

## Free Energies, Barriers, and Reactivity Patterns in Oxidation-Reduction Reactions

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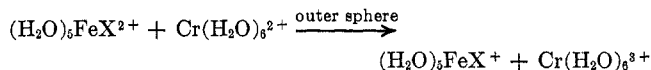
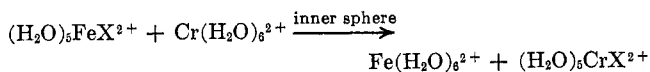
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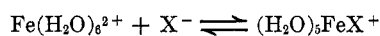
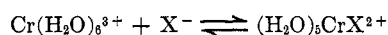
Mechanisms of electron transfer in solution are discussed. The evidence that rates of reduction by vanadium(II) are primarily determined by the rate of water replacement on the reducing agent is reviewed. The effects of azide, thiocyanate, hydroxide, and halide ions on electron-transfer rates are considered, and the question of normal and inverted bridging orders is discussed. Variations in electron-transfer rates are interpreted in terms of changes in the intrinsic and thermodynamic barriers.

It may be said that the study of oxidation-reduction reactions began about two centuries ago with the work of Lavoisier and his contemporaries. They reinterpreted a large area of chemistry in terms of the concepts of oxidation and reduction. By "oxidation" Lavoisier meant the addition of oxygen to a substance to form an "oxide." The term "reduction" had been used even earlier to describe the process of refining or restoring iron metal from ores or rusts, usually by treatment with charcoal. The modern meanings of oxidation and reduction are much more general. These terms are now used to describe any reaction in which electrons are transferred from one substance (the reducing agent) to another (the oxidizing agent).

In recent years there has been a great deal of interest in the mechanisms of these electron-transfer processes. As a result of work in this area it is now recognized that oxidation-reduction reactions involving metal ions and their complexes are of two main types,<sup>2</sup> called inner sphere and outer sphere reactions. The metal ions are connected by a common bridging group in inner sphere reactions, while the coordination shells of the metal ions remain intact during outer sphere reactions. Since transfer of the bridging group from the oxidizing agent to the reducing agent frequently occurs in inner sphere reactions, the immediate products of inner sphere reactions are usually different from those of outer sphere reactions, and consequently valuable information concerning the reaction mechanism can be obtained from the identities of the primary products of the reactions.



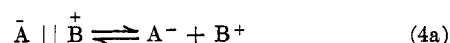
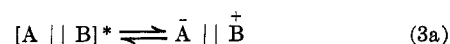
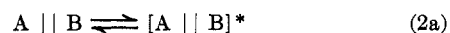
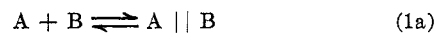
The immediate products of an oxidation-reduction reaction can be identified by conventional techniques if the substitution reactions are sufficiently slow or by the use of flow techniques if the substitution reactions



are rapid. By this means it has been shown that many reductions by  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{V}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Co}(\text{CN})_5^{3-}$ , and  $\text{Ru}(\text{NH}_3)_5^{2+}$  proceed *via* inner sphere mechanisms.<sup>3</sup> Indeed it now appears likely that the inner sphere mechanism provides the preferred pathway for reactions involving substitution-labile reductants.

Once an inner sphere or an outer sphere label has been assigned to a particular reaction, some of the remaining questions to be answered are: What is the detailed nature of the individual steps leading from the reactants to the products? How does the electron-transfer rate depend upon the structure of the metal ions and upon the nature of the bridging group? These questions will be discussed in the remainder of this article.

**The Elementary Steps.** In common with ordinary chemical processes, electron-transfer reactions proceed in a number of steps. In outer sphere reactions these steps are given by eq 1a-4a, where || denotes that no



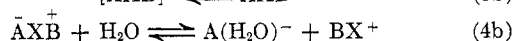
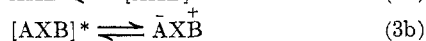
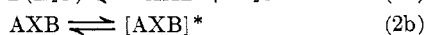
chemical bonds have been made or broken. The steps

(3) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

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(2) H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75**, 4118 (1953); H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

in inner sphere reactions are given by eq 1b-4b. The



first step involves the formation of a precursor complex from the separated reactants. The distance between the centers of the reactants in the precursor complex is approximately the same as in the activated complex. No chemical bonds are made or broken in forming the precursor complex in outer sphere reactions, whereas substitution (or addition) is involved in forming the precursor complex in inner sphere reactions. Reorganization of the precursor complex to form the activated complex occurs in the second step. In this step the inner coordination shells of the reactants, as well as the polarization of the surrounding medium, adjust to the configuration appropriate to the activated complex. The electron transfer may, and usually does, take place during the latter stages of the reorganization of the precursor complex. However, in some instances, the precursor complex may acquire the nuclear configuration of the activated complex without any resulting electron transfer.

The third step involves the deactivation of the activated complex to form the successor complex (or to re-form the precursor complex if no electron transfer had occurred in the activated complex). While the electron distribution in the precursor complex corresponds to that of the reactants, the electron distribution in the successor complex corresponds to that of the products of the reaction. Dissociation of the successor complex to form the separated products occurs in the fourth step. Although transfer of the bridging group usually accompanies the dissociation of the successor complex in an inner sphere mechanism, such transfer need not necessarily occur, and is not an essential feature of an inner sphere reaction.

