viations such as arise from nonbonded interactions. This approach is now being extended to molecules of increasing complexity.

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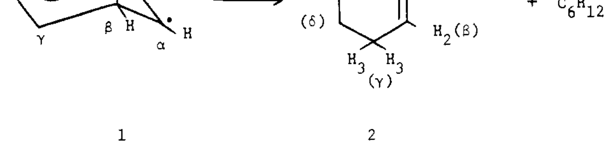
CIDNP Evidence for Stereoselectivity in the Disproportionation of Two Cyclohexyl Radicals

Sir:

The ESR spectrum of the cyclohexyl radical, **1** (Scheme I), observed under a variety of conditions,[1] reveals that the two β-protons adjacent to the carbon containing the unpaired electron are nonequivalent. The proton hyperfine splittings of 41 and 5 G are presumed to be due to the pseudoaxial and pseudoequatorial protons, respectively, in a chair-like conformation of the radical.[1i] The possibility thus exists for preferential reactivity of the two stereochemically different β-hydrogens in a reaction involving removal of a hydrogen atom from the cyclohexyl radical. We wish to report the observation of an NMR spectrum exhibiting CIDNP in a manner which implies that the disproportionation reaction between two cyclohexyl radicals to give cyclohexene, **2**, does indeed display preferential reactivity of one of the two types of β-hydrogen.

Scheme I



1 **2**

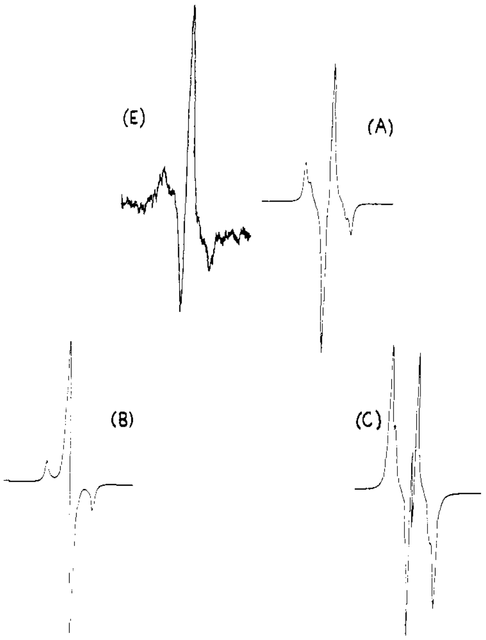


Figure 1. NMR spectra of the olefinic protons of cyclohexene formed by the disproportionation of two cyclohexyl radicals: (E) experimentally observed spectrum obtained during the reaction of cyclohexyl bromide with metallic magnesium in THF at room temperature; simulated spectra calculated assuming (A) removal of pseudoequatorial hydrogen, (B) removal of pseudoaxial hydrogen, and (C) conformational equilibration of radicals before hydrogen removal.

While observing the NMR spectrum of a tetrahydrofuran solution of cyclohexyl bromide reacting with magnesium metal we have obtained the CIDNP spectrum of the olefinic protons of **2** reproduced in Figure 1E. In other studies of the reaction between alkyl halides and magnesium,[2] alkenes have been observed to exhibit CIDNP consistent with their formation via encounters between freely diffusing alkyl radicals. We thus interpret Figure 1E as a record of the disproportionation reaction between two free cyclohexyl radicals.

Using published values for the hyperfine splittings in cyclohexyl radical[1g] and the spin-spin coupling constants in **2**,[3] we have carried out a calculation of the CIDNP intensity pattern for the olefinic protons of **2** using three difference models for the disproportionation process: (A) removal of a pseudoequatorial β-hydrogen (a = 5 G); (B) removal of a pseudo-axial β-hydrogen (a = 41 G); (C) removal of a β-hydrogen whose hyperfine splitting is the mean of models A and B. Model C serves as an approximation to the case where ring flipping in **1** is fast compared to the radical pair lifetime. The computation of NMR spin state populations in the radical pair included the α- and β-protons on both radicals ($a_\alpha = -21$ G[1g]) and was carried out using a modified NMR simulation program[4] to incorporate the radical pair model for CIDNP proposed by Adrian.[5] A calculation based on the CKO model[6] gave nearly identical spectra in this case. The simulations for the models A–C are shown in Figures 1A–1C, respectively.

The nearly perfect agreement between simulation A and the 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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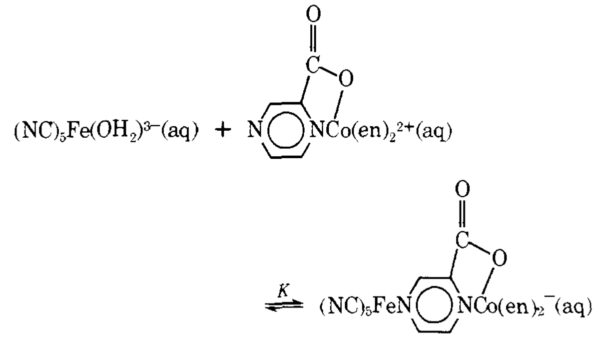
Intramolecular Electron Transfer Induced by Visible Light

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