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Fast Complex Formation Reactions of Divalent First-Row Transition-Metal Ions in Aqueous Solution: Mechanistic Information from Volumes of Activation

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The complex formation reactions of Mn^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} with 2,2'-bipyridine and 2,2':6',2''-terpyridine in aqueous solution were studied as a function of metal ion and ligand concentrations for pressures up to 100 MPa. The corresponding volumes of activation range from -3.4 ± 0.7 (for Mn^{2+}) to $+6.7 \pm 0.2$ cm^3 mol^{-1} (for Ni^{2+}) and parallel the earlier reported data for solvent exchange for the aquated metal ions. This study is the first to report an activation volume for a complex formation reaction involving Fe^{2+} , viz. $+3.5 \pm 0.5$ cm^3 mol^{-1} for the reaction with terpyridine. The results are discussed in reference to data for closely related systems and in terms of a changeover in the nature of the ligand-exchange process, i.e. from I_a to I_d , along the first-row transition-metal elements.

Introduction

In a recent report¹ on the present standing of substitution reactions of divalent and trivalent metal ions, Swaddle pointed out by way of some introductory remarks that the well-understood state of such reactions of a decade ago² has lately been disturbed by new findings and challenging reports. One of these areas concerns the fast substitution reactions of solvated divalent first-row transition-metal ions. Prior to the work of Merbach and co-workers³⁻¹⁴ nobody had ever seriously questioned the dissociative nature of such reactions; i.e. the traditional "Eigen-Wilkins" (or I_d) mechanism^{15,16} was well accepted. However, the Merbach group³⁻¹⁴ reported a gradual mechanistic changeover from I_a to I_d for the exchange of water, methanol, acetonitrile, and dimethylformamide on divalent solvated metal ions in going from V^{2+} to Ni^{2+} along the first-row transition-metal elements. Their conclusions were based on the volumes of activation determined for such processes by employing high-pressure NMR techniques.^{17,18} These results demonstrated that the volume of activation is a valuable mechanistic criterion to characterize the intimate nature of such processes, a claim that has been made by various other groups for mechanistic studies in general.¹⁹⁻²⁵

A consequent and important step in the argumentation is to investigate whether this mechanistic changeover also occurs for complex formation reactions of these metal ions. Earlier papers²⁶⁻³⁰ have reported volumes of activation for some complex formation reactions of Co^{2+} and Ni^{2+} . These are in close agreement with the solvent-exchange data¹² and support the I_d character of the substitution process. A later investigation from this laboratory³¹ presented a negative volume of activation for the reaction of Mn^{2+} with bipyridine in aqueous solution, thus underlining the I_a character of the process. In a very recent study Merbach et al.³² also found a negative volume of activation for the complex formation reaction between V^{2+} and thiocyanate ion. These are the only two examples available at the present time to illustrate that the mechanistic changeover referred to above also occurs for the corresponding complex formation reactions.

We have now undertaken a complete study to determine the volumes of activation for the complex formation reactions of aquated Mn^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} with bipyridine and terpyridine. Preliminary accounts of some of this work have been reported elsewhere.^{33,34}

Experimental Section

Materials. Perchlorate salts of Mn^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} (Fluka and Ventron) were used as source for the metal ions. 2,2'-Bipyridine (bpy), 2,2':6',2''-terpyridine (terpy), and all other chemicals were of analytical reagent grade and used without any further purification. Doubly distilled water was used to prepare all solutions. In most cases the ligand terpy was dissolved in a few drops of ethanol and then diluted to the required volume. The presence of such small quantities of ethanol (<1%) had no significant influence on the kinetic measurements. Deviations only occurred at concentrations higher than 5%. All concentrations quoted refer to normal pressure and room temperature; no corrections for variations

in these parameters were made.^{35,36}

Kinetic and Other Measurements. Kinetic measurements at ambient and elevated pressures (up to 1 kbar) were performed on an Aminco and a self-constructed high-pressure stopped-flow instrument, respectively. The reactions were followed under pseudo-first-order conditions, i.e. by use of at least a 10-fold excess of metal ion or ligand over the other reactant. The corresponding first-order plots were linear for at least 3