In terms of the above reaction scheme the free energy of activation for the electron-transfer reaction is given by<sup>4-7</sup>

$$k = pZe^{-\Delta G^*/RT} \quad (5)$$

where  $Z$  is the collision frequency between two uncharged reactants in solution,  $\Delta G^*$  is the free energy required to form the activated complex from the separated reactants, and  $p$  is the probability of electron transfer in the activated complex.  $p$  is equal to unity in adiabatic reactions and is less than unity in nonadiabatic reactions.

In some instances the electron-transfer process may be more complicated than indicated above. A recent example is the reaction of isonicotinamidopentaaminocobalt(III) with chromium(II).<sup>8</sup> It has been

(4) R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960).

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

(6) R. A. Marcus, *J. Chem. Phys.*, **44**, 679 (1965).

(7) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

(8) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1162 (1968).

Table I

Comparison of Rates of Substitution and of Electron-Transfer Reactions Involving Vanadium(II)<sup>a</sup>

Reaction	$k$ , $M^{-1} \text{ sec}^{-1}$	$\Delta H^\ddagger$ , $\text{kcal mol}^{-1}$	$\Delta S^\ddagger$ , $\text{cal deg}^{-1}$ $\text{mol}^{-1}$	Ref
$V^{2+} + SCN^-$	$28 \pm 3^b$	13.5	$-7 \pm 4$	c
$V^{2+} + CrSCN^{2+}$	$15 \pm 2^d$			11
$V^{2+} + VO^{2+}$	8.0	13.0	-11	e
$V^{2+} + cis-Co(en)_2(N_3)_2^+$	$1.6^{f,i}$	$12.3^i$	$-16.5^i$	g
$V^{2+} + Co(NH_3)_5X^{2+}$ , X =	32.9			h
Azide	13	11.7	-14	12
Binoxalate	12.5	12.2	-13	10
Oxalate	$45 \pm 5$			10
Glyoxalate	8.2	11.0	-17	10
Pyruvate	10.2	11.6	-15	10
Trimethylpyruvate	2.1	11.9	-17	10
Oxamate	20.7	11.6	-14	10

<sup>a</sup> Rate constants at 25° and 1.0 M ionic strength. <sup>b</sup> Ionic strength 0.84 M. <sup>c</sup> J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968). According to these authors  $\Delta S^\ddagger = -2$  eu. However we calculate  $\Delta S^\ddagger = -7$  eu from their data. <sup>d</sup> Rate constant at 24°. <sup>e</sup> M. Orhanović, H. N. Po, and N. Sutin, to be published. <sup>f</sup> Ionic strength 2.0 M. <sup>g</sup> T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964). <sup>h</sup> J. H. Espenson, *J. Am. Chem. Soc.*, **89**, 1276 (1967). <sup>i</sup> These are the observed parameters and contain the contribution of an outer sphere path. The outer sphere path accounts for about 35% of the observed rate at 0° [T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964)]. The value of the enthalpy of activation for the inner sphere path is 12.8 kcal mol<sup>-1</sup> if it is assumed that the extinction coefficient of the dinuclear complex is independent of temperature.

proposed that this reaction proceeds by a radical intermediate mechanism in which the electron transfer is initially to the ligand rather than to the cobalt center.

**Reductions by Vanadium(II).** The reorganization of the precursor complex is believed to be the rate-determining step in most electron-transfer reactions. However, there is evidence that the formation of the precursor complex is rate determining in certain systems. For example, there are a number of electron-transfer reactions involving vanadium(II) in which the rate of the oxidation-reduction reaction is similar to the rate of substitution of vanadium(II) by thiocyanate.<sup>9-12</sup>



Because of its stable d<sup>3</sup> electronic configuration, substitution on vanadium(II), as on chromium(III), is relatively slow. The relevant data are summarized in Table I. It seems likely that the rates of the electron-transfer reactions presented in the table are primarily determined by the rates of formation of the precursor complexes and that the nature of the entering group does not have a large effect on the rate of replacement of a water molecule coordinated to vanadium(II). The faster reaction rates of the oxalato and diazido complexes can be ascribed to electrostatic effects, while the slower reaction rate of the trimethylpyruvate complex may be due to steric effects.<sup>10</sup> The identification

(9) B. Baker, M. Orhanović, and N. Sutin, *ibid.*, **89**, 722 (1967).

(10) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(11) W. Kruse and D. Thusius, *ibid.*, **7**, 464 (1968).

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

**Table II**  
Comparison of the Acid-Independent and Inverse Acid Paths in Electron-Transfer Reactions<sup>a</sup>

Reaction	$k_{M^{2+}}$ , $M^{-1} \text{ sec}^{-1}$	$k_{\text{MOH}^{2+}}/k_{\text{MOH}_2^{3+}}$	Ref
$\text{Fe}^{2+} + \text{Fe}^{3+}$	4.0	$7.8 \times 10^2$	<i>b</i>
$\text{Cr}^{2+} + \text{Fe}^{3+}$	$2.3 \times 10^3$	$1.4 \times 10^3$	<i>c</i>
$\text{V}^{2+} + \text{Fe}^{3+}$	$1.8 \times 10^4$	$\leq 20$	<i>g</i>
$\text{Cr}^{2+} + \text{Cr}^{3+}$	$\leq 2 \times 10^{-5}$	$\geq 3 \times 10^4$	<i>d</i>
$\text{V}^{2+} + \text{V}^{3+}$	$1.0 \times 10^{-2}$	$1.8 \times 10^2$	<i>e</i>
$\text{Cr}^{2+} + (\text{NH}_3)_5\text{CoOH}_2^{3+}$	0.5	$3 \times 10^3$	<i>g</i>
$\text{V}^{2+} + (\text{NH}_3)_5\text{CoOH}_2^{3+}$	$\sim 0.5$	$\leq 1 \times 10^5$	<i>g</i>
$\text{Ru}(\text{NH}_3)_6^{2+} +$ $(\text{NH}_3)_5\text{CoOH}_2^{3+}$	3.0	$10^{-2}$	<i>f</i>
$\text{Cr}(\text{bipy})_3^{2+} +$ $(\text{NH}_3)_5\text{CoOH}_2^{3+}$	$5 \times 10^4$	$10^{-2}$	<i>g</i>

