The Kinetics of the Oxidation of Vanadium(II) by Iron(III) and Chromium(III) Complexes[1]

Sir:

Important information concerning the mechanisms of oxidation–reduction reactions can be obtained when the rates of substitution of the reactants or products are slower than, or comparable to, the rates of the electron-transfer reactions.[2–5] Reductions by hexaaquovanadium(II) ions satisfy these conditions since, by suitable choice of the oxidizing agent, the rate of the electron-transfer reaction can be made either faster or slower than the rate of water replacement on vanadium(II) and vanadium(III).[6] This communication is concerned with the mechanism of oxidation of hexaaquovanadium(II) by iron(III) and chromium(III) complexes.

The $(H_2O)_5FeX^{2+}$–$V(H_2O)_6^{2+}$ Reaction. The kinetics of the oxidation of vanadium(II) by iron(III) were studied under pseudo-first-order conditions (with the vanadium(II) present in excess) by use of the flow apparatus which has been previously described.[7] The oxidations were followed at the absorption maxima of the iron(III) complexes. The rate constant for the V^{2+}–Fe^{3+} reaction is $(1.8 \pm 0.1) \times 10^4$ M^{-1} sec^{-1} at 25.0° and ionic strength 1.0 *M* and was found to be independent of $(HClO_4)$ in the range 1.0–0.25 *M*. From the acid independence of the rate constant and the hydrolysis constant[8] of Fe^{3+}, we estimate that the rate constant for the V^{2+}–$FeOH^{2+}$ reaction is less than 4×10^5 M^{-1} sec^{-1} at 25.0°. The rate constants for the oxidation of V^{2+} by $FeCl^{2+}$, $FeNCS^{2+}$, and FeN_3^{2+} are $(4.6 \pm 0.5) \times 10^5$, $(6.6 \pm 0.7) \times 10^5$, and $(5.2 \pm 0.6) \times 10^5$ M^{-1} sec^{-1}, respectively, at 25.0° and ionic strength 1.0 *M*.[9] No spectrophotometric evidence indicating that VX^{2+} complexes were formed in the oxidation–reduction reaction was obtained.[10]

The relatively small effect of hydroxide on the rate of the vanadium(II)–iron(III) reaction is particularly striking in view of its marked effect on other oxidations by iron(III)[11] and suggests that hydroxide is not functioning as a bridging group in the $FeOH^{2+}$–V^{2+} reaction.[12] The similar effects of chloride, azide, and thiocyanate suggests that these anions, too, are not acting as bridging groups in the electron-transfer reaction. There is good evidence that azide is a much better bridging group than thiocyanate in certain inner-sphere reactions.[13]

The conclusion that the anions are not directly bonded to both metal centers in the activated complex for the $(H_2O)_5FeX^{2+}$–V^{2+} reactions receives strong support from studies of the rate of water replacement on $V(H_2O)_6^{2+}$. The water exchange rate of $V(H_2O)_6^{2+}$ has not been measured directly; however, the rate constant for the formation of $(H_2O)_5VNCS^+$ from vanadium(II) and thiocyanate is 9 ± 1 M^{-1} sec^{-1} at 25.0°, $(HClO_4) = 0.5$ *M*, and ionic strength 1.0 *M*.[14] By analogy with the substitution reactions of other aquo ions,[6] it is likely that this rate constant provides a measure of the rate of replacement of a water molecule coordinated to vanadium(II). It is seen that this rate is several orders of magnitude slower than the rate of the $(H_2O)_5FeX^{2+}$–V^{2+} reactions, and consequently water replacement on $V(H_2O)_6^{2+}$ cannot occur prior to the electron-transfer step.[15] However, while these studies suggest strongly that the $Fe(H_2O)_6^{3+}$–$V(H_2O)_6^{2+}$ reaction is outer sphere, they do not require an outer-sphere mechanism for the $(H_2O)_5FeX^{2+}$–V^{2+} reactions since the latter reactions could proceed *via* inner-sphere, water-bridged activated complexes. Such activated complexes (in which X acts as a nonbridging ligand) could be formed by the loss of a water molecule coordinated to the iron(III). There is some evidence that water substitution on $(H_2O)_5FeX^{2+}$ is sufficiently rapid for this reaction to occur prior to the electron-transfer step.[6]

The $(H_2O)_5CrSCN^{2+}$–$V(H_2O)_6^{2+}$ Reaction. This reaction proceeds in two stages.

