

oxide over a period of 2 hr. The reaction was exothermic and the temperature was permitted to rise to room temperature toward the end of the addition.

The contents of the autoclave then were transferred with water to a 2-liter three-necked round-bottomed flask. One hundred milliliters of water and 100 ml. of concentrated hydrochloric acid were added, and the chromium carbonyl was co-distilled with water at atmospheric pressure with stirring. The yield of chromium carbonyl recovered was 35.2 g. (80%), m.p. 152–155°.

Essentially the same procedure was employed for the preparation of molybdenum carbonyl and tungsten carbonyl

except for the quantities of the reactants, which are shown in Table II.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, STATE UNIVERSITY OF NEW YORK, LONG ISLAND CENTER, OYSTER BAY, AND BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK]

The Kinetics of the Oxidation of Iron(II) Ions and of Coordination Complexes^{1a}

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The kinetics of the oxidation of iron(II) ions by $\text{Ag}(\text{phen})_2^{+2}$, $\text{Ag}(\text{dipy})_2^{+2}$, $\text{Ru}(\text{dipy})_3^{+3}$, $\text{Os}(\text{dipy})_3^{+3}$ and IrCl_6^{-2} have been investigated in perchloric and sulfuric acid solutions. The rates of oxidation of the iron(II) ions were found to increase with the standard free energy changes of the reactions. The oxidation of iron(II) ions by IrCl_6^{-2} is more rapid than the oxidation by $\text{Fe}(\text{phen})_3^{+3}$ although the standard free energy changes of the two reactions are identical. The increased rate of the former reaction was found to be due to a less negative entropy of activation. The reactions between positively-charged complexes as well as those between oppositely-charged complexes proceed with rate constants which are larger than $10^8 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. On the other hand the oxidations of ferrocyanide ions by IrCl_6^{-2} , MnO_4^- and OsCl_6^{-2} are considerably slower and increase with the standard free energy changes of the reactions. The oxidation-reduction reactions between the complex ions are discussed in terms of the Marcus theory of these reactions, and the free energies required to reorganize the inner coordination shells of the various complexes are estimated.

Introduction

Recent investigations^{2,3} of the kinetics of the oxidation of iron(II) ions by substituted 1,10-phenanthroline complexes of iron(III) ions have shown the existence of a linear relationship between the free energies of activation and the standard free energy changes of the reactions. It was found that the rate constants determined for the oxidation of iron(II) ions by the 4,4'-dimethyl-2,2'-dipyridine, 2,2'-dipyridine and 2,2',2''-tripyridine complexes of iron(III) did not satisfy the linear relationship found for the phenanthroline complexes. We have extended these studies to other reactions between oxidizing and reducing agents, which differ in their sizes, structures and charges.

Sheppard and Wahl⁴ have reported that the permanganate-manganate isotopic exchange reaction is catalyzed by ferrocyanide ions. They suggested that this catalysis could be explained in terms of the permanganate-ferrocyanide oxidation-reduction reaction and calculated a second order rate constant of approximately $10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ for this reaction. Such a rate can be measured with a flow apparatus.

Experimental

Chemicals.—Solutions of ferrous perchlorate and the substituted phenanthroline and dipyridine complexes of iron(III) were prepared as previously described.^{2,3} Tris-(2,2'-dipyridine)-osmium(II) perchlorate was prepared from osmium tetroxide according to the procedures described by Dwyer and Hogarth⁵ and by Burstall, Dwyer and Gyrfas.⁶

