BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2101—2105 (1973)

Electron-transfer Kinetics of Transition-metal Complexes in Lower Oxidation States. Part I. Electron Spin Resonance Measurements of the Electron-exchange Rate between $Cr(bipy)_3{}^{1+}$ and $Cr(bipy)_3$

Tetsuo SAJI and Shigeru AOYAGUI
Faculty of Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

(Received November 2, 1972)

The rate of the electron-exchange reaction between $Cr(bipy)_3{}^{1+}$ and $Cr(bipy)_3$ was measured in *N,N*-dimethylformamide by the ESR method, with the line-broadening procedure. The width of the partly-overlapped hyperfine lines was determined by comparing the observed spectrum with the computer-simulated one. The observed second-order rate constant was $(1.5\pm0.4)\times10^9\ M^{-1}\ sec^{-1}$ at 25 °C. When corrected for diffusion, this yielded the activation-controlled rate constant of $2.0\times10^9\ M^{-1}\ sec^{-1}$. It was pointed out that the rate constant obtained here was the largest of all those ever reported for the electron-exchange reactions in which the transition-metal complexes participated. The observed rate constant was in good agreement with the one calculated non-empirically according to the theory of R. A. Marcus. Although the value for the molecular radius must be chosen somewhat arbitrarily in applying this theory, the "good" radius was a reasonable one in view of the molecular geometry and dimensions of the reactants. The rate constant of the Heisenberg spin-exchange process was also determined to be $1.8\times10^9\ M^{-1}\ sec^{-1}$ at 25 °C in the same solvent.

From the mechanistic point of view, the electron-transfer reactions of transition-metal complexes may be divided into two groups: one is the group of reactions proceeding *via* an outer-sphere activated complex, and the other, an inner-sphere activated complex.[1,2] In the reactions of the former group, the inner coordination shells of the reactant complex ions are left intact in the transition state; in the latter, two reactants share the ligands of their first coordination spheres in the transition state. In general, it may be difficult to show which mechanism is realized in an electron-transfer reaction. However, it is known that reactions of some kind proceed with the outer-sphere mechanism: they are the fast electron-transfer reactions between substitution-inert complexes. Particularly, the electron-exchange rate constant is very large for a pair of complexes differing by one in the number of electrons in the lower t_{2g} orbitals, which are not used in ligand bondings.[1] For example, the electron-exchange reaction between $Fe(phen)_3{}^{3+}(t_{2g}{}^5)$ and $Fe(phen)_3{}^{2+}(t_{2g}{}^6)$ is too fast to be measured by the NMR method; the largest second-order rate constant observable by this method is of the order of $10^7\ M^{-1}\ sec^{-1}$. The lower limit of the rate constant of this reaction has been reported by Larsen and Wahl to be $3\times10^7\ M^{-1}\ sec^{-1}$ at 25 °C in aqueous solutions.[3]

Among the methods for measuring the rates of isotopic exchange-reactions, the ESR method is probably the only one which is applicable to such fast reactions as were mentioned above. This method has been applied extensively to electron-transfer reactions between aromatic hydrocarbons and their anion radicals. On the other hand, there has been only one report on the application of this procedure to the transition-metal complexes.[4] This may be because of the following difficulties: most of the ESR spectra of these complexes thus far reported are very broad at ordinary temperatures, and they scarcely ever exhibit a hyperfine structure. Moreover, the rate constants measurable by this method must be larger than $10^6\ M^{-1}\ sec^{-1}$.

The present investigation deals with the ESR measurement of the rate of electron-exchange between

---

[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., John Wiley & Sons Inc., New York, N.Y. (1967), Chap. 6.

[2] W. L. Reynolds and R. W. Lamry, "Mechanisms of Electron Transfer," The Ronald Press Co., New York, N. Y. (1966).

[3] D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **43**, 3765 (1965).

