TABLE VI

LIGAND FIELD SPECTRAL DATA[a]

Complex	$\lambda_{\max}$, cm.$^{-1}$	ϵ
$[NiS_4C_4(CF_3)_4]^{-2}$	12,900	18
$[PdS_4C_4(CF_3)_4]^{-2\,b}$	16,950	40
$[((C_6H_5)_3P)_2NiS_2C_2(CF_3)_2]$	~15,200 (sh)	~70
$[((C_6H_5)_3P)_2PdS_2C_2(CF_3)_2]$	19,050	84
$[((C_6H_5)_3P)_2PtS_2C_2(CF_3)_2]$	25,320	141
$[((C_6H_5)_3P)_2NiS_2C_2(CN)_2]$	14,900	<100
$[((C_6H_5)_3P)_2PdS_2C_2(CN)_2]$	19,050	74

[a] Measured in dichloromethane solution unless otherwise noted. [b] Measured in DMF.

anions is the much reduced separation of $\sigma^*(b_{1g})$ and the next highest d-type orbital compared to the tetrahalo or tetracyano complexes.[41] A slightly smaller energy separation has already been observed in $[NiS_4C_4(CN)_4]^{-2}$.[12a] It is tempting to place $R_2C_2S_2^{-2}$ near the weak end of the spectrochemical series for planar complexes. However, this cannot be meaningfully done until d-orbital energy differences have been firmly established in a series of d^8 planar complexes. The designation of such energies requires consistent assignment of ligand field transitions, concerning which disagreement exists.[41,42] An overriding consideration may be that the ligand field is in fact quite strong due to significant covalency in the metal–ligand π- and σ-bonds. A particular feature of this ligand system could be the participation in relatively strong in- and out-of-plane π-bonding which promotes the $\pi^*_{1,2}$ (b_{2g} or b_{3g}) and $\pi^*(a_g)$ orbitals closer to $\sigma^*(b_{1g})$ than, for example, in $M(CN)_4^{-2}$ complexes. In these complexes in-plane π-bonding may be less important, and the out-of-plane π-orbitals (d_{xz} and d_{yz}) are believed to be the most stable metal orbitals.[41] These π-bonding effects could then account for the relatively small transition energies observed in the dianions. Although the ligand field may be weak in the sense of a spectrochemical series, it is believed that the metal–ligand bonds are quite robust.[44]

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(41) (a) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963); (b) H. B. Gray and C. J. Ballhausen, *ibid.*, **85**, 260 (1963).

(42) If the assignment of the lowest energy spin-allowed transition in MX_4^{-2} and $M(CN)_4^{-2}$ complexes is accepted to be $\pi^*(b_{2g}) \rightarrow \sigma^*(b_{1g})$,[41b] and if the analogous assignment, $\pi^*(a_g) \rightarrow \sigma^*(b_{1g})$, is made for the dianions, the following orbital energy differences Δ_1 are obtained: Ni, 16,400 cm.$^{-1}$, Pd, 19,400 cm.$^{-1}$. These values were calculated using $F_2 = 10F_4 = 1000$ cm.$^{-1}$ (Ni), 700 cm.$^{-1}$ (Pd). Comparison with other Δ_1 values [41b] gives the series $Br^- < Cl^- \lesssim (CF_3)_2C_2S_2^{-2} << CN^-$ for Pd. Taking the same assignment for type **3** complexes, the presence of triphenylphosphine increases Δ_1. In other complexes it has been found that $Cl^- < (C_6H_5)_3P$.[43]

(43) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

(44) NOTE ADDED IN PROOF.—The structure of $[(n\text{-}C_4H_9)_4N][CuS_4C_4(CN)_4]$ has recently been completed and shows the monoanion to be planar.[12b] The ions $[MS_4C_4(CN)_4]^-$ form isomorphous crystals.[2] This result tends to confirm the general supposition that electron-transfer reactions between mono- and dianions involve planar species.