Bis-(1,10-phenanthroline)-silver(II) nitrate and bis-(2,2'-dipyridine)-silver(II) nitrate were prepared by dissolving silver(II) oxide in 6*F* nitric acid which had been cooled to about -10° . Excess base (1,10-phenanthroline and 2,2'-dipyridine, respectively) was added, and the color of the solutions changed from deep brown to deep red. More nitric acid was added and the solutions cooled in a salt-water-ice bath, whereupon the nitrate salts of the respective silver(II) complex ions crystallized. The crystals were filtered off, rapidly washed with cold water and dried in air. The preparation of the stock solutions for the kinetic runs was accompanied by appreciable reduction to the silver(I) state. A sample of ammonium hexachloroiridium(IV), prepared from hexachloroiridic acid and ammonium chloride, was kindly donated by Dr. Garman Harbottle of Brookhaven National Laboratory. The following compounds were used without further purification: tris-(2,2'-dipyridine)-ruthenium(II) chloride (G. Frederick Smith Chemical Co.), potassium permanganate (Baker Analyzed Reagent), potassium hexacyanoiron(II) (Baker Analyzed Reagent), ammonium hexachlorosmium(IV) (Johnson, Mathey and Co.), perchloric acid (Baker Analyzed Reagent) and sulfuric acid (Baker and Adamson). Tris-(2,2'-dipyridine)-osmium(III) and tris-(2,2'-dipyridine)-ruthenium(III) were prepared from the corresponding osmium(II) and ruthenium(II) complexes by oxidation with lead dioxide and sulfuric acid.

Triply-distilled water was used in preparing the solutions for the kinetic measurements.

Procedure.—The reactions were followed using the rapid-mixing and flow apparatus which has been previously described.^{2,3} The "continuous flow" rather than the "stopped flow" procedure was used to follow the faster reactions. Temperature was maintained by circulating water from a constant temperature bath through the jacket which housed the mixing chamber and flow tube and was constant to $\pm 0.1^\circ$. Activation energies were calculated from determinations of the rate constants at 15, 25 and 35°.

Results

The reactions were found to be first order with respect to each of the reactants by independent variations of the concentration of each reactant

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. (b) Summer student from Hollins College, Virginia.

(2) N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

(3) M. H. Ford-Smith and N. Sutin, *ibid.*, **83**, 1830 (1961).

(4) J. C. Sheppard and A. C. Wahl, *ibid.*, **79**, 1020 (1957).

(5) F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc., N. S. Wales*, **84**, 194 (1951).

(6) F. Burstall, F. P. Dwyer and E. Gyrfas, *J. Chem. Soc.*, 1953 (1950).

(7) M. H. Ford-Smith, N. Sutin and R. W. Dodson, to be published.

TABLE I
SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF
IRON(II) IONS BY VARIOUS COMPLEX IONS AT 25.0°

Oxidizing agent ^a	E ⁰ , volts	k(0.5 F HClO ₄), F ⁻¹ sec. ⁻¹	k(0.5 F H ₂ SO ₄), F ⁻¹ sec. ⁻¹	$\frac{k(0.5 F H_2SO_4)}{k(0.5 F HClO_4)}$
Ag(phen) ₂ ⁺²	1.7 × 10 ⁸	..
Ag(dipy) ₂ ⁺²	1.43 ^b	1.4 × 10 ⁸	..
Ru(dipy) ₂ ⁺³	1.27 ^c	7.2 × 10 ⁸
Fe(phen) ₃ ⁺³	1.06 ^d	3.7 × 10 ^{4b}	3.0 × 10 ^{4b}	8.1
IrCl ₆ ⁻³	1.06 ^e	3.2 × 10 ⁸
Fe(dipy) ₂ ⁺³	0.97 ^c	2.7 × 10 ^{4b}	2.2 × 10 ^{4b}	8.2
Fe(tripy) ₂ ⁺³	.93 ^f	8.5 × 10 ^{4b}	7.4 × 10 ^{4b}	8.7
Os(dipy) ₂ ⁺³	.83 ^g	1.43 × 10 ³	1.35 × 10 ⁴	9.4