[4] R. A. Stewart, L. W. Reeves and S. Fujiwara,, This Bulletin, **41**, 2832 (1968).

$Cr(bipy)_3^{1+}$ and $Cr(bipy)_3$ in *N*,*N*-dimethylformamide (DMF). The latter complex is diamagnetic,[5] while the former complex yields the ESR spectra with the most resolved nitrogen hyperfine splittings of all the tris-bipyridyl complexes of transition metals ever reported.[6,7] Furthermore, the electronic configurations of $Cr(bipy)_3^{1+}$ and $Cr(bipy)_3$ are t_{2g}^5 and t_{2g}^6 respectively, as in $Fe(phen)_3^{3+}$ and $Fe(phen)_3^{2+}$; it may thus be expected that the reaction rate for this pair of complexes is sufficiently fast for it to be measured by the ESR method. The determination of the hyperfine linewidth is made by comparing the observed ESR spectrum with the computer-simulated one. The observed rate constants are discussed in comparison with those predicted by the theory of R. A. Marcus on the electron-transfer reactions with the adiabatic outer-sphere mechanism.[8]

The present discussion is based on the following premises: (1) both complexes, $Cr(bipy)_3^{1+}$ and $Cr(bipy)_3$, are substitution-inert, and (2) the electron-transfer reaction between them proceeds *via* an outer-sphere activated complex. Experimental evidence for the validity of the former premise will be described elsewhere. In regard to the latter one, there is no data which assures us of its validity. However, it may reasonably be considered that this reaction has a fair chance of being an outer-sphere reaction because of its very large rate constant, which will be seen in the later part of this article.

Experimental

Reagents. All the reagents and solvents were commercially obtained. The 2,2′-bipyridine was supplied by the Tokyo Chemical Industry Co., Ltd. The DMF used as the solvent was refluxed over calcium hydride, distilled *in vacuo*, and then stored in an evacuated ampoule already containing solid $Cr(bipy)_3(ClO_4)_2$ and magnesium powder in order to remove the trace of oxygen.

Complexes. Tris(2,2′-bipyridyl)chromium(1+) perchlorate[9] and tris(2,2′-bipyridyl)chromium(0)[10] were prepared in a nitrogen atmosphere or in a vacuum, according to the procedures described in the literature cited. They were identified by means of their electronic spectra[11] and by elemental analyses.

Found: C, 57.8; H, 3.79; N, 13.9. Calcd for $Cr(bipy)_3ClO_4$: C, 58.1; H, 3.90; N, 13.6.

Found: C, 67.0; H, 4.60; N, 16.0. Calcd for $Cr(bipy)_3$: C, 69.2; H, 4.65; N, 16.2.

Solutions. Solutions of $Cr(bipy)_3ClO_4$ with various concentrations were required in order for us to evaluate the contribution to the linewidth of the $Cr(bipy)_3^{1+}$ spectrum from the Heisenberg spin-exchange process. They were prepared separately in the ESR sample tubes by diluting each aliquot from the stock solution of $Cr(bipy)_3ClO_4$ to a desired concentration with the solvent distilled from the stock solution *in vacuo*. Their concentrations were determined ESR-spectroscopically.

The sample solutions used in the measurement of the electron-exchange rates contained both $Cr(bipy)_3ClO_4$ and $Cr(bipy)_3$; they were prepared by dissolving a known amount of solid $Cr(bipy)_3$ into a $Cr(bipy)_3ClO_4$ solution of a known concentration in such an ampoule as is shown in Fig. 1.

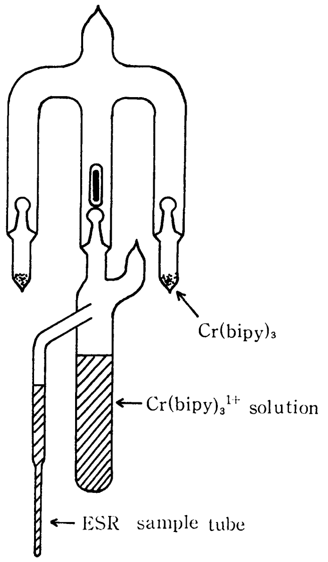

Fig. 1. Apparatus for preparation of ESR sample solutions.