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Kinetics of Fast Electron-Transfer Reactions

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The temperature-jump method has been used to determine the rate constants for a series of rapid, "outer-sphere" oxidation–reduction reactions of the type

$$\mathrm{ox_1}^{2-} + \mathrm{red_2}^{2+} \underset{k_r\,(M^{-1}\,\mathrm{sec.}^{-1})}{\overset{k_f\,(M^{-1}\,\mathrm{sec.}^{-1})}{\rightleftharpoons}} \mathrm{red_1}^{3-} + \mathrm{ox_2}^{3+}$$

The symbol $\mathrm{ox_1}^{2-}$ represents $IrCl_6^{2-}$, $IrBr_6^{2-}$, or $RhCl_6^{2-}$. The symbol $\mathrm{red_2}^{2+}$ represents a substituted phenanthroline or bipyridine complex of iron(II) or ruthenium(II). It has been found that a diffusion-controlled limit of about 2×10^9 (M^{-1} sec.$^{-1}$) is approached when the equilibrium quotient is equal to or greater than unity. The rate of reaction for a given electron donor is then independent of the relative acceptor strength once the diffusional limit has been reached. Evidence was also found that steric restrictions can affect a diffusion-controlled electron-transfer reaction, causing the rate constant to fall somewhat short of the theoretical value.

As indicated by experiments utilizing the rapid mixing technique, electron transfer between large metal complexes is rapid.[1] The reactions are often so rapid that in many cases only the lower limits of rate constants are obtained. By applying the temperature-jump method it has been possible to determine the rate constants for electron-transfer reactions of the type

$$\mathrm{ox_1}^{2-} + \mathrm{red_2}^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{red_1}^{3-} + \mathrm{ox_2}^{3+}$$

where k_f (M^{-1} sec.$^{-1}$) and k_r (M^{-1} sec.$^{-1}$) are the bimolecular forward and reverse rate constants, respectively. The symbol $\mathrm{ox_1}^{2-}$ represents $IrCl_6^{2-}$, $IrBr_6^{2-}$, or $RhCl_6^{2-}$. The symbol $\mathrm{red_2}^{2+}$ represents a complex of iron(II) or ruthenium(II).

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(1) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

The temperature-jump method is one of the relaxation methods.[2] A small perturbation is rapidly applied to the equilibrium system under study, and the subsequent shift to a new equilibrium is then measured. In this study, all relaxation spectra were characterized by one relaxation time, τ, given in eq. 1 where K is the

$$1/\tau = 2C_0k_r\sqrt{K} \tag{1}$$

equilibrium quotient and C_0 is the initial molar concentration. This simplified expression is obtained for those reaction mixtures which have equal initial stoichiometric concentrations, C_0, of ox_1^{2-} and red_2^{2+}.[3]

Experimental

The temperature-jump apparatus used for the present experiments was essentially the same as that described by Czerlinski and Eigen.[4] The temperature jump, of about 7°, was caused by discharging a 0.1-μf. capacitor, charged to approximately 25 kv., through the solution. The heating time was about 5 μsec., for ionic strength $\mu = 0.1$ M. The initial temperature of about 3° was controlled to within $\pm 2°$ by circulating water from an ice bath through the temperature-jump cell compartment.

The light source was a G.E. T3Q/1CL-100W tungsten filament lamp powered by a suitably stabilized voltage supply. The light passed through a monochromator; however, unlike earlier arrangements, the light beam was not split, but passed directly from the monochromator through the cell and impinged upon an RCA 1P28 photomultiplier (*cf.* Hammes and Steinfeld[5] for a more detailed description of the single-beam method). The change in absorbancy (optical density), which occurs as the equilibrium is shifted after the temperature jump, is oscilloscopically recorded and photographed. The shift could be followed directly, without employing coupled indicators, by utilizing the fact that the reactants absorbed considerably more light than did the products at 500 mμ (*cf.* Table I).

