

[CONTRIBUTION FROM THE LABORATORY FOR BIOPHYSICAL CHEMISTRY, SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

## Measurement of the Rate of Electron Transfer between Tris-(4,7-dimethyl-1,10-phenanthroline)-iron(II) and Hexachloroiridate(IV) by the T-Jump Method

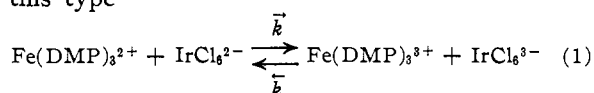
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The kinetics of the electron transfer reaction 1 (where DMP = 4,7-dimethyl-1,10-phenanthroline) have been measured in aqueous solution using the temperature-jump relaxation method. In the temperature range 10° to 30° the rate constants (for 0.1 *M* ionic strength) are given by  $\vec{k} = 1.1 \times 10^9 M^{-1} \text{sec}^{-1}$  and  $\bar{k} = 4.0 \times 10^{13} \exp -(6000/RT) M^{-1} \text{sec}^{-1}$  ( $= 1.0 \times 10^9 M^{-1} \text{sec}^{-1}$  at 10°). These are among the highest rates yet observed for electron transfer between metal complexes, and appear to be close to the diffusion-controlled limit. It is concluded that the solvent- and ligand-rearrangement barriers to electron transfer in this system are very small.

### Introduction

Electron transfer reactions between "large" metal complexes, particularly those with a high degree of covalent character (*e.g.*, phenanthrolines, cyanides, etc.), are generally very rapid, in many cases beyond the range of rapid mixing flow techniques.<sup>3,4</sup> In this paper we report measurements of the rate of a reaction of this type



(where DMP = 4,7-dimethyl-1,10-phenanthroline)<sup>5</sup> using the temperature-jump relaxation method recently developed by Eigen<sup>6</sup> and previously applied<sup>7</sup> to measure the rate of electron transfer between  $\text{Fe}(\text{CN})_6^{4-}$  and dichlorophenol indophenol.

### Experimental

The T-jump apparatus employed was substantially the same as that described by Czerlinski and Eigen.<sup>6</sup> The cell (originally developed for measurement of optical rotation changes)<sup>8</sup> had a heated optical path length of 6.4 cm. (and a heated solution volume of about 2 ml.), permitting the use of reactant concentrations as low as  $5 \times 10^{-6} M$ . The temperature jump, corresponding to about 8°, was effected by discharging a 0.5  $\mu\text{f}$ . capacitor, charged to 16,500 volts, through the solution. The heating time ( $\sim 90\%$  total temperature rise) was about 20  $\mu\text{sec}$ . for 0.05 *M*  $\text{KNO}_3$  and 14  $\mu\text{sec}$ . for 0.1 *M*  $\text{KNO}_3$ . Control of the initial temperature (to at least  $\pm 2^\circ$ ) was effected by circulating water from a constant temperature bath through the cell housing and by pre-cooling the solution and cell to the reaction temperature.

The scanning light source was an Osram HBO 100 W/2 mercury arc lamp, powered by four 12-v. storage batteries. The light beam was passed through Corning No. 3-72 and No. 5-56 filters (maximum transmittance region 480-510  $\mu\text{m}$ ) and split into two components, one of which passed through the solution. The intensities of the two beams were measured with a pair of RCA IP28 photomultiplier tubes and compared. The change in optical density, resulting from the shift in equilibrium following the temperature jump, was observed on a Tektronix type 545 oscilloscope equipped with a Polaroid camera.

$\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$  was obtained from Platinum Chemicals Co. and 4,7-dimethyl-1,10-phenanthroline (DMP) from G. Frederick Smith Chemical Co. The  $\text{Fe}(\text{DMP})_3^{2+}$  solution was prepared by dissolving DMP and reagent grade  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in water. The electrolyte was reagent grade  $\text{KNO}_3$ . All solutions were prepared from doubly distilled water.

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(3) E. Eichler and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 4145 (1958).