In handling the sample solutions, all the operations were performed on a vacuum line by the use of glassware fitted with a breakable seal.

ESR Measurements. The ESR spectra of $Cr(bipy)_3^{1+}$ were measured in solutions with and without $Cr(bipy)_3$ added under experimental conditions otherwise identical. A JEOL-3SB spectrometer was operated at a frequency near 9.7 kMHz, with a 100 kHz field modulation and with a modulation amplitude of 0.5 gauss. The measurements were carried out at room temperature maintained at 25±1 °C. Calculations of the linewidth were performed on a FACOM 270-20/30 computer using a FORTRAN program.

Results and Discussion

Let the rate of the electron-transfer reaction between a diamagnetic and a paramagnetic molecule be described by the following equation:

$$\text{rate} = k[P][D] = [P]/\tau_p$$

where k is the second-order rate constant and τ_p, the mean life of the paramagnetic species; [D] and [P] are the concentrations of $Cr(bipy)_3$ and $Cr(bipy)_3^{1+}$ respectively, in this case. The hyperfine linewidth as a function of τ_p can be linearlized with regard to τ_p and $1/\tau_p$ respectively, under the following fast-limit and slow-limit conditions:[12]

$$\text{fast-limit:}\ |\omega_i-\omega_j|\tau_p \ll 1 \quad \text{for all i's}$$

$$\text{slow-limit:}\ |\omega_i-\omega_j|\tau_p \gg 1 \quad \text{for all i's}$$

---

[5] S. Herzog and K. Renner, *Chem. Ber.*, **92**, 872 (1959).

[6] B. Elschner and S. Herzog, *Arch. Sci.* (Geneva), **11**, 160 (1958).

[7] E. König, *Z. Naturforsch.*, *A*, **19**, 1139 (1964).

[8] R. A. Marcus, *J. Chem. Phys.*, **24**, 966, 979 (1956).

[9] V. F. Hein and S. Herzog, *Z. Anorg. Allgem. Chem.*, **267**, 337 (1952).

[10] S. Herzog, K. Renner, and W. Schön, *Z. Naturforsch.*, *B*, **12**, 809 (1957).

[11] E. König and S. Herzog, *J. Inorg. Nucl. Chem.*, **32**, 585 (1970).

[12] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y. (1959), Chap. 10.

where ω's are the resonance frequencies of the designated hyperfine lines. As will be seen below, it is necessary that [D] be larger than 1 M to fulfill the fast-limit condition. This is not possible in the present investigation, however, because of the poor solubility of the D species; thus, in the present experiment the rate constant is determined by the line-broadening procedure, with the slow-limit approximation. The rate constant is, then, given by Eq. (1), when the broadened hyperfine lines are assumed to maintain the Lorentzian lineshape:[13]

$$k = (1.5\times10^7)\Delta(\Delta H_{pp})/[D] \qquad (1)$$

where $\Delta(\Delta H_{pp})$ is the increase in the peak-to-peak linewidth of the first derivative spectra caused by electron exchange.

Although evidence has been reported for the disproportionation of $Cr(bipy)_3^{1+}$ ions,[14] their absorption spectrum obtained in DMF exhibited no sign of absorption due to either $Cr(bipy)_3^{2+}$ or $Cr(bipy)_3$; it was identical with the spectrum reported by König and Herzog in methanol.[11] Hence, the disproportionation was not taken into consideration.

