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### Mechanistic Information on Base Hydrolysis and Base-Promoted Linkage Isomerization Reactions of Chromium(III) Amine Complexes from Volumes of Activation

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Whereas base hydrolysis reactions of aminocobalt(III) complexes are generally accepted as proceeding by a  $S_N1CB$  mechanism,<sup>2</sup> the mechanism for analogous chromium(III) systems is less certain. Although reactions are accelerated in base, almost invariably aminochromium(III) compounds with halide leaving groups are slower to react in aqueous base than cobalt(III) analogues, but this may be tied to less acidic amine protons or a less labile conjugate base. The positive activation entropies for reactions of both haloaminochromium(III) and -cobalt(III) systems in aqueous base certainly support a common mechanism for cobalt(III) and chromium(III).<sup>2</sup> In an extensive study of base hydrolysis reactions of haloaminocobalt(III) systems, we have established that large positive activation volumes ( $\Delta V^*_{\text{exptl}}$ ) in the range +19 to +43  $\text{cm}^3 \text{mol}^{-1}$  are observed for these reactions, and interpretation underlines the validity of the  $S_N1CB$  process in those systems.<sup>3-5</sup> It was of interest to us to determine  $\Delta V^*_{\text{exptl}}$  values for some chromium(III) complexes in base for comparison, and some preliminary results are reported here and compared with data for cobalt(III).

Further, it has recently been observed that some pentaaminochromium(III) complexes with neutral O-bound donor ligands with the capacity for N- as well as O-coordination do not hydrolyze in aqueous base but undergo an intramolecular O  $\rightarrow$  N isomerization to form the deprotonated N-bonded species.<sup>6</sup> Ligands such as urea and formamide are candidates for this process. Clearly, this reaction is different from the behavior of halo amine complexes in aqueous base, yet no activation parameters have been reported. (It was considered valuable to investigate whether  $\Delta V^*_{\text{exptl}}$  is distinctly different for this type of reaction.) A clear distinction is reported here for reactions of  $\text{Cr}(\text{NH}_3)_5\text{L}^{3+}$  (L =  $\text{OC}(\text{NH}_2)_2$ ,  $\text{OCHNH}_2$ ) in base compared with those of haloamminochromium(III) complexes.

#### Experimental Section

The complexes  $[\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{NH}_2)_2)](\text{S}_2\text{O}_8)_{3/2} \cdot \text{H}_2\text{O}$ ,  $[\text{Cr}(\text{NH}_3)_5(\text{OCHNH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)_2$ ,  $[\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{CH}_3)\text{N}(\text{CH}_3)_2)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ ,  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ,  $[\text{Cr}(\text{NH}_2\text{CH}_3)_5\text{Cl}]\text{Cl}_2$ , and  $[\text{Cr}(\text{NH}_3)_5\text{I}]\text{I}_2$  were prepared as previously described,<sup>7-10</sup> with chemical analyses and electronic spectral data consistent with the formulations. Kinetic measurements were performed on thermostated ( $\pm 0.1$  °C) stopped-flow or high-pressure stopped-flow equipment,<sup>11</sup> except for slow reactions, which were studied in a high-pressure cell in a standard spectrophotometer.<sup>12</sup> The base hydrolysis reactions were studied under pseudo-first-order conditions and the observed rate constants determined by standard methods, with first-order plots linear for at least 3 half-lives of the reaction. The isomerization reactions were performed at high pH values