(4) B. M. Gordon, L. L. Williams and N. Sutin, *ibid.*, **83**, 2061 (1961).

(5) The choice of the substituted phenanthroline complex was dictated by the requirement of the method that the reaction equilibrium must not lie too far on either side in order that the small shift of equilibrium with temperature be observable. For the unsubstituted tris-(1,10-phenanthroline)-iron complex, the corresponding equilibrium lies too far to the left.

(6) G. Czerlinski and M. Eigen, *Z. Elektrochem.*, **63**, 652 (1959).

(7) H. Diebler, *ibid.*, **64**, 128 (1960).

(8) The apparatus will be described in a forthcoming paper by R. Legare and R. Lumry.

The reaction solutions exhibited some instability on standing in the T-jump cell, apparently due to reduction of the  $\text{IrCl}_6^{2-}$  by the electrodes of platinum-plated brass. The reduction was, however, sufficiently slow that it did not interfere with the relaxation measurements.

The equilibrium constant of the reaction, needed for the interpretation of the relaxation spectra, was determined spectrophotometrically, the reaction being accompanied by a large spectral change in the region of 500  $\mu\text{m}$ , where the reactants absorb strongly and the products negligibly. The absorption characteristics of the various species involved are

	$\lambda_{\text{max}}, \mu\text{m}$	$\epsilon_{\text{max}}$
$\text{Fe}(\text{DMP})_3^{2+}$	510	14,000
$\text{IrCl}_6^{2-}$	490	3,200
$\text{Fe}(\text{DMP})_3^{3+}$	560	1,500
$\text{IrCl}_6^{3-}$	415	76

A Cary model 11 recording spectrophotometer with a thermostated cell compartment was used for these measurements.

### Results and Discussion

Table I lists values for various temperatures and ionic strengths of the equilibrium constant, *K*, of reaction 1, defined by eq. 2

$$K = \vec{k}/\bar{k} = [\text{Fe}(\text{DMP})_3^{3+}][\text{IrCl}_6^{3-}]/[\text{Fe}(\text{DMP})_3^{2+}][\text{IrCl}_6^{2-}] \quad (2)$$

As expected for a reaction in which the magnitude of the ionic charges increases,  $\Delta S^\circ$  is negative, and *K* increases with ionic strength. The heat of reaction is sufficient for the shift in equilibrium resulting from a temperature jump of 8° to be readily observable.

TABLE I  
EQUILIBRIUM DATA FOR REACTION 1

Ionic strength ( $\text{KNO}_3$ )	$K_2^\circ$	$K_{25^\circ}$	$\Delta H^\circ$ , kcal./mole	$\Delta S^\circ$ , e.u./mole
0.05	0.71	0.34	-5.6	-21
0.10	1.55	0.82	-4.9	-17

The relaxation spectra (Fig. 1) were characterized by a single relaxation time,  $\tau$ , defined by eq. 3<sup>9</sup>

$$-d\Delta C/\Delta C = dt/\tau \quad (3)$$

which gives, on integration

$$\ln(\Delta C/\Delta C_0) = -t/\tau \quad (4)$$

In eq. 4,  $\Delta C_0$  is the initial displacement and  $\Delta C$  the displacement at time *t* of the reactant concentrations from their final equilibrium values. In accord with eq. 4 the relaxation spectra yielded linear plots of  $\log(\Delta C/\Delta C_0)$  vs. time (Fig. 2). Values of the relaxation time were determined from the slopes of such plots and used to compute the rate constants through the relation, eq. 5.

(9) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).