^a phen = 1,10-phenanthroline; dipy = 2,2'-dipyridine; tripy = 2,2',2''-tripyridine. ^b E. Scrocco, G. Marmani and P. Mirone, *Boll. Sci. Fac. Chim. Ind. Bologna*, **8**, 119 (1950). ^c F. P. Dwyer, *J. Proc. Roy. Soc., N. S. Wales*, **83**, 134 (1949). ^d G. F. Smith and F. P. Richter, *Ind. Eng. Chem., Anal. Ed.*, **16**, 580 (1944). ^e F. P. Dwyer, H. A. McKenzie and R. S. Nyholm, *J. Proc. Roy. Soc., N. S. Wales*, **78**, 260 (1944). ^f F. P. Dwyer and E. C. Gyrfas, *J. Am. Chem. Soc.*, **76**, 6312 (1954). ^g F. P. Dwyer, N. A. Gibson and E. C. Gyrfas, *J. Proc. Roy. Soc., N. S. Wales*, **84**, 80 (1950). ^h Ref. 2. ⁱ Ref. 3.

over a range which was usually twofold or greater. Individual determinations differed from the mean by less than 10%. In Table I are given mean values of the second order rate constants determined at 25° for the oxidation of iron(II) ions by various complex ions in 0.50 F HClO₄ and in 0.50 F H₂SO₄. The formal oxidation potentials of the complex ions are also included in this table.

The free energy of activation, the activation energy and the entropy of activation for the oxidation of iron(II) ions by IrCl₆⁻² ions and by Fe(phen)₃⁺³ ions in 0.50 F HClO₄ are presented in Table II. Table III shows the second order rate constants for various oxidation-reduction reactions between complex ions as well as the formal oxidation potentials of the various ions. The reactions for which lower limits of the rate constant are given were complete within the time required for the reaction solution to reach the observation point. Using the known flow rates and dimensions of the flow tube this time was calculated to be eighteen milliseconds. Since the concentrations of the reagents were always less than 2 × 10⁻⁶ F, lower limits of 10⁸ F⁻¹ sec.⁻¹ were estimated for the rate constants assuming that reactions with half times greater than five milliseconds would have been detected.

TABLE II
FREE ENERGY OF ACTIVATION, ACTIVATION ENERGY AND ENTROPY OF ACTIVATION FOR THE OXIDATION OF IRON(II) IONS AT 25.0°

Reaction	ΔG*, kcal. mole ⁻¹	Ea*, kcal. mole ⁻¹	ΔS*, cal. deg. ⁻¹ mole ⁻¹
IrCl ₆ ⁻² -Fe(H ₂ O) ₆ ⁺²	8.6	1.9	-25.2
Fe(phen) ₃ ⁺³ -Fe(H ₂ O) ₆ ⁺² ^a	11.2	0.8	-37.2

^a N. Sutin and B. M. Gordon, ref. 2.

Discussion

Ferrous Ion Oxidations.—It can be seen from Table I that the second order rate constants for the oxidation of iron(II) ions tend to increase with the increasing formal oxidation potential of the

complex ions with the marked exception of the hexachloroiridium(IV) ion. Thus, the oxidation of ferrous ions by hexachloroiridium(IV) ions proceeds about a hundredfold faster than the oxidation by tris-(1,10-phenanthroline)-iron(III) ions although the standard free energy changes of the reactions are the same. As can be seen from Table II, the faster rate of the IrCl₆⁻²-Fe(H₂O)₆⁺² reaction is due to a more favorable entropy of activation. Several factors may be responsible for this increase in the entropy of activation. Since the activated complex formed from IrCl₆⁻² and Fe(H₂O)₆⁺² has zero charge, the ordering of the solvent molecules around the activated complex should be less than around the separate reactants and this will tend to make the entropy of activation less negative. On the other hand, the activated complex formed from Fe(phen)₃⁺³ and Fe(H₂O)₆⁺² has a high positive charge and may well be more strongly solvated than the separate ions. The value of this contribution to the entropy of activation is given approximately by⁸

$$\Delta S_{a1}^* = \frac{-e_1^* e_2^*}{r} \frac{\partial(1/D_s)}{\partial T}$$

where e_1^* and e_2^* are the charges on the reactants, and r is the distance between the centers of the reactants in the activated complex. D_s is the static dielectric constant of the medium. At infinite dilution this factor will tend to make the entropy of activation of the IrCl₆⁻²-Fe(H₂O)₆⁺² reaction about 22 cal. deg.⁻¹ mole⁻¹ more positive than the entropy of activation of the Fe(phen)₃⁺³-Fe(H₂O)₆⁺² reaction. However, this difference will be smaller at the ionic strength of the kinetic measurements.