**Table I.** Observed Rate Constants for the Reaction of Aminochromium(III) Compounds in Aqueous Base

complex <sup>a</sup>	$[\text{OH}^-]$ , M <sup>b</sup>	temp, °C	$\lambda$ , nm	P, MPa	$k_{\text{obsd}}$ , s <sup>-1</sup> <sup>c</sup>
$\text{Cr}(\text{NH}_3)_5(\text{OCHNH}_2)^{3+}$	0.1	25.0	260	5	0.307
				25	0.344
				50	0.370
				75	0.390
				100	0.417
$\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{NH}_2)_2)^{3+}$	1.0	23.5	500	5	0.095
				25	0.109
				50	0.119
				75	0.129
				100	0.141
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$	0.2	33.5	410	5	$5.00 \times 10^{-4}$
				50	$3.48 \times 10^{-4}$
				100	$2.49 \times 10^{-4}$
				145	$1.98 \times 10^{-4}$
				150	$1.84 \times 10^{-4}$
$\text{Cr}(\text{NH}_2\text{CH}_3)_5\text{Cl}^{2+}$	0.5	25.0	420	5	0.0610
				25	0.0508
				50	0.0375
				75	0.0247
				95	0.0180
				97.5	0.0173
$\text{Cr}(\text{NH}_3)_5\text{I}^{2+}$	0.1	17.2	290	5	0.0772
				25	0.0620
				50	0.0511
				75	0.0395
				100	0.0320
$\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{CH}_3)\text{N}(\text{CH}_3)_2)^{3+}$	1.0	29.0	520	5	0.150
				25	0.118
				50	0.0930
				75	0.0730
				100	0.0580

<sup>a</sup>  $[\text{Cr}(\text{III})]$  from 3 to 50 mM, depending on  $[\text{OH}^-]$ . <sup>b</sup> All at 1.0 M ionic strength ( $\text{NaClO}_4$ ). <sup>c</sup> Averages of from 3 to 10 runs; standard error  $\leq 4\%$ .

**Table II.** Activation Volumes for Selected Base-Catalyzed Hydrolysis Reactions

complex	$\Delta V^*_{\text{exptl}}$ , $\text{cm}^3 \text{mol}^{-1}$	
	M = Cr(III) <sup>a</sup>	M = Co(III) <sup>b</sup>
$\text{M}(\text{NH}_3)_5\text{Cl}^{2+}$	$+17.0 \pm 0.9$	$+33.8 \pm 1.0$
$\text{M}(\text{NH}_2\text{CH}_3)_5\text{Cl}^{2+}$	$+34.8 \pm 1.7$	$+32.8 \pm 1.7$
$\text{M}(\text{NH}_3)_5\text{I}^{2+}$	$+22.2 \pm 0.6$	$+33.6 \pm 1.0$
$\text{M}(\text{NH}_3)_5(\text{OC}(\text{CH}_3)\text{N}(\text{CH}_3)_2)^{3+}$	$+25.0 \pm 0.7$	$+43.2 \pm 1.7$

<sup>a</sup> This work. <sup>b</sup> Reference 3.

**Table III.** Activation Parameters for Linkage Isomerization Reactions of (Urea)- and (Formamide)pentaaminochromium(III) Ions in Aqueous Base

complex <sup>a</sup>	$\Delta H^*$ , kJ mol <sup>-1</sup>	$\Delta S^*$ , J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^*$ , cm <sup>3</sup> mol <sup>-1</sup>
$\text{Cr}(\text{NH}_3)_5(\text{OCHNH}_2)^{3+}$ <sup>b</sup>	$54.3 \pm 1.0$	$-73 \pm 3$	$-7.6 \pm 0.8$
$\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{NH}_2)_2)^{3+}$ <sup>c</sup>	$62.2 \pm 1.5$	$-58 \pm 5$	$-9.8 \pm 0.9$

<sup>a</sup> Ionic strength 1.0 M ( $\text{NaClO}_4$ ); fully deprotonated ligand.

<sup>b</sup> Temperature dependence: 16.0 °C, 0.1485 s<sup>-1</sup>; 24.8 °C, 0.2907 s<sup>-1</sup>; 36.9 °C, 0.7293 s<sup>-1</sup>. <sup>c</sup> Temperature dependence: 24.9 °C, 0.092 s<sup>-1</sup>; 31.9 °C, 0.158 s<sup>-1</sup>; 40.0 °C, 0.32 s<sup>-1</sup>; 46.8 °C, 0.542 s<sup>-1</sup>.

above the  $pK_a$  values for the coordinated ligands (formamide,  $pK_a = 11.7$ ; urea,  $pK_a \approx 13.5$ )<sup>6</sup> to limit consideration of the deprotonation equilibrium. Under the conditions employed, the simple isomerization of the deprotonated O-bound ligand was followed.

