experimentally observed spectrum, E (allowing for some overlap of the center peak with unenhanced **2**), and the large qualitative differences among the three simulations seem to indicate that (a) the cyclohexyl radical is "locked" on the CIDNP time scale, and (b) there is a preference for abstraction of the pseudoequatorial β-hydrogen. These two qualitative conclusions are discussed below.

By observing temperature-dependent selective line broadening, Fessenden and Ogawa[1j] have estimated a barrier to chair–chair interconversion in **1** of 4.9 ± 0.5 kcal/mol and a rate constant which makes it possible to estimate a mean lifetime of 2×10^{-9} s for the process at 40 °C, the temperature at which the spectrum in Figure 1 was obtained. This is in accord with our conclusion that, on the average, **1** will remain in one conformation for approximately the length of time (10^{-9} to 10^{-10} s[4c]) required for a cyclohexyl-cyclohexyl radical pair to undergo nuclear spin dependent singlet–triplet mixing leading to CIDNP of the observed intensity.

More surprising is the conclusion that the pseudoequatorial proton is removed selectively. One might have expected just the opposite mode of selectivity: The 41 G hyperfine splitting of the pseudoaxial β-proton suggests that this hydrogen participates to a greater extent than the pseudoequatorial hydrogen in hyperconjugative ("no-bond") resonance, lowering the bond order of the C–H (axial) bond relative to that of C–H (equatorial). Furthermore, a least-motion argument would predict the nearly trans-anti-pseudoaxial β-hydrogen as the one most likely to depart. In fact, in a pseudochair conformation of **1** the pseudoequatorial β-hydrogen has nearly achieved the coplanarity with the α-hydrogen which the double bond of **2** demands.

Two possible explanations for the unexpected preference for transfer of a pseudoequatorial β-hydrogen between two cyclohexyl radicals come readily to mind: (1) the steric bulk of a cyclohexyl radical might favor its abstraction of the less hindered, pseudoequatorial, hydrogen from a partner radical, or (2) the disproportionation reaction might take place via a severely distorted conformation of the six-membered ring in which the normally pseudoequatorial hydrogen occupies a position relative to the unpaired electron which resembles that of the pseudoaxial hydrogen in the chair-like conformation. It also remains to be seen whether steric preference for hydrogen atom removal from **1** may be detected by more conventional chemical means such as the use of specifically labeled radical precursors.

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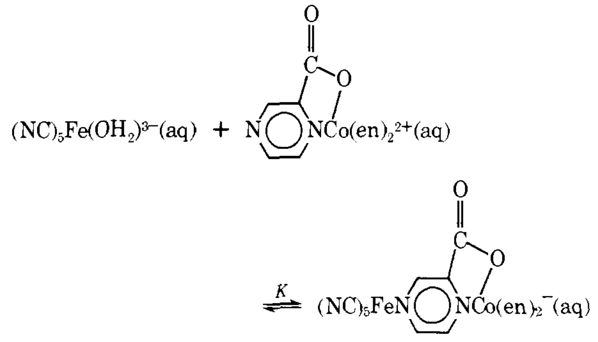
Intramolecular Electron Transfer Induced by Visible Light

Sir:

The mechanisms of light-induced electron transfer processes are presently being investigated intensively.[1] However, as in mechanistic studies of thermal redox reactions an exact interpretation of experiments is often impossible because the extent of association of oxidant with reductant is not known. Recently, a new approach to the problem was provided via the use of "precursor" complexes, containing electron source and sink joined by a common bond system.[2-6]

Among the few precursor complexes synthesized thus far, several are bleached on exposure to ultraviolet or visible light.[3,4] Accurate quantum yields for electron transfer, ϕ_{et}, have been determined in one study, in the ultraviolet region.[4] We report here our measurements of ϕ_{et} at 620 nm in two related precursor complexes. The results are of interest because of the relatively long wavelength of light employed, the manner in which ϕ_{et} reflects the reactivity of the oxidants used, and because of the simplicity of the photolysis procedure, performed in a stopped-flow instrument.

Toma[6] has shown that the 2-pyrazinecarboxylatobis(ethylenediamine)cobalt(III) ion reacts rapidly with the aqueous pentacyanoaquoferrate(II) complex according to eq 1. An intensely blue-colored species, A, is formed (λ_{max} 635 nm, ϵ_{max} 9.5×10^3 M^{-1} cm^{-1}, $K = 8.3 \times 10^6$ M^{-1}, 25 °C, $\mu = 0.10$ M). The strong optical absorption is due to iron(II)-to-heterocycle (MLCT) charge-transfer excitation. In the absence of light, A is stable with respect to electron transfer. However, it reacts on exposure to visible light, producing aqueous cobalt(II) and iron(III)-containing species.



(1)

A

To utilize the increased driving force for electron transfer offered by tetraamminecobalt(III) relative to a bis(ethylenediamine)cobalt(III) oxidant,[7] we have produced by a reaction analogous to eq 1, the intermediate B. This species is generated rapidly upon mixing 2.0×10^{-5} M pentacyanoaquoferrate(II) with 2.0×10^{-3} M pyrazinecarboxylatotetraamminecobalt(III) ion in the cuvette of a stopped-flow spectrophotometer (Durrum Model D-110, pathlength 2.0

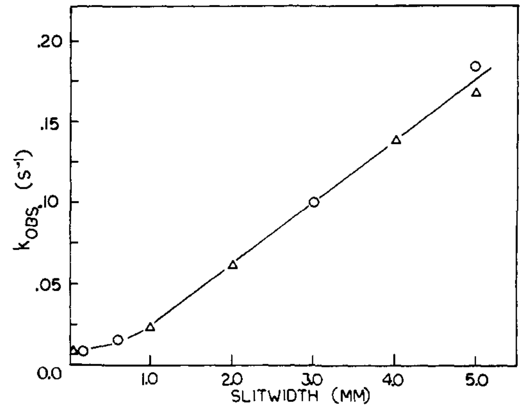
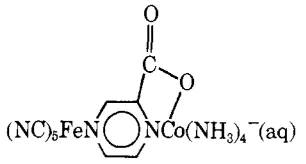


Figure 1. Specific rate of electron transfer in B vs. spectrophotometer slit width: [Co_{total}] = 1.0 × 10^{-3} M, [Fe_{total}] = 1.0 × 10^{-5} M. 24 °C, pH 6.5, μ = 0.15 M ($LiClO_4$). Triangles denote added ascorbic acid (5 × 10^{-4} M).