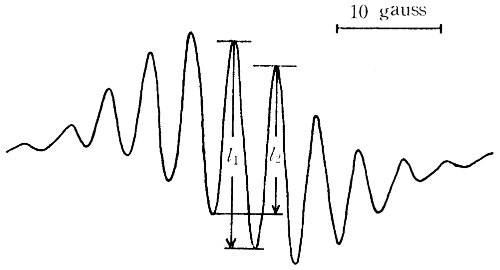

Fig. 2. ESR spectrum of 0.7 mM $Cr(bipy)_3^{1+}$ in DMF.

The ESR spectrum of $Cr(bipy)_3^{1+}$, shown in Fig. 2, exhibits eleven poorly-resolved lines with a spacing of about 3.05 gauss. They may be attributed to the hyperfine interaction due to six equivalent nitrogen nuclei of three bipyridyls. Such an interaction would give rise to thirteen lines. Because of the broadening in linewidth and poor signal-to-noise ratio, not all the thirteen lines were observed. The following procedure was used in order to determine the hyperfine linewidth of such a poorly-resolved spectrum as this. A linewidth parameter is defined here as l_2/l_1, where l_1 and l_2 are taken in the way shown in Fig. 2. The parameter was calculated for each given width of the hypothetical unoverlapping hyperfine lines and is shown plotted *vs.* the latter quantity in Fig. 3. From the observed values for the linewidth parameter, the true or unoverlapped hyperfine linewidths are obtained by the use of this figure.

Figure 4 illustrates a plot of the linewidth *vs.* the concentration of $Cr(bipy)_3ClO_4$. The experimental points lie on a straight line; this may serve to support this procedure for the linewidth determination. From the slope of this line, the second-order rate constant

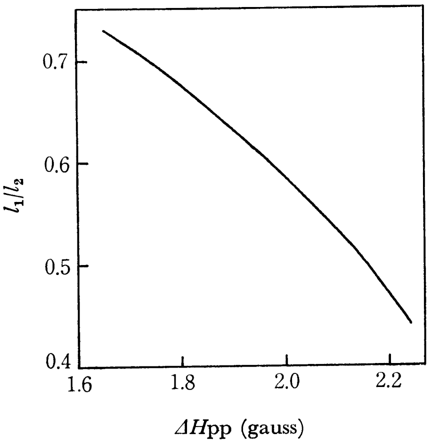

Fig. 3. Linewidth parameter *vs.* unoverlapped hyperfine linewidth.

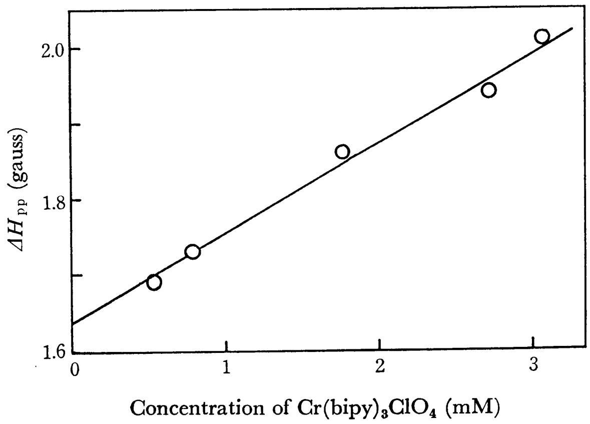

Fig. 4. Observed linewidth of ESR spectrum *vs.* concentration of $Cr(bipy)_3ClO_4$.

of the Heisenberg spin-exchange process[15] was estimated to be $1.8\times10^9\ M^{-1}\,sec^{-1}$. An inevitable increase in the concentration of $Cr(bipy)_3ClO_4$ is caused by the addition of $Cr(bipy)_3$;[16] this can be corrected by a procedure described elsewhere.[17] The increase, however, was less than 0.02 mM; its effect on the linewidth is negligible.