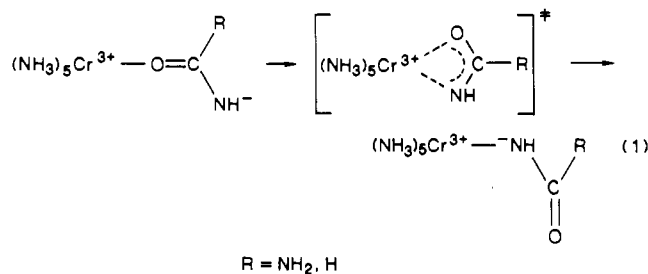
#### Results and Discussion

Reactions of the urea and formamide complexes in strong basic solution are accelerated by the application of pressure, whereas other reactions are significantly retarded (Table I). Plots of  $\ln k_{\text{obsd}}$  versus pressure are linear within experimental error limits for all systems studied up to 1 kbar, with  $\Delta V^*_{\text{exptl}}$  values derived

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from the slope<sup>3,13</sup> collected in Tables II and III. Distinctly different  $\Delta V^{\ddagger}_{\text{exptl}}$  values occur for linkage isomerization versus base hydrolysis reactions.

The reactions of  $\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{NH}_2)_2)^{3+}$  and  $\text{Cr}(\text{NH}_3)_5(\text{OCHNH}_2)^{3+}$  in strong base involve isomerization of the deprotonated ligand.<sup>6</sup> A process as outlined in eq 1 is presumably

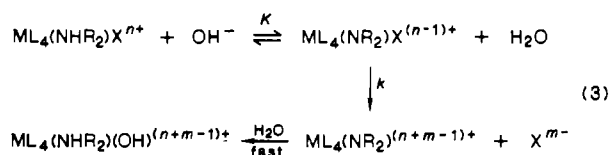


involved, since no competition by hydroxide ion or water occurs. This intramolecular process could involve an intermediate of the type drawn (perhaps even viewed as a tight ion pair). A conjugate base (coordinated ammonia) mechanism, as originally suggested,<sup>6</sup> is ruled out on the basis of the negative  $\Delta V^{\ddagger}_{\text{exptl}}$ , since such a mechanism requires a positive  $\Delta V^{\ddagger}_{\text{exptl}}$ .<sup>3-5</sup> The negative  $\Delta V^{\ddagger}_{\text{exptl}}$  presumably arises as a result of solvent electrostriction around separated charge centers in the transition state. The values observed are not unlike values for spontaneous aquation of halopentaamminechromium(III) compounds;  $\Delta V^{\ddagger}_{\text{exptl}}$  for  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$  aquation is  $-10.6 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>14</sup> Although the anion is recaptured in the present examples, a similar movement of a monoanion from a cationic complex is presumably involved. The negative  $\Delta V^{\ddagger}_{\text{exptl}}$  values observed here are paralleled by negative activation entropies (Table III). Because of the relatively low  $\text{p}K_a$  values for the amine groups in the O-bound ligands (at least compared with those of coordinated ammonia), we were able to operate in pH regimes where essentially complete deprotonation occurs, simplifying the reaction to consideration of the isomerization step. As will be seen below, this is not the case in other reactions, where a conjugate base equilibrium is involved in the kinetic equation. The formamide and urea complexes exhibit rate-limiting behavior at high pH; i.e., the rate constant is independent of hydroxide ion where complete deprotonation has occurred. The  $\text{p}K_a$  of coordinated ammonia is too high to permit operation in such a regime in water, and a simple first-order dependence on  $[\text{OH}^-]$  is normally found for base-promoted isomerization reactions where a conjugate ammine base is involved. This is the case for the nitrito-nitro isomerization reaction of  $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$  in base, which shows a large positive  $\Delta V^{\ddagger}_{\text{exptl}}$  of  $+27.0 \text{ cm}^3 \text{ mol}^{-1}$ ,<sup>15</sup> markedly different from the values observed for the chromium(III) compounds here and similar to values for base-catalyzed hydrolysis reactions of cobalt(III) compounds.<sup>3-5</sup>