B

cm). B is characterized by its close similarity in spectrum with A. For B, λ_{max} 630 ± 10 nm, ϵ_{max} (9 ± 1) × 10^3 M^{-1} cm^{-1}. Decay of the absorption due to B is a first-order process described by rate plots that are linear over at least three half-lives.[8] Aqueous cobalt(II) and an iron(III)-containing product, presumably the 2-pyrazinecarboxylate complex of pentacyanoferrate(III) ion, are the products of the reaction.

We find that k_{obsd}, *the first-order specific rate of disappearance of B is approximately a linear function of the optical slit width employed in the stopped-flow instrument.* This dependence is shown in Figure 1. The bandwidth of the spectrophotometer (3 nm/mm) is inside the charge-transfer envelope even at the widest slit setting used (5 mm). Also, the rate of reaction at a given slit width is relatively independent of wavelength in the range 615–640 nm. Therefore the increase in k_{obsd} given in Figure 1 is ascribed to an increase in light intensity, I_0, entering the observation cuvette. At narrow slitwidth (0.10–0.15 mm) k_{obsd} reaches a constant value, 0.012 s^{-1}, the specific rate of the dark reaction (k_{th}). Reaction conditions were 24 °C, μ = 0.15 M ($LiClO_4$), pH 6.5 (phosphate buffer).

To determine ϕ_{et}, the quantum yield for photoredox decomposition of the intermediates, it is necessary to find I_0. This was accomplished by measuring the rate of photolysis of aqueous hexaureachromium(III) ioin the stopped-flow cuvette under the same physical conditions employed in studying the precursor complexes. At 620 nm, 5.0 mm slitwidth, I_0 was (4.2 ± 0.4) × 10^{15} quanta cm^{-3} s^{-1} ((1.4 ± 0.13) × 10^{-8} einsteins cm^{-2} s^{-1}). The wavelength 620 nm was chosen because it corresponds to an absorbance peak of the primary actinometer[9] and is near the absorbance maxima of A and B.

By working at very low initial concentrations of Fe(II) (1.0 × 10^{-5} M after dilution) it could be ensured that the total optical absorbance was always 0.1 or less and that the light intensity throughout the cuvette was therefore close to I_0. ϕ_{et} could then be calcted using eq 2.[10]

$$\phi_{et} = k_l/(2.303 \times 10^3 I_0 \epsilon) \qquad (2)$$

For B, ϕ_{et} equals 0.9 ± 0.15, computed using k_l and ϵ values that are, respectively, 0.17 ± 0.01 s^{-1} and 6.1 ± 0.3 × 10^3 M^{-1} cm^{-1}. k_l was found at 5.0 mm slitwidth using the equation $k_l = k_{obsd} - 0.012\ s^{-1}$. ϵ_{620} was measured directly at 5.0 mm slitwidth.

For A, k_{th} was not detected. Therefore k_l was considered equal to k_{obsd} (4.1 × 10^{-3} s^{-1}, 24 °C, 5.0 mm slitwidth). The values of I_0 and ϵ at 5.0 mm slitwidth in this case were (1.1 ± 0.1) × 10^{-8} einsteins cm^{-2} s^{-1} and (8.4 ± 0.3) × 10^3 M^{-1} cm^{-1}. Substitution in eq 2 yields ϕ_{et} = (2.0 ± 0.3) × 10^{-2}.

The difference in the photoreactivities of A and B can be rationalized if the mechanism in each case involves an excited state in which iron(III) is linked to cobalt(III) via a short-lived, bridging pyrazine radical. In the species formed by MLCT excitation of B, the tetraamminecobalt(III) moiety evidently is sufficiently reactive to oxidize the bridging radical after virtually every excitation event. From the radiative lifetime estimated for a $Fe^{II}(d) \rightarrow pyrazine(\pi^*)$ excited state,[11] the lower limit for photoinduced electron transfer to tetraamminecobalt(III) would be ca. 10^9 s^{-1}. The low quantum yield in the case of A indicates that the bis(ethylenediamine)cobalt(III) oxidant is considerably less reactive in competing for the electron, just as A is thermally unreactive compared to B.

In Figure 1 the value of k_{th} is 0.012 ± 0.001 s^{-1}. This value is larger than those found previously for thermal intramolecular electron transfer between $Fe(CN)_5^{3-}$ and $Co(NH_3)_5^{3+}$ mediated by 4,4′-bipyridine (2.6 × 10^{-3} s^{-1})[3a] or by 4-pyridine carboxylate (1.8 × 10^{-4} s^{-1}),[3b] yet much smaller than k_{obsd} for intramolecular electron transfer between Co(III) and Ru(II) bridged by 4-pyridine carboxylate (ca. 200 s^{-1}).[2]

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The Remarkable Alcoholysis Reaction and Structure of *trans*-Bis(α-chlorovinyl)bis(dimethylphenylphosphine)-platinum(II)

Sir:

Although simple vinyl halides are known to be highly unreactive in solvolytic processes,[1] α-chlorovinylplatinum(II)