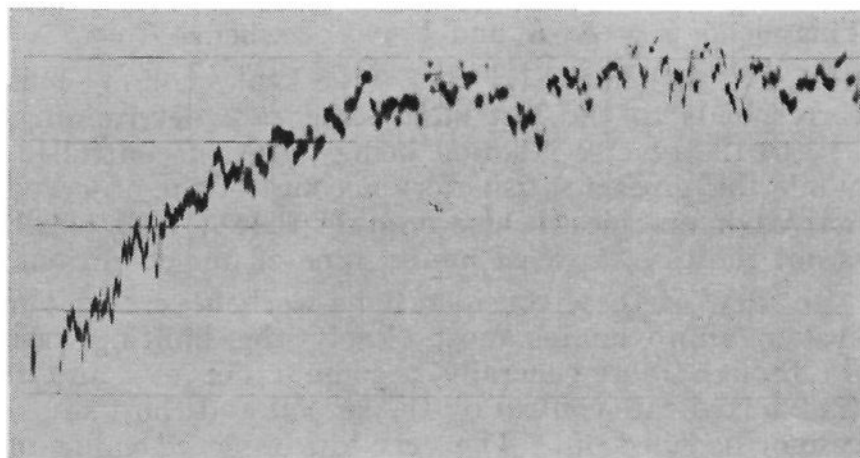


Fig. 1.—Sample temperature-jump relaxation spectrum. The sweep rate is 20  $\mu\text{sec./cm}$ . This spectrum was obtained with initial concentrations of  $1.0 \times 10^{-5} M$ . The  $\text{KNO}_3$  concentration was 0.1  $M$  and the temperature was about 18°.

$$\tau = \frac{1}{\bar{k}([\text{Fe}(\text{DMP})_3^{2+}] + [\text{IrCl}_6^{2-}]) + \bar{k}([\text{Fe}(\text{DMP})_3^{3+}] + [\text{IrCl}_6^{3-}])} \quad (5)$$

In the present experiments, the solutions always contained initially equal concentrations ( $C_{\text{total}}$ ) of  $\text{IrCl}_6^{2-}$  and  $\text{Fe}(\text{DMP})_3^{2+}$ ; hence

$$[\text{Fe}(\text{DMP})_3^{2+}] = [\text{IrCl}_6^{2-}] \quad (6)$$

and

$$[\text{Fe}(\text{DMP})_3^{3+}] = [\text{IrCl}_6^{3-}] = C_{\text{total}} - [\text{Fe}(\text{DMP})_3^{2+}] \quad (7)$$

Under these conditions, eq. 5, in combination with eq. 2, reduces to

$$1/\tau = 2C_{\text{total}} \bar{k} \sqrt{K} = 2C_{\text{total}} \bar{k}'/\sqrt{K} \quad (8)$$

The data obtained using these relations are summarized in Table II. Each value of  $\tau$  is the average of at least 3 determinations whose agreement was generally well within  $\pm 10\%$ . The rate constants are independent of  $C_{\text{total}}$  which, in each case, was varied between  $5 \times 10^{-6}$  and  $1 \times 10^{-5} M$ . At higher concentrations  $\tau$  approached the heating time, while at lower concentrations the optical density changes were too small for measurement. The temperature coefficients of  $\bar{k}$  and  $\bar{k}'$  provided apparent activation energies  $\bar{E} = 0.5 \pm 0.5 \text{ kcal./mole}$  and  $\bar{E}' = 6 \pm 1 \text{ kcal./mole}$ .

The values of  $\bar{k}$  and  $\bar{k}'$ , both of which exceed  $10^9 M^{-1} \text{ sec.}^{-1}$  under the conditions of these experiments, appear to be the highest yet reported for electron transfer reactions between two metal complexes, and of the same order as those found by Ward and Weissman,<sup>10</sup> using electron spin resonance methods, for electron transfer between [naphthalene]<sup>-</sup> and naphthalene in dimethoxyethane solution. A few experiments with tris-(5,6-dimethyl-1,10-phenanthroline)-iron(II) instead of the 4,7-dimethyl complex yielded very similar relaxation times.