<sup>a</sup> Rate constants at 25°. <sup>b</sup> J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). <sup>c</sup> G. Dulz and N. Sutin, *J. Am. Chem. Soc.*, **86**, 829 (1964). <sup>d</sup> A. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954). <sup>e</sup> K. V. Krishnamurty and A. C. Wahl, *ibid.*, **80**, 5921 (1958). <sup>f</sup> J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964). <sup>g</sup> A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

of the products of the electron-transfer process has shown that the reactions of vanadium(II) with  $\text{CrSCN}^{2+}$ ,  $\text{VO}^{2+}$ ,  $\text{cis-Co(en)}_2(\text{N}_3)_2^+$ , and  $\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)^+$  proceed mainly by inner sphere mechanisms.

#### Comparison of the Effects of Hydroxide and Water.

The rates of reduction of aqua complexes generally increase with decreasing acidity. This increase in rate is ascribed to displacement of the hydrolysis equilibrium



with  $\text{MOH}^{2+}$  undergoing more rapid reduction than  $\text{MOH}_2^{3+}$ . The rates of reduction of some hydrolyzed and unhydrolyzed complexes are compared in Table II. It will be seen that  $\text{MOH}^{2+}$  generally reacts some  $10^2$  to  $10^4$  times more rapidly than  $\text{MOH}_2^{3+}$ . The vanadium(II)-iron(III) reaction appears to be an exception in that  $\text{V}^{2+}$  does not react much more rapidly with  $\text{FeOH}^{2+}$  than with  $\text{Fe}^{3+}$ . The rate of the reaction between  $\text{V}^{2+}$  and  $\text{Fe}^{3+}$  is much faster than the rate of reaction of vanadium(II) with thiocyanate (and is also faster than the rate of water replacement on iron(III)), indicating that the electron transfer in the  $\text{V}^{2+}$ - $\text{Fe}^{3+}$  reaction proceeds by an outer sphere mechanism. As discussed above, the fastest rate of an inner sphere vanadium(II) reaction is about  $40 M^{-1} \text{ sec}^{-1}$  (unless electrostatic or other factors are very favorable). Consequently hydroxide ion cannot act as an efficient bridging ligand in the reaction of vanadium(II) with  $\text{FeOH}^{2+}$  (since the rate constant for the bridging reaction would have to be  $\leq 40 M^{-1} \text{ sec}^{-1}$ ). Thus the observation that vanadium(II) does not react much more rapidly with  $\text{FeOH}^{2+}$  than with  $\text{Fe}^{3+}$  indicates that it is necessary for the hydroxide ion to function as a bridging ligand for it to exert a large catalytic effect (and that formation of the precursor complex not be rate determining). Conversely, the observation of a large discrimination between hydroxide and water indicates that the hydroxide-catalyzed reaction is proceeding by an inner sphere mechanism.<sup>13</sup>

(13) See Table II, footnote *g*.

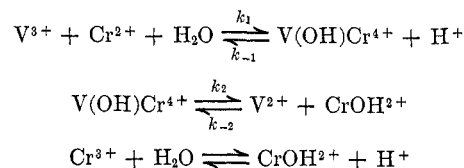
The rates of reaction of  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$  and  $(\text{NH}_3)_5\text{CoOH}^{2+}$  with various reducing agents are also included in Table II. It will be seen that the discrimination between hydroxide and water is very marked with chromium(II) but not with the substitution-inert reducing agents  $\text{Cr}(\text{bipy})_3^{2+}$  and  $\text{Ru}(\text{NH}_3)_6^{2+}$ . It has been shown that  $^{18}\text{O}$  is transferred in the reactions of labeled  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$  and labeled  $(\text{NH}_3)_5\text{CoOH}^{2+}$  with chromium(II), thus establishing that these reactions proceed by oxygen-bridged transition states.<sup>14</sup> The reaction of  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$  with vanadium(II) shows no change in rate over an acidity range which changes the rate of the chromium(II) reaction by a factor of 40.<sup>13</sup>

Evidence of oxygen- or hydroxide-bridged intermediates has been obtained in other cases from the rate law for the reaction.<sup>15-17</sup> For example, the rate law for the reaction of chromium(II) with vanadium(III) is:<sup>17</sup>

$$\text{rate} = \frac{q(\text{V}^{3+})(\text{Cr}^{2+})}{r + (\text{H}^+)}$$

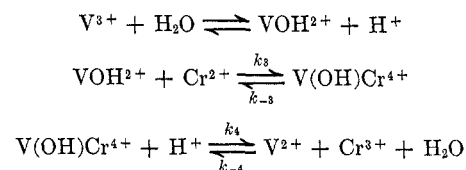
Although the form of this rate law has been questioned,<sup>18</sup> it has recently been established that the above rate law does indeed accurately describe the acid dependence of the reaction.<sup>19</sup> The rate law is consistent with the following mechanisms, both of which involve the formation of a hydroxide-bridged intermediate.<sup>17,20</sup>

#### Mechanism I



which gives  $k_1 = 5.76 M^{-1} \text{ sec}^{-1}$  and  $k_2/k_{-1} = 0.108 M$  at 25°.

