

lylic anilines and allylic methylanilines;<sup>10,11</sup> the reported products, which include neither aziridines nor Schiff bases, may be derived from allylic and amino radicals produced by bond homolysis.<sup>10,11</sup> It seems plausible that the fragmentation reactions we report here may similarly involve homolysis, although the interesting possibility of a hydrocarbon analog<sup>12</sup> of a Norrish type II cleavage with the tertiary amine **3e** remains to be excluded.<sup>13</sup> While it is premature to speculate in detail upon the mechanisms of the rearrangements to aziridines and to Schiff bases, appropriate labeling experiments may provide data useful to this end. For the present, we consider the intermediacy of a zwitterion, analogous to the intermolecular exciplexes derived from photoexcited arenes and amines,<sup>14</sup> as highly likely for the aziridine formation. Further analogy may be seen in the additions of primary, secondary, and tertiary amines to olefins and to benzene, where similar exciplexes may be proposed.<sup>15</sup>

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## References and Notes

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- Solutions were prepared under nitrogen from olefin-free deaerated solvents. Amines were freshly distilled under nitrogen from KOH. Direct irradiations were conducted with a type L Hanovia lamp using Vycor filters and sensitized irradiations with Pyrex filters. Quantum yield studies used sealed quartz ampoules degassed at  $10^{-5}$  Torr and 254-nm light.
- Yields and product ratios (a) were determined by vpc analysis on  $\frac{1}{8}$  in. 15% Carbowax 20-M + 5% KOH columns using hydrocarbon internal references, (b) are approximate in 1a irradiations since the areas were determined using a TC detector and are uncorrected, and (c) are exact in 1b-e irradiations, determined using flame ionization techniques and appropriate molar response ratios. Products were isolated by distillation under nitrogen through a Vigreux column to yield a product concentrate from which individual components were isolated by vpc collection on a  $\frac{1}{4}$  in. Carbowax-KOH column.
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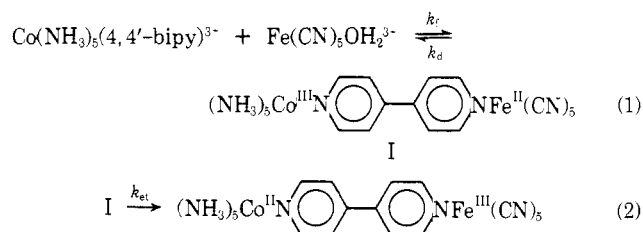
## Formation of a Precursor Binuclear Complex and Intramolecular Electron Transfer Mediated by 4,4'-Bipyridine<sup>1</sup>

Sir:

Inner sphere redox reactions proceed by a sequence of steps: formation of a precursor complex, intramolecular

electron transfer, and dissociation of the successor complex.<sup>2</sup> For most systems, the first step is an unfavorable, rapid equilibrium ( $Q$ ), and electron transfer is rate-determining ( $k_{et}$ ). The measured rate constants are, therefore, composite quantities ( $Qk_{et}$ ). Many attempts have been made to measure rates of elementary steps, but only partial success has been achieved.<sup>3-5</sup>

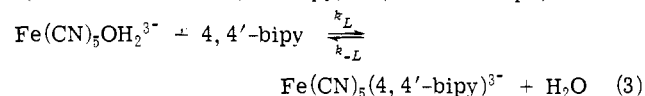
For the reduction of 4,4'-bipyridinepentaamminecobalt(III) by aquopentacyanoferrate(II),<sup>6</sup> we have measured the rate of formation and dissociation of the precursor complex I (eq 1) and the rate of intramolecular electron transfer (eq 2).



The formation of I was monitored at 480 nm, 25°, pH 8.0 (tris(hydroxymethyl)aminomethane buffer),  $\mu = 0.10$  M ( $\text{LiClO}_4$ ),  $[\text{Co}] = (0.39\text{--}72) \times 10^{-5}$  M, and  $[\text{Fe}] = (0.92\text{--}17.4) \times 10^{-5}$  M<sup>7</sup> and yielded  $k_f = (5.5 \pm 0.3) \times 10^3$  M<sup>-1</sup> sec<sup>-1</sup>.