TABLE I

OPTICAL ABSORPTION CHARACTERISTICS

Metal complex	$\lambda_{\max}$, mμ	$\epsilon_{\max}$, mole^{-1} cm.$^{-1}$
$Fe(DMP)_3^{2+}$	512	12,400
$Fe(DMBPY)_3^{2+}$	529	8,470
$IrCl_6^{2-}$	490	3,920
$Fe(DMP)_3^{3+}$	600	550
$Fe(DMBPY)_3^{3+}$	543	350
$IrCl_6^{3-}$	415	76
$RhCl_6^{2-}$	390	1,320
$RhCl_6^{3-}$	505	150
$Ru(PH)_3^{2+}$	450	3,100
$Ru(PH)_3^{3+}$	415, 445	1,200
$IrBr_6^{2-}$	585	3,800
$IrBr_6^{3-}$	440	210
$Fe(4,7\text{-}DMP)_3^{2+}$	512	11,700
$Fe(4,7\text{-}DMP)_3^{3+}$	562	1,200

Potassium hexachloroiridate, potassium hexabromoiridate, and sodium hexachlororhodite–18-water from Platinum Chemicals Co.; ferrous 5,6-dimethyl-1,10-phenanthroline [$Fe(DMP)_3^{2+}$] sulfate, ferrous 4,4′-dimethyl-2,2′-bipyridine [$Fe(DMBPY)_3^{2+}$] perchlorate, ruthenous 1,10-phenanthroline [$Ru(PH)_3^{2+}$] dichloride, and 4,7-dimethyl-1,10-phenanthroline [4,7-DMP] monohydrate from the G. Frederick Smith Chemical Co.; and ferrous sulfate heptahydrate from the J. T. Baker Chemical Co. were used without further purification. Reagent grade potassium nitrate from the Fisher Scientific Co. was used as an inert electrolyte to maintain a constant ionic strength in all experiments except those involving rhodium. In this case reagent grade sodium chloride from the same company was used to establish an ionic strength of 0.05 M. All solutions were prepared with doubly distilled water.

It was found that each reaction solution containing K_2IrCl_6 as well as the stock solution of K_2IrCl_6 decomposed upon standing. The reason was that the oxidized forms of both the iridium and the iron complexes were unstable compared to their respective reduced states. However, this instability did not interfere with the measurements, since the rates of decomposition were slow compared to the time required for the experiment. As an added precaution, fresh solutions of both the reaction and the stock K_2IrCl_6 solutions were prepared for each measurement.

The equilibrium quotients for the reactions studied were determined spectrophotometrically, using a Beckman DU spectrophotometer. These measurements were carried out in a temperature controlled room. The relevant absorption characteristics of the various reaction species are given in Table I.

Results

The results of the equilibrium quotient determinations are given in Table II.

TABLE II

EQUILIBRIUM DATA

Reaction	μ, M	$K_{10°}$
(A) $IrCl_6^{2-} + Fe(DMP)_3^{2+}$	0.10	0.0764
(B) $IrCl_6^{2-} + Fe(DMBPY)_3^{2+}$	0.10	4.85
(C) $IrBr_6^{2-} + Fe(4,7\text{-}DMP)_3^{2+}$	0.10	0.083
(D) $IrBr_6^{2-} + Fe(DMP)_3^{2+}$	0.30	0.061
(E) $IrBr_6^{2-} + Fe(DMBPY)_3^{2+}$	0.10	0.320
(F) $RhCl_6^{2-} + Ru(PH)_3^{2+}$	0.05	9.08

The results of the kinetic determinations are listed in Table III. The rate constants were calculated from (1) except as noted.

Each relaxation time is an average of three photographic determinations, for which agreement is within ±10%. The low extinction coefficients of the species in reaction F necessitated the use of relatively high concentrations in order to obtain an observable effect. Thus the chemical relaxation time and the instrumental temperature rise time overlapped, precluding a concentration dependence study, as in the other reactions. A few experiments with ferrous 4,7-dimethyl-1,10-phenanthroline sulfate yielded results similar to those obtained by Halpern, Legare, and Lumry[6] for this system. Their values have been included in Table III in order to facilitate comparison (*vide infra*).