#### Mechanism II



which yields  $k_3 = 3.12 \times 10^2 M^{-1} \text{ sec}^{-1}$  and  $k_{-3}/k_4 = 0.108 M$  at 25.0°.

The above reaction parameters may be combined with the equilibrium constant for the vanadium(II)-chromium(III) reaction to yield values for  $k_{-2}$  and  $k_{-4}$ . These are the rate constants for the reverse reactions and involve substitution on vanadium(II). It might prove possible to rule out one (or both) of the above mechanisms if  $k_{-2}$  or  $k_{-4}$  turned out to be much

- (14) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **82**, 526 (1960).  
 (15) T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).  
 (16) T. W. Newton and F. B. Baker, *ibid.*, **67**, 1425 (1963).  
 (17) J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).  
 (18) A. G. Sykes, *Chem. Commun.*, 442 (1965).  
 (19) A. Adin and A. G. Sykes, *J. Chem. Soc.*, **A**, 351 (1968).  
 (20) A. Haim, *Inorg. Chem.*, **5**, 2081 (1966).

**Table III**  
Formation of Dinuclear Complexes in Electron-Transfer and Substitution Reactions

Reaction	Dinuclear species <sup>a, b</sup>	Ref
Cr <sup>II</sup> + Cr <sup>IV</sup>	Cr <sup>III</sup> (OH) <sub>2</sub> Cr <sup>III</sup>	c, d
Cr <sup>III</sup> + Cr <sup>III</sup>		
V <sup>II</sup> + V <sup>IV</sup>	V <sup>III</sup> (OH) <sub>2</sub> V <sup>III</sup>	e, f
V <sup>III</sup> + V <sup>III</sup>		
Fe <sup>II</sup> + Fe <sup>IV</sup>	Fe <sup>III</sup> (OH) <sub>2</sub> Fe <sup>III</sup>	g, h
Fe <sup>III</sup> + Fe <sup>III</sup>		
Cr <sup>II</sup> + Np <sup>IV</sup>	Cr <sup>III</sup> ONp <sup>V</sup>	i
Cr <sup>III</sup> + Np <sup>V</sup>		
Cr <sup>II</sup> + U <sup>VI</sup>	Cr <sup>III</sup> O <sup>U</sup> V	j
Cr <sup>II</sup> + V <sup>IV</sup>	Cr <sup>III</sup> (OH) <sub>2</sub> V <sup>III</sup>	k

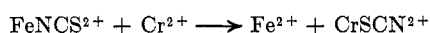
<sup>a</sup> The dinuclear products are sufficiently long lived so that their decomposition could be followed by conventional or flow techniques. <sup>b</sup> Different dinuclear species are produced under different conditions. <sup>c</sup> M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959). <sup>d</sup> R. W. Kolaczowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964). <sup>e</sup> T. W. Newton and F. B. Baker, *ibid.*, **3**, 569 (1964). <sup>f</sup> L. Pajdowski and B. Jezowska-Trzebiatowska, *J. Inorg. Nucl. Chem.*, **28**, 443 (1966). <sup>g</sup> T. J. Conoccholi, E. J. Hamilton, and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965). <sup>h</sup> R. M. Milburn, *ibid.*, **79**, 537 (1957), H. Schugar, C. Walling, R. Jones, and H. B. Gray, *ibid.*, **89**, 3712 (1967). <sup>i</sup> J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964). <sup>j</sup> T. W. Newton and F. B. Baker, *ibid.*, **1**, 368 (1962). <sup>k</sup> J. H. Espenson, *ibid.*, **4**, 1533 (1965).

larger than the rate constant for substitution on vanadium(II). Unfortunately the equilibrium constant for the vanadium(II)–chromium(III) reaction is not accurately known at the present time. However, the values of  $k_{-2}$  and  $k_{-4}$  calculated from the available data are 3 and  $4 \times 10^{-3} M^{-1} \text{ sec}^{-1}$ , respectively, at 25°. These values are consistent with both of the proposed mechanisms, although the former value is remarkably similar to some of the rate constants presented in Table I.

The formation and/or dissociation of oxygen- or hydroxide-bridged intermediates (successor complexes) have been directly observed in a number of electron-transfer reactions. These reactions are summarized in Table III. In most of these cases it has also proved possible to form the dinuclear complexes by recombining the final products of the reaction under somewhat different conditions. Successor complexes have also been observed in other systems<sup>21</sup> and appear to be quite common in reactions between chromium(II) and ruthenium(III).<sup>22, 23</sup>

#### Comparison of the Effects of Azide and Thiocyanate.

Interesting chemical effects have been observed when the bridging ligand is an unsymmetrical group. The transfer of an unsymmetrical group in an inner sphere reaction may yield a product in which the "wrong end" of the bridging ligand is attached to the metal center.