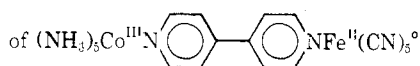
The spectrum of I was obtained by repetitively scanning equimolar mixtures of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  and  $\text{Co}(\text{NH}_3)_5(4,4'\text{-bipy})^{3+}$  and extrapolating to the time of mixing.<sup>8</sup> I exhibits a maximum at ~505 nm ( $\epsilon \sim 6 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>).  $\text{Fe}(\text{CN})_5\text{L}^{3-}$  complexes with L = pyridine, 4,4'-bipyridine, and pyrazine exhibit metal to ligand electron transfer bands at 362 ( $\epsilon 3.5 \times 10^3$ ), 432 ( $\epsilon 5.6 \times 10^3$ ), and 452 ( $\epsilon 5.0 \times 10^3$ ) nm, respectively.<sup>9</sup> The wavelength of maximum absorption of  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$  increases upon coordination of the remote N. Thus, with  $\text{CH}_3^+$  and  $\text{H}^+$ , the maximum shifts to 520 ( $\epsilon 5.6 \times 10^3$ )<sup>9</sup> and 515 ( $\epsilon 4.7 \times 10^3$ )<sup>10</sup> nm, respectively. Therefore, the 505 nm ( $\epsilon \sim 6 \times 10^3$ ) band observed for I represents strong evidence for the proposed structural assignment.

The measurement of  $k_{et}$  posed serious difficulties, even in the presence of  $\text{EDTA}^{2-}$  (added to sequester the cobalt(II) produced and prevent precipitation) and ascorbic acid (added to reduce the  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{2-}$  produced and prevent its rapid reaction with I). In order to drive reaction 1 to more than 98% completion, and because of rapid reduction of I by  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ ,  $\text{Co}(\text{NH}_3)_5(4,4'\text{-bipy})^{3+}$  was in excess. Under these circumstances, I is regenerated by reaction of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  produced by aquation of  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$  (reverse of eq 3) with the



excess Co(III), and the kinetics of disappearance of I are quite complicated. Initial rates from a dozen runs, with  $[\text{Co}] = (1.0\text{--}29.2) \times 10^{-5}$  M,  $[\text{Fe}] = (4.3\text{--}19.1) \times 10^{-6}$  M,  $[\text{ascorbic acid}] = (1.0\text{--}2.2) \times 10^{-3}$  M,  $[\text{EDTA}^{2-}] = (1.0\text{--}7.0) \times 10^{-4}$  M, pH 8.0 (Tris buffer), and  $\mu = 0.10$  M ( $\text{LiClO}_4$ ), yielded values of  $k_{et}$  in the range  $(2\text{--}4) \times 10^{-3}$  sec<sup>-1</sup>.

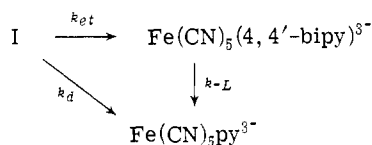
Since the quality of the measurements of  $k_{et}$  was unsatisfactory, we sought to obtain  $k_{et}$  by a procedure which provided unequivocal evidence for the intramolecular electron transfer pathway. This was achieved by allowing I to be formed by reaction of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  with  $\text{Co}(\text{NH}_3)_5(4,4'\text{-bipy})^{3+}$ , and then, before much of reaction 2 took place, adding pyridine in excess. Since pyridine reacts rapidly<sup>11</sup>

**Table I.** Kinetics of Dissociation and Internal Electron Transfer

$10^8[\text{Co}(\text{NH}_3)_5(4,4'\text{-bipy})^{3+}]_0, M$	$10^6[\text{Fe}(\text{CN})_5\text{OH}_2^{3-}]_0, M$	$10^3(k_d + k_{et}),^b \text{ sec}^{-1}$	$10^4k_{-L},^c \text{ sec}^{-1}$	$10^3k_{et}, \text{ sec}^{-1}$
5.50	14.1	6.9	7.7	2.4
7.28	20.0	6.8	7.7	2.5
7.75	19.5	7.0 <sup>d</sup>	7.6 <sup>d</sup>	2.6
8.57	9.3	7.5	7.6	2.5
9.75	9.9	6.9	7.7	2.7
10.0	8.4	7.1	7.6	2.5
10.0	22.9	7.3	8.0	2.7
10.4	9.9	7.1	7.9	2.9
10.4	20.0	7.2	7.8	2.8
11.1	9.6	7.3	8.0	2.8
11.1	11.5	6.7 <sup>d</sup>	8.0 <sup>d</sup>	2.8
	7.1 <sup>e</sup>		7.6	
	7.1 <sup>e</sup>		7.6	

<sup>a</sup> At 25°, pH 8.0 (trizma buffer  $5.0 \times 10^{-3} M$ ),  $\mu = 0.10 M$  (LiClO<sub>4</sub>), [ascorbic acid] =  $(0.51\text{--}2.42) \times 10^{-3} M$ , [EDTA<sup>2-</sup>] =  $(0.93\text{--}1.86) \times 10^{-4} M$ , [pyridine] =  $(4.14\text{--}11.0) \times 10^{-2} M$ . <sup>b</sup> From measurements at 550 nm. <sup>c</sup> From measurements at 450 nm. <sup>d</sup> Measurements at 455 nm from time of mixing and fitted simultaneously to a two exponential decay with constants  $k_d + k_{et}$  and  $k_{-L}$ , respectively. <sup>e</sup> This is the concentration of  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$ .