Discussion

Since these rate constants are very large, we shall first discuss them in terms of the fastest possible bimolecular reactions in solution; namely, diffusion limited reactions. The rate constant for such a reaction can be calculated from an equation derived by Debye.[7] For reactants of the size,[6] charge type, and

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[2] M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., John Wiley and Sons, New York, N. Y., 1963.

[3] *Cf.* ref. 2 for an exact derivation of τ for reactions of the type $A + B \rightleftharpoons C + D$.

[4] G. Czerlinski and M. Eigen, *Z. Elektrochem.*, **63**, 652 (1959).

[5] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[6] J. Halpern, R. J. Legare, and R. Lumry, *ibid.*, **85**, 680 (1963).

[7] P. Debye, *Trans. Electrochem., Soc.*, **82**, 265 (1942).

TABLE III

SINGLE-STEP ELECTRON-TRANSFER RATE CONSTANTS

Temp., °C.	μ, M	$C_0 \times 10^5$, M	$K_{10°}$	τ, μsec.	k_f, M^{-1} sec.$^{-1}$	k_r, M^{-1} sec.$^{-1}$
		(A) $IrCl_6^{2-} + Fe(DMP)_3^{2+} \rightleftharpoons IrCl_6^{3-} + Fe(DMP)_3^{3+}$				
10	0.10	3.0	0.0764	21	2.2×10^8	2.8×10^9
10	0.10	2.0	0.0764	33	2.1×10^8	2.7×10^9
10	0.10	1.0	0.0764	61	2.3×10^8	2.9×10^9
				Av.	$(2.2 \pm 0.2) \times 10^8$;	$(2.8 \pm 0.3) \times 10^9$
		(B) $IrCl_6^{2-} + Fe(DMBPY)_3^{2+} \rightleftharpoons IrCl_6^{3-} + Fe(DMBPY)_3^{3+}$				
10	0.10	5.0	4.85	23	9.6×10^8	2.0×10^8
10	0.10	3.75	4.85	31	9.6×10^8	2.0×10^8
10	0.10	2.5	4.85	45	9.6×10^8	2.0×10^8
				Av.	$(9.6 \pm 1.0) \times 10^8$;	$(2.0 \pm 0.2) \times 10^8$
10	0.10	$C_0(Ir) = 3.0^3$ $C_0(Fe) = 2.5$	4.85	38	1.07×10^9	2.2×10^8
		(C) $IrBr_6^{2-} + Fe(DMP)_3^{2+} \rightleftharpoons IrBr_6^{3-} + Fe(DMP)_3^{3+}$				
10	0.30	4.0	0.061	16	1.9×10^8	3.2×10^9
10	0.30	3.0	0.061	24	1.7×10^8	2.8×10^9
10	0.30	2.0	0.061	37	1.7×10^8	2.8×10^9
				Av.	$(1.8 \pm 0.2) \times 10^8$;	$(2.9 \pm 0.3) \times 10^9$
		(D) $IrBr_6^{2-} + Fe(4,7\text{-}DMP)_3^{2+} \rightleftharpoons IrBr_6^{3-} + Fe(4,7\text{-}DMP)_3^{3+}$				
10	0.10	4.0	0.083	22	1.7×10^8	2.0×10^9
10	0.10	3.0	0.083	31	1.6×10^8	1.9×10^9
10	0.10	2.0	0.083	50	1.4×10^8	1.7×10^9
				Av.	$(1.6 \pm 0.2) \times 10^8$;	$(1.9 \pm 0.2) \times 10^9$
		(E) $IrBr_6^{2-} + Fe(DMBPY)_3^{2+} \rightleftharpoons IrBr_6^{3-} + Fe(DMBPY)_3^{3+}$				
10	0.10	3.0	0.320	13	7.4×10^8	2.3×10^9
10	0.10	2.0	0.320	22	6.4×10^8	2.0×10^9
10	0.10	1.0	0.320	41	6.7×10^8	2.1×10^9
				Av.	$(6.8 \pm 0.7) \times 10^8$;	$(2.1 \pm 0.2) \times 10^9$
		(F) $RhCl_6^{2-} + Ru(PH)_3^{2+} \rightleftharpoons RhCl_6^{3-} + Ru(PH)_3^{3+}$				
10	0.05	7.75	9.08	8	2.5×10^{9}[a]	2.7×10^{8}[a]
		(G) (ref. 6) $IrCl_6^{2-} + Fe(4,7\text{-}DMP)_3^{2+} \rightleftharpoons IrCl_6^{3-} + Fe(4,7\text{-}DMP)_3^{3+}$				
10	0.10		1.2		Av. 1.2×10^9	1.0×10^9

