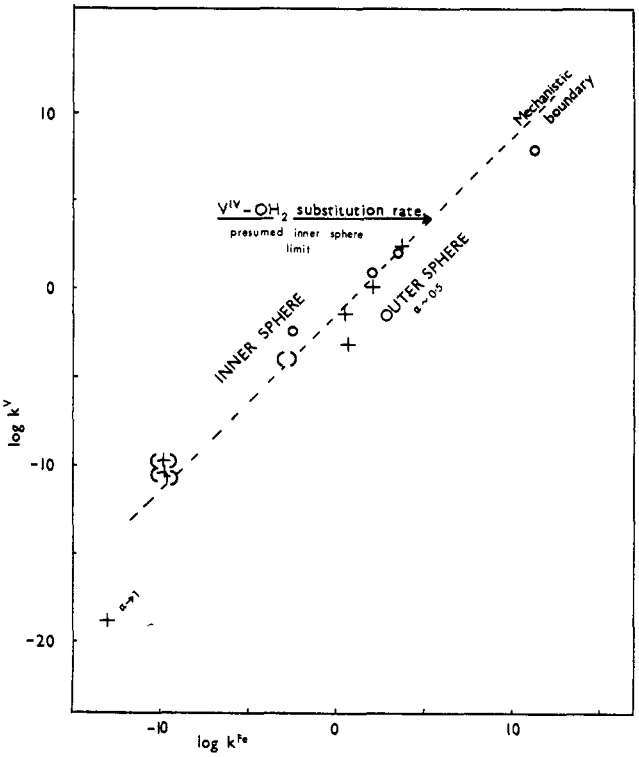

Figure 6. Summary of mechanistic interpretation. Points exactly as in Figure 5.

D. SUMMARY

The mechanistic rationalization of the results is presented in Figure 6. To recapitulate, rate constants for oxidations of V^{IV} are almost invariably smaller than those for Fe^{II} but become less small relatively when the evidence suggests a probably inner-sphere oxidant. This view is reinforced when rate constant for particular $[H^+]$ dependences ($[H^+]^m$ for Fe^{II} and $[H^+]^{m-1}$ for V^{IV}) replace experimental values in the plot. The enhanced acceleration with bridging at V^{IV} accords with the enhanced equilibrium stability of V^{IV} complexes. For inner-sphere oxidants V^{IV} rates approach Fe^{II} rates, while for putatively outer-sphere reactions V^{IV} can be up to several hundred fold slower. At VO^{2+}, inner-sphere reaction probably occurs by attachment of oxidant at an equatorial coordination site, outer-sphere by juxtaposition at a pyramidal face. Both mechanisms might conceivably accord with the cross-reaction relation (section II.C), but the relevant vanadium self-exchange rate (for hypothetical inner- *and* outer-sphere mechanism first order in each oxidation state) would be required; this problem is faced in the next section.

The effect of bridging favors V^{IV} only to the extent of *equalizing* the rates, no V^{IV} reaction proceeding much faster than its Fe^{II} counterpart. There may be a hint of a law in this observation, but there are insufficient data to generalize. It is tempting but facile to suggest, contrary to section II.D, that $\alpha \to 0$ for the bridged reactions, $\alpha \to 1$ having been invoked for the opposite deviation.

E. SEPARABILITY OF ELECTRON-TRANSFER MECHANISMS

Any implication in the foregoing of an all-or-nothing choice between inner- and outer-sphere mechanism must be discounted, experimental evidence for concurrence of both being widespread for a variety of systems.[73] By an inner-sphere classification we mean a probable, not exclusive, predominance of this process, correspondingly, the outer-sphere. Our graphs indicate such a gradation of mechanism. Furthermore, the oversimplification implicit in the outer-sphere *model*

---

(108) W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1962).

(109) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964).

(section II.C) should be admitted here. The separation *a* chosen must in general be a representative one of a possible range (through which a particular electron transfer could proceed), from close bridging to something greater than outer-sphere contact. The outer-sphere classification is largely an assertion of belief in the predominance of the latter.