Differences in the steric requirements might also be responsible for the different entropies of activation of the two reactions. The large negative entropy of activation of the Fe(phen)₃⁺³-Fe(H₂O)₆⁺² reaction can be explained in part by a necessity for the ferrous ion to penetrate the space between the phenanthroline groups in order to approach the ferric ion more closely for reaction. Such a steric requirement probably is less in the IrCl₆⁻²-Fe(H₂O)₆⁺² reaction.

All the oxidizing agents listed in Table I are low-spin complexes.^{9,10} Fe(phen)₃⁺³ has five electrons in the 3d_z level, while IrCl₆⁻² has five electrons in the 5d_z level. Thus, the difference in the entropies of activation of the Fe(phen)₃⁺³-Fe(H₂O)₆⁺² and IrCl₆⁻²-Fe(H₂O)₆⁺² reactions is unlikely to be due to markedly different multiplicity restrictions in the two reactions.¹¹

The standard entropy changes of the two reactions may be estimated from the differences in the entropies of the appropriate ions. The difference in the entropies of Fe(H₂O)₆⁺² and Fe(H₂O)₆⁺³ is 43.0 cal. deg.⁻¹ mole⁻¹ with that of Fe(H₂O)₆⁺³ more negative.¹² George, Hanania and Irvine have reported that the difference in the entropies

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TABLE III

SECOND ORDER RATE CONSTANTS FOR OXIDATION-REDUCTION REACTIONS BETWEEN COMPLEX IONS AT 25.0°

Oxidizing agent ^a	E° ox. ag., volts	Reducing agent ^a	E° red. ag., volts	Medium	ΔE°, volts	F ⁻¹ k _s , sec. ⁻¹
IrCl ₆ ⁻³	1.02 ^b	Fe(CN) ₆ ⁻⁴	0.36 ^c	H ₂ O	0.66	1.20 × 10 ⁸
IrCl ₆ ⁻³	1.06 ^b	Fe(CN) ₆ ⁻⁴	.72 ^d	0.5 F HClO ₄	.34	4.1 × 10 ⁵
MnO ₄ ⁻	0.56 ^e	Fe(CN) ₆ ⁻⁴	.46 ^f	0.1 F NaOH	.10	1.34 × 10 ⁴
OsCl ₆ ⁻²	0.45 ^d	Fe(CN) ₆ ⁻⁴	.38 ^c	H ₂ O	.07	1.79 × 10 ⁻¹
IrCl ₆ ⁻³	1.06 ^b	Os(dipy) ₃ ⁺³	.83 ^f	0.5 F HClO ₄	.23	>10 ⁸
Fe(phen) ₃ ⁺³	1.06 ^e	Fe(CN) ₆ ⁻⁴	.72 ^d	.5 F HClO ₄	.23	>10 ⁸
Os(dipy) ₃ ⁺³	0.83 ^f	Fe(CN) ₆ ⁻⁴	.72 ^d	.5 F HClO ₄	.11	>10 ⁸
Ru(dipy) ₃ ⁺³	1.27 ^g	Fe(<i>t</i> -phen) ₃ ⁺²	.81 ^h	.5 F H ₂ SO ₄	.46	>10 ⁸
Ru(dipy) ₃ ⁺³	1.27 ^g	Os(dipy) ₃ ⁺²	.83 ^f	.5 F HClO ₄	.44	>10 ⁸
Fe(phen) ₃ ⁺³	1.06 ^e	Os(dipy) ₃ ⁺²	.83 ^f	.5 F HClO ₄	.23	>10 ⁸
Ru(dipy) ₃ ⁺³	1.27 ^g	Fe(<i>p</i> -phen) ₃ ⁺²	1.08 ⁱ	.5 F H ₂ SO ₄	.19	>10 ⁸
Fe(<i>d</i> -dipy) ₃ ⁺³	0.95 ^h	Fe(<i>t</i> -phen) ₃ ⁺²	0.81 ^h	.5 F H ₂ SO ₄	.14	>10 ⁸
Fe(phen) ₃ ⁺³	1.06 ^e	Fe(<i>d</i> -dipy) ₃ ⁺²	0.95 ^h	.5 F HClO ₄	.11	>10 ⁸