[a] Values of rate constants represent lower limits.

mobility (*ca.* 100 cm.^{2} (intern. ohm)$^{-1}$ equiv.$^{-1}$) reported on here $k_f = 6 \times 10^{10}$ M^{-1} sec.$^{-1}$, $k_r = 8 \times 10^{10}$ M^{-1} sec.$^{-1}$ at 10° and zero ionic strength. An appreciable ionic strength serves to retard the rate of the reaction, hence the diffusion limited rate constant at an ionic strength around 0.1 M would be somewhat lower.

Therefore, if we first consider reactions C, D, E, and F, it is apparent that for the hexabromoiridate reactions the reverse rate constants are close to the diffusional limit, whereas the forward rate constant is at the diffusional limit for the hexachlororhodate reaction. In a gross fashion, this result can be correlated with the difference in equilibrium quotient, which is less than unity for C, D, and E and greater than unity for F. Closer comparison cannot be made, however, since reaction C is at a different ionic strength, and the electron donor in F is not the same as that in D and E. A more significant comparison can be made for reactions A, B, and G, since the same electron donor ($IrCl_6^{3-}$) is involved in all of the reverse reactions. For reactions A, B, and G only k_f for A and k_r for B are less than diffusion limited, all the other rate constants for these three systems are close to being diffusion limited.

To understand this result, we utilize the fact that when the rate of the electron transfer for a given donor closely approaches the diffusion limit, the rate of the reaction becomes independent of the relative acceptor strength. The rate of the reverse reaction is then linearly proportional to the equilibrium constant in the supporting medium. Thus, we note that the free energy of the reaction, as expressed in the equilibrium quotient (Table II), is "spontaneous" for the reverse reaction of A. The opposite situation is represented by B. For the system studied by Halpern, Legare, and Lumry (G), the equilibrium quotient is essentially unity, resulting in the intermediate case, where both reactions are close to being diffusion controlled. The effect of free energy is, therefore, of greater significance in determining the rate than the coulombic attraction, which is greater for the reverse reaction in each case. This effect can also be derived from a theory by Marcus,[8] which may be applied to very rapid, "outer-sphere" electron-transfer reactions, for which the equilibrium quotient does not deviate too much from unity.

According to this theory, the rate constant for an elementary electron-transfer reaction is

$$k = Z \exp[-(w + m^2\lambda)/RT] \quad (M^{-1}\text{ sec.}^{-1}) \qquad (2)$$

where Z is the collision frequency between two uncharged particles in solution (10^{11} M^{-1} sec.$^{-1}$), w is the coulombic work term, and $m^2\lambda$ represents the work necessary to reorganize the inner and outer coordination shells of the reactants. Substitution of the

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[8] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963) (*cf.* for previous references).

measured k values and calculated w values into (2) yields values of $m^2\lambda$ ranging from 4 to 6.8 kcal./mole. Thus, the reorganizational energies are small (*cf.* ref. 1), which is reasonable in view of the rapidity of the reactions. Since w is the same for this series of reactions in any one direction, the variations in rate constant are due to the contributions of the different free energies to the $m^2\lambda$ term.