The reactions of simple inert octahedral aminometal(III) complexes with a leaving group that is not recaptured, i.e., hydrolysis, are in general base-catalyzed and frequently follow the rate law in eq 2, with terms for spontaneous ( $k_1$ ) and catalyzed ( $k_2$ ) paths, for which  $k_1 \ll k_2[\text{OH}^-]$  for the complexes studied here. The base-dependent term arises perhaps generally from

$$k_{\text{obsd}} = k_1 + k_2[\text{OH}^-] \quad (2)$$

the  $\text{S}_{\text{N}}1\text{CB}$  process (eq 3), which under pseudo-first-order con-



ditions yields an expression for the rate constant (eq 4), that

simplifies to eq 5 since usually  $K[\text{OH}^-] \ll 1$ . For an  $\text{S}_{\text{N}}1\text{CB}$

$$k_{\text{obsd}} = kK[\text{OH}^-]/(1 + K[\text{OH}^-]) \quad (4)$$

$$k_{\text{obsd}} = kK[\text{OH}^-] \quad (5)$$

mechanism, the observed  $\Delta V^{\ddagger}_{\text{exptl}}$  values are a composite of the effect of pressure on both  $k$  and  $K$ , according to eq 6, where the

$$\Delta V^{\ddagger}_{\text{exptl}} = \Delta V^{\ddagger}(k) + \Delta \bar{V}(K) \quad (6)$$

latter term has been estimated at  $+22 \text{ cm}^3 \text{ mol}^{-1}$  for a 2+ precursor.<sup>3</sup> The residual  $\Delta V^{\ddagger}(k)$  term represents the volume change in forming the transition state leading to the presumed five-coordinate intermediate. Detailed discussion of these effects for cobalt(III) systems has appeared elsewhere.<sup>3-5</sup> Like cobalt(III), the chromium(III) systems studied here exhibit large positive  $\Delta V^{\ddagger}_{\text{exptl}}$  values.

Comparison of data for the  $\text{M}(\text{NH}_2\text{CH}_2)_5\text{Cl}^{2+}$  systems ( $\text{M} = \text{Co}, \text{Cr}$ ) shows that  $\Delta V^{\ddagger}_{\text{exptl}}$  is insensitive to the metal ion. We have previously argued that, even in spontaneous aquation, the  $\text{Cr}(\text{NH}_2\text{CH}_2)_5\text{Cl}^{2+}$  ion may be mechanistically dissociative in character,<sup>13</sup> largely as a result of steric considerations. Hence, it is not unexpected to find a  $\Delta V^{\ddagger}_{\text{exptl}}$  value similar to the value for the cobalt(III) systems, where a well-defined  $\text{S}_{\text{N}}1\text{CB}$  mechanism operates,<sup>2</sup> obviously supporting the same mechanism for the chromium(III) complex. The smaller  $\Delta V^{\ddagger}_{\text{exptl}}$  value for  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$  (ca.  $17 \text{ cm}^3 \text{ mol}^{-1}$  lower than the value for the cobalt(III) analogue) indicates that the absence of non-leaving-group influence observed for cobalt(III)<sup>5</sup> does not hold for chromium(III). In fact,  $\Delta V^{\ddagger}_{\text{exptl}}$  for  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$  is smaller than the predicted  $\Delta \bar{V}(K)$  value, indicating a negative  $\Delta V^{\ddagger}(k)$  term. Given the apparently associative nature of the spontaneous aquation reaction for this ion,<sup>13</sup> the observation in base may imply far more association of water in the loss of  $\text{Cl}^-$  from the conjugate base in this sterically more accessible ion. The idea of association of some sort with the conjugate base would seem unprecedented. However, if this is so, the variation observed here for chromium(III) complexes again underlines the differences in the chemistries of cobalt(III) and chromium(III).