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Table I. Rate Data for the Process at Ambient Pressure

$$M^{2+} + L \xrightleftharpoons[k_r]{k_f} ML^{2+}$$

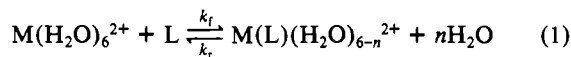
M	L	temp, °C	μ , M	λ , nm	[M], mM	[L], mM	k_f^a , M ⁻¹ s ⁻¹	k_r , s ⁻¹	$K (=k_f/k_r)$, M ⁻¹	ref
Mn	terpy	15	0.1	330	0.01	0.1–0.25	$(8.9 \pm 0.7) \times 10^4$	-0.5 ± 1.3	...	<i>b</i>
		25	0.1	330	0.002	0.05–0.12	$(1.2 \pm 0.1) \times 10^5$	4 ± 1	3.0×10^4	<i>b</i>
		25	~0		0.025	0.20	1.1×10^5	3.8	2.9×10^4	38
		15	0.1	325	0.1–0.6	0.015	$(8.3 \pm 0.6) \times 10^4$	4 ± 2	2.1×10^4	<i>b</i>
Fe	terpy	25	0.1	321	0.05–0.20	0.005	$(1.5 \pm 0.1) \times 10^5$	6 ± 1	2.5×10^4	<i>b</i>
		25	0.1	324	0.005	0.05–0.30	$(8.0 \pm 0.5) \times 10^4$	-0.9 ± 1.0	...	<i>b</i>
		25	~0		0.005	0.10	5.6×10^4	6.3×10^{-3}	8.9×10^6	38
Co	terpy	25	0.1	317	0.2–1.0	0.01	$(2.1 \pm 0.3) \times 10^4$	15 ± 2	...	<i>b</i>
		25	0.1	330	0.01	0.125–0.30	$(3.6 \pm 0.3) \times 10^4$	1.0 ± 0.7	...	<i>b</i>
		25	~0		0.005	0.12	2.4×10^4	10^{-4}	2.4×10^8	38
	bpy	25	0.1	320	0.5–1.0	0.05	$(9.4 \pm 1.1) \times 10^4$	-2 ± 8	...	<i>b</i>
		25	~0		0.03	0.3–0.8	$(6.5 \pm 0.6) \times 10^4$	3 ± 3	...	<i>b</i>
	25	~0		0.5	0.01	7.2×10^4	...	10^6	37	
	25	0.1	302	0.3–0.8	0.03	$(1.2 \pm 0.1) \times 10^5$	-0.5 ± 4.9	...	<i>b</i>	
Ni	terpy	25	0.1	335	0.005	0.05–0.15	$(1.2 \pm 0.1) \times 10^3$	<i>b</i>
		25	~0		0.005	0.08	1.4×10^3	2.5×10^{-8}	5.6×10^{10}	38
	25	0.1	330	2–6	0.1	$(3.00 \pm 0.05) \times 10^3$	<i>b</i>	
	bpy	25	0.1	303	0.02	0.2–0.8	$(2.0 \pm 0.2) \times 10^3$	<i>b</i>
		25	~0		5	0.01	1.5×10^3	5×10^{-5}	3×10^7	37
25	0.1	303	1.0–2.5	0.1	$(5.1 \pm 0.2) \times 10^3$	<i>b</i>		

^a Calculated according to eq 2 or 3 with use of the k_{obsd} values reported in Table A (supplementary material). ^b This work.

half-lives of the reaction. UV-visible absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer. pH measurements were performed on a Radiometer PHM 64 instrument, the reference electrode of which was filled with a 3 M NaCl solution.

