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Non-aqueous, outer-sphere electron transfer kinetics of transition metal complexes

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CONTENTS

A. INTRODUCTION

The kinetics of electron transfer by transition metal complexes are studied specifically in non-aqueous solution for two general purposes. One is to characterize the electron transfer reactivity of the diverse array of complexes that are only stable in such media. The second is to use the reactions in non-aqueous solution to further test the developing theory of electron transfer kinetics, both through the study of types of compounds that cannot be studied in aqueous solution and in order to test predictions of the dependence of electron transfer reactivity on the medium.

The characterization of electron transfer reactivity is important from the practical standpoint that many complexes, typically classed as organometallic, that are soluble and stable in non-aqueous solution have a variety of oxidation states. Thus their synthesis and reactions frequently involve electron transfer. The compounds discussed below are substitution inert, and their reactivity is limited to acting as oxidizing or reducing agents and thus electron mediators between electrodes or

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photogenerated electron donors or acceptors and catalytically competent compounds. However, the patterns and principles of reactivity that are being developed should carry over to those related complexes that can carry out more complex reactions when they reach the appropriate oxidation state. Organometallic compounds often involve transition metal oxidation states, ligands, geometries, and charge types that are not found in complexes that are stable in aqueous solution. Furthermore, since the stability of organic solvents to oxidation and reduction is typically much greater than that of water, complexes with a much wider range of reduction potential are amenable to study.

The best way to characterize the electron transfer reactivity of a compound is to specify the reduction potential and the electron self-exchange rate constant between a pair of oxidation states. Because of difficulties in establishing a common reference for reduction potentials in non-aqueous solution and the scattered data on the electron transfer kinetics, it has been a rather difficult process to search for well-characterized electron transfer reagents. One purpose of this review is to present a table of transition metal complexes, their potentials, and their measured or apparent electron self-exchange rate constants.

The theory of electron transfer kinetics by transition metal complexes is well developed, especially as compared with the theory of more complex reactions. A good recent review of inorganic electron transfer reactions has been prepared by Creutz et al. [1]. Rather accurate predictions of electron transfer rate constants can now be made, both from first principles and from correlations between self-exchange and cross-reaction reactivity. As the theory has evolved, greater demands have been put on the experimentalists to design experiments that can test specific predictions of the theory. As is common to many areas, the parameters and assumptions of the theory do not all match the independent variables in the experimental design. For example, it is convenient to assume a spherical molecule, but it is more difficult to make one; it is easy to change the size of a molecule by modifying a ligand, but the size is seldom the only property of the complex that has changed. A principal prediction that must be tested is the dependence of the electron transfer rate constant on the properties of the solvent. The predictions of the standard theory are based on the assumption that the medium can be treated as a dielectric continuum. This convenient assumption must eventually break down for fast reactions and there must be some influence of the molecular nature and shape of the solvent molecules, but the continuum assumption may very well cover a large number of reactions. The more complex problem of treating the molecular nature of the solvent and the contribution of solvent dynamics to electron transfer reactivity has also been pursued, both by theoreticians and experimentalists, and is a new area of focus in non-aqueous electron transfer chemistry [2].

The vast majority of the data that are available and that have been used in the development of the theories involve reactions of complexes of first row transition metals in aqueous solution. Because neutral complexes are seldom soluble in water, and because the common oxidation states are III and II, reactions between +3 and

+2 complexes are most commonly studied. By switching to non-aqueous solvents, a broader range of complexes is amenable to study. Still, however, neutral complexes that are soluble in less polar solvents are often much less soluble in the more polar solvents, and the more highly charged complexes are not soluble in the less polar solvents. Most of the reactions in non-aqueous solution involve complexes that are −1, 0, 1, or 2 in charge. Since single-electron transfer cannot be studied without involving at least one ionic reactant, and since many of the solvents that are studied have a rather low polarity, ion pairing often occurs. Thus, one of the major concerns in the studies that are to be described will be the establishment of the influence of counter ions on the reactivity of the complexes.

(i) Scope

The general scope of this review is limited to thermal, bimolecular, outer-sphere electron transfer reactions by substitution-inert transition metal complexes in solvents other than water. In addition, some atom/electron transfer reactions are discussed, particularly as they relate to discussion of $\Delta V^{\ddagger}$. The literature has been surveyed via *Chemical Abstracts* through March 1992. The topic of the contribution of solvent dynamics to these reactions has recently been reviewed, and thus will be considered only by reference to that work [2].

(ii) Available data

In order to provide an overview, the systems that have been studied will be briefly described. Because NMR methods have made them reasonably straightforward to measure, many electron self-exchange rate constants have been determined. Table 1 lists the systems which have been studied and indicates a typical rate constant and other information that is available. The largest class of compounds investigated in this way is the metallocenes. Various metals (Co, Fe, and Ni), and ligands (cp, alkylated cp, and others) have been studied, and the full range of conditions of temperature, pressure, solvent, and added electrolyte that have been examined for any system have been studied for metallocenes. These reactions have been the primary testing ground for theories of the dependence of electron transfer rate constants on solvent dynamics. Closely related are the studies, by EPR, on dibenzene chromium and substituted arenes.

The second class of compounds that has been studied with particular thoroughness includes the hexakis(isocyanide) complexes of Mn(I,II) and Cr(0,I,II). For the Mn systems in particular, a range of ligands which differ in size and extent of conjugation (methyl, ethyl, isopropyl, *t*-butyl, cyclohexyl, benzyl, and various phenyl isocyanides) have been examined as a function of temperature, pressure, solvent, including mixed solvents, and added salt.

The third, rather large class of compounds includes the tris(bipyridine) and tris(phenanthroline) complexes of Fe, Os, and Cr as well as various substituted

TABLE 1

Self-exchange reactions

Reaction no.	*Oxidized*[a] form	I^b (M)	k^c ($M^{-1}\,s^{-1}$)	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal $mol^{-1}\,K^{-1}$)	$\Delta V^\ddagger$ (cm^3 mol^{-1})	Salt[d]	Solv.[e]	Comments
1	$[Co(cpCO_2Me)_2]BF_4$	ca. 0.02	2.0×10^8					×9	f
2	$[Co(cp^*)_2]BF_4$	0.1	4.3×10^8					×7	f,g,h,i
3	$[Co(cp)_2]BF_4$	0.1	3.8×10^7				×4	×7	f,g,h,i
4	$[Co(nor)_4]BF_4$	0.06	7.0×10^5	12	8			×3	j,ai
5	$[Co(P(OMe)_3)_4]BF_4$	0.071	8.8×10^3	6.6	−18				k,ai
6	$[Cr(bpy)_3]ClO_4$	ca. 0.002	2.0×10^9						l,aj
7	$[Cr(CNdipp)_6](BF_4)_2$	ca. 0.03	1.5×10^7	3.1	−15.0			×5	m,al
8	$[Cr(CNdipp)_6]BF_4$	ca. 0.003	1.8×10^8	1.5	−16			×2	n,al
9	$[Cr(PhMe)_2]BPh_4$	5×10^{-4}	3.3×10^7	4	−11				o,am
10	$[Cr(PhCl)_2]BPh_4$	5×10^{-4}	2.0×10^8	2.3	−13				o,am
11	$[Cr(PhCO_2Et)_2]BPh_4$	5×10^{-4}	3.2×10^8	1.7	−14				o,am
12	$[Cr(PhOMe)_2]BPh_4$	5×10^{-4}	7.7×10^7	3	−12				o,am
13	$[Cr(PhPh)_2]BPh_4$	5×10^{-4}	3.8×10^8	2.1	−12			×4	o,ak,an
14	$[Cr(Ph)_2]BPh_4$	5×10^{-4}	6.0×10^7	3.4	−12				o,am
15	$[Cu(2,9\text{-}Me_2phen)_2](CF_3SO_3)_2$	0.099	5.0×10^3	6.7	−19	−3	×4	×2	p,ao,ap
16	$[Cu(5\text{-}MeimidH)_2DAP](BF_4)_2$	0.025	3.5×10^4	3.9	−25				q
17	$[Cu((py)_2DAP)](BF_4)_2$	0.05	1.7×10^3						r
18	$[Fe(3,4,7,8\text{-}Me_4phen)_3](PF_6)_3$	0.32	1.7×10^7	1.4	−21				s
19	$[Fe(4,4'\text{-}Me_2bpy)_3](ClO_4)_3$	0.14	9.0×10^6				×7		t,aq
20	$[Fe(4,7\text{-}chx_2phen)_3](ClO_4)_3$	ca. 0.1	4.1×10^5	2.8	−23				t
21	$[Fe(4,7\text{-}Me_2phen)_3](PF_6)_3$	ca. 0.1	3.0×10^7	1.6	−19				t,aq
22	$[Fe(4,7\text{-}Ph_2phen)_3](ClO_4)_3$	ca. 0.1	1.5×10^7	1.5	−21				t,aq
23	$[Fe(bpy)_3](PF_6)_3$	ca. 0.1	3.7×10^6	2.1	−22				t
24	$[Fe(cpcpCH_2NMe_2)_2]PF_6$	ca. 0.1	1.8×10^6	4.3	−16		×6		v
25	$[Fe(cpcpCO_2Me)]PF_6$	ca. 0.01	6.8×10^7	4.7	−12				v
26	$[Fe(cp^*)_2]BF_4$	0.093	2.5×10^7	3.4	−12		×4	×6	f,h,j,v
27	$[Fe(cp(CH_2)_3cp)]PF_6$	ca. 0.01	1.5×10^7	1.1	−22				v
28	$[Fe(cp)_2]BF_4$	0	9.1×10^6	5.3	−9	−7	×7	×9	w,f,v,x,h,as
29	$[Fe(cp)(cpCH_2OH)]BF_4$	ca. 0.02	5.5×10^6					×8	f
30	$[Fe(Me_4phen)_3](PF_6)_3$	0.32	1.7×10^7	1.5	−21				s

31	$[Fe(Mecp)_2]PF_6$	ca. 0.01	8.3×10^6	5.4–9					v
32	$[Fe(nBucp)_2]PF_6$	ca. 0.015	4.9×10^6	4.7	−12				v
33	$[Fe(phen)_3](ClO_4)_3$	ca. 0.1	1.4×10^7	2	−19	−6	×3	×3	t,y,aq
34	$[Fe([9]aneS_3)_2](PF_6)_3$	0.1	5.3×10^4	2.5	−28				z,ap,at
35	$[Mn(CNC_6H_{11})_6](BF_4)_2$	0.1	4.4×10^5	3.4	−21	−20	×12	×6	aa,ab,ac,au, av,aw
36	$[Mn(CNCH_2Ph)_6](BF_4)_2$	0.1	1.3×10^6	2.0	−24				ab,aw
37	$[Mn(CNCH(Me)_2)_6](BF_4)_2$	0.1	2.6×10^5	4.9	−18				ab,aw
38	$[Mn(CNEt)_6](BF_4)$	0.1	2.0×10^6	3.6	−18	−6	×9	×4	ab,ad,aa
39	$[Mn(CNMe)_6](BF_4)_2$	0.1	2.1×10^7	1.8	−20	−2	×9		aa,ab
40	$[Mn(CNnBu)_6](BF_4)_2$	0.1	6.4×10^5	3.6	−21	−20			aa
41	$[Mn(CNPhMe)_6](BF_4)_2$	0.1	3.0×10^7	2.4	−16.0				ae
42	$[Mn(CNPhOMe)_6](BF_4)_2$	0.1	4.5×10^7	3.4	−12				ae
43	$[Mn(CNtBu)_6](BF_4)_2$	0.1	6.5×10^4	5.4	−19	−10	×9	×8	ab,ac,aa,ad,au, av,aw,ax,ay
44	$[Ni(cp)_2]BF_4$	0.008	2.1×10^8	1.7	−15				af,al
45	$[Os(3,5,6,8\text{-}Me_4phen)_3](PF_6)_3$	ca. 0.007	1.5×10^6						u,az
46	$[Os(3,4,7,8\text{-}Me_4phen)_3](PF_6)_3$	ca. 0.008	3.4×10^6						u,az
47	$[Os(4,4'\text{-}Me_2bpy)_3](PF_6)_3$	ca. 0.1	2.2×10^6						t,az
48	$[Os(4,7\text{-}Me_2phen)_3](PF_6)_3$	ca. 0.01	3.6×10^6	1.5	−25.0		×8		u,az
49	$[Os(bpy)_3](PF_6)_3$	ca. 0.1	2.2×10^6						t,az
50	$[Os(phen)_3](PF_6)_3$	0.006	2.0×10^6	1.5	−25				t,az
51	$[Ru(bpy)_3](PF_6)_3$	ca. 0.03	8.3×10^6	3.7	−15				t
52	$[Rh_2(OAc)_4(MeCN)_2](ClO_4)$	0.002	5.3×10^4					×2	ag
53	$[Ru(hfac)_3]Bu_4N$	ca. 0.02	4.4×10^6	6.4	−7	−6	×4	×8	ah,ba
54	$[Ru(Me_2bpy)(acac)_2]PF_6$	ca. 0.01	1.4×10^8	2.7	−12				ah
55	$[Ru(Me_2bpy)(hfac)_2]PF_6$	ca. 0.005	4.5×10^6					×3	ah