To pursue the issue a little further, we subsequently investigated the behavior of  $\text{Cr}(\text{NH}_3)_5\text{I}^{2+}$  and  $\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{CH}_3)\text{N}(\text{CH}_3)_2)^{3+}$  in aqueous base. In the former complex,  $k_{\text{OH}}$  approaches most closely that of its cobalt(III) analogue for simple pentaamines, whereas the latter represents a neutral leaving group, related to the ligands that can isomerize but is itself unable to do so because of N-methylation. The value for the iodo pentaamine complex is somewhat larger than that for the chloro analogue, and this may arise because the much larger iodide ion prevents as close an approach for water molecules in the transition state as is the case with chloride departing. Again,  $\Delta V^{\ddagger}_{\text{exptl}}$  is well below the average value for several cobalt(III) halo pentaamines of  $\sim +34 \text{ cm}^3 \text{ mol}^{-1}$ , supporting a mechanistic difference for the pentaamminechromium(III) system. This view is further supported by the value for the neutral leaving group hydrolysis from the chromium(III) 3+ ion, which is again ca.  $17 \text{ cm}^3 \text{ mol}^{-1}$  below the value for the analogous cobalt(III) system, although it is larger than the values for base hydrolysis from 2+ ions of pentaamminechromium(III). Hence, for both 3+ and 2+ ions, we observe the ca.  $17 \text{ cm}^3 \text{ mol}^{-1}$  less positive value for chromium(III), reflecting the more associative process. We do not expect  $\Delta \bar{V}(K)$  to be significantly different, since we have demonstrated earlier that  $\Delta \bar{V}$  for neutralization reactions similar to conjugate base formation is mainly determined by changes in the overall charge, i.e., electrostriction, and not the nature of the central metal atom.<sup>16</sup>

Although the determined  $\Delta V^{\ddagger}_{\text{exptl}}$  values for base hydrolysis of  $\text{Cr}(\text{NH}_3)_5\text{X}^{n+}$  ( $\text{X} = \text{Cl}^-, \text{I}^-, \text{OC}(\text{CH}_3)\text{N}(\text{CH}_3)_2$ ) and  $\text{Cr}(\text{NH}_2\text{CH}_2)_5\text{Cl}^{2+}$  support the operation of a conjugate base mechanism, the negligible influence of non leaving groups observed for cobalt(III) systems does not hold for chromium(III). At least for the pentaamminechromium(III) system, the existence of a

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genuine five-coordinate intermediate in basic solution must be questioned on the basis of our results. It is on the basis of the available data appropriate to think in terms of a more associative process for the reaction of the conjugate base species, and a type of interchange mechanism would account best for the observed effects. This would require the introduction of an ICB (interchange conjugate base) mechanism, in line with our more recent findings for associative character in aquation reactions of pentaamminechromium(III) complexes.<sup>13,17,18</sup> On the other hand, for the methylamine complex steric hindrance obviously forces the conjugate base species to react in a dissociative way similar to that found for the Co(III) complexes.

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### Rate Constants for the Scavenging of Ru(bpy)<sub>3</sub><sup>3+</sup> by EDTA in Aqueous Solution

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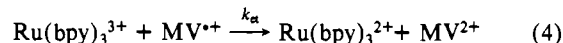
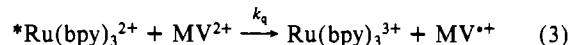
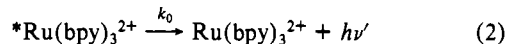
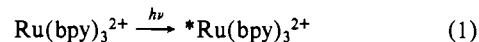
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In the model system for the photosensitized reduction of water, containing Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine) as the photosensitizer and methylviologen (1,1'-dimethyl-4,4'-bipyridinium dication; MV<sup>2+</sup>) as the quencher,<sup>1</sup> a sacrificial electron donor, which upon one-electron oxidation transforms rapidly and irreversibly into a species that lacks the ability to oxidize the methylviologen radical cation (MV<sup>•+</sup>), is required to scavenge the Ru(bpy)<sub>3</sub><sup>3+</sup> generated in the oxidative quenching reaction in order to permit the MV<sup>•+</sup> to accumulate in solution.<sup>2</sup> In the absence of the sacrificial donor, the rapid and highly exoergic back-electron-transfer reaction between Ru(bpy)<sub>3</sub><sup>3+</sup> (E<sub>red</sub><sup>o</sup> = 1.26 V)<sup>3</sup> and MV<sup>•+</sup> (E<sub>ox</sub><sup>o</sup> = 0.45 V)<sup>4</sup> would annihilate these redox charge carriers.<sup>5</sup>