Results and Discussion

Experiments at Ambient Pressure. Complex formation reactions of the type investigated can be presented by the overall reaction



where $n = 2$ and 3 for $L = \text{bpy}$ and terpy , respectively. Higher substituted species such as $M(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$ and $M(\text{terpy})_2^{2+}$ are produced in the presence of an excess of L .^{37,38} In most cases the formation of the 1:1 complex is the rate-determining step of the process.^{37,38} Alternatively, reaction 1 can be studied very effectively by working in an excess of M^{2+} compared to the amount of L such that only the 1:1 complex can be formed. Furthermore, kinetic experiments demonstrated that ring-closing processes of the coordinated ligand are non-rate-determining steps.

An important variable in such studies is pH since the aquated metal ions can deprotonate to produce hydroxy species and the ligands L can protonate to produce LH^+ , LH_2^{2+} , etc. depending on the acidity of the solution. The acid dissociation constants for the aquated metal ions are as follows¹⁶ (pK_a): Mn^{2+} , 10.6; Fe^{2+} , 9.5; Co^{2+} , 8.9; Ni^{2+} , 10.6. The acid association constants for the unprotonated ligand are as follows (pK): bpy , 4.5;³⁹ terpy , 4.7.⁴⁰ It follows from these constants that in neutral aqueous medium ($\text{pH} \sim 6$) no significant interference from the various acid-base equilibria is expected (see further discussion).

The earlier studies at ambient pressure^{37,38} were mostly performed in the presence of an excess of L under pseudo-first-order conditions. In this study we have investigated the complex formation process (1) under both conditions of excess of M and L , such that

$$k_{\text{obsd}} = k_f[\text{L}] + k_r \quad (2)$$

$$k_{\text{obsd}} = k_f[\text{M}] + k_r \quad (3)$$

respectively. For this reason the ionic strength of the solution was

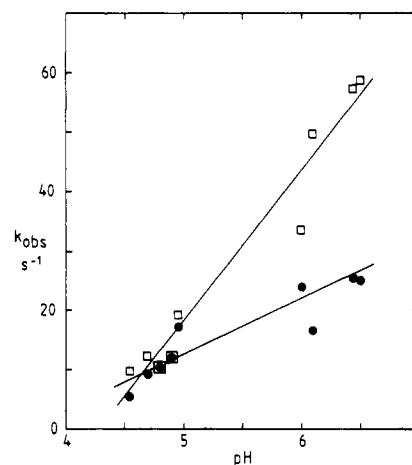


Figure 1. pH dependence of k_{obsd} for the reaction $\text{Fe}^{2+} + \text{bpy} \rightarrow \text{Fe}(\text{bpy})_2^{2+}$ (temperature 12 °C, ionic strength 0.1 M, $[\text{Fe}^{2+}] = 0.6$ mM, $[\text{bpy}] = 0.06$ mM, wavelength 296 nm): (●) first reaction step, k_{obsd} vs. pH; (□) second (slow) reaction step, $10^3 k_{\text{obsd}}$ vs. pH.

adjusted to 0.1 M with NaClO_4 since changes in $[\text{M}]$ are accompanied by significant changes in the ionic strength of the medium. It follows that plots of k_{obsd} vs. $[\text{L}]$ or $[\text{M}]$ should be linear with slopes k_f and intercepts k_r . In the majority of cases the equilibrium constant for reaction 1, i.e., $K = k_f/k_r$, is so large^{37–39} that such plots do not exhibit a meaningful intercept; i.e., k_r is very small. Furthermore, it is likely that the contribution of k_r will disappear in the case of a rapid subsequent substitution process in the presence of an excess of L .