with  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ , the reaction scheme becomes that shown in Scheme I. Values of  $k_{et} + k_d$  were obtained by fitting the observed absorbances  $A_t$  at 550 nm to  $A_t = A_\infty + (A_0 - A_\infty) \exp[-(k_{et} + k_d)t]$ .  $A_\infty$  and  $k_{et} + k_d$  were taken as adjustable parameters. Values of  $k_{-L}$  were obtained by fitting the observed absorbances  $A_t$  at 450 nm to  $A_t = A_\infty + (A_1 - A_\infty) \exp(-k_{-L}t)$ , where values of  $A_t$  were taken at sufficiently long times to ensure that less than 2% of I remained,  $A_1$  was the first value of  $A_t$ , and  $A_\infty$  was measured after ten half-lives. Values of  $k_{et} + k_d$  and  $k_{-L}$  are listed in columns 3 and 4 of Table I. Additional confirmation for the proposed scheme comes from the ex-

**Scheme I**

cellent agreement between measurements of the rate of dissociation of  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$  prepared by reaction of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  with 4,4'-bipyridine (experiments 12 and 13) and measurements in the presence of cobalt.

To obtain values of  $k_{et}$  and  $k_d$ , the yields of  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$  and  $\text{Fe}(\text{CN})_5\text{py}^{3-}$  before equilibration must be known. Extrapolating the absorbance at 450 nm to the time of addition of pyridine, yielded the fraction of  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$ ,  $f$ , produced in the reaction if no equilibration takes place as  $(A_{\text{extrap}} - A_\infty)/(A_{\text{bipy}} - A_{\text{py}})$ , where  $A_{\text{bipy}}$  and  $A_{\text{py}}$  are the absorbances  $\text{Fe}(\text{CN})_5(4,4'\text{-bipy})^{3-}$  and  $\text{Fe}(\text{CN})_5\text{py}^{3-}$ , respectively, at a concentration equal to the iron concentration in the run. Values of  $k_{et}$ , calculated from  $k_{et} = f(k_{et} + k_d - k_{-L})$ , are listed in column 5 of Table I.

From the average values of  $k_{et} + k_d = 7.1 \times 10^{-3} \text{ sec}^{-1}$  and  $k_{-L} = 2.6 \times 10^{-3} \text{ sec}^{-1}$ , we calculate  $k_d = 4.5 \times 10^{-3} \text{ sec}^{-1}$ . From the latter and  $k_f = 5.5 \times 10^3 M^{-1} \text{ sec}^{-1}$ , we obtain  $1.2 \times 10^6 M^{-1}$  for the equilibrium constant of reaction 1. This compares favorably with the range  $(0.3\text{--}2.0) \times 10^6$  for the equilibrium constants of reactions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  with nitrogen heterocycles.<sup>11</sup> The value of  $k_f$  is somewhat higher than the values  $(3\text{--}4) \times 10^2 M^{-1} \text{ sec}^{-1}$

for neutral nitrogen heterocycles, and the increase in rate with increasing positive charge of the entering ligand suggests an ion pair, dissociative mechanism for the substitution reactions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ .<sup>12</sup>

The radicals derived by one-electron reduction of protonated 4,4'-bipyridine<sup>13</sup> or the dimethyl derivative (methyl viologen)<sup>14</sup> are relatively stable, and it is appropriate to inquire if a chemical mechanism is operative in the electron transfer mediated by 4,4'-bipyridine. However, the low reducing power of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  ( $E^0 = -0.54 \text{ V}$ )<sup>15</sup> combined with the difficulty in reducing protonated 4,4'-bipyridine or methyl viologen ( $E^0 = 0.44 \text{ V}$ )<sup>13</sup> render the chemical mechanism unlikely.<sup>16</sup> We suggest that the resonance exchange mechanism is operative and that the slow rate of intramolecular electron transfer is associated with two factors: a symmetry factor with iron(II) being a  $\pi$ -donor and 4,4'-bipyridine a  $\pi$ -conductor, but cobalt(III) being a  $\sigma$ -acceptor, and a spatial factor, the large distance between the two metal centers preventing the coupling of inner-sphere and solvation shell reorganizations necessary for electron transfer.<sup>17</sup> Additional work using other nitrogen heterocycles as electron mediators is in progress.

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## Spin Density Distribution in and Rearrangement of a Naphthobicyclobutane Radical Anion

Sir:

A few examples of ring cleavage reactions in radical anions are known<sup>1</sup> which, if concerted, are cycloreversion reactions<sup>2</sup> of the type  $\sigma_2s + \sigma_2s$ . In this communication, we wish to report the results of our nmr and esr studies of the NaK alloy reduction of the naphthobicyclobutane (**1**)<sup>3</sup> (formally [1',8']naphthotricyclo[4.1.0.0<sup>5,7</sup>]hept-2-ene), which