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[a] Ligand abbreviations: cp*, pentamethylcyclopentadienide; nor, norbornyl; bpy, bipyridine; CNdipp, 2,6-diisopropylphenylisocyanide; phen, phenanthroline; OAc, acetate; DAP, 2,6-diiminoethylpyridine; py, pyridine; Meimid, methylimidazole; chx, cyclohexyl; acac, acetylacetonate; hfx, hexafluoroacetylacetonate. [b] Ionic strength. [c] Second-order rate constant at 25°C in acetonitrile unless otherwise indicated. [d] Number of different salt concentrations studied. [e] Number of other solvents studied. [f] Ref. 3. [g] Ref. 4. [h] Ref. 5. [i] Ref. 6. [j] Ref. 7. [k] Ref. 8. [l] Ref. 9. [m] Ref. 10. [n] Ref. 11. [o] Ref. 12. [p] Ref. 13. [q] Ref. 14. [r] Ref. 15. [s] Ref. 16. [t] Ref. 17. [u] Ref. 18. [v] Ref. 19. [w] Ref. 20. [x] Ref. 21. [y] Ref. 22. [z] Ref. 23. [aa] Ref. 24. [ab] Ref. 25. [ac] Ref. 26. [ad] Ref. 27. [ae] Ref. 28. [af] Ref. 29. [ag] Ref. 30. [ah] Ref. 31. [ai] Solvent was tetrahydrofuran. [aj] Solvent was dimethylformamide. [ak] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in each solvent. [al] Solvent was dichloromethane. [am] Solvent was dimethylsulfoxide. [an] Solvent was benzonitrile. [ao] Molality units used. [ap] $\Delta V^\ddagger$ in acetone also. [aq] Anion varied. [ar] Salt dependence in other solvents. [as] Salt dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. [at] $T=0$°C. [au] $\Delta V^\ddagger$ in each solvent. [av] Conductivity studied. [aw] Ion pairing analyzed. [ax] Salt dependence of $\Delta V^\ddagger$ studied. [ay] Mixed solvents studied. [az] $T=30$°C. [ba] Cation varied.

ligands, and the bis(2,9-dimethylphenanthroline) complexes of Cu. Some of these compounds, especially $Fe(phen)_3^{2+/3+}$, have also been investigated extensively in aqueous solution. These reactions have been studied less extensively than the first two classes, but examples of all of the types of measurement described above are available. The remaining systems represent individual compounds, or small groups of related compounds. $Ru(hfac)_3^{0/-}$ has been examined extensively, including volume of activation measurements, and is one of the few couples involving anions. Related compounds with both acetylacetonate and bipyridine ligands have also been considered. Copper compounds often change their coordination environment significantly on reduction from Cu(II) to Cu(I), but some notable exceptions that have been carefully studied both structurally and kinetically are $Cu((py)_2DAP)^{+/2+}$ and $Cu(5MeimidH)_2DAP^{+/2+}$. $Rh_2(OAc)_4(MeCN)_2$ is the only polymetallic compound that has been studied, and more work has been done with it in cross-reactions. A few compounds, $Co(nor)_4^{-/0/+}$, $Co(P(OMe)_4)^{0/-}$, and $Fe([9]aneS_3)^{2+/3+}$ have had their self-exchange reactivity determined in conjunction with other aspects of their characterization.

Cross-reactions, reactions in which one type of complex reacts with another, provide a much more flexible venue for the study of electron transfer reactivity than does the study of self-exchange reactions. Questions of the effect of thermodynamic driving force on reactivity can be considered, along with the correlation of self-exchange and cross-reaction reactivity. The influence of varying the properties of the reactants, such as size, shape, charge, and electronic structure, can be explored to a greater extent than is possible in self-exchange reactions. Further, it is only cross-reactions that can ever lead to net energy transfer and thus they must eventually be understood. Since concentrations change in a cross-reaction, unlike a self-exchange reaction, they are inherently easier to follow. Many of the studies that will be discussed have included the use of Marcus theory to estimate self-exchange rate constants from cross-reaction data, and test the Marcus theory cross-reaction prediction. Table 2 shows the systems which have been studied, a representative rate constant and an indication of further information that is available. The largest number of studies has employed the family of cobalt clathrochelate complexes $Co(dioximate)_3(BX)_2^{0/+}$ in reactions with metallocenes, $Cr(CNdipp)_6^{2+}$, and each other. The clathrochelate complexes have been used because they are soluble and substitution inert in many solvents, and because their reactions are typically slow enough to be studied by stopped-flow methods. This is not the case for most of the reactions that could occur between the complexes with known self-exchange rate constants. Other reactions that have been studied include a large matrix of reactions of $Mn(urea)_6^{3+}$, $Co(bpyO_2)_3^{2+/3+}$, Ni macrocycles, $Rh_2(OAc)_4(MeCN)_2$, and bipyridine and phenanthroline complexes of Ru, Os, and Fe, a pseudo-exchange reaction between $Co(terpy)_2^{2+}$ and $Co(bpy)_3^{3+}$, and some reactions of the Cu complexes described above as well as $Ru(hfac)_3^{3-}$.

Table 3 is provided as a convenient summary of the electrochemical potentials

TABLE 2

Cross-reactions

Oxidant[a]	Reductant[a]	I[b] (M)	k ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal $mol^{-1}\,K^{-1}$)	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})	Salt[d]	Solv.[e]	k_{11}[f] ($M^{-1}\,s^{-1}$)	Comments
1 $[Co(bpy)_3](ClO_4)_3$	$[Co(terpy)_2](ClO_4)_2$	<0.01	1.0	7	−35			×10		g
2 $[Co(dmg)_3(BBu)_2]BF_4$	$Fe(Mecp)_2$	0				−11				h
3 $[Co(dmg)_3(BBu)_2]BF_4$	$Fe(cp^*)_2$	0.1	1.6×10^6	5.9	−10		×9	×9	Co = 550	i,af
4 $[Co(dmg)_3(BF)_2]BF_4$	$Co(dpg)_3(BPh)_2$	0.1	1.5×10^3	5.5	−26		×8			j,af
5 $[Co(dmg)_3(BF)_2]BF_4$	$Fe(Mecp)_2$	0.1	9.8×10^4	6.4	−15	−11			Co = 45	h,i,t
6 $[Co(dmg)_3(BF)_2]BF_4$	$Fe(cp)_2$	0.1	1.2×10^4	8.5	−12	−15	×10	×4		h,i,k,u,v,af
7 $[Co(dmg)_3(BPh)_2]BF_4$	$Fe(Mecp)_2$	0.1	3.9×10^3	9	−12	−4	×10		Co = 120	h,i,w,t,af
8 $[Co(dpg)_3(BPh)_2]BF_4$	$Fe(Mecp)_2$	0.1	6.8×10^4	6.2	−16				Co = 350	i
9 $[Co(dpg)_3(BPh)_2]BF_4$	$Fe(cp)_2$	0.1	8.1×10^3	7.9	−14				Co = 630	i
10 $[Co(dpg)_3(BPh)_2]BF_4$	$Co(nox)_3(BBu)_2$	0.1	2.4×10^3	8.1	−16		×10			j,af
11 $[Co(dpg)_3(BPh)_2]BF_4$	$Co(nox)_3(BPh)_2$	0.1	1.9×10^2	4.8	−31		×9			j,af
12 $[Co(dpg)_3BPh)_2]BF_4$	$Fe(Mecp)_2$	0				−14				h,x
13 $[Co(dpg)_3BPh)_2]BF_4$	$Fe(cp)_2$	0				−10				h
14 $[Co(nox)_3(BBu)_2]BF_4$	$Fe(cp^*)_2$	0.1	3.9×10^5	4	−15				Co = 130	i
15 $[Co(nox)_3(BF)_2]BF_4$	$Co(dpg)_3(BPh)_2$	0.1	6.0×10^3	8.1	−14		×10	×4		j,y,af
16 $[Co(nox)_3(BF)_2]BF_4$	$Fe(Mecp)_2$	0.1	2.0×10^5	6.4	−13				Co = 110	i
17 $[Co(nox)_3(BF)_2]BF_4$	$Fe(cp)_2$	0.1	2.5×10^4	7.1	−15	−12	×9		Co = 200	h,i,z,af
18 $[Co(nox)_3(BPh)_2]BF_4$	$Fe(Mecp)_2$	0.1	7.7×10^3	7.6	−16	−9	×10		Co = 270	h,i,t,af
19 $[Cr(CNdipp)_6](BF_4)_2$	$Co(dpg)_3(BPh)_2$	0	1.2×10^5	8.2	−8	11				i,z
20 $[Cr(CNdipp)_6](BF_4)_2$	$Co(nox)_3(BBu)_2$	0	1.2×10^6	4	−17					l
21 $[Cr(CNdipp)_6](BF_4)_2$	$Co(nox)_3(BPh)_2$	0	1.0×10^5	6.3	−15					
22 $[Cu((py)_2DAP)](BF_4 2)$	$[Cu((imidH)_2DAP)]BF_4$	0.01	2.4×10^4					×9	imidH = 1.6×10^3	m,aa,ab,ac,af
23 $[Cu((py)_2DAP)](BF_4)_2$	$[Cu((imidR)_2DAP)]BF_4$	0.01	1.7×10^4					×9	imidR = 3.3×10^3	m,ad,af
24 $[Fe(4,4'\text{-}Me_2bpy)_3](ClO_4)_3$	$[Os(4,4'\text{-}Me_2bpy)_3](ClO_4)_2$	<0.05	1.9×10^6					×9		n,ae,af
25 $[Fe(4,4'\text{-}Me_2bpy)_3](ClO_4)_3$	$[Os(phen)_3](ClO_4)_2$	<0.05	4.9×10^5							n,ag
26 $[Fe(5,6\text{-}Me_2phen)_3](ClO_4)_3$	$[Ni(Me_2[14]dieneN_4)](ClO_4)_2$	0.05	2.6×10^5						Ni = 2.0×10^3	o
27 $[Fe(5,6\text{-}Me_2phen)_3](ClO_4)_3$	$[Ni([14]aneN_4)](ClO_4)_2$	0.05	2.3×10^5						Ni = 1.1×10^3	o
28 $[Fe(5\text{-}Clphen)_3](ClO_4)_3$	$[Rh_2(OAc)_4(MeCN)_2$	0.05	3.3×10^6						Rh = 1.2×10^5	o
29 $[Fe(Me_2bpy)_3](ClO_4)_3$	$[Os(Me_2bpy)_3](ClO_4)_2$	0	5.2×10^5	0.11	−32		×7			p,af,ah
30 $[Fe(Ph_2bpy)_3](ClO_4)_3$	$[Os(Me_2bpy)_3](ClO_4)_2$	0	2.2×10^6				×7			p,af,ah
31 $[Fe(bpy)_3](ClO_4)_3$	$[Os(bpy)_3](ClO_4)_2$	0	1.3×10^5				×7			p,ae,af,ah
32 $[Fe(bpy)_3](ClO_4)_3$	$[Os(bpy)_3](ClO_4)_2$	<0.03	1.0×10^6							n,ag
33 $[Fe(bpy)_3](ClO_4)_3$	$[Os(phen)_3](ClO_4)_2$	<0.03	1.9×10^7							n
34 $[Fe(bpy)_3](PF6)_3$	$[Ru(bpy)_3](PF6)_2$	ca. 1	8.3×10^6	3.7	−15					q

(continued on next page)

TABLE 2 (*continued*)