A number of "wrong-bonded" complexes, or linkage

**Table IV**  
Comparison of the Effects of Azide and Thiocyanate on Electron-Transfer Rates<sup>a</sup>

Reaction	$k$		Ref
	$M^{-1} \text{ sec}^{-1}$	$k_{\text{N}_3^-} / k_{\text{NCS}^-}$	
(1) Cr <sup>2+</sup> + (NH <sub>3</sub> ) <sub>5</sub> CoN <sub>3</sub> <sup>2+</sup>	$3 \times 10^5$	$2 \times 10^4$	12
(2) Fe <sup>2+</sup> + (NH <sub>3</sub> ) <sub>5</sub> CoN <sub>3</sub> <sup>2+</sup>	$8.8 \times 10^{-3}$	$\geq 3 \times 10^3$	30
(3) V <sup>2+</sup> + (NH <sub>3</sub> ) <sub>5</sub> CoN <sub>3</sub> <sup>2+</sup>	13	43	12
(4) Cr(bipy) <sub>3</sub> <sup>2+</sup> + (NH <sub>3</sub> ) <sub>5</sub> CoN <sub>3</sub> <sup>2+</sup>	$4.1 \times 10^4$	4	12
(5) Co(CN) <sub>5</sub> <sup>3-</sup> + (NH <sub>3</sub> ) <sub>5</sub> CoN <sub>3</sub> <sup>2+</sup>	$1.6 \times 10^8$	1.6	c
(6) Cr <sup>2+</sup> + CrN <sub>3</sub> <sup>2+</sup>	6.1	$4 \times 10^4$	29, d
(7) Cr <sup>2+</sup> + FeN <sub>3</sub> <sup>2+</sup>	$2.9 \times 10^7$	~1	27
(8) Fe <sup>2+</sup> + FeN <sub>3</sub> <sup>2+</sup>	$(1.9 \times 10^3)^b$	10 <sup>2</sup>	e, f
(9) V <sup>2+</sup> + FeN <sub>3</sub> <sup>2+</sup>	$5.2 \times 10^6$	~1	9

<sup>a</sup> Rate constants at 25°. <sup>b</sup> Temperature is 0°. <sup>c</sup> J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963). <sup>d</sup> R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964). <sup>e</sup> D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961). <sup>f</sup> R. A. Horne, Ph.D. Thesis, Columbia University, 1955.

isomers, have recently been prepared in this manner.<sup>24–28</sup> The difference in rates observed with symmetrical and unsymmetrical bridging groups forms a basis for determining whether a particular reaction proceeds by an inner or an outer sphere mechanism. Comparisons between azide and thiocyanate have been widely used in this connection.<sup>29, 30</sup> If nitrogen-bonded thiocyanate is the stable isomer, and if transfer of the bridging group occurs in the reaction, then an inner sphere reaction should proceed faster when the bridging group is azide than when it is thiocyanate. The effects of azide and thiocyanate on electron-transfer rates are compared in Table IV.

It is apparent from Table IV that azide is much more efficient than thiocyanate in promoting reactions 1, 2, 6, and 8. This suggests that these reactions proceed by an inner sphere mechanism, a conclusion confirmed by identification of the products of reactions 1 and 6. The absence of discrimination between azide and thiocyanate in reaction 5 (which is inner sphere) is due to the fact that Co(CN)<sub>5</sub>SCN<sup>3-</sup> is the stable configuration of the cobalt(III) complex. It is likely that reaction 3 is also inner sphere and that the low ratio of rate constants arises from the rate of the reaction of V<sup>2+</sup> with Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>2+</sup> being primarily determined by the rate of water replacement on vanadium(II) (see Table I). Reactions 4 and 9 proceed faster than the rate of substitution on the reducing agents and are therefore outer sphere, confirming that azide and thiocyanate have similar effects on the rates of outer sphere reactions. The similarity in the rates of oxidation of chromium(II) by FeN<sub>3</sub><sup>2+</sup> and by FeNCS<sup>2+</sup> is surprising, particularly since identification of the products of these reactions has established that both reactions proceed

(21) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

(22) H. Taube, Award Address, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(23) D. Seewald and N. Sutin, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract M5.

(24) J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

(25) J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965).

(26) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

(27) M. Orhanović and N. Sutin, *ibid.*, **90**, 4286 (1968).

(28) J. P. Birk and J. H. Espenson, *ibid.*, **90**, 1153 (1968).

(29) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

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

by an inner sphere mechanism. It may be that the rates of these chromium(II) reactions, like the rates of some of the vanadium(II) reactions, are primarily determined by the rate of loss of a water molecule coordinated to the reducing agent.

**Theoretical Considerations.** The progress of the electron-transfer reaction may be described in terms of the motion of a point representing the system on a potential energy surface. If  $N$  is the number of independent variables necessary to define the separation of the reactants and the nuclear configurations of their coordination shells, the potential energy of the reactants may be represented by an  $N$ -dimensional surface in  $(N + 1)$ -dimensional nuclear configuration space. This surface will have valleys corresponding to the more stable nuclear configurations of the reactants. The potential energy of the products may be represented by a similar surface in the  $N + 1$  space. This surface will have its own valleys corresponding to the more stable nuclear configurations of the products. In the absence of interaction between the orbitals of the reactants involved in the electron transfer (in other words, the "redox orbitals" of the reactants), the two potential-energy surfaces will intersect on an  $(N - 1)$ -dimensional surface on which the reactants and products have the same nuclear configurations and the same energies. If there is interaction between the reactants, the degeneracy at the intersection will be removed and two new surfaces will be formed. The minimum separation between the two surfaces is equal to  $2E_{I,II}$  where  $E_{I,II}$  is the interaction energy of the system. The difference between the minimum potential energy of the reactants and the potential energy of the lowest pass through the intersection region is equal to the potential energy of activation for the reaction.