$$CrSCN^{2+} + V^{2+} \xrightarrow{k_1} Cr^{2+} + VNCS^{2+} \tag{1}$$

$$VNCS^{2+} \xrightarrow{k_2} V^{3+} + SCN^- \tag{2}$$

The rate constant for reaction 1, obtained by following the disappearance of $CrSCN^{2+}$ at 262 mμ (an absorption maximum of $CrSCN^{2+}$), is 7.1 ± 0.4 M^{-1} sec^{-1} at 25.0° and $(HClO_4) = 1.0$ *M*.[16] The formation of $VNCS^{2+}$ and its subsequent disappearance was followed at 350 mμ (an absorption maximum of $VNCS^{2+}$) and also at 400 mμ. The $VNCS^{2+}$ was identified by its spectrum and by its rate of dissociation.[17] In the concentration ranges used, $(V^{2+}) = 1.0 \times 10^{-3}$ to 0.15 *M* and $(CrSCN^{2+}) \sim 2 \times 10^{-6}$ to 2×10^{-4} *M* with $(V^{2+}) \geq 150(CrSCN^{2+})$, the rate of reaction 3 is negligible compared to that of reaction 1.[18,19] Consequently the

$$CrSCN^{2+} + Cr^{2+} \xrightarrow{k_3} Cr^{2+} + CrNCS^{2+} \tag{3}$$

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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

(3) J. Menashi, S. Fukushima, C. Foxx, and W. L. Reynolds, *Inorg. Chem.*, **3**, 1242 (1964).

(4) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *J. Am. Chem., Soc.*, **86**, 1453 (1964).

(5) A. Haim and N. Sutin, *ibid.*, **88**, 5343 (1966).

(6) For a recent review of this subject, see N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966)

(7) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963). The uncertainties quoted for the rate constants are the standard deviations from the mean.

(8) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(9) The rates of the oxidation–reduction reactions were rapid compared to the rates of formation of the FeX^{2+} complexes from Fe^{3+} and X^- ions under the experimental conditions used.[6]

(10) The dissociation of $VSCN^{2+}$, which could be a primary product of the $FeNCS^{2+}$–V^{2+} reaction, might be too rapid to be detected in these studies. We did, however, observe that the reaction of vanadium(III) and thiocyanate to form $VNCS^{2+}$ occurred after the $FeNCS^{2+}$–V^{2+} reaction was complete.

(11) E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **6**, 428 (1967).

(12) The $Co(NH_3)_5OH_2^{3+}$–V^{2+} reaction does not show any acid dependence over a range of acidity which changes the rate of the $Co(NH_3)_5OH_2^{3+}$–Cr^{2+} reaction by a factor of 40: A Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

(13) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

(14) B. R. Baker and N. Sutin, unpublished observations.

(15) The ratio of the rates of the V^{2+}–V^{3+} and V^{2+}–VOH^{2+} reactions is 1.8×10^2 at 25.0°: K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958). The rate constant for the latter reaction ($\sim$1.8 M^{-1} sec^{-1}) is sufficiently small for water replacement on vanadium(II) to occur prior to the electron-transfer step.

(16) The $CrSCN^{2+}$ solutions also contained some $CrNCS^{2+}$: A. Haim and N. Sutin, *ibid.*, **87**, 4210 (1965). However, the rate of reaction of $CrNCS^{2+}$ with vanadium(II) ($k = 1.7 \times 10^{-4}$ M^{-1} sec^{-1} in 1.0 *M* perchloric acid at 25°) is much slower than the rate of reaction 1.

(17) The rate constant for reaction 2 is 0.99 sec^{-1} at 25.0° and ionic strength 1.0 *M*: B. R. Baker, T. J. Conocchioli, and N. Sutin, to be published.

(18) The rate constant for reaction 3 is 42 M^{-1} sec^{-1} at 25.0° and 1.0 *M* perchloric acid.[16,19]

(19) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

chromium(II) produced in reaction 1 does not significantly affect the rate of disappearance of $CrSCN^{2+}$. This was further checked by adding $Co(NH_3)_5F^{2+}$ to react with the chromium(II) produced in reaction 1.[20-22] A solution 0.42 M in V^{2+} and 1 M in perchloric acid was mixed with a solution $\sim 2 \times 10^{-3}$ M in $CrSCN^{2+}$, 1.2×10^{-2} M in $Co(NH_3)_5F^{2+}$, and 1 M in perchloric acid, and the formation of $VNCS^{2+}$ and its subsequent disappearance were followed at 400 mμ, an absorption minimum of $Co(NH_3)_5F^{2+}$. The value of t_{max}, the time required for the concentration of $VNCS^{2+}$ to reach its maximum value, was 0.83 sec, in very good agreement with the value of 0.83 sec calculated for reactions 1 and 2.[23,24] We conclude, therefore, that, in contrast to the iron(III)–vanadium(II) reactions, the reaction of $CrSCN^{2+}$ with vanadium(II) proceeds *via* an anion-bridged transition state, in which the thiocyanate is bonded to both the vanadium and the chromium. It is noteworthy that the rate constant for reaction 1 is very similar to the rate constant for the formation of thiocyanatopentaaquovanadium(II) from vanadium(II) and thiocyanate ions.[25,26]

(20) The rate constants for the reaction of $Co(NH_3)_5F^{2+}$ with vanadium(II) and chromium(II) are 2.6 and 9×10^5 M^{-1} sec^{-1}, respectively, at 25.0° and ionic strength 1.0 M.[21,22]

(21) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, 86, 1019 (1964).

(22) J. P. Candlin and J. Halpern, *Inorg, Chem.*, 4, 766 (1965).

(23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 166.

(24) G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 71.