^a phen = 1,10-phenanthroline; dipy = 2,2'-dipyridine; tripy = 2,2',2''-tripyridine; d-dipy = 4,4'-dimethyl-2,2'-dipyridine; *t*-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; *p*-phen = 5-phenyl-1,10-phenanthroline. ^b F. P. Dwyer, H. A. McKenzie and R. S. Nyholm, *J. Proc. Roy. Soc., N. S. Wales*, **78**, 260 (1944). ^c W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 239. ^d F. P. Dwyer, J. E. Hummel and R. S. Nyholm, *J. Proc. Roy. Soc., N. S. Wales*, **80**, 242 (1947). ^e G. F. Smith and F. P. Richter, *Ind. Eng. Chem., Anal. Ed.*, **16**, 580 (1944). ^f F. P. Dwyer, N. A. Gibson and E. C. Gyarfas, *J. Proc. Roy. Soc., N. S. Wales*, **84**, 80 (1950). ^g F. P. Dwyer, *ibid.*, **83**, 134 (1949). ^h G. F. Smith Chemical Co., Columbus, Ohio, Catalogue, January 1960, p. 97. ⁱ I. M. Kolthoff and W. J. Tomicek, *J. Phys. Chem.*, **39**, 949 (1935). ^j E. H. Swift, "A System of Chemical Analysis," 1st Ed., Prentice-Hall, Inc., New York, N. Y., 1939, p. 542. ^k W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949). ^l W. W. Brandt and D. F. Gullstrom, *J. Am. Chem. Soc.*, **74**, 3532 (1952).

of Fe(phen)₃⁺² and Fe(phen)₃⁺³ is -5.2 cal. deg.⁻¹ mole⁻¹ with that of Fe(phen)₃⁺² more negative.¹³ The difference in the entropies of IrCl₆⁻³ and IrCl₆⁻² is -20 cal. deg.⁻¹ mole⁻¹ with that of IrCl₆⁻³ more negative.¹⁴ These values give ΔS° = -48.2 cal. deg.⁻¹ mole⁻¹ for the Fe(phen)₃⁺²-Fe(H₂O)₆⁺² reaction and ΔS° = -63.0 cal. deg.⁻¹ mole⁻¹ for the IrCl₆⁻²-Fe(H₂O)₆⁺² reaction. It thus is apparent that despite the fact that the standard entropy change of the IrCl₆⁻²-Fe(H₂O)₆⁺² reaction is more negative than that of the Fe(phen)₃⁺³-Fe(H₂O)₆⁺² reaction, the entropy of activation of the former reaction is more positive. This suggests that the entropies of activation of the two reactions are not directly related to their standard entropy changes. A possible reason for the absence of such a relation may lie in the large difference in the values of ΔS[‡]_{el} of the two reactions.

Oxidation-Reduction Reactions Between Complex Ions.—As can be seen in Table III, the second order rate constants for the oxidation of ferrocyanide ions by a series of negatively-charged complexes tend to increase with the standard free energy changes of the reactions. In the reactions studied those between oppositely-charged complexes as well as those between positively-charged complexes proceed with rate constants which are larger than 10⁸ F⁻¹ sec.⁻¹.