The above-described complex formation reactions are accompanied by significant spectral changes in the UV region, such that complexation by bpy and terpy can be followed at 280–300 and 320–330 nm, respectively. A summary of the obtained kinetic data is given in Table I; for comparison the available literature data are also included. Complexation of Mn^{2+} by bpy could not be followed by using a stopped-flow technique, and the corresponding information was obtained from T -jump measurements as reported elsewhere.^{31,41} Good reproducible kinetic data were obtained for the Fe^{2+} - terpy system in the presence of an excess of L . However, significantly different values of k_f and k_r were found where M was in excess, and the k_r value turned out to be

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Table II. Rate Data for the Process as a Function of Pressure^a

$$\text{M}^{2+} + \text{L} \xrightleftharpoons[k_r]{k_f} \text{ML}^{2+}$$

M	L	temp, °C	[M], mM	[L], mM	rate param	P, MPa					ΔV^\ddagger , ^c cm ³ mol ⁻¹
						3	25	50	75	100	
Mn	terpy	15	0.02	0.15–0.30	$10^{-4}k_f$, ^d M ⁻¹ s ⁻¹	7.8 ± 0.4	8.0 ± 0.3	8.0 ± 0.2	8.1 ± 0.3	8.3 ± 0.2	-1.3 ± 0.3
			0.1–0.5	0.015–0.03	$10^{-4}k_f$, ^d M ⁻¹ s ⁻¹	8.2 ± 0.4	8.3 ± 0.4	8.5 ± 0.6	8.7 ± 0.4	9.5 ± 0.4	-3.4 ± 0.7
					k_r , s ⁻¹	4.3 ± 1.4	4.9 ± 1.4	5.6 ± 1.9	6.1 ± 1.3	5.8 ± 1.3	-7.7 ± 2.2
Fe	terpy	25	0.02	0.20	k_{obsd} , ^b s ⁻¹	14.4 ± 0.3	13.9 ± 0.8	13.3 ± 0.8	12.5 ± 0.2	12.8 ± 0.4	+3.5 ± 0.7
			0.02	0.30		23.3 ± 1.6	22.6 ± 0.5	22.3 ± 0.8	20.8 ± 0.9	20.6 ± 0.7	+3.3 ± 0.4
			0.2	0.02		24.0 ± 0.9	21.1 ± 0.8	21.4 ± 1.5	19.6 ± 0.3	18.3 ± 0.4	+4.3 ± 1.2
			0.4	0.02		31.2 ± 1.2	30.2 ± 1.2	29.5 ± 1.4	29.0 ± 1.0	26.9 ± 0.7	+3.5 ± 0.6
			0.6	0.02		45 ± 4	45 ± 4	44 ± 4	42 ± 4	40 ± 2	+3.4 ± 0.6
Co	terpy	25	0.015–0.03	0.175–0.50	$10^{-4}k_f$, ^d M ⁻¹ s ⁻¹	4.5 ± 0.3	4.4 ± 0.2	4.3 ± 0.2	4.1 ± 0.1	3.7 ± 0.2	+4.5 ± 0.8
			0.6	0.03	k_{obsd} , ^b s ⁻¹	59 ± 2	60 ± 2	53 ± 2	53 ± 2	49 ± 1	+4.7 ± 0.7
			1.0	0.04		85 ± 4	79 ± 5	76 ± 3	76 ± 2	76 ± 1	+2.8 ± 0.9
Co	bpy	25	0.03	0.30–0.70	$10^{-4}k_f$, ^d M ⁻¹ s ⁻¹	7.6 ± 0.3	7.6 ± 0.4	7.0 ± 0.2	6.6 ± 0.6	6.9 ± 0.5	+3.4 ± 1.2
					$10^{-4}k_f$, ^d M ⁻¹ s ⁻¹	6.9 ± 0.2	7.0 ± 0.2	6.7 ± 0.1	6.3 ± 0.2	5.9 ± 0.3	+4.3 ± 1.0
			0.3–0.8	0.02–0.05	$10^{-4}k_f$, ^d M ⁻¹ s ⁻¹	9.1 ± 0.7	8.7 ± 0.7	7.2 ± 0.6	8.2 ± 0.4	8.2 ± 0.6	+2.8 ± 2.8
					$10^{-4}k_f$, ^d M ⁻¹ s ⁻¹	9.8 ± 0.5	8.4 ± 0.4	7.9 ± 0.4	7.4 ± 0.4	7.2 ± 0.3	+7.5 ± 1.4
Ni	terpy	25	0.03	0.275–0.6	$10^{-3}k_f$, ^d M ⁻¹ s ⁻¹	1.6 ± 0.2	1.7 ± 0.2	1.6 ± 0.2	1.5 ± 0.3	1.4 ± 0.2	+3.5 ± 1.2
					$10^{-3}k_f$, ^d M ⁻¹ s ⁻¹	1.45 ± 0.09	1.36 ± 0.11	1.27 ± 0.11	1.18 ± 0.12	1.12 ± 0.11	+6.7 ± 0.2
			1.5	0.1	k_{obsd} , ^b s ⁻¹	3.9 ± 0.0	3.9 ± 0.1	3.8 ± 0.1	3.4 ± 0.1	3.4 ± 0.0	+4.8 ± 0.9
			3.0	0.1		9.4 ± 0.2	9.1 ± 0.2	8.4 ± 0.5	8.1 ± 0.3	7.9 ± 0.3	+4.7 ± 0.5
			4.0	0.1		12.3 ± 0.5	11.9 ± 0.3	11.6 ± 0.4	11.1 ± 0.1	10.4 ± 0.4	+4.0 ± 0.4
Ni	bpy	25	0.03–0.08	0.35–1.0	$10^{-3}k_f$, ^d M ⁻¹ s ⁻¹	2.47 ± 0.03	2.47 ± 0.03	2.43 ± 0.08	2.29 ± 0.05	2.09 ± 0.11	+4.2 ± 1.1
					$10^{-3}k_f$, ^d M ⁻¹ s ⁻¹	2.22 ± 0.10	2.08 ± 0.17	2.00 ± 0.16	1.89 ± 0.16	1.77 ± 0.15	+5.5 ± 0.3
			2–6	0.2	$10^{-3}k_f$, ^d M ⁻¹ s ⁻¹	4.7 ± 0.3	4.5 ± 0.2	4.2 ± 0.2	4.2 ± 0.1	3.9 ± 0.2	+4.9 ± 0.6
					$10^{-3}k_f$, ^d M ⁻¹ s ⁻¹	5.2 ± 0.3	4.9 ± 0.1	4.8 ± 0.2	4.5 ± 0.1	4.2 ± 0.2	+5.1 ± 0.4