Using the Debye<sup>11</sup> formula with numerical integration, and estimating the radii of  $\text{IrCl}_6^{2-(3-)}$  and  $\text{Fe}(\text{DMP})_3^{2+(3+)}$  to be 4.3 and 7.0 Å, respectively,<sup>3</sup> we have computed the diffusion-limited rate constant for reaction between  $\text{IrCl}_6^{2-}$  and  $\text{Fe}(\text{DMP})_3^{2+}$  at 10° and zero ionic strength to be  $1 \times 10^{10} M^{-1} \text{ sec.}^{-1}$  ( $7 \times 10^9 M^{-1} \text{ sec.}^{-1}$  at  $\mu = 0.05$ ) and that for the reverse action between  $\text{IrCl}_6^{3-}$  and  $\text{Fe}(\text{DMP})_3^{3+}$  to be  $2 \times 10^{10} M^{-1} \text{ sec.}^{-1}$  ( $9 \times 10^9 M^{-1} \text{ sec.}^{-1}$  at  $\mu = 0.05$ ). Unfortunately, the ionic strengths which these experiments called for lie well outside the Debye-Hückel region so that the ionic strength correction is unreliable.

(10) R. L. Ward and S. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957).

(11) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

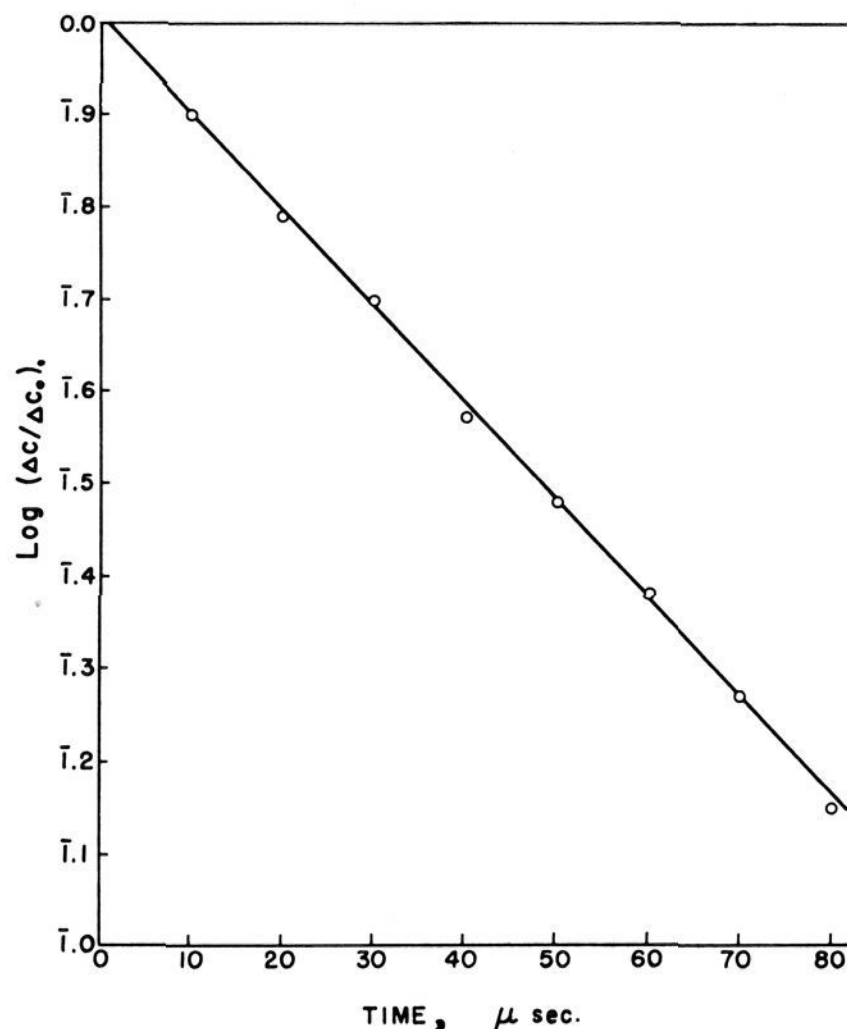


Fig. 2.—First-order plot obtained from the spectrum shown in Fig. 1. The relaxation time obtained from this plot is 42  $\mu\text{sec}$ .

Nevertheless, it is clear that the observed values of  $\bar{k}$  and  $\bar{k}'$  are close, probably within an order magnitude, to the diffusion-limited values.