Expressions for the free energy of activation for adiabatic, outer sphere electron-transfer reactions have been derived by Marcus<sup>4,6,7</sup> and Hush.<sup>5</sup> According to Marcus the free energy of activation is given by

$$\Delta G^* = w + \frac{\lambda}{4} + \frac{(\Delta G^\circ + w^p - w)}{2} + \frac{(\Delta G^\circ + w^p - w)^2}{4\lambda} \quad (6)$$

where

$$\lambda = \lambda_0 + \lambda_t$$

$$\lambda_0 = (ne)^2 \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left( \frac{1}{D_{op}} - \frac{1}{D_s} \right)$$

$$\lambda_t = \frac{f_1 f_1^p}{f_1 + f_1^p} (\Delta a_1^0)^2 + \frac{f_2 f_2^p}{f_2 + f_2^p} (\Delta a_2^0)^2$$

In the above expressions  $w$  is the work required to bring the reactants together and  $w^p$  is the corresponding term for the products,  $\Delta G^\circ$  is the standard free energy change for the reaction,  $n$  is the number of electrons transferred,  $a_1$  and  $a_2$  are the radii of the two reactants (assumed spherical), and  $r$ , the distance between the centers of the reactants in the activated complex, is equal to  $a_1 + a_2$ .  $D_{op}$  and  $D_s$  are the square of the refractive index

and dielectric constant, respectively,  $f_1$  and  $f_1^p$  are the force constants for the symmetrical breathing vibration of a species when it is a reactant and a product, respectively,  $\Delta a_1^0 (= a_1 - a_1^p)$  is the difference in the radius of species 1 when it is a reactant and a product, and  $\lambda_0$  and  $\lambda_t$  are parameters related to the reorganization of the outer and inner coordination shells of the reactants, respectively. In deriving the above expression for  $\lambda_t$  it was assumed that the symmetrical breathing motions of the inner coordination shells of the reactants and products are harmonic and that the force constant for this motion is the same when a particular species is a reactant as when it is a product. In particular, it was assumed that the breathing force constant of species  $i$  had the reduced value  $2f_i f_i^p / (f_i + f_i^p)$  regardless of whether it was in the oxidized or in the reduced state. A different expression for the potential energy of the inner coordination shells can be used, but this leads to a more complicated expression for the reorganization energy.

Without a significant loss in accuracy,  $\Delta G_{12}^*$  is given by

$$\Delta G_{12}^{**} = \frac{(\Delta G_1^{**} + \Delta G_2^{**})}{2} + \frac{\Delta G_r^\circ}{2} + \frac{(\Delta G_r^\circ)^2}{8(\Delta G_1^{**} + \Delta G_2^{**})} \quad (7)$$

where

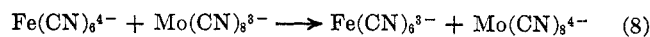
$$\Delta G_1^* = w_1 + \frac{f_1 f_1^p}{2(f_1 + f_1^p)} (\Delta a_1^0)^2 + \frac{(ne)^2}{4} \left( \frac{1}{2a_1} + \frac{1}{2a_1^p} - \frac{1}{a_1 + a_1^p} \right) \left( \frac{1}{D_{op}} - \frac{1}{D_s} \right)$$

$$\Delta G_2^* = w_2 + \frac{f_2 f_2^p}{2(f_2 + f_2^p)} (\Delta a_2^0)^2 + \frac{(ne)^2}{4} \left( \frac{1}{2a_2} + \frac{1}{2a_2^p} - \frac{1}{a_2 + a_2^p} \right) \left( \frac{1}{D_{op}} - \frac{1}{D_s} \right)$$

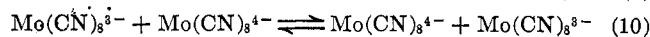
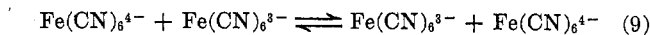
$$\Delta G^{**} = \Delta G^* - w$$

$$\Delta G_r^\circ = (\Delta G_{12}^\circ + w^p - w)$$

In eq 7,  $\Delta G_{12}^*$  and  $\Delta G_{12}^\circ$  are the free energy of activation and the standard free energy change, respectively, for an electron-transfer reaction accompanied by a net chemical change

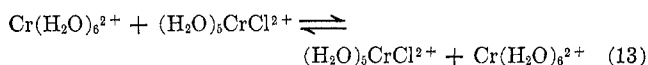
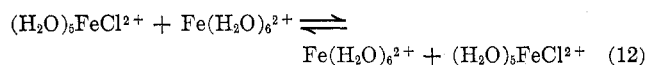
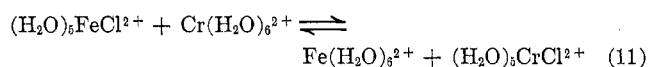


and  $\Delta G_1^*$  and  $\Delta G_2^*$  are the free energies of activation for the corresponding exchange reactions 9 and 10.



