ligand field absorption band (λ_{max} 360 nm). By comparing the change of absorbance of $Co(CN)_5N_3^{3-}$ to the yield of I_2^- in flash photolysis experiments, we estimate that $\phi_{aq}/\phi_{redox} \simeq 2$[20] for irradiation of the 281-nm CTTM band and $\phi_{aq}/\phi_{redox} > 1.7 \times 10^2$ for irradiation of the ligand field band (no I_2^- was detected). In the continuous irradiation of the 281-nm CTTM band we found that nitrogen (and no hydrogen; $3 \leqslant pH \leqslant 9$) was produced, permitting us to estimate $\phi_{redox} = (7.4 \pm 1) \times 10^{-3}$. Most of the N_2 could be quenched by radical scavengers; *e.g.*, irradiation of $Co(CN)_5N_3^{3-}$ in 10^{-3} *M* I^- reduced the yield of N_2 by 75%. The photoredox behavior in the deeper ultraviolet ($\lambda \leqslant 254$ nm) is far more complex with $\phi_{redox} \sim 7 \times 10^{-3}$ at 254 nm and $\phi_{redox} \sim 7 \times 10^{-2}$ at 214 nm. However, for irradiations at $\lambda \leqslant 254$ nm not all the nitrogen can be scavenged by I^- (*e.g.*, only 50% of the N_2 is scavengeable at 254 nm), indicating that irradiations at these wavelengths produce both $Co(CN)_5NH^{2-}$ and ($Co(CN)_5^{2-} + \cdot N_3$) intermediates. For those experiments in which I^- was in the solution during irradiation, $Co(CN)_5I^{3-}$ was found among the products.

The photochemical behavior of $Rh(NH_3)_5N_3^{2+}$ contrasts to that of $Co(CN)_5N_3^-$ in its simplicity; I^- scavenging experiments indicate that less than 10% of product nitrogen is scavengeable at any wavelength, so the simple photoredox process must be formation of $Rh(NH_3)_5NH^{3+}$ intermediates. However, this system is also very remarkable in that this product is associated *only* with irradiation of the 251-nm absorption band (*i.e.*, for excitations at 250 ± 30 nm); at 254 nm $\phi = 0.2$.

We find further that photoredox behavior seems to be a reasonably common feature of the photochemistry of acidopentacyanocobaltates. Thus flash irradiation of the ligand field absorption band of $Co(CN)_5I^{3+}$ in 10^{-3} *M* I^- did not produce I_2^- while irradiation of the 254–360-nm region of this complex resulted in the formation of appreciable I_2^-. Flash photolysis of $Co(CN)_5NCS^{3-}$ or of $Co(CN)_5SCN^{3-}$ in the presence of NCS^- resulted in the formation of $(NCS)_2^-$ (λ_{max} 475 nm[21]).

We infer that previous investigations have failed to find evidence for photoredox behavior in $Co^{III}(CN)_5X$ complexes either because they did not irradiate CTTM absorption bands or because they did not attempt to detect, possibly transient, redox products. It is evident that these complexes exhibit the general pattern of photochemical behavior characteristic of most complexes of d^6 metals: (1) low energy irradiation results predominantly in aquation of coordinated ligands; (2) irradiation of CTTM bands results in oxidation–reduction and in aquation processes, and (3) product yields are strongly wavelength dependent.

The photoredox chemistry of $Co(CN)_5N_3^-$ qualitatively appears to combine some features of the behavior of $Rh(NH_3)_5N_3^{2+}$ with those reported for $Co(NH_3)_5N_3^{2+}$.[15] However, the photochemical behavior of $Co(NH_3)_5N_3^{2+}$ has not been examined with care in the deep ultraviolet and the differences between the pentaammine- and pentacyanocobaltates may be more apparent than real. More specifically, we cannot rule out the possibility that nitrene production is characteristic of the population of a ligand-centered state which does not communicate efficiently with other states in the molecules. Nevertheless the azido complexes of rhodium(III) (and probably iridium(III)) appear to be unique in that there is no appreciable formation of azide radicals on irradiating any CTTM band (*i.e.*, with $\lambda \leqslant 214$ nm). A very likely source of this difference in behavior is the difference in radial extension of the metal-centered nonbonding 3d and 4d electrons; the back-bonding interaction, possible in the latter cases but not for cobalt,[13] could sufficiently stabilize the CTTM excited states that N–N cleavage becomes the preferred mode of excited-state reactive decomposition.

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[20] α_{aq} = quantum yield for aquation = decomposition yield of $Co(CN)_5N_3^{3-}$ less the yield of I_2^- and corrected for the yield resulting from irradiation of the ligand field band only.

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Theoretical Analysis of Long-Range Hyperfine Interactions in Aliphatic Free Radicals. Origin of the W and Anti-W Rules

Sir:

We wish to report the main results of an *ab initio* investigation of long-range interactions in the *n*-propyl radical, the simplest compound in which hyperfine splittings have been observed for α, β, and γ protons separated from the paramagnetic site by one, two, and three bonds, respectively.[1,2]

The spin-restricted SCF equations of the doublet ground state have been solved by the open-shell IBMOL program[3] based on Roothaan's method.[4] A (9s,5p/4s) Gaussian basis set reduced to a double-ζ form by the usual contraction technique[5] has been chosen.