F. THE CROSS-REACTION RELATION AND THE V(IV)-V(V) EXCHANGE RATE

Were V^{V} to react partly as a bridging oxidant, from our correlation in Figures 4 to 6 the exchange rate for $V^{IV} + V^{V}$ can be inferred as being *ca.* $3 \times 10^{3}\ M^{-1}\ sec^{-1}$ in 1 M $HClO_4$. This figure is obtained from the observation of rate equality in Fe^{II} and V^{IV} reactions with bridging oxidants, and hence by equating the rate observed[57] for $V^{V} + Fe^{II}$ with that for $V^{V} + V^{IV}$. If, on the other hand, the reaction were outer sphere, a value *ca.* $10\ M^{-1}\ sec^{-1}$ may be inferred from the *ca.* 300-fold rate decrement from bridged to unbridged reactions. This argument can be framed in terms of the cross-reaction relation. If the vanadium self-exchange rate is close to that for the $Fe^{II,III}$ self-exchange,[8] $10\ M^{-1}\ sec^{-1}$, then the cross-reaction relation (section II.C), with f for the time being assumed unity, indicates oxidations of Fe^{II} to be faster by $K^{1/2}$ than oxidations of V^{IV}. K, the equilibrium constant[65] for $Fe^{II} + V^{V} = Fe^{III} + V^{IV}$, gives $K^{1/2}$ as 260, close to the 300 quoted above. (Note that even if the major rate law for the $V^{IV,V}$ exchange involves $[V^{IV}][V^{V}]^2$, which would then represent the fastest path, indirect estimates, as above, of rate constant for both a slower inner-sphere $V^{IV} + V^{V}$ bimolecular path and a possibly even slower outer-sphere bimolecular path are not invalidated. The latter values would, in such case, not be directly observable.)

Further independent argument for this rate estimate is obtained as follows, if the surmise of section II.C, that $\alpha \rightarrow 0$ for very negative values of ΔF°_{12}, is correct. This implies that the equilibrium constant should be omitted from the cross-reaction relation, which then takes the form

$$k_{12} = \text{function}(k_1, k_2)$$

We examine the nearly equal rates of the reactions with negative ΔF°_{12} and $\Delta F^{\circ}_{1'2}$, $V^{V} + V^{II}$ and $Fe^{III} + V^{II}$. Here 1 represents V^{V} and 1′ Fe^{III}, and $k_{12} \approx k_{1'2}$ then indicates approximate equality of the self-exchange rates k_1 and $k_{1'}$. The supposition $\alpha \rightarrow 0$ prompted by the correlation of section IV(A–C) thus leads to internal consistency in conclusions regarding the self-exchanges.

The application of Marcus's equations[10] to reactions involving hydrolysis or protonations is not rigorously valid, but a transition-state quasi-equilibrium formulation[11] involves less objection. Particularly, the Marcus model[10] requires binary collision, but it is possible that hydrolyzed[58] V^{IV} is the major reactant, hence colliding entity, or, in the reverse direction, protonated V^{V}, $VOOH^{2+}$. If so, the equilibrium constant appearing in the cross-reaction relation should be increased from its value for the predominant V^{IV}/V^{V} species by the factor $K_p/K_h = 10^{6}K_p\ M^{-1}$, where K_p is the VO^{2+} hydrolysis[58] and K_p the VO_2^{+} protonation value (unknown). Use of $K^{1/2} = 260$ above carries the implicit assumption that K_p is of the same order of K_h. (The vanadium rate constants need modification by the factors K_h or K_p when appropriate.)

The factor f might, better than as above being presumed unity, be taken to vary by approximately the same amount for both Fe^{II} and V^{IV} as reductant. The difference of factor 6.7×10^{4} in redox equilibrium constants has by itself little differentiating effect. By way of illustration, for $k_1 = k_2 = 10\ M^{-1}\ sec^{-1}$ and $K_{12} = 10^{5}$, f introduces a factor 0.7 in predicted k_{12}, not very significant for our approximate correlations.