Figure 5 shows with circles the observed increase in the linewidth plotted *vs.* the concentration of added $Cr(bipy)_3$. The second-order rate constant of the electron-exchange reaction was determined from the slope of the straight line drawn through the point of origin and the circles as $k_{obs}=(1.5\pm0.4)\times10^9\ M^{-1}\,sec^{-1}$. No such a large rate constant exceeding $10^9\ M^{-1}\,sec^{-1}$ has, to our knowledge, ever been reported for the electron-exchange reactions of transition-metal complexes. The observed rate constant must be corrected for diffusion because of its large value, approaching the value for the diffusion-controlled rate constant. The correction was performed using the following relation:

---

[13] R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957).

[14] U. P. Geiger and E. Class, *Experientia*, **17**, 444 (1961).

[15] M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.*, **51**, 2690 (1969). M. P. Eastman, G. V. Bruno J. H. Freed, *ibid.*, **52**, 2511 (1970).

[16] When a known amount of $Cr(bipy)_3$ is added to the solution of $Cr(bipy)_3^{1+}$, a part of $Cr(bipy)_3$ may inevitably be oxidized by oxygen to yield $Cr(bipy)_3^{1+}$.

[17] S. Suga and S. Aoyagui, This Bulletin, **45**, 1375 (1972).

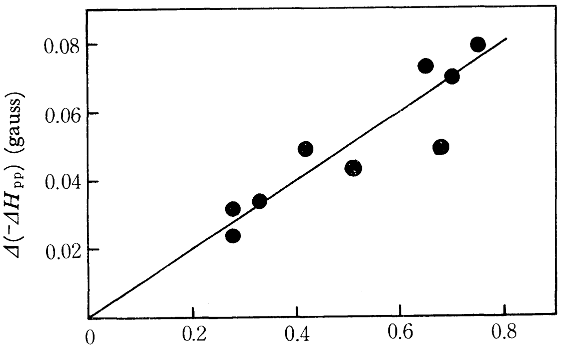

Fig. 5. Increase in linewidth of ESR spectrum *vs.* concentration of added Cr(bipy)$_3$.

$$k_{act}^{-1} = k_{obs}^{-1} - k_{dif}^{-1}$$

where k_{act} is the corrected or activation-controlled rate constant, and k_{obs} and k_{dif} are the observed and the diffusion-controlled rate constant respectively. The last one was estimated in the following way. When one of the reactants is neutral and when, accordingly, the electrostatic interaction between the reactants is negligibly small or zero, the diffusion-controlled second-order rate constant in $M^{-1}\,sec^{-1}$ may be given by:[18)]

$$k_{dif} = 4\pi\sigma DN/1000 \tag{2}$$

where σ is the collision diameter; D, the sum of the diffusion coefficients of the two reactants, and N, Avogadro's number. The value for σ was assumed to be equal to the sum of the molecular radii of the reactants; the latter quantities were estimated from the molecular geometry of Cr(bipy)$_3$, drawn in Fig. 6 on the basis of the X-ray diffraction data[19)] as well as the van der Waals radius of the hydrogen atom (1.2 Å). It may reasonably be assumed that a common value can be attributed to the radii of Cr(bipy)$_3^{1+}$ and Cr(bipy)$_3$. In the subsequent calculations, this common molecular radius is designated by a and taken in the two ways shown in Fig. 6: 7.1 and 6.1 Å. The diffusion coefficients of Cr(bipy)$_3$ and Cr(bipy)$_3^{1+}$ are both $3.2\times10^{-6}\,cm^2\,sec^{-1}$ at 25 °C in DMF.[20)] The diffusion-controlled rate constants calculated from Eq. (2) with the a values of 7.1 and 6.1 Å were 7×10^9 and $6\times10^9\,M^{-1}\,sec^{-1}$ respectively. Both k_{dif} values, however, actually yielded the same k_{act} value, $2.0\times10^9\,M^{-1}\,sec^{-1}$. The limiting condition for slow-exchange is obviously fulfilled with the observed k value of $1.5\times10^9\,M^{-1}\,sec^{-1}$ and the minimum value for $|\omega_i-\omega_j|$, 3.05 gauss, as well as the maximum value for $[D]$, 0.7 mM. On the other hand, the limiting condition for fast-exchange requires that $[D]$ be significantly larger than 0.4 M when the maximum value for $|\omega_i-\omega_j|$, *ca.* 30 gauss, is applied.