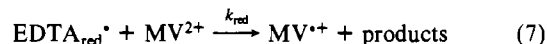
Because the formation of H<sub>2</sub> from the interaction of MV<sup>•+</sup> with colloidal metal catalysts is most efficient in mildly acidic solution,<sup>6</sup> the sacrificial donor of choice for this particular application over the past decade has been EDTA (pK<sub>a</sub> 0.0, 1.5, 2.0, 2.7, 6.1, 10.2).<sup>7</sup> At pH ~ 5, EDTA exists primarily as a dianion; in increasingly basic solution, first the trianion and then the tetraanion predominate. The one-electron oxidation of EDTA (>N-CH<sub>2</sub>-CO<sub>2</sub><sup>-</sup>) yields an amine-localized radical (EDTA<sub>ox</sub><sup>•</sup>; >N<sup>•+</sup>-CH<sub>2</sub>-CO<sub>2</sub><sup>-</sup>) that rapidly loses a proton from the carbon atom α to the amine and carboxylate moiety to generate a carbon-localized radical that is a strong reducing agent (EDTA<sub>red</sub><sup>•</sup>; >N-CH-CO<sub>2</sub><sup>-</sup>).<sup>8</sup> Our

work with EDTA as an electron donor indicates that the transformation step is very rapid (k<sub>tr</sub> > 10<sup>7</sup> s<sup>-1</sup>), and independent of pH.<sup>9-12</sup>

The relevant steps in the mechanism that deal with excitation, relaxation, quenching, back electron transfer, and scavenging are shown as reactions 1-5. Reaction 6 describes the overall transformation of EDTA<sub>ox</sub><sup>•</sup> to EDTA<sub>red</sub><sup>•</sup>.



The ultimate yield of MV<sup>•+</sup> is dictated by the efficiencies of quenching ( $\eta_q = k_q[\text{MV}^{2+}]/(k_q[\text{MV}^{2+}] + k_0)$ ), cage escape of the redox products in reaction 3 ( $\eta_{ce}$ ), and scavenging ( $\eta_{sc} = k_{sc}[\text{EDTA}]/(k_{sc}[\text{EDTA}] + k_{et}[\text{MV}^{\bullet+}])$ ), as well as those of the secondary reduction steps; knowledge of the kinetic details of the mechanism is required for the most efficacious use of the model photochemical system and for the design of better systems. Values of k<sub>0</sub> (1.6 × 10<sup>6</sup> s<sup>-1</sup>), k<sub>q</sub> (~10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, depending on [EDTA], pH, μ), η<sub>ce</sub> (0.1-0.3, depending on [MV<sup>2+</sup>], [EDTA], and μ), and k<sub>et</sub> (>10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, depending on μ), as well as the rate constant for reaction 7 (k<sub>red</sub> = 10<sup>6</sup>-10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> at pH 4.7-11), have been



extensively reported.<sup>5,9,10,13,14</sup> Interestingly, despite the obvious importance of knowing the value of k<sub>sc</sub> under photochemically relevant conditions, there have been very few direct determinations of that quantity, which still remains somewhat in doubt. As a result, a complete kinetic understanding of this model photochemical system, with an eye toward the maximization of the yields of charge-separated redox products, has not yet been achieved.

Sutin<sup>15</sup> first reported a value for k<sub>sc</sub> of 2 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> at pH 8.2; unfortunately, experimental details were not given in this review article. From the [EDTA]-dependent recovery of the bleaching of Ru(bpy)<sub>3</sub><sup>2+</sup> upon pulsed-laser flash photolysis, Keller et al.<sup>8</sup> obtained a value of 1.1 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> for solutions containing 0.5-5 mM MV<sup>2+</sup> at pH 5 in 0.5 M acetic acid/acetate buffer; the range of [EDTA] for these experiments was not specifically given. By using the stopped-flow technique to effect the direct reaction of Ru(bpy)<sub>3</sub><sup>3+</sup> with EDTA, Miller and McLendon<sup>16</sup> determined k<sub>sc</sub> as a function of pH: 8 × 10<sup>3</sup>, 7 × 10<sup>4</sup>, and 2 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> at pH 3, 5, and 7, respectively. They noted that the deprotonation of the acidic forms of EDTA would render the species a stronger reductant, thereby accounting for their observed "titration curve" of the rate constants. However, the details of the exact composition of the solutions, especially regarding the ionic strength, were not given.

Because of these very different values of k<sub>sc</sub>, Orellana et al.<sup>17</sup> made a redetermination. They obtained a value of 1.7 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> from a pulsed-laser flash photolysis study on a solution containing 25 mM MV<sup>2+</sup> at pH 5 in 0.05 M potassium hydrogen phthalate buffer; apparently, only one concentration of EDTA

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