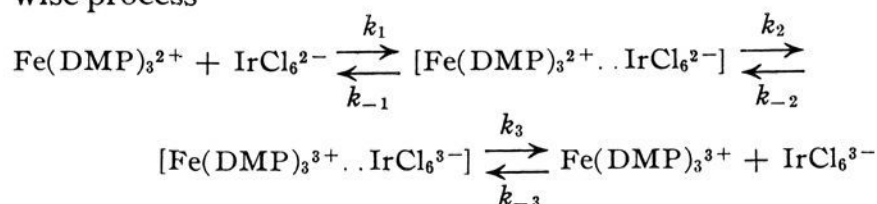
TABLE II  
SUMMARY OF KINETIC DATA

Temp., °C.	$\text{KNO}_3$ , $M$	$C_{\text{total}} \times 10^6$ , $M$	$K^a$	$\tau \times 10^6$ , sec.	$\bar{k} \times 10^{-9}$ , $M^{-1} \text{ sec.}^{-1}$	$\bar{k}' \times 10^{-9}$ , $M^{-1} \text{ sec.}^{-1}$
10	0.05	10	0.55	33	1.1	2.0
10	.05	7.5	.55	55	0.9	1.7
10	.05	5.0	.55	66	1.1	2.1
18	.05	10	.40	32	1.0	2.4
18	.05	7.5	.40	42	1.05	2.5
18	.05	5.0	.40	59	1.1	2.6
30	.05	10	.28	23	1.1	4.2
30	.05	7.5	.28	31	1.1	4.1
30	.05	5.0	.28	44	1.2	4.4
10	.10	10	1.2	45	1.2	1.0
10	.10	7.5	1.2	59	1.2	1.0
10	.10	5.0	1.2	98	1.1	0.9
18	.10	10	0.95	46	1.1	1.1
18	.10	7.5	.95	62	1.1	1.1
18	.10	5.0	.95	83	1.2	1.2
30	.10	10	.69	34	1.2	1.7
30	.10	7.5	.69	43	1.2	1.8
30	.10	5.0	.69	65	1.2	1.8

Activation energy (kcal./mole)  $0.5 \pm 0.5$   $6 \pm 1$

<sup>a</sup> Interpolated from the data in Table I.

The relation between the measured, and the diffusion-limited, rate constants, and the significance of the measured activation energies,  $\bar{E}$  and  $\bar{E}'$ , can be understood more clearly in terms of the following analysis in which the over-all reaction is considered as a stepwise process



where  $[\text{Fe}(\text{DMP})_3^{2+} \cdot \text{IrCl}_6^{2-}]$  and  $[\text{Fe}(\text{DMP})_3^{3+} \cdot \text{IrCl}_6^{3-}]$  refer to the reactant and product collision complexes and  $k_1$  and  $k_{-3}$  to the diffusion-limited rate constants for their formation. Assuming steady-state concentrations for the two collision complexes, it follows that

$$\vec{k} = \frac{k_1}{1 + \frac{k_{-1}}{k_2} + \frac{k_{-1}k_{-2}}{k_2k_3}} \quad (9)$$

$$\vec{k} = \frac{1}{\frac{1}{k_1} + \frac{k_{-1}}{k_1k_2} + \frac{1}{Kk_{-3}}} \quad (9')$$

$$\vec{k} = \frac{(1/K)}{\frac{1}{k_1} + \frac{k_{-1}}{k_1k_2} + \frac{1}{Kk_{-3}}} \quad (10)$$

whence

$$\vec{E} = \frac{-R\delta \ln \vec{k}}{\delta 1/T} = \frac{\vec{k}E_{1\ddagger}}{k_1} + \frac{\vec{k}k_{-1}}{k_1k_2} (E_{1\ddagger} + E_{2\ddagger} - E_{-1\ddagger}) + \frac{\vec{k}}{Kk_{-3}} (\Delta H^0 + E_{-3\ddagger}) \quad (11)$$