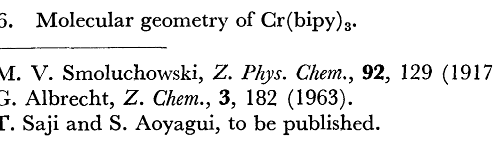

Fig. 6. Molecular geometry of Cr(bipy)$_3$.

According to the theory of Marcus,[8)] the rate constant of the electron-exchange reaction between a neutral and a charged species is, the inner-sphere reorganization being neglected:

$$\begin{aligned} k_{act} &= Z\exp(-\Delta G^*/RT) \\ &= Z\exp[-(e^2/8a)(1/D_{op}-1/D_s)] \end{aligned} \tag{3}$$

where Z, the collision number between two uncharged species in solution, is assumed to be $10^{11}\,M^{-1}\,sec^{-1}$; ΔG^* is the reorganization free energy of solvent molecules in forming the activated complex; e is the electronic charge, and D_{op} and D_s are the optical and the static dielectric constants respectively. The activation-controlled rate constant was calculated from Eq. (3) for each radius mentioned above. They are listed in Table 1, together with the corrected observed rate constant. The agreement between k_{act} and k_{calc} was satisfactory. In order for k_{calc} to be in exact agreement with k_{act}, a should be taken as 8.2 Å, a reasonable value in view of the molecular dimensions of Cr(bipy)$_3$. This suggests that the inner-sphere reorganization energy contributes to the activation free energy to only a small extent in this reaction. However, the value of k_{calc} is quite sensitive to that of a, and unfortunately a is not a sufficiently definite quantity for the Marcus theory to be applied to the existing molecules. Thus, the theory must be tested experimentally with regard to a variety of aspects of its theoretical expression for the rate constant before we can consider that the theory is successful in the nonemipirical prediction of the electron-exchange rate constant. Such an extensive examination of this theory has recently been attempted for the electron-transfer reactions between aromatic hydrocarbons and their anion radicals.[21)] The theoretical calculation of the rate constant can be done more reasonably for the reactions participated by the octahedral complex ions than for those participated by the planar aromatic hydrocarbons, because of the premise of a spherical molecular shape in this theory. However, there may be more difficulties in finding a suitable reactant among the former complexes than among the latter.

Table 1. Comparison of the corrected observed rate constant with the calculated one in the electron exchange reaction between Cr(bipy)$_3^{+1}$ and Cr(bipy)$_3$

k_{act} ($M^{-1}\,sec^{-1}$)	Radius (Å)	k_{calc} ($M^{-1}\,sec^{-1}$)	ΔG^* (kcal/mol)
	6.1	3.7×10^8	3.3
	7.1	1.2×10^9	2.6
2.0×10^9	8.2	2.0×10^9	2.2

---

18) M. V. Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917).

19) G. Albrecht, *Z. Chem.*, **3**, 182 (1963).

20) T. Saji and S. Aoyagui, to be published.

21) K. Suga and S. Aoyagui, This Bulletin, **46**, 755, 808 (1973).

One of the most outstanding features of the Marcus theory is that it can treat the homogeneous and the electrochemical electron-transfer reactions in a unified way.[22] An attempt to test this theory in the electrochemical electron-transfer reaction of the $Cr(bipy)_3{}^{1+}$/$Cr(bipy)_3$ redox couple, the corresponding homogeneous reaction having been revealed to be the fastest of all the electron-transfer reactions participated by the transition-metal complexes, is now in progress in our laboratory. It will be reported in the near future.[20]

---

[22] R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).