$\Delta G_r^\circ$  is the free-energy change of the reaction when the two reactants are a distance  $r$  apart ( $\Delta G^\circ$  is the standard free energy change when the reactants are infinitely far apart).  $\Delta G_r^\circ$ , rather than  $\Delta G^\circ$ , affects the reorganization energy at the separation distance  $r$  in the medium.<sup>7</sup>  $\Delta G^{**}$  is the free energy required to reorganize the coordination shells of the two reactants prior to the electron transfer. It is apparent from eq 6 and 7 that  $\lambda$  is

equal to  $2(\Delta G_1^{**} + \Delta G_2^{**})$ ; in other words,  $\lambda$  can be written as the sum of two terms, one term depending only on the properties of species 1 in its initial and final states and the other depending only on the properties of species 2 in its initial and final states. In deriving eq 6, Marcus assumed that the splitting at the intersection was small enough so that it could be neglected in calculating the free energy of activation but large enough so that the value of  $p$  was close to unity. Some of the other approximations and assumptions made in deriving eq 6 and 7 have been examined.<sup>31</sup> More recently the assumption of small splitting at the intersection was removed, and the formulation was extended to include the application of eq 6 (with  $\lambda$  having a different meaning) to outer sphere reactions in which the splitting is considerable as well as to certain classes of inner sphere reactions.<sup>32</sup> In inner sphere mechanisms, the reactions corresponding to eq 8–10 are eq 11–13.



It is of interest to explore whether eq 6 could also be applied to nonadiabatic reactions. According to the Landau-Zener formulation,  $p$  is given by

$$p = 1 - \exp \left[ \frac{-4\pi^2 E_{I,II}^2}{\hbar v |s_I - s_{II}|} \right] \quad (14)$$

where  $v$  is the velocity with which the system moves through the intersection region and  $s_I - s_{II}$  is the difference between the slopes of the potential-energy surfaces at the intersection. If  $E_{I,II}$  is small, then

$$p = \frac{4\pi^2 E_{I,II}^2}{\hbar v |s_I - s_{II}|}$$

It thus becomes evident that eq 6 will also be satisfied by those nonadiabatic reactions for which the interaction energy in the cross reaction is approximately equal to the geometric mean of the interaction energies in the corresponding exchange reactions, in other words, by those reactions for which

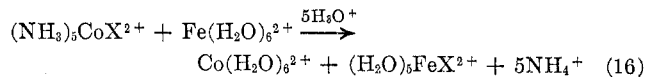
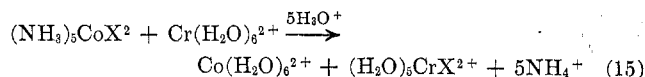
$$(E_{I,II})_{12} = [(E_{I,II})_1(E_{I,II})_2]^{1/2}$$

a condition which does not appear too restrictive. However it should be noted that most inner sphere reactions, particularly those involving simple inorganic ions and conjugated organic systems as bridging groups, are very probably adiabatic. It will be recalled that in adiabatic reactions the potential energy of the reacting system changes in a continuous manner from that of the reactants to that of the products.

**Intrinsic and Thermodynamic Barriers.** The above treatment shows that the barrier to electron transfer is made up of two parts.<sup>32</sup> There is an intrinsic contribution

( $\Delta G_1^{**} + \Delta G_2^{**}$ ) and a thermodynamic contribution ( $\Delta G^\circ$ ). Difference in reaction rates may arise from differences in either or both of these contributions. For example, it is likely that the azide-thiocyanate rate comparisons made earlier reflect changes which occur primarily in the thermodynamic contribution. So also are the changes produced in the rate of oxidation of a series of tris(phenanthroline)iron(II) complexes when different substituents are introduced into the phenanthroline ring system.<sup>33</sup> Other rate comparisons reflect changes in both the thermodynamic and the intrinsic contributions.<sup>33,34</sup> The rates of inner sphere reactions<sup>3,26,35,36</sup> as well as electron-transfer reactions involving actinide elements<sup>37</sup> have also been considered in terms of intrinsic and thermodynamic factors.

As a further example of the usefulness of resolving the electron-transfer barrier into its thermodynamic and intrinsic components we will consider the effect of halide ions on electron-transfer rates. A normal order of bridging efficiency ( $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ ) is observed in certain reactions, and an inverted order ( $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ ) in others. An interesting analysis of this reactivity pattern has recently been given in terms of the relative stabilities of the transition states.<sup>38</sup> For purposes of our treatment we will consider reactions 15 and 16. The normal reactivity order is observed in reaction 15 and the inverted order in reaction 16. Since the thermodynamic con-



tribution to the reaction barrier favors the inverted order in both reactions<sup>39</sup> and since the change in the thermodynamic barrier produced upon replacing fluoride by chloride is very nearly the same in the two reactions, we conclude that the reactivity pattern in these systems is primarily determined by differences in the intrinsic contributions to the barriers. Some information about the intrinsic barriers is available from the  $\text{Cr}^{2+}$ - $\text{CrX}^{2+}$  and  $\text{Fe}^{2+}$ - $\text{FeX}^{2+}$  exchange reactions. In the former exchanges the intrinsic barriers decrease in the order  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$ , while in the latter exchanges the intrinsic barriers decrease in the opposite order. These orders are precisely those needed to ex-

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

(34) R. J. Campion, N. Purdie, and N. Sutin, *ibid.*, **3**, 1091 (1964).

(35) N. Sutin, Proceedings of a Symposium on Exchange Reactions, Upton, N. Y., 1965, p. 7.

(36) T. W. Newton and N. A. Daugherty, *J. Phys. Chem.*, **71**, 3768 (1967).

(37) T. W. Newton and F. B. Baker, to be published.

(38) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).