(25) These studies do not establish the structure of the monothiocyanate complex of vanadium(III). However, the similarity of the spectra of the monoazide and monothiocyanate complexes of vanadium(III) (both have absorption maxima at 350 mμ) strongly suggests that the latter complex is nitrogen bonded. The observation that V^{2+} reacts 4×10^4 times more rapidly with $CrSCN^{2+}$ than with $CrNCS^{2+}$ is consistent with this view. Evidence has been previously presented[5,19,26] that the stable monothiocyanate complexes of chromium(III) and iron(III) are nitrogen bonded.

(26) T. J. Conocchioli and N. Sutin, *J. Am. Chem. Soc.*, **89**, 282 (1967).

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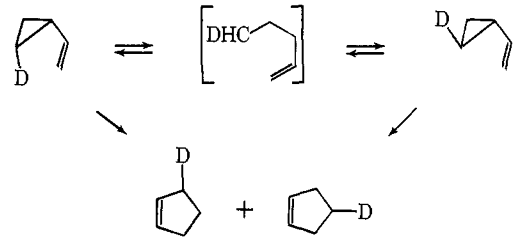
The Stereochemical Fate of the Cyclopropyl Ring in the Vinylcyclopropane Rearrangement

Sir:

Thermolysis of vinylcyclopropane to cyclopentene is a reaction whose course is securely established.[1-3] Interpretation of the kinetic parameters for the formation of cyclopentene have, on the one hand, led to the conclusion that the rearrangement is concerted,[2] and, on the other hand, that a discrete diradical intermediate is involved.[3] We present here experimental evidence that has a considerable bearing on this mechanistic question.

A 5:1 mixture of *cis*- and *trans*-2-bromo-1-vinylcyclopropane[4] was separated by vapor phase chromatography. These bromine compounds were reduced by sodium in moist methanol to vinylcyclopropane. Reduction of each isomer by sodium in methanol-O-*d* containing deuterium oxide produced vinylcyclopropane containing 1 deuterium atom/molecule. The upfield portion of the 100-MHz nmr spectrum of vinylcyclopropane consists of three complex multiplets centered at δ 1.3, 0.7, and 0.4, with intensities of 1:2:2. The nmr spectrum of the monodeuteriovinylcyclopropane prepared from the minor brominated isomer exhibits peaks with the same chemical shifts but having the intensities 1:1:2, while the spectrum of the compound prepared from the major brominated isomer exhibited intensities of 1:1.5:1.5. Since it is assured that the stereochemistry has been lost in the latter case, we turned our attention to the monodeuterio isomer with the 1:1:2 pattern of intensity.[5] Pyrolysis of this monodeuteriovinylcyclopropane at 300 mm in a base-washed Pyrex tube at 360° for 10 min caused a 6% conversion to cyclopentene. The intensities of the absorptions of the upfield portion of the nmr spectrum changed from 1:1.1:1.9 before pyrolysis to 1:1.5:1.5 in the recovered vinylcyclopropane. The precision and reproducibility of our integrated intensities are such that no more than 5% unrearranged deuteriovinylcyclopropane would have remained undetected. If both the scrambling of the deuterium label and the formation of cyclopentene are first-order reactions, we can then calculate that during the first 6% of the irreversible formation of cyclopentene complete equilibration of the stereochemistry at the labeled site occurred. We thus conclude that the loss of stereospecificity at the deuterium-labeled site in the cyclopropyl ring is at least five times as fast as the conversion to cyclopentene.



The most economical interpretation of this experiment is based on the trimethylene diradical model for the *cis*- and *trans*-1,2-dideuteriocyclopropane isomerization data of Rabinovitch, *et al.*[6,7] These authors assert that the geometrical and structural isomerization of cyclopropane involves formation of the trimethylene diradical as an intermediate, a process with an activation energy of 63 kcal/mole. The addition of a vinyl group to the cyclopropyl ring should lower the activation energy for formation of a diradical by

(1) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007 (1960).

(2) (a) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); (b) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962); (c) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4188 (1964); (d) C. J. Elliot and H. M. Frey, *ibid.*, 345 (1965); (e) C. J. Elliot and H. M. Frey, *ibid., Phys. Sect.*, 553 (1966).

(3) (a) B. Grzybowska, J. H. Knox, and A. F. Trotman-Dickenson, *ibid.*, 4402 (1961); (b) H. M. Frey, *Trans. Faraday Soc.*, **58**, Part I, 516 (1962); (c) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962); (d) R. J. Ellis and H. M. Frey, *ibid.*, 959 (1964); (e) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964).

(4) D. Seyferth, Y. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(5) The *trans* relationship of the deuterium atom and the vinyl group can be inferred from the nmr spectrum. However, since the observations reported here do not depend on this assignment in any critical fashion, we have decided to defer a more rigorous assignment of structure.

(6) (a) The contributions to the question are summarized in D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964); (b) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(7) (a) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *ibid.*, **28**, 504 (1958); (b) B. S. Rabinovitch and E. W. Schlag, *J. Am. Chem. Soc.*, 86, 5996 (1960).