Additional confirmation of the Marcus theory is possible when the rate constants for the exchange reactions of the two oxidation–reduction couples in each cross reaction are known.[9] In the cases of the $IrCl_6^{3-}$–$IrCl_6^{2-}$ and $Fe(DMP)_3^{2+}$–$Fe(DMP)_3^{3+}$ exchange reactions, for which some data exist, only lower limits on the rate constants have been reported. Thus, we calculate a value of about 2.5×10^4 M^{-1} sec.$^{-1}$ depending upon ionic radius for either exchange reaction, but the experimental values are $>3 \times 10^2$ and $>2 \times 10^3$ M^{-1} sec.$^{-1}$ for the iridium[10] and iron[11] systems, respectively. This comparison is, therefore, essentially in agreement with the Marcus theory.

Finally, it is to be noted that for the compounds studied, large changes in equilibrium quotient (and correspondingly in the E^0 values of the oxidation–reduction couples) result from the substitution of methyl groups on the chelating agent. To see if this substitution has a further steric effect on the rate, an experiment was carried out with hexabromoiridate and tris(bypyridine)iron(II). These ions are closer to being spherical than any of the others, and would therefore present the least steric hindrance. For a concentration as low as 10^{-5} M, however, it was not possible to observe a chemical relaxation, although a sizable "jump" was detected. The relaxation occurs at a time shorter than 5 μsec., which corresponds to a reverse rate constant around 10^{10} M^{-1} sec.$^{-1}$. Thus, even for these rapid electron-transfer reactions, there are severe spatial restrictions, the result of which is to cause the diffusion controlled rate constant to fall somewhat short of the theoretical limiting value.

Acknowledgment.—This investigation was supported by PHS research grant GM-08893-03 from the National Institute of General Medical Sciences, Public Health Service.

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[9] R. Campion, N. Purdie, and N. Sutin, *J. Am. Chem. Soc.*, **85**, 3528 (1963).

[10] E. N. Sloth and C. S. Garner, *ibid.*, **77**, 1440 (1955).

[11] L. Eimer and A. I. Medalis, *ibid.*, **74**, 1592 (1952).

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Kinetics of the Acid and Base Hydrolyses of the Chloropentaammineruthenium(III) Ion[1]

BY JOHN A. BROOMHEAD, FRED BASOLO, AND RALPH G. PEARSON

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A study of the rates of hydrolysis of $[Ru(NH_3)_5Cl]^{2+}$ shows that base hydrolysis is very much faster than acid hydrolysis, the ratio of rate constants being more than 10^6. This result resembles that for cobalt(III) complexes, but is quite different from the behavior of rhodium(III) and chromium(III) complexes. The rates for the different metal ions can be explained satisfactorily by an SN1CB mechanism for base hydrolysis. The data for acid hydrolysis are not as well explained by a single mechanism. The equilibrium constant for the acid hydrolysis has been determined as a function of temperature. The aquopentaammineruthenium(III) ion is a relatively strong acid with a pK_a of 4.2 ± 0.1 at 25°.

Reactions of ruthenium complexes, in particular those possessing nonchelate ligands, are often complicated by disproportionation, olation, and precipitation phenomena. The formation of the well known ruthenium red cation is a pertinent example.[2] It is not surprising, therefore, that few mechanistic studies have been made on these systems. Details of the acid and base hydrolysis reactions for complexes of the type $[Ru(NH_3)_5X]^{2+}$ where X is a replaceable anionic ligand are a desirable prerequisite to the general investigation of substitution reactions of ruthenium(III). In this work acid and base hydrolysis studies of the chloropentaammineruthenium(III) complex are reported together with equilibrium data for acid hydrolysis. A recent report[3] of electron-transfer processes in ruthenium(II) and ruthenium(III) ammine complexes included an estimate of the equilibrium constant and half-life for the acid hydrolysis of the $[Ru(NH_3)_5Cl]^{2+}$ cation, but there have been no detailed studies reported.

In preliminary experiments it was found that substitution of the bromide ligand in $[Ru(NH_3)_5Br]^{2+}$ was faster than for the corresponding chloro complex. Attempts were made to follow the reaction rate by spectrophotometric and titrimetric methods in various phosphate and borate buffers but reproducibility was poor and depended upon the nature and concentration

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[1] Supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-1087.

[2] J. M. Fletcher, *et al.*, *J. Chem. Soc.*, 2000 (1961).

[3] J. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).