(39) Although the equilibrium constants for the formation of  $(\text{NH}_3)_5\text{CoX}^{2+}$ ,  $\text{CrX}^{2+}$ , and  $\text{FeX}^{2+}$  run parallel in the series of halide complexes, the ratios of the formation constants  $K_F/K_{Cl}$  are 20,  $1.5 \times 10^5$ , and  $0.4 \times 10^5$  for the  $(\text{NH}_3)_5\text{CoX}^{2+}$ ,  $\text{CrX}^{2+}$ , and  $\text{FeX}^{2+}$  complexes, respectively. Consequently, reactions 15 and 16 are both more exothermic when  $\text{X} = \text{F}$  than when  $\text{X} = \text{Cl}$ . Note also that  $K_F/K_{Cl}$  is not too different for the  $\text{CrX}^{2+}$  and  $\text{FeX}^{2+}$  complexes.

(31) T. W. Newton, *J. Chem. Educ.*, in press.

(32) R. A. Marcus, 18th CITCE meeting, Elmau, Germany, April 1967, published in *Electrochim. Acta*, **13**, 995 (1968); R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

plain the reactivity patterns in reactions 15 and 16, indeed, the relative rates of reactions 15 and 16 have been calculated using the appropriate exchange rate constants and thermodynamic barriers.<sup>3</sup>

In comparing the (intrinsic) barriers in the  $\text{Cr}^{2+}$ - $\text{CrX}^{2+}$  and  $\text{Fe}^{2+}$ - $\text{FeX}^{2+}$  exchange reactions it is also necessary to consider the effect of X on the interaction energies in addition to its effect on the reorganization energies. When the interaction energies are very small (less than  $\sim 100$  cal/mol) the reactions will not be adiabatic and the value of the preexponential factor in the expression for the free energy of activation (eq 5) may change as X is varied. On the other hand, the reactions will be adiabatic when the interaction energy is larger than about 500 cal/mol. This is probably the case in the exchange reactions considered here. However, if the interaction energy becomes too large it may no longer be neglected in calculating the energy of activation for the reaction. The interaction energy will be relatively large when the redox orbitals have the appropriate symmetries to overlap with the orbitals of the

bridging group. Since an  $e_g$  electron is transferred in the  $\text{Cr}^{2+}$ - $\text{CrX}^{2+}$  exchange reactions while a  $t_{2g}$  electron is transferred in the  $\text{Fe}^{2+}$ - $\text{FeX}^{2+}$  exchange reactions,  $\sigma$  interactions with the bridging group will be important when chromium(II) is the reducing agent while  $\pi$  interactions may be more important in reductions by iron(II). The reactivity pattern in the exchange reactions may thus reflect, in part, the relative  $\sigma$ - and  $\pi$ -bonding abilities of the halide ions as bridging groups.

The interpretation of the reactivity patterns obtaining in other systems remains an interesting and challenging problem. However, as suggested by theory,<sup>6,7,36</sup> electron-exchange reactions appear to provide a useful reference or standard state for considering more complex electron-transfer processes.

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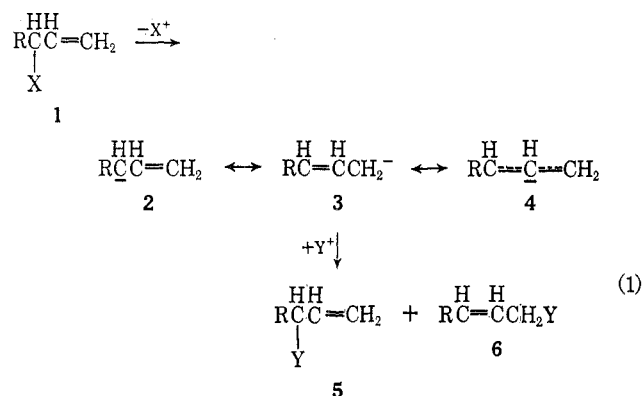
## Equilibria and Base-Catalyzed Exchange of Substituted Olefins

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Reactions at positions adjacent to double bonds, *i.e.*, allylic positions, are of interest for two basic reasons.<sup>1</sup> First, in unsymmetrically substituted systems two types of products may be formed. As shown in eq 1, generation of an allylic intermediate (in this case a negatively charged *carbanion*) can be followed by reaction at the original site of attachment of the departing group to give **5** or through an "allylic rearrangement" to give the isomeric product **6**. Examples of this type



of reaction are widespread and occur through positively charged (carbonium ions) and free-radical intermediates, as well as through allylic carbanions. It is then of interest to investigate what factors control

the product distributions from these various reactions.

Secondly, these processes proceeding through allylic intermediates are generally rapid as compared to the corresponding reactions in saturated systems. This has been attributed to electron delocalization in the transition states leading to allylic intermediates. Such delocalization (mesomerism) can be pictured as in structures **2-4**. While increased reactivity is generally observed, the extent of this increase is not well defined.

The present discussion is concerned primarily with anionic allyl intermediates.<sup>2</sup> The main points of interest are (1) the relative rates of formation of an anionic intermediate common to two unsaturated isomers (tautomers) and (2) the relative rates of protonation of the anionic intermediate to form the two isomers.

An early generalization of allyl anionic reactivity was stated by Ingold:<sup>3</sup> "when a proton is supplied by acids to the mesomeric anion of weakly ionizing tautomers of markedly unequal stability, then the tautomer which is most quickly formed is the thermodynamically least stable; it is also the tautomer from which the proton is lost most quickly to bases." This

(2) For reviews see (a) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 238; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter V; (c) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 418; (d) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 102 (1965).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 565.

(1) P. de la Mare in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 27.