The relationship of the over-all rate constants and activation parameters to those of the individual steps is thus seen to be rather complex and cannot be resolved in detail with the information available. It is of interest, however, to consider the simpler limiting cases which arise when one of the three consecutive free energy barriers is significantly higher than the others so that the step associated with this barrier becomes effectively rate-determining. These correspond to

$$(i) \quad (k_{-1}/k_2 + k_{-1}k_{-2}/k_2k_3) \ll 1$$

This yields  $\vec{k} = k_1$  and  $\vec{E} = E_{1\ddagger}$  corresponding to the first step being rate determining, *i.e.*, the forward reaction being diffusion-controlled. The observation that  $\vec{E} \sim 0$  precludes this case since  $E_{1\ddagger}$  (and  $E_{-3\ddagger}$ ) must be of the order of 4-5 kcal./mole, corresponding to the activation energy of the viscosity of water.

$$(ii) \quad k_{-1}/k_2 \gg (1 + k_{-1}k_{-2}/k_2k_3)$$

This yields  $\vec{k} = k_1k_2/k_{-1}$  and  $\vec{E} = E_{1\ddagger} + E_{2\ddagger} - E_{-1\ddagger}$ , corresponding to the second step, *i.e.*, the electron transfer step itself, being rate determining. The observed values of  $\vec{E}$  and  $\vec{E}$  can be readily reconciled with this case.

$$(iii) \quad k_{-1}k_{-2}/k_2k_3 \gg (1 + k_{-1}/k_2)$$

This yields  $\vec{k} = k_{-3}K$  and  $\vec{k} = k_{-3}$ , whence  $\vec{E} = E_{-3\ddagger} + \Delta H^0 (\sim 0)$  and  $\vec{E} = E_{-3\ddagger} (\sim 5 \text{ kcal./mole})$ . This corresponds to the last step being rate determining, *i.e.*, to the reverse reaction being diffusion controlled. While this gives a satisfactory account of the observed activation energies, it also requires that  $K \ll 1$  which is not the case, at least under some of our conditions.

In view of these considerations we believe that our system approximates most closely the limiting case ii although, more generally, a combination of ii and iii (*i.e.*, mixed rate-control by the second and third steps) cannot be ruled out. The very low observed value of  $\vec{E}$  does, however, argue against the first step contributing significantly to rate determination.

The identification of  $\vec{k}$  with  $k_1k_2/k_{-1}$ , suggested above, permits direct comparison of our rate constants with those computed from the Marcus<sup>12</sup> theory which (neglecting "inner-sphere" reorganization) gives  $k_1k_2/k_{-1} = Z \exp[-(W(R) + m^2\lambda)/RT]$  where  $Z$  is the collision number for neutral particles in solution,  $W(R)$  is the electrostatic work involved in bringing the reactants together to their separation in the activated complex ( $= z_1z_2e^2/DR$  at zero ionic strength) and  $m$  and  $\lambda$  have the definitions given by Marcus.<sup>12</sup> Choosing  $Z = 1 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$  and  $W(R) = -1.0 \text{ kcal./mole}$  (a compromise between the zero ionic strength value of  $-1.4$  and the value of  $-0.7$  for  $\mu = 0.05$  obtained using the Debye limiting law which is known to over-correct for ionic strength effects outside the limiting region), we obtain  $m = -0.46$ ,  $m^2\lambda = 3.5 \text{ kcal./mole}$  and  $k_1k_2/k_{-1} = 1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  which agrees well with the observed value of  $\vec{k}$  at  $18^\circ$ ,  $\mu = 0.05$ . Although the approximations involved in the calculations and in the identification of  $\vec{k}$  with  $k_1k_2/k_{-1}$  and the uncertainties in the value of  $Z$  and in the ionic strength correction introduce some latitude into this comparison, it nevertheless seems clear from the agreement that the barrier to electron transfer from "inner-sphere" reorganization must be extremely small in this reaction.

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(12) R. A. Marcus, *J. Chem. Phys.*, **26**, 867 (1957).