^aIonic strength = 0.1 M. ^bMean value of at least six kinetic runs; only quoted for systems where limited data are available; all other data are reported in Table B (supplementary material). ^cCalculated from the slope of the natural logarithms of k_{obsd} , k_f , and k_r vs. pressure plots. ^dCalculated by setting $k_r = 0$ —see Results and Discussion.

very pH dependent. We also encountered difficulties with the Fe²⁺–bpy system, where it was found that the kinetic data were very unreproducible in the presence of an excess of M. The system is extremely pH sensitive (see Figure 1), probably due to the acid–base equilibria referred to above. In addition, a second slower kinetic step was observed, presumably a pH-dependent (see Figure 1) chelation step. More than one reaction step is also observed in the presence of an excess of bpy, which can probably be ascribed to the different complex formation steps.

The results in Table I illustrate that k_r can only be determined for the aquation of Mn(terpy)²⁺. In the remaining cases k_r is very small, i.e., K is very large, and subject to large errors. The quoted literature values for k_r ^{37,38} were determined in a different way.³⁴ In general, our data show good agreement with those published before, especially when the difference in ionic strength is taken into consideration. The two procedures adopted to determine k_f and k_r , i.e. using an excess of M or L, result in k_f values of the same order of magnitude. It is, however, significant to notice that k_f is in some cases approximately 2–3 times larger when determined in the presence of an excess of M as compared to the determination in an excess of L. Whether this is due to a statistical factor, a specific solvational effect, or ion-pair formation in the presence of an excess of metal ions remains to be cleared. We performed various experiments in an effort to solve this discrepancy but cannot offer a definite explanation at the present time.