Oxidant[a]	Reductant[a]	I^b (M)	k ($M^{-1}\,s^{-1}$)	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal $mol^{-1}\,K^{-1}$)	$\Delta V^\ddagger$ (cm^3 mol^{-1})	Salt[d]	Solv.[e]	$k_{11}{}^f$ ($M^{-1}\,s^{-1}$)	Comments
35 $[Fe(cp)_2]BF_4$	$Co(dmg)_3(BF)_2$	0				−13				h
36 $[Fe(phen)_3](ClO_4)_3$	$[Os(phen)_3](ClO_4)_2$	<0.03	1.4×10^7					×2		n
37 $[Mn(urea)_6](ClO_4)_3$	$[Fe(3,4,7,8\text{-}Me_4phen)_3](ClO_4)_2$	0.1	1.0×10^4						Mn $=4.4\times10^{-6}$	r
38 $[Mn(urea)_6](ClO_4)_3$	$[Fe(4,4'\text{-}Me_2bpy)_3](ClO_4)_2$	0.1	3.4×10^3						Mn $=6.7\times10^{-5}$	r
39 $[Mn(urea)_6](ClO_4)_3$	$[Fe(4,7\text{-}Me_2phen)_3](ClO_4)_2$	0.1	4.5×10^3						Mn $=1.4\times10^{-5}$	r
40 $[Mn(urea)_6](ClO_4)_3$	$[Fe(4,7\text{-}Ph_2phen)_3](ClO_4)_2$	0.1	8.5×10^2						Mn $=1.7\times10^{-5}$	r
41 $[Mn(urea)_6](ClO_4)_3$	$[Fe(5,6\text{-}Me_2phen)_3](ClO_4)_2$	0.1	1.8×10^3						Mn $=1.2\times10^{-4}$	r
42 $[Mn(urea)_6](ClO_4)_3$	$[Fe(bpy)_3](ClO_4)_2$	0.1	7.5×10^2						Mn $=1.4\times10^{-3}$	r
43 $[Mn(urea)_6](ClO_4)_3$	$[Ni(Me_2[14]4,11\text{-}dieneN_4)](ClO_4)_2$	0.1	2.9×10^2						Mn $=0.19$	r
44 $[Mn(urea)_6](ClO_4)_3$	$[Ni([14]aneN_4)](ClO_4)_2$	0.1	5.1×10^2						Mn $=0.14$	r
45 $[Mn(urea)_6](ClO_4)_3$	$[Ni([19]aneN_3)_2](ClO_4)_2$	0.1	1.2×10^3						Mn $=0.19$	r
46 $[Mn(urea)_6](ClO_4)_3$	$[Os(4,4'\text{-}Me_2bpy)_3](ClO_4)_2$	0.1	1.1×10^5						Mn $=2.4\times10^{-5}$	r
47 $[Mn(urea)_6](ClO_4)_3$	$[Os(4,4'\text{-}Ph_2bpy)_3](ClO_4)_2$	0.1	7.1×10^4						Mn $=2.3\times10^{-4}$	r
48 $[Mn(urea)_6](ClO_4)_3$	$[Os(4,7\text{-}Ph_2phen)_3](ClO_4)_2$	0.1	1.1×10^5						Mn $=3.7\times10^{-4}$	r
49 $[Mn(urea)_6](ClO_4)_3$	$[Os(5,6\text{-}Mephen)_3](ClO_4)_2$	0.1	3.2×10^5						Mn $=2.8\times10^{-4}$	r
50 $[Mn(urea)_6](ClO_4)_3$	$[Os(5\text{-}Clphen)_3](ClO_4)_2$	0.1	4.8×10^4						Mn $=6.2\times10^{-3}$	r
51 $[Mn(urea)_6](ClO_4)_3$	$[Os(5\text{-}Mephen)_3](ClO_4)_2$	0.1	1.9×10^5						Mn $=8.5\times10^{-4}$	r
52 $[Mn(urea)_6](ClO_4)_3$	$[Os(bpy)_3](ClO_4)_2$	0.1	1.7×10^5						Mn $=4.1\times10^{-3}$	r
53 $[Mn(urea)_6](ClO_4)_3$	$[Os(phen)_3](ClO_4)_2$	0.1	1.7×10^5						Mn $=2.8\times10^{-3}$	r
54 $[Mn(urea)_6](ClO_4)_3$	$[Ru(3,4,6,8\text{-}Me_4phen)_3](ClO_4)_2$	0.1	5.0×10^2						Mn $=1.4\times10^{-4}$	r
55 $[Mn(urea)_6](ClO_4)_3$	$[Ru(3,4,7,8\text{-}Me_4phen)_3](ClO_4)_2$	0.1	1.5×10^3						Mn $=5.7\times10^{-5}$	r
56 $[Mn(urea)_6](ClO_4)_3$	$[Ru(4,7\text{-}Me_2phen)_3](ClO_4)_2$	0.1	8.2×10^2						Mn $=3.8\times10^{-4}$	r
57 $[Ni(Me_6[14]dieneN_4)](ClO_4)_3$	$[Rh_2(OAc)_4(MeCN)_2$	0.1	1.6×10^4						Rh $=1.8\times10^5$	o
58 $[Ni(Me_6[14]dieneN_4)](ClO_4)_3$	$[Ru(bpy)_3](ClO_4)_2$	0.1	1.7×10^4						Ni $=1.1$	o
59 $[Ni(mesoMe_6[14]aneN_4)](ClO_4)_3$	$[Rh_2(OAc)_4(MeCN)_2$	0.1	2.2×10^4						Rh $=5.3\times10^5$	o
60 $[Ni(mesoMe_6[14]aneN_4)](ClO_4)_3$	$[Ru(bpy)_3](ClO_4)_2$	0.1	1.2×10^4						Ni $=19$	o
61 $[Ni(racMe_6[14]aneN_4)](ClO_4)_3$	$[Rh_2(OAc)_4(MeCN)_2$	0.1	1.5×10^4						Rh $=5.0\times10^5$	o
62 $[Ni(racMe_6[14]aneN_4)](ClO_4)_3$	$[Ru(bpy)_3](ClO_4)_2$	0.1	8.8×10^3						Ni $=9.7$	o
63 $[Rh_2(OAc)_4(MeCN)_2]ClO_4$	$[Ni(Me_2[14]dieneN_4)](ClO_4)_2$	0.1	8.1×10^5						Rh $=4.3\times10^5$	o
64 $[Rh_2(OAc)_4(MeCN)_2]ClO_4$	$[Ni([14]aneN_4)](ClO_4)_2$	0.1	7.3×10^5						Rh $=3\times10^5$	o
65 $[Rh_2(OAc)_4(MeCN)_2]ClO_4$	$[Ru(4,4'\text{-}Ph_2bpy)_3](ClO_4)_2$	0.1	2.0×10^6						Rh $=2.7\times10^5$	o
66 $(Bu_4N)[Ru(hfac)_3]$	$[Cu(2,9\text{-}Me_2phen)_2](CF_3SO_3)$	0.04	2.9×10^5	8.6	−4					s,ai
67 $Fe(phen)_3(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	1.7×10^4				×6		Co $=0.08$	aj,ae
68 $Fe(5\text{-}Mephen)_3(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	1.1×10^4						Co $=0.1$	aj
69 $Fe(5,6\text{-}Me_2phen)_3(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	1.0×10^3						Co $=0.2$	aj
70 $Fe(5\text{-}Clphen)_3(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	1.7×10^5						Co $=0.2$	aj
71 $Fe(bpy)_3(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	1.4×10^4						Co $=0.4$	aj

72	$Fe(4,4'\text{-}Ph_2bpy)_3(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	6.1×10^3	Co = 0.1	[aj]
73	$Ni([14]aneN_4)(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	5.1×10^3	Co = 600	[aj]
74	$Ni([9]aneN_3)(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	3.0×10^3	Co = 400	[aj]
75	$Ni(racMe_6[14]aneN_4)(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	8.7×10^3	Co = 90	[aj]
76	$Ni(Me_6[14]dieneN_4)(ClO_4)_3$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	1.0×10^4	Co = 50	[aj]
77	$Rh_2(OAc)_4(MeCN)_2(ClO_4)$	$Co(bpyO_2)_3(ClO_4)_2$	0.1	5.3×10^4	Co = 4	[aj]
78	$[Co(bpyO_2)_3(ClO_4)_3$	$Fe(4,4'\text{-}Me_2bpy)_3(ClO_4)_2$	0.1	1.4×10^3	Co = 0.1	[aj]
79	$[Co(bpyO_2)_3(ClO_4)_3$	$Fe(4,7\text{-}Me_2phen)_3(ClO_4)_2$	0.1	2.6×10^3	Co = 0.3	[aj]
80	$[Co(bpyO_2)_3(ClO_4)_3$	$Os(5\text{-}Clphen)_3(ClO_4)_2$	0.1	8.8×10^3	Co = 2	[aj]
81	$[Co(bpyO_2)_3(ClO_4)_3$	$Os(phen)_3(ClO_4)_2$	0.1	2.7×10^4	Co = 0.2	[aj]

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[a] Ligand abbreviations: bpy, bipyridine; terpy, terpyridine; dmg, dimethylglyoximate; dpg, diphenylglyoximate; nox, cyclohexanediondioximate; CNdipp, 2,6-diisopropylphenylisocyanide; DAP, 2,6-diiminoethylpyridine; py, pyridine; imid, imidazole; phen, phenanthroline; OAc, acetate; hfac, hexafluoroacetylacetonate; cp*, pentamethylcyclopentadienide; $bpyO_2$, 1,1′-dioxo-2,2′-bipyridine. [b] Ionic strength, typically from added tetrabutylammonium salts, or from reactants. [c] Second-order rate constant in acetonitrile at 25°C unless otherwise indicated. [d] Number of different salt concentrations studied in a salt dependence. [e] Number of other solvents studied. [f] Electron self-exchange rate constant calculated from the Marcus cross-reaction equation. [g] Ref. 32. [h] Ref. 33. [i] Ref. 34. [j] Ref. 35. [k] Ref. 36. [l] Ref. 37. [m] Ref. 15. [n] Ref. 38. [o] Ref. 30. [p] Ref. 39. [q] Ref. 17. [r] Ref. 40. [s] Ref. 13. [t] $\Delta V^\ddagger$ measured with no added salt. [u] Salt dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ determined. [v] Anion dependence with four anions. [w] Solvent dependence of $\Delta V^\ddagger$. [x] $\Delta V^\ddagger$ in dichloromethane also. [y] Solvent dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. [z] Salt dependence of $\Delta V^\ddagger$. [aa] Conductivity studied for ion pair analysis. [ab] Ion paired path negligible. [ac] Activity coefficients used in analysis. [ad] $R = CH_2PhCH_3$. [ae] Anion dependent. [af] Ion pairing analysis. [ag] Solvent was HCO_2H. [ah] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are for the ion free path. [ai] Molality units. [aj] Ref. 41.

TABLE 3

Reagent summary

No.	Reagent[a]	Oxidation states	E^{0} [b] (V)	k_{11} [c] ($M^{-1}\ s^{-1}$)	Comments
1	$Co(cp^{*})_2$	III/II	−1.3	4×10^{8}	d
2	$Co(P(OMe)_3)_4$	0/−I	−1.1	9×10^{3}	e,f
3	$Co(bpy)_3$	III/II	0.6		g
4	$Co(bpyO_2)_3$	III/II	1.2	0.1–600	ab
5	$Co(cp)_2$	III/II	−0.7	4×10^{7}	d
6	$Co(dmg)_3(BBu)_2$	III/II	0.3	6×10^{2}	h
7	$Co(dmg)_3(BF)_2$	III/II	0.6	1×10^{2}	h
8	$Co(dmg)_3(BPh)_2$	III/II	0.5	1×10^{2}	h
9	$Co(dpg)_3(BPh)_2$	III/II	0.6	5×10^{2}	i
10	$Co(nor)_4$	IV/III	0.0	7×10^{5}	j
11	$Co(nox)_3(BBu)_2$	III/II	0.4	1×10^{2}	h
12	$Co(nox)_3(BF)_2$	III/II	0.7	2×10^{2}	h
13	$Co(nox)_3(BPh)_2$	III/II	0.5	3×10^{2}	h
14	$Co(terpy)_2$	III/II	0.5		l
15	$Cr(CNdiip)_6$	I/0	−0.1	2×10^{8}	l
16	$Cr(CNdiip)_6$	II/I	0.7	2×10^{7}	l
17	$Cr(ClPh)_2$	I/0	−0.1	2×10^{8}	m
18	$Cr(MePh)_2$	I/0	−0.6	3×10^{7}	m
19	$Cr(PhCO_2Et)_2$	I/0	−0.3	3×10^{8}	m
20	$Cr(Ph)_2$	I/0	−0.5	6×10^{7}	d
21	$Cr(PhCOMe)_2$	I/0	−0.5	8×10^{7}	m
22	$Cr(PhPh)_2$	I/0	−0.4	4×10^{8}	m
23	$Cu(2,9\text{-}Me_2phen)_2$	II/I	1.1	5×10^{3}	n
24	$Cu(5\text{-}MeimidH)_2DAP$	II/I		4×10^{4}	o
25	$Fe(5\text{-}Clphen)_3$	III/II	1.5	2×10^{7}	ab,x
26	$Fe(3,4,7,8\text{-}Me_4phen)_3$	III/II	1.0	2×10^{7}	p
27	$Fe(5\text{-}Mephen)_3$	III/II	1.4	2×10^{7}	x,ab
28	$Fe(4,4'\text{-}Me_2bpy)_3$	III/II	1.2	2×10^{7}	p,x,ab
29	$Fe(4,7\text{-}Me_2phen)_3$	III/II	1.1	3×10^{7}	p
30	$Fe(4,7\text{-}Ph_2phen)_3$	III/II	1.2	2×10^{7}	p
31	$Fe(4,7\text{-}(chx)_2phen)_3$	III/II	1.1	4×10^{5}	q
32	$Fe(5,6\text{-}Me_2phen)_3$	III/II	1.2	2×10^{7}	p
33	$Fe(9aneS_3)_2$	III/II		5×10^{4}	
34	$Fe(Bucp)_2$	III/II		5×10^{6}	
35	$Fe(cp^{*})_2$	III/II	0.2	3×10^{7}	
36	$Fe(Mecp)_2$	III/II	0.6	8×10^{6}	h
37	$Fe(4,4'\text{-}Ph_2bpy)_3$	III/II	1.1	2×10^{7}	r
38	$Fe(bpy)_3$	III/II	1.3	4×10^{6}	s
39	$Fe(cp(CH_2)_3cp)_2$	III/II		2×10^{7}	
40	$Fe(cp)_2$	III/II	0.7	9×10^{6}	d,s
41	$Fe(cpcpCH_2NMe_2)$	III/II		2×10^{6}	
42	$Fe(cpcpCO_2Me)$	III/II		7×10^{7}	
43	$Fe(phen)_3$	III/II	1.4	1×10^{7}	s
44	$Mn(CNC_6H_{11})_6$	II/I	0.7	4×10^{5}	t
45	$Mn(CNCH_2Ph)_6$	II/I	0.9	1×10^{6}	t
46	$Mn(CNCHMe_2)_6$	II/I	0.7	3×10^{5}	t