V. Correlations in Other Redox Sequences

Guenther and Linck[110] find that for many Co^{III} complexes of structure $Co^{III}A_4LCl^{2+}$ (A being NH_3 or half-ethylenediamine, and the L a variety of ligands) the rates of reduction by Fe^{II} correlate well with rates of reduction by V^{2+} and by $Ru(NH_3)_6{}^{2+}$. The correlation equations, for rate constants in $M^{-1}\ sec^{-1}$, are

$$\log k_{V(II)} = 0.49 \log k_{Fe(II)} + 2.68$$

$$\log k_{Ru(II)} = 0.83 \log k_{Fe(II)} + 5.09$$

Now these are akin to the correlations examined above for Fe^{II} and V^{IV} except that a commonality of mechanism, at least for each reductant, is inferrable here, and the oxidants are structurally much more uniform, with constant Co^{III} core. (In consequence, the rate range for each reductant is $<10^{6}$.) Linck is noncommittal regarding the possibility of bridging of Fe^{II} to Co^{III} through Cl (see ref 23–25, and comments where cited). Linck suggests that the sensitivity of rate to change of oxidant diminishes, reductant by reductant, with increasing equilibrium constant K. The E° values for the $M^{II,III}$ are Fe 0.75, Ru 0.1, V −0.26 V, which represent a 10^{17}-fold increase in K, from Fe to V. Such variation of sensitivity has been hitherto neglected in the widely quoted[16] rate correlation of Candlin, Halpern, and Trimm.[111]

For V^{IV} and Fe^{II} we aimed to rationalize the facts in terms of the cross-reaction relation. The equilibrium constants for the two reductants there were not greatly dissimilar, likewise (probably) the f factors. For Linck's data the cross-reaction relations for a series of oxidants "i" and two reductants "1" and "2" are for each series

$$k_{1i} = (k_1k_iK_{1i}f_{1i})^{1/2}$$

$$k_{2i} = (k_2k_iK_{2i}f_{2i})^{1/2}$$

If neglecting the f factors we eliminate k_i, a relationship is obtained predicting unit slope for $\log k_{1i}$ *vs.* $\log k_{2i}$, contrary to observation. Unless the unknown f values, requiring a knowledge of k_i, the Co^{III}–oxidant self-exchange rates, hold the key to the correlations, the cross-reaction relations unmodified appear to be unsuccessful here, which is disappointing.

Huchital, Sutin, and Warnqvist[81] compare a pair of oxidants, Co^{III} and Ag^{II}, in reactions with a series of reductants. The data have been plotted in Figure 7. It is the reviewer's prejudice that such series should provide the best correlations, since oxidants, usually having the higher core charge, would seem thereby to possess the factor dominating the potential energies, in u_{reorg}, for example. Thus a constant pair of oxidants should ensure constancy of a larger contribution to $\Delta F^{\ddagger}$ values than would reductants. Figure 7 shows a scatter in fact not very different from that in correlations for fixed reductants. Perhaps the most notable feature is the probable value unity

---

(110) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969).

(111) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

for the slope, as might have been expected for oxidants of comparable strength ($E°$ values).