Experiments at Elevated Pressures. Typical results for the pressure dependence of k_{obsd} as a function of [M] and [L] are summarized in Table II. These data were analyzed in the same way as the normal-pressure data to determine k_f and k_r as functions of pressure. In some cases k_r was set to zero such that k_f could be determined from the quantities $k_{\text{obsd}}/[M]$ or $k_{\text{obsd}}/[L]$. The latter procedure was adopted to obtain better data fits since it must be kept in mind that the pressure dependence of k_f is obtained from the pressure dependence of k_{obsd} measured at

different [M] or [L]. Alternative data-fitting procedures have been adopted elsewhere.^{34,42} Plots of the natural logarithms of k_{obsd} , k_f , and k_r vs. pressure turned out to be linear in all cases, and the corresponding volumes of activation were calculated from the slopes ($=-\Delta V^\ddagger/RT$)^{35,36} of these plots. In some cases additional data points at intermediate pressures (not quoted in Table II) were included in the calculations. The values of ΔV^\ddagger estimated from the k_{obsd} data exhibit no specific trend for a particular reaction in the case where no significant contribution from k_r exists and coincide with the average value of ΔV^\ddagger estimated from the k_f data. In the case of the Mn²⁺–terpy system, however, the data could be analyzed in terms of the pressure dependencies of k_f and k_r .

The results presented in Table II clearly indicate that negative volumes of activation are only observed for substitution reactions of Mn²⁺. This correlates with our earlier results for the Mn²⁺–bpy system,³¹ as well as with the solvent-exchange data for Mn²⁺.¹² A similar result was reported for the solvent-exchange and complex formation reactions of V²⁺³² referred to in the Introduction. These negative volumes of activation are compatible with an I_a type of ligand-exchange process, and a more detailed discussion of these data is presented elsewhere.³⁴ We therefore focus on the ΔV^\ddagger data for Fe²⁺, Co²⁺, and Ni²⁺ in the remainder of the discussion.

This study is the first to report volumes of activation for a complex formation reaction of Fe²⁺. The two sets of data (excesses of L and M, respectively) are in close agreement despite the difficulties encountered in the case of an excess of M mentioned above. The data are in excellent agreement with the solvent-exchange value of $+3.8 \pm 0.2$ cm³ mol⁻¹,¹² thus emphasizing the probable I_d nature of the substitution process. The present results clearly underline the previously suggested mechanistic changeover

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Table III. Volumes of Activation for Complex Formation Reactions of Co^{2+} and Ni^{2+} with Neutral Ligands in Aqueous Solution

entering ligand	ΔV^\ddagger , $\text{cm}^3 \text{mol}^{-1}$		ref
	Co^{2+}	Ni^{2+}	
H_2O	$+6.1 \pm 0.2$	$+7.2 \pm 0.3$	12
bpy	$+4.3 \pm 1.0$	$+5.5 \pm 0.3$	this work ^a
	$+7.5 \pm 1.4$	$+5.1 \pm 0.4$	this work ^b
terpy	$+4.5 \pm 0.8$	$+6.7 \pm 0.2$	this work ^a
	$+3.7 \pm 1.3$	$+4.5 \pm 0.4$	this work ^b
NH_3	$+4.8 \pm 0.7$	$+6.0 \pm 0.3$	26
pada ^c	$+7.2 \pm 0.2$	$+7.7 \pm 0.3$	26
	$+11.2 \pm 2.5$	$+8.2 \pm 2.1$	30
	$+5.3 \pm 0.5$		43
imidazole		$+11.0 \pm 1.6$	29
isoquinoline		$+7.4 \pm 1.3$	44

^a Determined from the data for $[\text{L}] \gg [\text{M}]$ in Table II.