TABLE 3 (*continued*)

No.	Reagent[a]	Oxidation states	E^0 [b] (V)	k_{11} [c] ($M^{-1}\,s^{-1}$)	Comments
47	$Mn(CNEt)_6$	II/I	0.7	2×10^6	t
48	$Mn(CNMe)_6$	II/I	0.7	2×10^7	t
49	$Mn(CNPhMe)_6$	II/I	1.1	3×10^7	t
50	$Mn(CNPhOMe)_6$	II/I	1.0	5×10^7	t
51	$Mn(CNtBu)_6$	II/I	0.7	7×10^4	t
52	$Mn(urea)_6$	III/II	1.1	10^{-2}–10^{-5}	p
53	$Ni(Me_2[14]dieneN_4)$	III/II	1.2	2×10^3	p,u,v
54	$Ni(Me_6[14]aneN_4)$	III/II	0.1	1.1	v
55	$Ni([14]aneN_4)$	III/II	1.2	3×10^3	p,u,v,ab
56	$Ni([9]aneN_3)$	III/II	1.2	6×10^3	p,ab
57	$Ni(cp)_2$	III/II	0.3	2×10^8	w
58	$Ni(meso\text{-}Me_6[14]aneN_4$	III/II	0.0	19	v
59	$Ni(rac\text{-}Me_6[14]aneN_4$	III/II	0.0	9	v
60	$Os(3,4,6,8\text{-}Me_4phen)_3$	III/II	0.7	2×10^6	s,y
61	$Os(3,4,7,8\text{-}Me_4phen)_3$	III/II	0.7	3×10^6	s,y
62	$Os(4,4'\text{-}Me_2bpy)_3$	III/II	0.9	2×10^6	s,x
63	$Os(4,4'\text{-}Ph_2bpy)_3$	III/II	1.0	8×10^7	p
64	$Os(4,7\text{-}Me_2phen)_3$	III/II	1.0	4×10^6	y
65	$Os(4,7\text{-}Ph_2phen)_3$	III/II	0.9	9×10^7	p
66	$Os(5,6\text{-}Me_2phen)_3$	III/II	1.0	1×10^8	p
67	$Os(5\text{-}Clphen)_3$	III/II	1.2	4×10^7	s,x,ab
68	$Os(5\text{-}Mephen)_3$	II/II	1.0	9×10^7	p
69	$Os(bpy)_3$	III/II	1.1	2×10^6	s,x
70	$Os(phen)_3$	III/II	1.1	4×10^7	s,x,ab
71	$Rh(OAc)_4(MeCN)_2$	+/0	1.4	5×10^4	v
72	$Ru(3,4,7,8\text{-}Me_4phen)_3$	III/II	1.3	1×10^8	p
73	$Ru(3,5,6,8\text{-}Me_4phen)_3$	III/II	1.3	1×10^8	p
74	$Ru(4,4'\text{-}Ph_2bpy)_3$	III/II	1.4		z
75	$Ru(4,7\text{-}Me_2phen)_3$	III/II	1.3	1×10^8	p
76	$Ru(5\text{-}Clphen)_3$	III/II	1.6		z
77	$Ru(Me_2bpy)(acac)_2$	III/II	0.1	5×10^6	r
78	$Ru(Me_2bpy)(hfac)_2$	III/II	1.2	1×10^8	r
79	$Ru(bpy)_3$	III/II	1.5	8×10^6	s,x
80	$Ru(hfac)_3$	III/II	0.9	4×10^6	aa

[a] Charges are omitted. Ligand abbreviations: bpy, bipyridine; terpy, terpyridine; dmg, dimethylglyoximate; dpg, diphenylglyoximate; nox, cyclohexanediondioximate; CNdipp, 2,6-diisopropylphenylisocyanide; DAP, 2,6-diiminoethylpyridine; py, pyridine; imid, imidazole; phen, phenanthroline; OAc, acetate; hfac, hexafluoroacetylacetonate; cp*, pentamethylcyclopentadienide; $bpyO_2$, 1,1'-dioxo-2,2'-bipyridine. [b] Potentials have been referenced to the hydrogen electrode, after the example of ref. 42. This has required a variety of assumptions and thus the potentials are of limited accuracy. [c] The second-order rate constants are from directly measured or calculated using the Marcus cross-reaction relationship; the values are taken from Tables 1 and 2. [d] Ref. 43. [e] Solvent was THF. [f] Ref. 8. [g] Ref. 44. [h] Ref. 34. [i] Ref. 35. [j] Ref. 45. [k] Ref. 32. [l] Ref. 46. [m] Ref. 12. [n] Ref. 13. [o] Ref. 14. [p] Ref. 40. [q] chx assumed equal to Me_2 for E^0 estimate. [r] Equation and parameters of ref. 42. [s] Ref. 42. [t] Ref. 59. [u] Ref. 48. [v] Ref. 30. [w] Ref. 49. [x] Ref. 17. [y] Ref. 18. [z] Ref. 50. [aa] Ref. 51. [ab] Ref. 41.

and self-exchange reactivity of the compounds that have been studied. The approximate nature of the potential is dictated by the problem of producing stable reference electrodes in non-aqueous solvents, and of relating potentials in different solvents. The best current solution is to use any arbitrary but stable reference electrode and relate the measured potentials to the potential of a standard compound such as ferrocene. Table 4 displays some available results on atom/electron transfer reactions.

(iii) Factors affecting electron transfer reactivity

Before presenting the discussion of the available results, which forms the bulk of this review, it is appropriate to present briefly the factors which current electron transfer theory indicates should control electron transfer reactivity.

Before electron transfer takes place, the reactants must come together. How frequently they encounter each other, how long these encounters last, and their geometry is going to be influenced by electrostatic and non-electrostatic interactions between the reactants, which in turn are influenced by the solvent and other solutes, particularly ions. In addition to affecting the Coulombic interaction between charged reactants, added salts control the extent of ion pairing in any given solvent. Ion pairing becomes an important consideration in non-aqueous solvents and ion paired reactants can be considered as derivatives of the free ions with their own reactivity properties. Relatively little work has been done on the problem of measuring or estimating these important parameters, partially because much of the statistical mechanical and solution thermodynamics theory is most developed for aqueous solution. In the limit of slow encounters or rapid electron transfer, reactions will become diffusion controlled and only the encounter will be relevant to the kinetics. To the extent that transfer within a complex is understood, including the influence of solvent dynamics as well as solvation thermodynamics, electron transfer kinetics become a way to study the encounter step which is common to all bimolecular reactions.

Marcus theory and elaborations from that model treat unimolecular electron transfer within a defined precursor complex. The activation energy is considered in terms of an inner-sphere reorganization component and an outer-sphere or solvent reorganization component. The inner-sphere component is the energy required to distort the complex to a compromise geometry between that of the oxidized and reduced forms. Calculation of this energy can be accomplished if all of the force constants are known and if the ground state structures are precisely known. The small structural change occurring on electron transfer for most of the complexes that have been studied in non-aqueous solvents leads to small inner-sphere reorganization energies. However, the complex structures and lack of detailed force constant information can also make it difficult to estimate this factor precisely. The solvent reorganization energy is typically estimated by treating the solvent as a dielectric continuum and the precursor complex as a charged cavity assumed to have a spherical or

TABLE 4

Atom/electron transfer reactions

Reaction no.	Oxidant[a]	Reductant	I^b (M)	k^c ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal $mol^{-1}\,K^{-1}$)	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})	Salt[d]	Solv.[e]	Comments
1	$(cp)Mo(CO)_3Br$	$[(cp)Mo(CO)_3]PPN$	ca. 0.05	1.6×10^1	12	−12				f
2	$(cp)Mo(CO)_3Cl$	$[(cp\text{-}d_5)Mo(CO)_3]PPN$	ca. 0.05	9.0×10^{-2}		18.9	0			f
3	$(cp)Mo(CO)_3I$	$[(cp)Mo(CO)_3]PPN$	ca. 0.05	1.5×10^4	6.4	−18				f
4	$(cp)W(CO)_3Br$	$[(cp)W(CO)_3]PPN$	ca. 0.05	1.5E+00	15.1	−7				f
5	$(cp)W(CO)_3Cl$	$[(cp\text{-}d_5)W(CO)_3]PPN$	ca. 0.05	2.1E−03	17.7	−11				f
6	$(cp)W(CO)_3I$	$[(cp)W(CO)_3]PPN$	ca. 0.05	4.5×10^3	7.5	−17				f
7	$[Os(cp)_2I]CF_3SO_3$	$Os(cp)_2$	0.001	1.8×10^4	7.5	−13	−8	×15	×9	g,h,l,m,o
8	$[Ru(cp)_2Br]PF_6$	$Ru(cp)_2$	0.01–0.02	1.6×10^3	8.2	−15.7	−5.9	×8		i,j,l,m,n
9	$[Ru(cp)_2I]CF_3SO_3$	$Ru(cp)_2$	0.001	7.4×10^5	6.7	−9	−6	×12	×6	j,m,n
10	$[Ru(cp)_2Cl]PF_6$	$Os(cp)_2$	0.002	1.4×10^2	9	−18				k

[a] Abbreviations: PPN, bis(triphenylphosphineiminium). [b] Ionic strength. [c] Second-order rate constant at 25°C in acetonitrile unless otherwise indicated. [d] Number of different salt concentrations studied. [e] Number of other solvents studied. [f] Ref. 52. [g] Ref. 53. [h] Ref. 54. [i] Ref. 55. [j] Ref. 56. [k] Ref. 57. [l] Solvent dependence of temperature dependence. [m] Solvent dependence of $\Delta V^{\ddagger}$. [n] Anion dependence. [o] Mixed solvent.

ellipsoidal shape. This is clearly a major simplification, but it forms a point of reference in the treatment of solvent effects. The total reorganization energy is also influenced by the free energy change for electron transfer in the precursor complex. The dependence predicted is a parabolic one, with the rate constant increasing with driving force up to a maximum value beyond which, in the "Marcus inverted region", the rate constant decreases with further increases in driving force. None of the systems discussed in this review involved such large free energy changes.

The probability of electron transfer also depends on electronic interaction between the two reactants. Factors here include electronic coupling between the initial and final states which determines whether the reaction will be adiabatic, as is commonly assumed, or non-adiabatic and thus inhibited compared with the adiabatic case. The electronic coupling is controlled by the nature of the orbitals which gain and lose the electron (or hole), their relative orientation, and the electron transfer distance. The exponential dependence of the electron transfer rate constant on distance, which is typically expected for a given orientation, makes it necessary not only to know the most likely orientations of complexes in the precursor complex, but the time they spend at the whole range of distances that are still viable for electron transfer. Nuclear tunneling can also modify the electron transfer rate constant, particularly at low temperatures.

After electron transfer, the successor complex must separate into the products. This process is seldom resolved in the kinetics, but it is important to understand it in evaluating the free energy change for the electron transfer within the precursor complex, since it is the overall free energy change for the reaction corrected for the difference in the free energy for formation of the precursor and successor complexes that is properly to be considered.

The most commonly used result of current theory is the Marcus cross-reaction relationship, which correlates a cross-reaction rate constant with the electron self-exchange rate constants of the reactant couples and the equilibrium constant for the reaction. Much work has been done to establish whether this relationship is valid. It is clear that agreement within 1 to 2 orders of magnitude between the observed and calculated cross-reaction rate constant is to be expected. Much larger deviations and systematic trends in deviations are most profitably attributed to changes in the donor and acceptor orbitals involved or the structure of the reactants between the cross-reaction and the self-exchange reaction, in other words deviations from the assumptions of the theory, rather than failure of the theory. When the cross-reaction relationship is used to estimate self-exchange reactivity for a new reactant couple, and when several reactions give consistent results, the value obtained is likely to be a reliable estimate. On a practical level, if the self-exchange rate constant is later measured and found to deviate, it may well be the self-exchange value obtained directly which represents a less typical mode of reaction. For particular reactions, further testing of electron transfer theory is probably best pursued through the attempt at detailed predictions of particular rate constants from first principles.