The more rapid rate of oxidation of Fe(CN)₆⁻⁴ by Fe(phen)₃⁺³ than by IrCl₆⁻² is in contrast to the relative rates of oxidation of Fe(H₂O)₆⁺² by these ions. In going from Fe(H₂O)₆⁺² to Fe(CN)₆⁻⁴ the rate of oxidation by Fe(phen)₃⁺³ ions relative to that by IrCl₆⁻² ions increases by more than ten thousandfold. These comparisons substantiate further the conclusions reached above concerning the importance of electrostatic factors

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(14) P. George and D. H. Irvine, *Biochem. J.*, **60**, 603 (1955).

in determining the rates of the oxidation-reduction reactions.

It is interesting to speculate about the possible causes of the relative slowness of those reactions in which both the oxidizing and the reducing agents are negatively charged. The relatively larger charge-products and smaller sizes of the negatively-charged reactants will increase the amount of work required to bring them together to form the activated complex. Moreover, the conducting natures of the phenanthroline and dipyridine ring systems may facilitate the transfer of electrons between the reactants. In this connection, the introduction of various groups in the phenanthroline and dipyridine ring systems might prevent the close approach of the reactants necessary for conduction through the ring systems. However, as is apparent from Table III, substitution on the periphery of the ligand ring systems does not reduce the rate constants for the oxidation-reduction reactions below 10⁸ F⁻¹ sec.⁻¹.

Application of the Marcus Theory.—Since the reactants listed in Table III do not undergo substitution readily, it is likely that they react *via* outer-sphere activated complexes. If this is the case, the Marcus theory⁸ should be applicable to them. In terms of the Marcus theory

$$\Delta G^* = m^2\lambda + w^*$$

where

$$2m + 1 = -[\Delta G^0 + (w - w^*)]/\lambda$$

and

$$1/\lambda = (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{n^2} - \frac{1}{D_s} \right)$$

In these equations, w^* is equal to the coulombic work required to bring the reactants together at the prevailing ionic strength and w the corresponding quantity for the products. ΔG^0 is the standard free energy change for the reaction at the prevail-

ing ionic strength. a_1 and a_2 are the radii of the reactants. r , the distance between the centers of the reactants in the activated complex, is set equal to $(a_1 + a_2)$. Δe is the charge transferred. n is the refractive index of the medium.

In order to calculate the amount of work required to bring the reactants together, we have used¹⁵

$$w^* = \frac{e_1^* e_2^*}{D_s r} e^{-\kappa r}$$

where

$$\kappa = \left(\frac{4\pi \sum n_i e_i^2}{D k T} \right)^{1/2}$$

In these equations, e_i is the charge and n_i the concentration of species i .

The observed and calculated free energies of activation for several of the reactions studied are shown in Table IV. It will be seen that the calculated free energies of activation are consistently lower than the observed values.

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED FREE ENERGIES OF ACTIVATION OF OXIDATION-REDUCTION REACTIONS BETWEEN COMPLEX IONS AT 25.0°

Reaction	a_1 $\times 10^3$, cm.	a_2 $\times 10^3$, cm.	ΔG^\ddagger , kcal. mole ⁻¹	$\Delta G^*_{\text{obsd.}}$, kcal. mole ⁻¹	$\Delta G^*_{\text{calcd.}}$, kcal. mole ⁻¹
Fe(CN) ₆ ⁻³ -Fe(CN) ₆ ^{-4a}	4.5 ^d	4.5 ^d	0.0	12.8 ^b	8.8
IrCl ₆ ⁻² -Fe(CN) ₆ ^{-4b}	4.3 ^e	4.5 ^d	-15.2	9.2	4.2
IrCl ₆ ⁻² -Fe(CN) ₆ ^{-4c}	4.3 ^e	4.5 ^d	-7.8	9.8	2.4
OsCl ₆ ⁻² -Fe(CN) ₆ ^{-4b}	4.2 ^f	4.5 ^d	-1.6	18.5	8.5
IrCl ₆ ⁻² -Os(dipy) ₃ ^{+2c}	4.3 ^e	7 ^g	-5.3	6.5	2.0
Fe(phen) ₃ ⁺² - Os(dipy) ₃ ^{+2c}	7 ^g	7 ^g	-5.3	6.5	1.2
Ru(dipy) ₃ ⁺² - Os(dipy) ₃ ^{+2c}	7 ^g	7 ^g	-10.1	6.5	0.2