Two contributions to hyperfine splitting have been considered. The direct or delocalization contribution (a_{dir}) is given by the restricted SCF ground-state wave function ψ_0. The indirect or spin-polarization contribution (a_{ind}) arises from a configuration interaction which has been limited to monoexcited states and computed by a first-order perturbation treatment.[6]

For protons, the resulting coupling constants are

$$a_H = a_{dir} + a_{ind} = (8\pi/3)(g_e/g_0)g_H\beta_H(\rho_{dir} + \rho_{ind}) \quad (1)$$

with

$$\rho_{dir} = |\phi_u(\mathbf{r}_H)|^2 \quad (2)$$

$$\rho_{ind} = -2\sum_d\sum_{v^*}\rho_{d\rightarrow v^*} \quad (3)$$

$$\rho_{d\rightarrow v^*} = \frac{\langle\phi_d\phi_u|\phi_u\phi_{v^*}\rangle}{E_0 - E_{d\rightarrow v^*}}\phi_d(\mathbf{r}_H)\phi_v(\mathbf{r}_H) \quad (4)$$

where ϕ_d and ϕ_{v^*} are doubly occupied and virtual orbitals and ϕ_u is the orbital containing the unpaired

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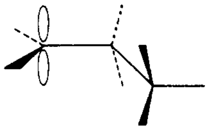
electron in ψ_0. In order to obtain a better understanding of spin-polarization effects, we have converted the delocalized MO's into quasilocalized equivalent MO's by the Foster–Boys procedure;[7] each term of the perturbation expansion is then described as the result of a well-defined local excitation.

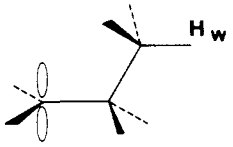
We shall first describe the stable conformation found for this propyl radical. Assuming a planar-trigonal carbon (angle HCC = 120°) for the radical site, fixed bond angles, and fixed bond lengths (CH = 1.093 Å, CC = 1.534 Å), the lowest energy is found for a conformation where the two α hydrogens are in the plane of the three carbon atoms, the methyl group being staggered ($E_{\text{staggered Me}} = -117.572018$ au).

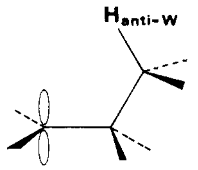


The rotation barrier of the methyl group is 4.8 kcal ($E_{\text{eclipsed Me}} = -117.564385$ au). According to epr results,[1,2] this conformation, in which both H_α are in the carbon plane but with the methyl group in free rotation, is predicted to be the most stable one. In this conformation, *ab initio* calculated hyperfine splittings are −34.34 G for α hydrogens and come exclusively from spin polarization. As shown previously for the ethyl radical,[8] β-hyperfine splittings in that conformation (+23.58 G) result from the combined effect of direct (+13.50 G) and indirect (+10.08 G) mechanisms. Delocalization has no appreciable contribution to the splittings of freely rotating γ hydrogens in this conformation, but spin polarization leads to an average value of −0.21 G on each γ atom. These results are in agreement with experimental determinations[2] of both geometry and hyperfine splittings (exptl: $a_{H\alpha} = -22.14$ G; $a_{H\beta} = +30.33$ G; $a_{H\gamma} = \pm 0.27$ G).

These calculations throw some light on the problem of long-range interactions; in this connection conformations of higher energies, in which the methyl group eclipses the p_z orbital containing the unpaired spin, are of structural interest. In one of these conformations ($E_W = -117.571544$ au), a "W-plan arrangement"[9a] of the bonds between the γ proton and the p_z orbital can be found. This situation is usually taken as being responsible for strong long-range interactions.[9]

On the contrary, the anti-W arrangement is associated with small hyperfine interactions; its energy is $E_{\text{anti-W}} = -117.564053$ au.





The present investigations confirm the above statements. In various conformations, the contribution of spin polarization to γ-proton splittings is weak and negative, the contribution of spin delocalization being negligible. However, on the anti-W hydrogen, delocalization (+1.11 G) and spin-polarization (−0.91 G) contributions are opposite in sign and of the same order of magnitude; they cancel to give a small value. On the W hydrogen, delocalization (+2.64 G) and spin-polarization (+1.73 G) contributions are both positive and relatively large; this gives a large positive hyperfine splitting (+4.37 G) for H_γ in the W conformation.

This *ab initio* calculation clearly shows that long-range interactions are critically dependent on stereochemical conditions; in the first-order perturbation, 90% of the total spin polarization always comes from the excitation of the CH bond under consideration ($\phi_d = CH_\gamma$; $\phi_{v*} = CH_{\gamma*}$ in eq 4). The change in sign of the spin polarization at H_γ is directly correlated with the change in sign of the bielectronic integral $\langle \phi CH_\gamma\text{-}\phi_u | \phi_u \phi CH_{\gamma*} \rangle$, the remaining terms in eq 4 being practically independent of the conformation as a consequence of localization.

The strong long-range interactions in γ position result from an appropriate arrangement of bonds permitting a cumulative effect of delocalization and spin-polarization contributions. This is well illustrated in a number of epr studies, especially on bicyclic radicals where geometrical requirements are satisfied by a rigid molecular framework.[9,10]

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Activation of Homogeneous Catalysts by Polymer Attachment

Sir:

The attachment of homogeneous catalysts to polystyrene–divinylbenzene copolymer produces a new class of catalysts with many of the best properties of both heterogeneous and homogeneous catalysts.[1] These catalysts also showed selectivity toward substrates of different molecular bulk[2] and polarities.[3]

We now wish to report that catalysts can be significantly activated by such attachment. A basic requirement for homogeneous catalysis by a transition metal complex is the presence of an open coordination site. In most cases, attempts to open a coordination site on a metal result in the polymerization of the complex, and the production of bridged species in which the required site of unsaturation is blocked.[4] Attach-

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