B. DISCUSSION

The general values of rate constants observed deserve some comment. For cross-reactions, the observed second-order rate constants are typically in the range of 10^0–10^5 M^{-1} s^{-1}. This range is limited on the high end by the stopped-flow method with mixing times of a few milliseconds. This is a severe limitation since so many of the complexes of interest have such high inherent reactivity that cross-reactions between them cannot be studied. This also limits many studies to reactions with low equilibrium constants. No particularly slow reactions are in the table because the less reactive complexes of the first row transition metals are insoluble or have not been studied, and none of the organometallic compounds so far studied are so unreactive.

Electron self-exchange studies suffer from the opposite technical problem. These reactions are typically studied by NMR line broadening. Since NMR characterization of new organometallic complexes is routine, the extension to line broadening studies is often pursued. The observed rate constants are in the range of 10^3–10^9 M^{-1} s^{-1}. Unlike the case for stopped-flow studies, here the faster reactions are more easily studied and slow reactions are much more difficult.

These experimental limitations are complementary. Directly measured self-exchange rate constants are possible for reactant couples that have appropriate NMR properties and which have a reasonably high reactivity. If a compound of interest is not particularly reactive, then cross-reactions can be studied by the stopped-flow method, using optical changes that commonly accompany electron transfer and using well-characterized oxidants or reductants. The heavy emphasis in our laboratory on the reactions of the cobalt clathrochelates is a direct result of these compounds being soluble in the solvents of interest while being of inherently low reactivity.

For the fastest reactions, especially if studied at low temperatures or in more viscous solvents, there is the concern that the diffusion-controlled limit is being approached. In general, this has not proven to be the case with the exception of the fastest rate constant on the list, $Cr(bpy)_3^{0/+}$, which yielded a rate constant of 2×10^9 M^{-1} s^{-1} in dimethylformamide from ESR data. The different limitation of solvent dynamics control is more commonly influential, as has been discussed by Weaver [2], especially for the faster metallocene self-exchange processes.

The rest of the discussion will be organized in terms of the experimental variables studied in the various investigations. These are reactant structure, added electrolyte, solvent, pressure, and temperature. The influence of these factors is not independent, and reference between them will be made while attempting to minimize repetition.

(i) Reactant structure

Reactant structure is the most basic variable available to the experimentalist. Many of the studies have been done to evaluate the intrinsic reactivity of a given class of compounds. Such studies rely on either directly measuring the electron self-exchange rate constant, which is the best single indicator of inherent reactivity, or on cross-reaction studies of the reactant of interest with well-characterized oxidants or reductants in order to extract the apparent self-exchange rate constant through application of the Marcus cross-reaction equation. Study of a series of cross-reactions of the same complex can be used to establish the reliability of the cross-reaction equation calculations as well as to establish situations in which inconsistencies are apparent.

An extensive study of cross-reactions was pursued by Macartney to establish the reactivity of $Mn(urea)_6^{3+/2+}$ (Table 2: 37–56). In that study, apparent self-exchange rate constants varied by a factor of 3×10^4. The highest values were from cross-reactions with Ni(II,III) macrocycles, while the lowest were from reactions with alkylated tris-phenanthroline complexes of Fe, Ru, and Os. The variation was attributed to changes in adiabaticity, and particularly to the orbital symmetry mismatch that occurs in the cross-reaction of the $Mn(urea)_6^{3+}$, which accepts the electron into a σ symmetry orbital while the polypyridine complexes of Fe, Ru, and Os provide an electron from a π symmetry orbital. The π/π pathway that is available for the self-exchange process of the polypyridine complexes gives them a high intrinsic reactivity but is not available for the cross-reaction. Macartney and co-workers also studied the reactivity of $Rh_2(OAc)_4(MeCN)_2^{0/+}$ (Table 2: 28, 57, 59, 61, 63–65) through cross-reactions with Ni macrocycles and Fe and Ru polypyridine complexes. In this case, the apparent self-exchange rate constant calculated for the $Rh_2(OAc)_4(MeCN)_2^{0/+}$ complex is consistent, and agrees well with the directly measured value (Table 1: 52). It should be noted that the self-exchange values used for the Ni macrocycles, unlike those for the polypyridine complexes, are not measured directly but are calculated from cross-reactions with the polypyridine complexes. Thus cycles of cross-reaction and self-exchange rate constants are developed and it becomes more clear, even when some of the self-exchange values are not available, that a particular reaction, such as $Mn(urea)^{3+/2+}$ is not showing the Marcus cross-reaction correlation in all of its reactions.

A result similar to that observed for $Mn(urea)_6^{3+/2+}$ was obtained in another study from the Macartney laboratory. In this study, 15 cross-reactions of $Co(bpyO_2)_3^{2+/3+}$ were investigated (Table 2: 67–81) and apparent self-exchange rate constants for the Co complex calculated. Again there was a large range (0.08–600 M^{-1} s^{-1}) in the calculated value and there were two categories. The faster apparent self-exchange values were derived from reactions with Ni(II,III) macrocycles while the slower ones again came from cross-reactions with polypyridine complexes.

An extensive series of cross-reaction studies from our laboratory has involved the reactivity of Co(II,III) clathrochelates of the general form $Co(dioximate)_3(BX)_2^{+/0}$, where the dioximes are dimethylglyoxime, diphenylglyoxime, and cyclohexanedionedioxime, and the X is F, phenyl, or butyl (Table 2: 2–21, 35). This is another case in which the self-exchange has not been measured. The matrix of cross-reactions studied has shown consistency with the Marcus cross-reaction equation and some patterns of varying reactivity with the substituents on the cage structure.

Direct measurement of self-exchange rate constants permits a study of how structural factors lead to differences in reactivity without the complication of considering two different reactants and products, and the necessary thermodynamic driving force. The ideal study isolates one structural contribution and considers a series of compounds. We attempted to study the effect of reactant size, and especially electron transfer distance, on bimolecular reactions through the series $Mn(CNR)_6^{+/2+}$ (Table 1: 35–43). The R groups studied were methyl, ethyl, isopropyl, *n*-butyl, *t*-butyl, cyclohexyl, benzyl, tolyl, and methoxyphenyl. The rate constant decreased by a factor of over 300 with increasing size of the alkyl substituents and after consideration of other possible contributions to the rate constant variation, it was concluded that the effect was due to decreased orbital overlap produced by the increased electron transfer distance. Introduction of a phenyl group that could be conjugated with the $Mn{-}C{\equiv}N$ center produced reactivity comparable with that of $CNCH_3$, further establishing that orbital overlap was being decreased by the bulkier alkyl substituents. Size also changes the outer-sphere reorganization energy since this decreases with increasing volume. When ion pairing is influential, it too will decrease as size increases. These factors will be discussed in later sections. Related to the $Mn(CNR)_6^{+/2+}$ studies is the investigation of $Cr(CNdipp)_6^{0/+/2+}$ (Table 1: 7, 8). Here, both self-exchange and cross-reactions (of the Cr(II) complex with Co(II) clathrochelates) allowed the investigation of a variation in charge and electronic structure through the consideration of three oxidation states of a single complex.

Metallocene self-exchange has been extensively studied, both through variation of substituents on the cp ligands and through variation of the central metal ion and thus the electronic structure (Table 1: 1–3, 24–29, 31, 32, 44). As in structural, and electrochemical studies, ferrocene is the reference point for a great deal of work in electron transfer kinetics. The pioneering work in this area was done by Wahl and co-workers. This has been extended and refined by work from Weaver's laboratory aimed at solvent dynamics effects. Generally, for a given central metal ion, the rate constant increases when the ring is methylated and cobaltocenes are more reactive than ferrocenes. For the one case in which it has been studied, nickelocene is more reactive than cobaltocene. The increase in rate constant with alkylation, contrary to the manganese isocyanide result, indicates that the increase in electron transfer distance brought about by the alkyl group is not enough to bring the orbital overlap below that threshhold necessary to produce adiabatic behavior. A significant question for metallocenes is whether a stacked or some side-by-side geometry is preferred. This will depend on the electronic structure, thus on the central metal ion, and has been investigated through electronic structure calculations by Newton and co-workers [58] who found that ferrocene electron transfer corresponds to electron transfer and cobaltocene to hole transfer superexchange, and that the stacked (D_{5h})

geometry provides the best overlap. Related to the metallocene studies are the investigation of dibenzene chromium(0,I) and related compounds (Table 1: 9–14).

The next large structural class involves the polypyridyl ligand complexes (phenanthroline, bipyridine, terpyridine, and alkylated derivatives) of M(II,III) including Co, Fe, Ru, and Os (Table 1: 18–23, 30, 33, 45–51). These had been extensively studied in aqueous solution, but maintain adequate solubility for reactions to be studied in organic solvents also. Again, Wahl and co-workers did much of the early self-exchange work. The lower oxidation state $Cr(bpy)_3^{0/+}$ self-exchange reaction has also been studied, and is one of the fastest reactions known in this category.

Copper complexes offer a particular challenge since the coordination number and geometry often vary considerably between the Cu(I) and Cu(II) oxidation states. However, $Cu(2,9\text{-}Me_2phen)_2^{0/+}$ and some copper macrocycle complexes have been amenable to study (Table 1: 15–17).

(ii) Added electrolyte and ion pairing

Many of the classical, aqueous electron transfer kinetics studies involved high ionic strength and often high acid media. This evolved from the need to suppress hydrolysis of aqua ions through high acid concentrations and the recognition that constant ionic strength should be maintained. In a high dielectric constant medium such as water, even +3 ions form on ion pairs only weakly with the large −1 ions of the added salts. When added electrolyte dependences are pursued, it is the influence on the electrostatic work required to form the precursor complex that is affected. For typical +2/+3 ions, added salt significantly increases rate constants and this is reasonably analyzed through a consideration of the ionic strength of the medium.

For solvents of much lower dielectric constant than water, the situation is much more complex. Ion pairing is extensive, even for large +1 cations in a solvent as polar as acetonitrile, if an anion such as BF_4^- or PF_6^- is present at 0.5 M. For solvents with a dielectric constant near 10, such as dichloromethane, ion pairing is extensive even without added electrolyte. Larger aggregates must also be considered, and ion pairing of the added electrolyte must also be considered. Aqueous solutions have been so extensively studied and modeled that activity coefficients can be reasonably estimated, but this is not true for the non-aqueous solutions at the higher concentrations of electrolytes typically involved in the kinetics studies. Thus, in addition to the influence on any electrostatic work required to form the precursor complex, the possibility of the formation of ion pairs which are effectively structural derivatives of the parent ions, must be considered. Fortunately, the systems available for study in non-aqueous solution have a variety of charge types, which help in designing systems to study these effects in isolation.

Much of the work on the influence of added electrolyte has been done on cross-reactions. This is because the electrolytes typically used in non-aqueous solvents, such as tetrabutylammonium tetrafluoroborate, produce overwhelming ^1H NMR signals which interfere with those from the reactants.

The best way to separate the effect of ion pairing from that of electrostatic work forming the precursor complex is to eliminate the electrostatic work by studying a reaction involving a neutral reactant. A neutral reactant often has a large dipole or quadrupole moment, but such orientation-dependent quantities have not yet been considered in any detail. Several studies involving $Co(dioximate)_3(BX)_2^{0/+}$ and $Fe(cp)_2^{0/+}$ have included consideration of the added salt dependence. For the ferrocene self-exchange reaction in acetonitrile (Table 1: 28), Wahl and co-workers found that added PF_6^- or ClO_4^- cause a decrease of up to a factor of about 2 in the rate constant. This was consistent with inhibition by ion pair formation if the association constant for the ion pair was 10–20 M^{-1}. Attempts at conductivity measurements for $Co(cp)_2PF_6$ indicated that ion pairing was weak, with an association constant of less than approximately 20 M^{-1} in acetonitrile and other polar, aprotic solvents. Higher values were found in methanol (120 M^{-1}), dichloroethane (5600 M^{-1}) and dichloromethane (25000 M^{-1}). The reduction of $Co(dmg)_3(BF)_2^+$ by $Fe(cp)_2$ (Table 2: 7) has been extensively studied in a series of papers from our laboratory. Conductivity measurements on the $Co(dmg)_3(BF)_2BF_4$ in acetonitrile indicated that it was only weakly associated ($K \approx 10$ M^{-1}). The kinetic results showed a reduction in the second order rate constant by a factor of ca. 5 as Bu_4NBF_4 was added. Similar results for other clathrochelate/ferrocene reactions were also found (Table 2: 3, 6, 17, 18). As for the ferrocene self-exchange data, the dependence on added electrolyte fit a rate law with an ion association constant, a path for the free ion and a path involving reduction of the ion paired cation. The apparent association constant was 17 M^{-1}.