^a C. F. Deck, *Diss. Abstracts*, 16, 1578 (1956). ^b In H₂O. ^c In 0.50 *F* HClO₄. ^d R. A. Marcus, *J. Chem. Phys.*, 26, 867 (1957). ^e Tables of Interatomic Distances, Special Publication Number 11, The Chemical Society, London (1958). ^f J. D. McCullough, *Z. Krist.*, 94, 143 (1936). ^g J. E. Dickens, F. Basolo and H. M. Neumann, *J. Am. Chem. Soc.*, 79, 1289 (1957), have determined the maximum radius of Fe(phen)₃⁺³ from a Fischer-Hirschfelder model to be about 7 Å. We shall use this value for the phenanthroline and dipyrindine complexes listed in Table III. ^h $T = 0.0^\circ$.

The foregoing equations from the Marcus theory require that there be no change in the interatomic distances in the innermost coordination shell of the reactants in forming the activated complex. Thus, the difference between the observed and calculated free energies of activation can be interpreted in terms of a "reorganization energy," which is the energy required to reorganize the innermost coordination shells of the reactants before the electron transfer can occur. By comparing ΔG^*_{obsd} with $\Delta G^*_{\text{calcd}}$ for the Fe(CN)₆⁻³ Fe(CN)₆⁻⁴ exchange reaction, the reorganization energy of the ferrocyanide ion can be estimated at approximately 2 kcal. mole⁻¹. Similar compari-

sons now can be made for the other ferrocyanide reactions, with the result that the IrCl₆⁻² reorganization energy is about 3-5 kcal. mole⁻¹ and the OsCl₆⁻² reorganization energy even greater. As can be seen in Table IV, the lowest values of $\Delta G^*_{\text{calcd}}$ tabulated are for those reactions which have rate constants larger than 10⁸ *F*⁻¹ sec.⁻¹. One of these reactions, that between IrCl₆⁻² and Os(dipy)₃⁺², can be interpreted to indicate the reorganization energy of Os(dipy)₃⁺² to be very small since the energy required to reorganize IrCl₆⁻² is 3-5 kcal./mole. When this value is subtracted from a maximum difference ($\Delta G^*_{\text{obsd}} - \Delta G^*_{\text{calcd}}$) of 4.5 kcal./mole, it is apparent that very little energy is required for reorganization of the Os(dipy)₃⁺² ion. This result probably applies to the other nitrogen-base complex ions in view of the fact that they are all very large complexes with similar structures.

The reorganization energy estimates can be summarized in the sequence OsCl₆⁻² > IrCl₆⁻² > Fe(CN)₆⁻⁴ > dipyrindines, phenanthrolines. The order of the reactants in this series is tentative, since there is evidence that small cations may catalyze the oxidation-reduction reactions between negatively-charged complexes.⁴ However, this effect is unlikely to be large under the conditions in which the reactions listed in Table IV have been investigated since it is apparent from this table that the reorganization energy estimated for the IrCl₆⁻² ion does not appear appreciably different in water and 0.5 *F* perchloric acid. The problem of obtaining good estimates of the coordination shell reorganization energies is complicated by the fact that the free energy available for solvent reorganization is no longer equal to [$\Delta G^0 + (w - w^*)$] in those reactions in which inner shell reorganization occurs. In such cases it is necessary to use a more complicated expression which allows for the free energy change associated with the reorganization of the inner coordination shells. This energy can be calculated provided the appropriate force constants and internuclear distances are known.¹⁶ However, since the free energy available for both solvent and inner shell reorganization is zero in isotopic exchange reactions, the solvent reorganization energies in such reactions are still given by the above equations from the Marcus model. Thus the differences between the solvent reorganization energies calculated from the above equations and the observed activation energies should be good estimates of the inner shell reorganization energies in the isotopic exchange reactions and less reliable estimates in all the other reactions.

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