VI. Some Oxidations by Vanadium(V) and Iron(III)

In some cases inaccessibility of equilibrium constants frustrates estimates of reverse rates from observed Fe^{III} and V^{V} oxidation rates. Thus, Sn^{III} being a fleeting intermediate, $Fe^{III} + Sn^{II}$ and $V^{V} + Sn^{II}$ can yield only relative, not absolute rates for the reverse directions. The $Fe^{III} + Sn^{II}$ reaction[112] was investigated 35 years ago, at 55 and 70°. The treatment of hydrolytic preequilibria probably requires reexamination in the light of current knowledge and methodology,[60] but from the data recorded the observed bimolecular rate constant in 0.1 M $HClO_4$ (from the values 4.5×10^{-4} and 3×10^{-3}, respectively), extrapolated to 20°, is *ca.* 2×10^{-6} M sec^{-1}; no higher orders were contemplated.[112] The vanadium(V) reaction[113] shows two paths, $V^{V} + Sn^{II}$ and $2V^{V} + Sn^{II}$, with rate constants 0.46 M^{-1} sec^{-1} and 3000 M^{-2} sec^{-1} (ionic strength 2 M, 1 M $HClO_4$, 20°). We compare the former with the Fe^{III} result. While the Fe^{III} rate at 20° must be uncertain by at least tenfold, and would be accelerated at a higher ionic strength, by perhaps up to tenfold again, use of equilibrium constants for hypothetical reaction rates of $Sn^{III} + V^{IV}$ and $Sn^{III} + Fe^{II}$ leads to roughly equal rates, or, taking into account the uncertainties, Fe^{II} reaction possibly up to a 100-fold faster. This again accords with the limits of behavior observed for V^{IV} and Fe^{II} reactions generally.

The $V^{V} + I^{-}$ reaction[61] is simple second order, but iron(III) with iodide,[114] examined in nitrate solution, appears to follow a different mechanism involving I_2^{-} as reductant. A reexamination in $HClO_4$ solution seems worthwhile.

Another reaction pair is[115] $V^{V} + Fe(CN)_6^{4-}$ and[116] $Fe^{III} + Fe(CN)_6^{4-}$. Both form adducts, the latter remaining so as a solid, the well-known Prussian or Turnbull's Blue, the former ultimately decomposing to reduced and oxidized products. The adducts also differ in that the Prussian Blue has iron(II) in the cyano complex,[116] whereas the vanadium adduct is[115] V^{IV}-$Fe(CN)_6^{3-}$. While the distribution of oxidation states in Prussian Blue might be partly an effect of lattice forces, the vanadium adduct has a structure well in keeping with the stated views on complexing with vanadium(IV) (section III.C).

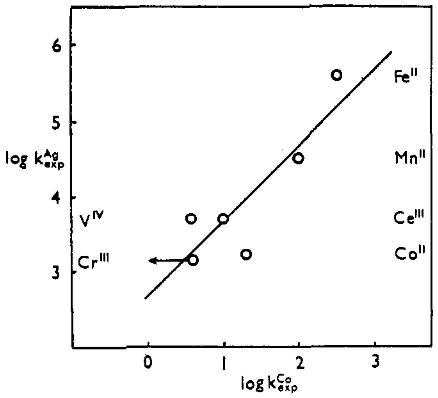

Figure 7. Log k for oxidations by Ag^{II} against log k for oxidations by Co^{III} (4 M $HClO_4$, 25°). Line of unit slope indicated.

VII. Conclusion

The comment *Se non e vero, e ben trovato* is as much as any mechanistic analysis including this one can aspire to.

Acknowledgments. I wish to acknowledge valuable discussion, verbal or written, with Drs. A. G. Sykes and J. M. Ottaway, Professors M. T. Pope, J. H. Espenson, and G. Gordon, and Drs. M. H. Ford-Smith, G. Davies, and G. St. Nikolov. I am deeply indebted to Dr. M. J. Nicol for fruitful and prolonged cooperation, and to my colleague Dr. K. Kite for generous aid and advice. Finally I would thank Professor R. E. Connick for his valuable comments as referee.

---

(112) M. H. Gorin, *J. Amer. Chem. Soc.*, **58**, 1787 (1936).

(113) N. A. Daugherty and B. Schiefelbein, *ibid.*, **91**, 4328 (1969).

(114) A. J. Fudge and K. W. Sykes, *J. Chem. Soc.*, **119**, 124 (1952).

(115) J. P. Birk, *Inorg. Chem.*, **9**, 125 (1970).

(116) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 295 (1967).