A concern in treating the data using the parallel path rate law is that activity coefficients are being ignored. Attempts to use available equations involving estimates of the activity coefficients were not successful, presumably because of the inaccuracy of these estimates at 0.1–0.5 M ionic strength in acetonitrile. However, another approach was attempted. The added electrolyte dependence was repeated using Br^-, PF_6^-, and $B(C_6H_5)_4^-$ as the anion. The first two anions gave results quite similar to those for BF_4^-, whereas $B(C_6H_5)_4^-$ did not affect the rate constant within the concentration range accessible, up to 0.1 M. This is consistent with the ion pair model if the large anion does not form ion pairs, but it is inconsistent with the effect as being due to activity coefficient variation, since this is not influenced, within the approximations used, by the size of the ion. Variation of solvent showed the same pattern of reactivity, but with an increase in the apparent ion pair association constant with a reduction in the dielectric constant of the solvent (200 M^{-1} in acetone, 53 M^{-1} in nitrobenzene, and 29000 M^{-1} in dichloroethane). Nitrobenzene showed a larger change in reactivity, with the rate constant for the ion paired form being a factor of 19 smaller than the rate constant for the free ion. In dichloroethane, there was some evidence for further ion association. A study on reactions between $Co(diphenylglyoxime)_3(BC_6H_5)^{0/+}$ and other clathrochelates (Table 2: 4, 10, 11, 15) also showed the now familiar decrease in rate constant with added electrolyte and an increase in the apparent association constant for the ion pair with decreasing solvent dielectric constant. The origin of the inhibitory effect of ion pairing can be sought both in the precursor formation and the electron transfer steps. The arguments which have been used here leave a good deal of room for more detailed analysis. If it is assumed that the transition state has the two reactants and the anion mutually tangential (other combinations of geometries are possible, but are limited to a certain extent by the principle of microscopic reversibility), many trajectories that would have led to adequate precursor complexes when the anion was not present do not lead to reactive geometries when the anion is present. To the extent that reactants must approach each other very closely, even to the extent of particular geometries with interpenetrating ligands, in order to get the most favorable orbital overlap, then the presence of the anion may block the optimal geometry attainable by the free ion. The driving force for the electron transfer within the precursor complex may vary, although no evidence for a change in apparent reduction potential has been found for the reactants at high salt concentrations. Relevant to this question are the observations from Hupp's [59] and Lewis's [60,61] laboratories of significant effects on the energies of intervalance electronic transitions brought on by ion pairing. Lastly, the detailed dynamics of the inner and outer coordination spheres will now involve the anion and the effect is not clearly predictable.

The other reactions that have been studied in detail involve positive charge on both reactants, either $+1/+2$ or $+2/+3$. This further complicates the analysis, but also allows a connection to be made to the $+2/+3$ systems studied in aqueous solution. The two $+1/+2$ reactions are the $\mathrm{Mn(CNR)_6^{+/2+}}$ self-exchange (Table 1: 35, 38, 39, 43) and the $\mathrm{Cu((imidH)_2DAP)^+}$ and $\mathrm{Cu((imidR)_2DAP)^+}$ reduction of $\mathrm{Cu((py)_2DAP)^{2+}}$ (Table 2: 22, 23). Both studies included conductivity analysis which is particularly well done for the Cu system from Stanbury's laboratory. For the Cu(I,II) cross-reaction, the ion pairing constant of the Cu(II) reactant with $\mathrm{BF_4^-}$ in acetonitrile was found to be 300 $\mathrm{M^{-1}}$ and further ion pairing was not considered within the range of salt concentrations used, up to 52 mM. The data were treated with a Debye–Huckel expression, which could describe the observed increase of observed rate constant with increasing ionic strength reasonably well, although the slope of the plot used was not quite the theoretical value. This indicates that changes in ion and transition state activity coefficients (comparable with changes in the electrostatic work to form the precursor complex) with ionic strength dominate the observed effects. Further attempts were made to take into account the ion pairing of the Cu(II) reactant and the possibility that it has different reactivity. The authors found that the data could be adequately described even if the ion pair was assumed to be totally unreactive.

The most detailed study of the $\mathrm{Mn(CNR)_6^{+/2+}}$ systems was performed on $\mathrm{Mn(CNC_6H_{11})_6^{+/2+}}$ in the presence of varying concentrations of $\mathrm{Bu_4NBF_4}$ in a series of solvents of varying dielectric constant (Table 1: 35). It was possible to study the self-exchange reactions by NMR in the presence of added salt because it was the ^{55}Mn resonance that was observed. Conductivity studies of both Mn complexes and Bu_4NBF_4 were performed to estimate the ion pairing constants. Using an equation for the dependence of the activity coefficients on the ionic strength, an estimate was made of the concentrations of the various ion paired species in the different solvents. This is more approximate than in the Cu(I,II) study cited above because total BF_4^- (free and ion paired) up to 0.4 M was investigated. The results showed that the most polar solvents, MeCN and $(CH_3)_2SO$, involved only free ions and the increase in rate constant could be attributed to the decrease in electrostatic work to assemble the transition state which accompanies higher ionic strength. For ethanol and acetone, the Mn(II) complex occurred only as the ion pair, and the further path with the complexes completely ion paired to make neutral reactants was also possible. The rate constant increased with ionic strength but to a smaller extent than for the $+1/+2$ path observed for the more polar solvents. This is attributable to an increase in the rate constant for the $+1/+1$ path being balanced by a decrease in rate constant for the path which involved the fully ion paired reactants. In the lowest dielectric constant solvents studied, chloroform and bromobenzene, only the fully ion paired species and more highly associated species should be present. The rate constants decreased with added Bu_4NBF_4. The general pattern observed was that the rate constants decreased with increasing extent of ion pairing, but this effect is dominated by the electrostatic work term when two ionic reactants are involved.

The next reactant charge type which has been studied in detail involves M(polypyridine)$^{2+/3+}$ complexes of Fe and Os, and the work is from Wahl's laboratory. These studies were done at very low ionic strength, 0.1–0.4 mM from added $NaClO_4$ or KPF_6, and with only 0.05 mM reactant concentrations in acetonitrile. Conductivity studies were also done, which established that only ion pairs with the $+3$ ions were significant at the concentrations studied. As above, activity coefficients were included in the analysis. It was found that the rate constants increased more with added salt than could be predicted from the activity coefficients. Using the measured ion association constants, this was attributed to higher reactivity of the ion paired reactant than the free ion. This is the only case where this has been shown. It is supported by a greater effect of $NaClO_4$ than KPF_6 which correlates with a greater extent of ion pairing by the ClO_4^- ion (Table 1: 19, 33, 48).

The last reaction to be considered has a charge type that is only accessible for a cross-reaction, $0/+2$. The reduction of $Cr(CNdipp)_6^{2+}$ by $Co(nox)_3(BBu)_2$ in acetonitrile (Table 2: 20) showed no salt dependence. Based on just the work term effect arising from the charged products, which causes the driving force for the overall reaction to be different from that in the precursor complex, the rate constant should have increased by about a factor of 2. Thus any inhibition from lower reactivity of the ion paired Cr reactant can only be this small factor. The insensitivity of this particular system to ion pairing may arise from the highly delocalized acceptor orbitals on the Cr which lead to better orbital overlap (more nearly adiabatic reactivity) and thus less influence of the BF_4^- counterion when it is in the transition state.

The study of the effects of ion pairing would be greatly facilitated if the structures, concentrations and lifetimes of the various ion paired species could be more directly evaluated, especially at the higher concentrations of added electrolytes.

(iii) Solvent

The study of the influence of the solvent on electron transfer reactivity is one of the primary concerns of the area of non-aqueous electron transfer kinetics. There is a prediction of the effect of varying the solvent on electron transfer reactivity that comes from Marcus theory. If the solvent is treated as a continuum with a dielectric constant (ε) and an index of refraction (n), then the outer-sphere reorganization energy will be proportional to a size and shape factor multiplied by $[(1/n^2)-(1/\varepsilon)]$. This comes about because the high frequency response of the solvent, n^2, can respond as rapidly as the change in electric field produced by the transferring electron, but the lower frequency motions which contribute to ε do not, leading to the need for a non-equilibrium orientation of the solvent about the precursor complex which must be attained before the electron is transferred. It is not simple to design experiments to test this factor. The shape and size term is not universally agreed on, but a commonly used form is $\{(1/2r_a)+(1/2r_b)-[1/(r_a+r_b)]\}$ where r_a and r_b are the radii of the reactants, which are assumed to be spheres. Clearly this is a crude definition of shape; however, it brings out the general principle that larger reactants and precursor complexes will have smaller solvent reorganization energies. The description of the solvent as a dielectric continuum must be inadequate at some level. The molecular nature of the solvent must eventually become important as must the actual composition and surface features of the solutes. The dynamics of solvent movement are also important in some cases. A practical problem is that solvent variation is necessarily a discontinuous process. Studies in mixed solvents can lead to a smoother variation, but they also raise the problem that certain solutes will remain preferentially solvated. This has been observed for intervalence compounds [62,63]. As will be discussed later, pressure and temperature change solvent properties continuously over a small range. Lastly, varying the solvent dielectric constant over a wide range also leads to changes in the extent of ion pairing and otherwise affects precursor complex formation.

The type of reaction that should lead to the fewest ancillary concerns is of the $0/+$ or $0/-$ charge type with reactants that are as much like hard spheres as possible. Self-exchange reactions are preferred since there is no need to determine the dependence of the driving force on solvent and rely on some way of taking this into account. Thus reactions that are especially appropriate for starting to test the solvent effect predictions are the self-exchange reactions of $Fe(cp)_2^{0/+}$ (Table 1: 28), $Co(cp)_2^{0/+}$ (Table 1: 3), $Ru(hfac)_3^{0/-}$ (Table 1: 53), and $Cr(C_6H_5)_2^{0/+}$ (Table 1: 13) as well as similar compounds with ligands bearing substitutions. The ferrocene self-exchange rate constants, as redetermined in Weaver's laboratory in a series of eight polar solvents, as well as the $Ru(hfac)_3^{0/-}$ and $Cr(C_6H_5)_2^{0/+}$ reactions, show a reasonable correlation with the dielectric parameter $\{(1/n^2)-(1/\varepsilon)\}$, indicating that solvent variation influences the rate constants primarily through the energetics of solvent reorganization. The cobaltocene rate constants show no such correlation. Weaver and co-workers pursued an extensive analysis of the metallocene results to seek solvent effects that originated in the details of solvent motion, and thus they first factored out the calculated outer-sphere reorganization energy (inner-sphere reorganization energies in these systems are small and solvent-independent) and looked for trends that remained. An important technique in this critical step is to use the solvent effect on an intervalence band of a structurally related compound, in this case the bis(ferrocenyl)acetylene cation, instead of relying only on theoretical equations. The details of these and later studies are beyond the scope of this review, especially since they have been recently reviewed [2]. However, as an introduction to a major conclusion of that work, it appears that, particularly for the fastest metallocene self-exchange reactions, cobaltocene and decamethylcobaltocene, solvent dynamics are strongly affecting the observed rate constants, while for somewhat slower reactions such as ferrocene self-exchange, the contribution is much less. The origin of this difference is in the weaker electronic coupling in the Fe cases. The lowest dielectric solvents, such as dichloromethane, did not fit the analysis.

A large number of cross-reactions of a neutral reductant with a +1 oxidant have been studied using the cobalt clathrochelate family, $Co(dioximate)_3(BX)_2^{0/+}$ (Table 2: 3, 6, 15). When solvents of much lower dielectric constant than acetonitrile are used, such as dichloroethane, the observed change in rate constant, corrected for the varying driving force for the reactions, correlates at best poorly with the solvent dielectric parameter. These are much more complex systems to analyze in detail because ion pairing must be considered and precursor complex structure may be varying, but it is clear that more than the outer-sphere reorganization energy is contributing to the rate enhancements observed in the less polar solvents.

Self-exchange reactions between +1 and +2 ions have been studied as a function of solvent for the $Mn(CNR)_6^{+/2+}$ series of compounds (Table 1: 35, 38, 43) for $Cr(CNdipp)_6^{0/+/2+}$ (Table 1: 7, 8) and for two solvents with $Cu(2,9\text{-}Me_2\text{-}phen)_2^{+/2+}$ (Table 1: 15). The limitation to self-exchange simplifies the interpretation somewhat, but ion association options further complicate it. The most detailed study is for $Mn(CNC_6H_{11})_6^{+/2+}$ in six solvents. Within that analysis, the measured rate constants were assigned to different paths involving varying numbers of counter ions (BF_4^-). Thus there were few comparisons that could be made of the same path in different solvents. The most extensive comparison that could be made was for the reaction between fully ion paired (neutral) complexes, which appeared to give an increase in rate constant with the solvent parameter rather than the predicted decrease. A later, more limited study of the $Mn(CNC(CH_3)_3)_6^{+/2+}$ self-exchange reaction showed a significantly different solvent dependence, further indicating that the molecular details of the interaction between the solvent and the reactant surface are influential. For the Cr isocyanide system, which was studied in five solvents, there was a much smaller variation in the measured rate constants compared to the Mn systems with alkyl isocyanide ligands. The small solvent dependence was consistent with predictions based on solvent reorganization and electrostatic work required to form the precursor complex only if the reactants were assigned +1 and +2 charges even in dichloromethane. No correlation with the solvent dynamics model was found.