^b Determined from the data for $[\text{M}] \gg [\text{L}]$ in Table II. ^c pada = pyridine-2-azo-(*p*-dimethylaniline).

from I_3 to I_4 for Mn^{2+} and Fe^{2+} , respectively.^{3-14,31} Unfortunately the extreme pH sensitivity of the Fe^{2+} -bpy system prevented further studies of this system, and we are presently in search of suitable alternatives.

The activation volumes for the complex formation reactions of Co^{2+} and Ni^{2+} with bpy and terpy fit well into the range of values summarized for various complex formation reactions of these ions in Table III. No effort is made to compare these data with those for systems involving charged entering ligands,^{27,28,44-48}

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since significant corrections of the measured ΔV^\ddagger for ion-pair formation is required in such cases. These corrections are usually based on theoretical predictions^{49,50} and cause some uncertainties with respect to the resulting ΔV^\ddagger values. The results in Table III underline the validity of the I_d mechanism for such ligand-exchange processes involving Co^{2+} and Ni^{2+} .

To summarize, the present study has shown that the earlier suggested changeover in the solvent-exchange mechanism for the first-row transition-metal elements also applies to complex formation reactions involving these metal ions and neutral ligands. Two complete sets of volume of activation data for complex formation of Mn^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} with bpy and terpy are now available, and these underline the mechanistic discrimination ability of this activation parameter. We therefore cannot go along with general statements casting doubt on the value of volumes of activation in mechanistic investigations.⁵¹ Plausible theoretical explanations for the observed mechanistic changeover along the first-row transition-metal elements have been given elsewhere.¹⁴

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Registry No. bpy, 366-18-7; terpy, 1148-79-4; Mn, 7439-96-5; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0.

Supplementary Material Available: Tables A and B including all averaged k_{obsd} values as a function of $[\text{M}]$, $[\text{L}]$, and pressure (7 pages). Ordering information is given on any current masthead page.

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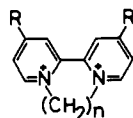
Kinetics of Reduction of Cobalt(III) Complexes by Viologen Radicals

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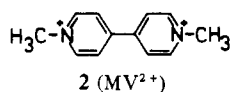
The second-order rate constants are reported for reduction of 11 cobalt(III) complexes by viologen radicals, derived from diquaternary salts of 4,4'-bipyridine and 2,2'-bipyridine. Rate constants vary from 1.5×10^2 to $6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and an excellent correlation with the Marcus expression for 14 redox reactions is observed. These data conform, on the basis of a unity transmission coefficient, to a self-exchange rate constant for the viologens ($\text{X}^{2+/+}$ couple) of $1.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. It is suggested however that this value is about 10^2 too low.

Diquaternary salts of 2,2'-bipyridine, 4,4'-bipyridine, and 1,10-phenanthroline form very interesting radicals by one-electron reduction.^{1,2} Most studied have been those from diquat (1,1'-ethylene-2,2'-bipyridylium ion, **1a**) and (particularly) paraquat



- 1a**, $n = 2$, $\text{R} = \text{H}$ (DQ^{2+})
b, $n = 2$, $\text{R} = \text{CH}_3$ (MDQ^{2+})
c, $n = 3$, $\text{R} = \text{H}$ (PDQ^{2+})
d, $n = 4$, $\text{R} = \text{H}$ (BDQ^{2+})

(1,1'-dimethyl-4,4'-bipyridylium ion, **2**), which are employed as



herbicides³ and used as mediators of one-electron-transfer processes in, for example, solar energy conversion and storage.^{4,5} No systematic study of the kinetics of reduction of metal complexes by these types of radicals has been reported. We have chosen as oxidants a variety of cobalt(III) complexes with neutral ligands (hence all are +3 charged). These have been well characterized with respect to both reduction potentials and self-exchange rate constants, and this is important for use in Marcus-type calculations. The five viologen radicals chosen can be easily prepared from the viologens (**1**, **2**) by dithionite reduction, and the radicals are relatively stable in anaerobic media.⁶ Some kinetic data on MV^{+} reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ have been reported previously.^{7,8}

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