A cross-reaction of the +2/+3 charge type, $Co(terpy)_2^{2+}/Co(bpy)_3^{3+}$, has been studied in a series of 15 solvents with no additional electrolyte and at a total ionic strength of 3–5 mM. The equilibrium constants were evaluated and found to vary little, except in acetophenone for which it was larger, while the rate constants varied by a factor of 20, except of acetophenone which was again larger. The general correlation was that expected just from electrostatic work terms, assuming that the ions are not ion paired.

A mention should be made of the particularly heroic attempts of Schmid et al. who have attempted to analyze the solvent dependence of the Fe(II) reduction of the Fe(III) solvates. These reactions involve changes in the first coordination sphere ligands with solvent and thus involve large changes in structure and driving force with solvent [64,65].

(iv) Activation parameters: $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$

Temperature and pressure dependence data provide a much more severe test of electron transfer theory than rate constants alone, especially to the extent that solvation effects are significant. Rate constants which may give an easily interpreted pattern at one temperature may give a different pattern, even the inverse, at another temperature. The Marcus cross-reaction equation can be extended to the correlation of $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$ given the corresponding parameters for the overall reaction, ΔH^0, ΔS^0, ΔV^0. However, the precision of the activation and equilibrium constant parameters is less than that of the rate constants, thus the precision of the predictions from the cross-reaction equation calculations is often sufficiently low to make interpretation of the apparent variations difficult. This is not to discourage such calculations; they should be done to pursue the origin of large variations of reactivity or activation parameters, but care must be taken in evaluating the precision of the results. Thus, it is again especially useful to consider the directly measured activation parameters of self-exchange reactions.

Before presenting the trends, some general points can be made about the activation parameters. With the rather low inner-sphere reorganization energies characteristic of most of the reactants, solvent and precursor complex contributions are dominant. Still, values of $\Delta H^\ddagger$ below 2–3 kcal mol^{-1} are certainly indicative of low barriers or significant exothermic contributions from precursor complex formation or other prior equilibria. In the case of $Cr(CNdipp)_6^{0/+}$, $\Delta H^‡$ is only 1.5 kcal mol^{-1} in dichloromethane. This is above a value of $\Delta H^‡$ of 1.0 kcal mol^{-1} that is estimated for diffusion in dichloromethane, but not much. The $\Delta S^‡$ values obtained are typically negative and can be quite negative. This result must also reflect precursor formation in some cases.

The largest set of data for one solvent is that for acetonitrile. The simple electron exchange reaction data from Table 1 give a range 1–7.5 kcal mol^{-1} for $\Delta H^‡$ and −7 to −28 cal mol^{-1} K^{-1} for $\Delta S^‡$. The overall range is limited because the range of rate constants is limited by the nature of the compounds and the NMR techniques. There is a general trend of decreasing (more negative) $\Delta S^‡$ with decreasing (less positive) $\Delta H^‡$. Some of this trend is due to correlation of errors in the calculation of the activation parameters, as demonstrated by some of the same compounds measured in different laboratories or at different times giving the described trend, but on a much larger scale the trend is clearly apparent. The best example is the $Mn(CNR)_6^{+/2+}$ family when R is ethyl, methyl, cyclohexyl, *t*-butyl, *n*-butyl, benzyl and isopropyl (Table 1: 35–40, 43), which give a range of 3.5 kcal mol^{-1} and 8 cal mol^{-1} K^{-1}. The aryl isocyanides give smaller entropies. There is some indication from the CNEt and CN*t*Bu reactions that increased ionic strength, from 0.1 to 0.3 M, also lowers $\Delta H^‡$ and produces a more negative $\Delta S^‡$. The +2/+3 phenanthroline and bipyridine complexes of Fe and Os (Table 1: 18, 20–23, 48, 50) have small $\Delta H^‡$ (1–3 kcal mol^{-1}) and a highly variable $\Delta S^‡$ (−12 to −25 cal mol^{-1} K^{-1}).

The activation parameters for several self-exchange reactions have been studied as a function of solvent. $Ru(hfac)_3^{0/-}$ (Table 1: 53) shows a substantial variation of ca. 5 kcal mol^{-1} and 11 cal mol^{-1} K^{-1} between acetic acid and acetone, as well as ca. 2 kcal mol^{-1} variation with different cations present. The $Cr(CNdipp)_6^{+/2+}$ reaction (Table 1: 7) gives a change of 3 kcal mol^{-1} and 11 cal mol^{-1} K^{-1} on changing from dichloromethane to acetone. The $Mn(CNR)_6^{+/2+}$ reactions also show significant solvent sensitivity. It remains a challenge to separate the ion pairing and solvation contributions to these activation parameters.

Volumes of activation are obtained from the pressure derivative of the rate constant, and are measured even less frequently than $\Delta H^‡$ and $\Delta S^‡$, particularly for electron transfer reactions in non-aqueous solvents. All of the entries in Tables 1 and 2 are from our laboratory and that of Thomas Swaddle. More work has been done on aqueous systems, particularly by European and Japanese groups, and a great deal more work has been done on substitution reactions particularly by van Eldik et al. An extensive review of $\Delta V^‡$ results is available [66].

The appeal of $\Delta V^‡$ measurements is that they should reflect strongly the changes in solvation in the activation process. At least superficially, they should also be easier to interpret than $\Delta S^‡$. Since electron transfer rate constants typically increase as distance decreases and since the volume of the precursor complex should decrease as the ions are brought closer together, there should be a discernible effect if pressure leads to shorter electron transfer distances. Pressures used for reactions in solution should not lead to significant changes in bond lengths, but they can lead to changes in ligand conformation which would change reactant–reactant separation. Since pressure influences solvent properties such as the index of refraction and dielectric constant, pressure variation is like a continuous solvent variation. Thus, it will affect electrostatic interaction, both between ionic reactants and in the formation of ion pairs between reactants and counter ions. The possibility that several different factors can influence $\Delta V^{\ddagger}$ is also one of its difficulties. The molar volume of an ion, $\Delta V^{\ddagger}$, or ΔV^0 in solution will be the sum of contributions from an intrinsic volume occupied and an electrostatic term arising from the interaction of the ion with the solvent. The electrostatic term can be large, and thus lead to negative molar volumes for ions, and all electron transfer reactions involve ions at some stage. This problem is exacerbated by the lack of molar volume data for solutes in solvents other than water, especially for large ions such as are involved in the electron transfer reactions of interest here. This latter problem has been partially alleviated by a recent study from our laboratory on apparent molar volumes (at 1–10 mM concentration) of a variety of complexes that we have studied, and some related compounds in acetonitrile and dichloromethane, along with a presentation of data from the literature on solutes in water and methanol. The principal result of use here is that the molar volumes of ions are a linear function of the volume of the molecules that can be calculated from computer graphics techniques ("van der Waals volumes"). For acetonitrile, neutral compounds give a parallel line that lies 28 cm^3 mol^{-1} above the line that desribes the 1–1 electrolytes. For dichloromethane there is no such distinction [67].

A particularly thorough extension of Marcus theory to the prediction of $\Delta V^{\ddagger}$ for self-exchange reactions has been presented by Swaddle [68], which leads to the conclusion that, for some reactions, particularly $MnO_4^{-/2-}$ in aqueous alkali, the increase in rate constant from a decrease in electron transfer distance contributes significantly to $\Delta V^{\ddagger}$. The electrostatic work required to form a precursor complex is influenced by pressure because the dielectric constant is influenced by pressure. This has been long appreciated, but the sign of the contribution was incorrect in an early treatment by Stranks, thus some of the first measurements of $\Delta V^{\ddagger}$ for an electron self-exchange reaction were thought to be in agreement with theory when they were not. This apparent agreement probably discouraged work in the field. We corrected the sign error, but wish to point out that in that paper there are also typographical errors in the example [69]. It seems that some degree of confusion is permanently associated with this subject. Further application of the Marcus cross-reaction to the correlation of volumes of activation from cross-reactions and self-exchange reactions is discussed below.

The $\Delta V^{\ddagger}$ for electron self-exchange in MeCN has been measured for $Mn(CNR)_6^{+/2+}$ where R is methyl, ethyl, *t*-butyl, isopropyl and cyclohexyl (Table 1: 35, 38–40, 43), $Fe(cp)_2^{0/+}$ (Table 1: 28), $Ru(hfac)_3^{0/-}$ (Table 1: 53), $Fe(phen)_3^{2+/3+}$

(Table 1: 33), and $Cu(2,9\text{-}Me_2phen)_2^{+/2+}$ (Table 1: 15). Further solvents were studied for the Cu, Ru and two of the Mn systems, and salt dependence data are available for $Mn(CNC(CH_3)_3)_6^{+/2+}$ and $Mn(CNC_6H_{11})_6^{+/2+}$. The values obtained span a small range including -2 to $-6\ cm^3\ mol^{-1}$ for $Mn(CNR)_6^{+/2+}$ when R is methyl and ethyl, $Cu(2,9\text{-}Me_2phen)_2$, $Ru(hfac)_3^{0/-}$, and $Fe(phen)_3^{2+/3+}$, $-7\ cm^3\ mol^{-1}$ for $Fe(cp)_2$, and -10 to -20 for $Mn(CNR)_6^{+/2+}$ when R is cyclohexyl, *t*-butyl, and isopropyl. These data indicate a rather consistent sign, and no particular influence of the overall charge. In the series of Mn systems, there is an indication that the more flexible ligands, that could adopt more compact conformations with increased pressure, lead to more negative $\Delta V^\ddagger$ values. This lack of a charge effect is surprising, and may be a result of compensating factors. The general negative sign, even for the reactions which include a neutral reactant ($Fe(cp)_2$ and $Ru(hfac)_3$), indicate that simple charge density arguments which would lead to solvent release on forming a +1 or −1 precursor complex, are not adequate. A requirement in these reactions for some degree of ligand interpenetration which is enhanced by pressure and leads to increased rate constants is apparently required. $Mn(CNC(CH_3)_3)_6^{2+/3+}$ and $Mn(CNC_6H_{11})_6^{2+/3+}$ were studied as a function of solvent in a large series of solvents and solvent mixtures. The $\Delta V^\ddagger$ remained in the range of -9 to $-22\ cm^3\ mol^{-1}$. Predictions based on a Marcus model, as presented by Swaddle, and consideration of ion pairing as only changing the charge on the complexes, led to the conclusion that much of the variation that would have been expected was attenuated by ion pairing. Added salt, 0.2 to 0.7 m, produced no resolvable effect in MeCN.

Two studies of cross-reactions are available, both involving $Co(dioximate)_3(BX)_2^{0/+}$ complexes (Table 2: 2, 5–7, 12, 13, 17–19) studied by the high pressure stopped-flow method. The first paper presented eight reactions involving the reduction of Co(III) clathrochelates by ferrocene or 1,1′-dimethylferrocene in acetonitrile, one reaction was also studied in the reverse direction, two reactions were further studied as a function of solvent and added salt. Studying a cross-reaction instead of a self-exchange reaction has added complexity, including the possibility that the equilibrium constant for the reaction is pressure-dependent, but it also allows studies such as the salt dependence to be done which are difficult in most self-exchange reactions and it allows extension of the Marcus cross-reaction relationship to the correlation of volumes of activation and the prediction of volumes of activation for the self-exchange process when one self-exchange and the cross-reaction volume of activation are known as well as the volume of reaction.

$$\Delta V_{12}^\ddagger = \frac{(\Delta V_{11}^\ddagger + \Delta V_{22}^\ddagger + \Delta V^0)}{2} \quad (\text{for } K_{12} \approx 1)$$

The $\Delta V_{12}^\ddagger$ values obtained in this study ranged from -4 to $-14\ cm^3\ mol^{-1}$, generally becoming more negative with increasing reactant bulk. Again, negative values are not predicted from simple solvent electrostriction arguments and nor are most of the values predicted from the pressure dependence of the solvent reorganization term in

Marcus theory. It appears again that some ligand interpenetration and pressure-dependent electron transfer distance term contributes to making the $\Delta V^{\ddagger}$ negative. Solvent variation showed that acetonitrile and nitrobenzene gave comparable results, while acetone gave 3–8 $cm^3\ mol^{-1}$ more negative volumes of activation than acetonitrile. Four reactions were studied in dichloromethane with 0.1 M Bu_4NBF_4 and all gave $\Delta V^{\ddagger}_{12}$ values of -14 or $-15\ cm^3\ mol^{-1}$. The more negative values were attributed to the ion paired pathway. This was further investigated by a study of the added salt dependence of $\Delta V^{\ddagger}_{12}$ in acetonitrile. Here the ion pairing constant will decrease with pressure and both the ion paired and free ion paths must be considered. The variation observed, more negative $\Delta V^{\ddagger}$ values at 0.1 M salt and slightly less negative values at 0.4 and 0.5 M, could be fit to such a model.

The most recent study involved the oxidation of Co(II) clathrochelates with $Cr(CNdipp)_6^{2+}$, thus exploring a different charge type, and an oxidant of particularly high intrinsic reactivity. The results give positive volumes of activation, ranging from $+2$ to $+11\ cm^3\ mol^{-1}$, increasing with the size and number of phenyl rings on the clathrochelate. Further, $\Delta V^{\ddagger}$ showed a dependence on the concentration of added Bu_4NBF_4 similar in shape to, but smaller in magnitude than that observed for the reduction of Co(III) clathrochelates by ferrocene. In this case, however, the rate constant at ambient pressure was insensitive to the concentration of added salt. This is the only case, except for reactions in aqueous solution between oppositely charged ions and some atom/electron transfer reactions, for which a positive volume of activation is observed. This is the expected result if the primary contribution to $\Delta V^{\ddagger}$ is solvent release brought on by the decrease in charge density on the formation of the precursor complex from a charged and a neutral reactant. If the negative $\Delta V^{\ddagger}$ values obtained for the ferrocene reductions of the Co(III) clathrochelates were due to an increase in rate constant brought about by a pressure-induced decrease in electron transfer distance, then this factor must have overcome the positive contribution to $\Delta V^{\ddagger}$ from solvent release. Further, the observation of a positive $\Delta V^{\ddagger}$ for the $Cr(CNdipp)_6^{2+}$ reductions must then indicate that either pressure does not decrease the electron transfer distance, or that these reactions are adiabatic and do not benefit, through improved donor/acceptor orbital overlap, from decreased electron transfer distance. The latter interpretation is consistent with the high self-exchange reactivity of $Cr(CNdipp)_6^{0/+/2+}$ and their insensitivity to added salt, as well as the insensitivity of the $Cr(CNdipp)_6^{2+}$ oxidations of the clathrochelates to added salt.

The results of some studies of halogen/electron transfer are presented in Table 4. Possible mechanisms for such reactions include X^+ transfer, or X and one electron transfer in the opposite direction, or X^- and two electron transfer in the opposite direction. For the current purpose, the most important limitation is that the reactions are assumed to take place via a halogen-bridged transition state. This is supported by the processes occurring in the absence of free halide and without decomposition of the halogenated species. The most striking result is the solvent dependence of $\Delta V^{\ddagger}$ for $Os(cp)_2/[Os(cp)_2I]CF_3SO_3$, which ranges from -8 and $-5\ cm^3\ mol^{-1}$ for

CD_3CN and CH_3NO_2 as solvent to 0 cm^3 mol^{-1} for $(CD_3)_2SO$ and 10 cm^3 mol^{-1} for $(CD_3)_2CO$. There should be no particular concern about a variation in adiabaticity for any electron transfer component to these reactions, so the variation must reflect changes in the contribution to $\Delta V^\ddagger$ from the formation of the bridged precursor complex and the release of solvent required in forming the bridge. This effect seems to be particularly pronounced for the iodo system, since the $Ru(cp)_2$/$[Ru(cp)_2Br]CF_3SO_3$ reaction shows little if any dependence of $\Delta V^\ddagger$ on solvent, in a more limited series of solvents.

C. CONCLUSIONS

Outer-sphere electron transfer reactions in non-aqueous solvents are just starting to be thoroughly investigated. The range of metal ion oxidation states, ligand structures, and complex geometries available are much broader than in the more thoroughly studied aqueous systems. However, the charge types and, so far, the range of reactivity, are not so diverse as for the aqueous reactions. The organometallic reactions are particularly rapid, and expose factors such as solvent dynamics and diffusion effects. The influence of the solvent and of the ionic strength and ion pairing, are highly interrelated and make it difficult to separate the various contributions. Of major importance in separating the factors is the future establishment of the concentrations, lifetimes, and structures of the ion paired species. The influence of ion pairing, typically an inhibitory effect, is probably also a contributor to aqueous reactivity but it is seldom observed because of the larger affect of ionic strength on electrostatic interactions between ionic reactants. The interpretation of $\Delta V^\ddagger$ measurements is progressing, and it appears that $\Delta V^\ddagger$ is strongly influenced by the need to bring reactants close together when the reactions are non-adiabatic. Further, the displacement of tightly associated solvents is also a major contribution in some cases. Besides attempting to define ion paired species, further work should investigate slower reactions in order to further study the $\Delta V^\ddagger$ of non-adiabatic reactions, and continue to investigate important types of organometallic structures involved in electron transfer reactions such as metal ion cluster compounds and highly delocalized systems that involve ligand-centered electron transfer.

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REFERENCES

1 C. Creutz, R.G. Linck and N. Sutin, in J.J. Zuckerman (Ed.), Inorganic Reactions and Methods, Vol.15, VCH, Deerfield Beach, Fl, 1991, pp. 3–87.
2 M.J. Weaver, Chem. Rev., 92 (1992) 463.
3 G.E. McManis, R.M. Nielson, A. Gochev and M.J. Weaver, J. Am. Chem. Soc., 111 (1989) 5533.
4 R.M. Nielson, M.N. Golovin, G.E. McManis and M.J. Weaver, J. Am. Chem. Soc., 110 (1988) 1745.
5 R.M. Nielson, G.E. McManis, L.K. Safford and M.J. Weaver, J. Phys. Chem., 93 (1989) 2152.
6 R.M. Nielson, G.E. McManis, M.N. Golovin and M.J. Weaver, J. Phys. Chem., 92 (1988) 3441.
7 E.K. Byrne and K.H. Theopold, J. Am. Chem. Soc., 111 (1989) 3887.
8 J.D. Protasiewicz, K.H. Theopold and G. Schulte, Inorg. Chem., 27 (1988) 1133.
9 T. Saji and S. Aoyagui, Bull. Chem. Soc. Jpn., 46 (1973) 2101.
10 K.A. Anderson and S. Wherland, Inorg. Chem., 29 (1990) 3822.
11 K.A. Anderson and S. Wherland, Inorg. Chem., 28 (1989) 601.
12 T.T. Li and C.H. Brubaker, Jr., J. Organomet. Chem., 216 (1981) 223.
13 H. Doine, Y. Yano and T.W. Swaddle, Inorg. Chem., 28 (1989) 2319.
14 D.K. Coggin, J.A. Gonzalez, A.M. Kook, C. Bergman, T.D. Brennan, W.R. Scheidt, D.M. Stanbury and L.J. Wilson, Inorg. Chem., 30 (1991) 1125.
15 J.A. Goodwin, D.M. Stanbury, L.J. Wilson, C.W. Eigenbrot and W.R. Scheidt, J. Am. Chem. Soc., 109 (1987) 2979.
16 M. Chan, J.B. DeRoos and A.C. Wahl, J. Phys. Chem., 77 (1973) 2163.
17 M. Chan and A.C. Wahl, J. Phys. Chem., 82 (1978) 2542.
18 D.M. Triegaardt and A.C. Wahl, J. Phys. Chem., 90 (1986) 1957.
19 E.S. Yang, M. Chan and A.C. Wahl, J. Phys. Chem., 84 (1980) 3094.
20 K. Kirchner, S. Dang, M. Stebler, H.W. Dodgen, S. Wherland and J.P. Hunt, Inorg. Chem., 28 (1989) 3605.
21 E.S. Yang, M. Chan and A.C. Wahl, J. Phys. Chem., 79 (1975) 2049.
22 H. Doine and T.W. Swaddle, Inorg. Chem., 27 (1988) 665.
23 H. Doine and T.W. Swaddle, Can J. Chem., 68 (1990) 2228.
24 R.M. Nielson, J.P. Hunt, H.W. Dodgen and S. Wherland, Inorg. Chem., 25 (1986) 1964.
25 R.M. Nielson and S. Wherland, J. Am. Chem. Soc., 107 (1985) 1505.
26 M. Stebler, R.M. Nielson, W.F. Siems, J.P. Hunt, H.W. Dodgen and S. Wherland, Inorg. Chem., 27 (1988) 2893.
27 D.S. Matteson and R.A. Bailey, J. Am. Chem. Soc., 91 (1969) 1975.
28 R.M. Nielson and S. Wherland, Inorg. Chem., 25 (1986) 2437.
29 J.D. Gribble and S. Wherland, Inorg. Chem., 29 (1990) 1130.
30 M.A.S. Aquino, D.A. Foucher and D.H. Macartney, Inorg. Chem., 28 (1989) 3357.
31 M. Chan and A.C. Wahl, J. Phys. Chem., 86 (1982) 126.
32 W.S. Prow, S.K. Garmestani and R.D. Farina, Inorg. Chem., 20 (1981) 1297.
33 M.A. Murguia and S. Wherland, Inorg. Chem., 30 (1991) 139.
34 D. Borchardt and S. Wherland, Inorg. Chem., 25 (1986) 901.
35 J. Gribble and S. Wherland, Inorg. Chem., 28 (1989) 2859.
36 D. Borchardt, K. Pool and S. Wherland, Inorg. Chem., 21 (1982) 93.
37 K.A. Anderson and S. Wherland, Inorg. Chem., 30 (1991) 624.
38 N.D. Stalnaker, J.C. Solenberger and A.C. Wahl, J. Phys. Chem., 81 (1977) 601.

39 T.G. Braga and A.C. Wahl, J. Phys. Chem., 89 (1985) 5822.

40 D.H. Macartney, Inorg. Chim. Acta, 127 (1987) 9.

41 D.H. Macartney and S. Mak, Can J. Chem., 70 (1992) 39.

42 A.B.P. Lever, Inorg. Chem., 29 (1990) 1271.

43 T. Gennett, D.F. Milner and M.J. Weaver, J. Phys. Chem., 89 (1985) 2787.

44 S.A. Richert, P.K.S. Tsang and D.T. Sawyer, Inorg. Chem., 28 (1989) 2471.

45 E.K. Byrne and K.H. Theopold, J. Am. Chem. Soc., 109 (1987) 1282.

46 D.A. Bohling, J.F. Evans and K.R. Mann, Inorg. Chem., 21 (1982) 3546.

47 R.M. Nielson and S. Wherland, Inorg. Chem., 24 (1985) 1803.

48 D.H. Macartney, A. McAuley and O.A. Olubuyide, Inorg. Chem., 24 (1985) 307.

49 J.D.L. Holloway and W.E. Geiger, Jr., J. Am. Chem. Soc., 101 (1979) 2038.

50 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, Coord. Chem. Rev., 84 (1988) 85.

51 G.S. Patterson and R.H. Holm, Inorg. Chem., 11 (1972) 2285.

52 C.L. Schwarz, R.M. Bullock and C. Creutz, J. Am. Chem. Soc., 113 (1991) 1225.

53 K.A. Anderson, K. Kirchner, H.W. Dodgen, J.P. Hunt and S. Wherland, Inorg. Chem., 31 (1992) 2605.

54 K. Kirchner, L. Han, H.W. Dodgen, S. Wherland and J.P. Hunt, Inorg. Chem., 29 (1990) 4556.

55 K. Kirchner, H.W. Dodgen, S. Wherland and J.P. Hunt, Inorg. Chem., 28 (1989) 605.

56 K. Kirchner, H.W. Dodgen, S. Wherland and J.P. Hunt, Inorg. Chem., 29 (1990) 2381.

57 T.P. Smith, D.J. Iverson, M.W. Droege, K.S. Kwan and H. Taube, Inorg. Chem., 26 (1987) 2882.

58 M.D. Newton, K. Ohta and E. Zhong, J. Phys. Chem., 95 (1992) 2317.

59 R.C. Blackbourn and J.T. Hupp, Chem. Phys. Lett., 28 (1988) 399.

60 N.A. Lewis, Y.S. Obeng and W.L. Purcell, Inorg. Chem., 28 (1989) 2796.

61 N.A. Lewis and Y.S. Obeng, J. Am. Chem. Soc., 110 (1988) 2306.

62 J.C. Curtis, R.L. Blackbourn, K.S. Ennix, S. Hu, J.A. Roberts and J.T. Hupp, Inorg. Chem., 28 (1989) 3791.

63 R.L. Blackbourn and J.T. Hupp, J. Phys. Chem., 92 (1988) 2817.

64 R. Schmid, K. Kirchner and F.L. Dickert, Inorg. Chem., 27 (1988) 1530.

65 R. Schmid, K. Kirchner and V.N. Sapunov, Inorg. Chem., 28 (1989) 4167.

66 R. van Eldik, T. Asano and W.J. le Noble, Chem. Rev., 89 (1989) 549.

67 D.T. Tran, J.P. Hunt and S. Wherland, Inorg. Chem., 31 (1992) 2460.

68 T.W. Swaddle, Inorg. Chem., 29 (1990) 5017.

69 S. Wherland, Inorg. Chem., 22 (1983) 2349. The corrections required are: $B = 4.284\times10^{9}$ kg mol$^{-1/2}$m^{-1} and $(\partial \ln \varepsilon/\partial P)_T = 4.71\times10^{-10}$ Pa^{-1}.