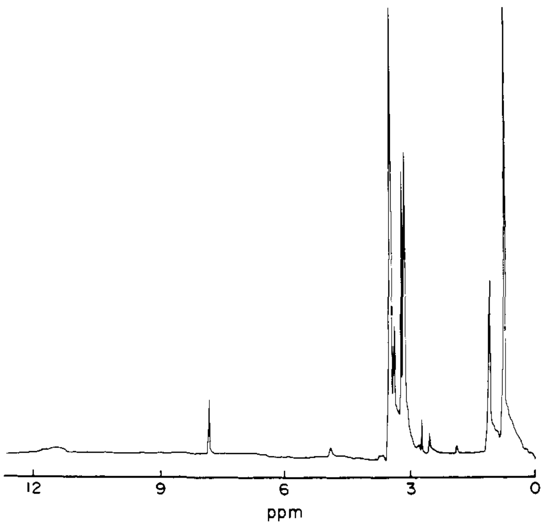

Figure 1. The 270-MHz ^{1}H spectrum of I, II, and *tert*-butyl cations in SO_2ClF at −110 °C.

was then dissolved in SO_2ClF at −125 °C. The 270-MHz proton spectrum at −103 °C demonstrated the presence of ion I and its rearrangement product ion II.[2] The resonances characteristic of ion I are 3.4 (m, 2 H), 3.1 (m, 6 H), and 1.1 ppm (s, 9 H) (external Me_4Si capillary).[3] Ion II had peaks at 3.2 (m, 2 H) and 1.8 ppm (m, 15). There was also a proton acid peak at 8.9 ppm. The spectrum showed no trace of further addition products of ion I with isobutylene. However, when the ratio of *tert*-butyl cation to olefin was reduced to 3:1, or when SbF_5 containing no proton acid was used, considerable amounts of apparent condensation products were formed.

We also prepared cation I from 2-chloro-2,4,4-trimethylpentane and excess SbF_5 (containing proton acid), using SO_2ClF as a solvent. When the sample was warmed to −80 °C it was observed that as the peaks of ion I disappeared, the acid peak also decreased at the same rate. A singlet appeared at 3.2 ppm corresponding to *tert*-butyl cation at twice the rate of decrease of ion I. These observations are explained by β-cleavage of ion I to give *tert*-butyl cation and isobutylene, which is protonated to give a second molecule of *tert*-butyl cation.

In another experiment, cation I was generated in the presence of a 5:1 excess of previously formed isopropyl cation. At −105 °C the solution (Figure 1) consists of cation I-isopropyl cation, 11.7 (heptet, 1 H) and 3.5 ppm (d, 6H), and un-ionized isopropyl chloride-SbF_5 charge-transfer complex 4.8 ppm[4] (heptet, 1 H) and 1.8 ppm (d, 6 H). The solution was allowed to warm in the NMR tube at −95 °C for 1 h and then returned to −105 °C (Figure 2). The spectrum shows a new resonance at 0.8 ppm. This peak corresponds to the upfield methyls of dimethylisobutyl carbonium ion. Although the other peaks of dimethylisobutyl carbonium ion occur under the doublet of the isopropyl cation and the singlet of the *tert*-butyl cation, the peak at 0.8 ppm, upon warming to −95 °C the line broadening due to the 1,3 hydride shift characteristic of this ion was observed.[5]

We feel that these observations can only be explained if isobutylene is formed as an intermediate via a β-cleavage mechanism. Oligomer or polymer is not detected since apparently the olefin is all trapped by reaction with excess isopropyl cation rather than reacting with the starting ion.

The addition of methyl fluoride-antimony pentafluoride complex[6] to isobutylene at −80 °C did not yield *tert*-amyl cation, but polymerization took place. This complex apparently does not react rapidly enough with the olefin at −80 °C to compete with reaction with the small amount of tertiary ions present.

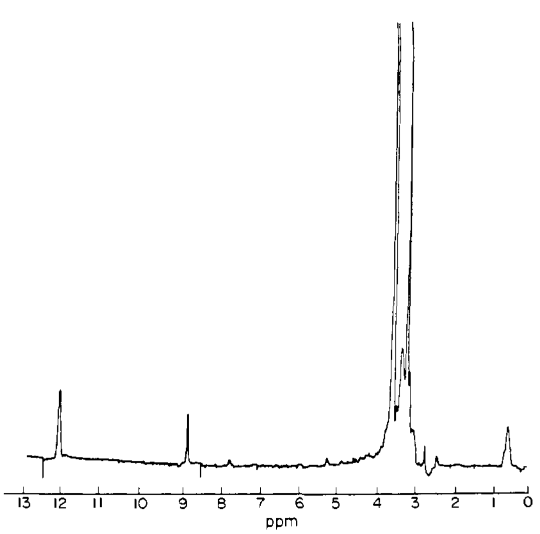

Figure 2. The 270 MHz ^{1}H spectrum of isopropyl, *tert*-butyl, and isobutyldimethyl carbonium ions at −105 °C.

A small amount of proton acid was present during the addition of isopropyl and *tert*-butyl cations to isobutylene. At −95 °C and below the cations react almost quantitatively without an observable decrease in the amount of proton acid present. The acid (presumably HF) is, therefore, less reactive than the carbonium ions in this addition reaction.

In this system, equilibrium must favor the addition step; otherwise, we would not observe it. Cleavage can be observed only because one of its products, isobutylene, is trapped.

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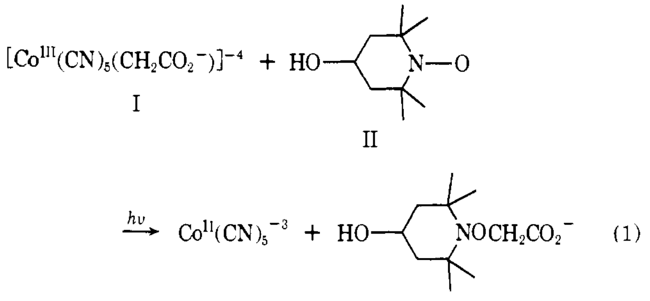
Photochemical Reaction of Alkylpentacyanocobaltates with Nitroxides. A New Biophysical Tool

Sir:

The photoinduced homolysis of the cobalt-carbon σ bond in vitamin B-12[1] and the related synthetic macrocycles[2] is well known. It was suggested by the mechanistic studies of Wood et al.[3] on vitamin B-12 that the alkyl radicals thus obtained should react readily with nitroxides and hence might provide a useful technique in spin-label studies;[4] however the restricted solubilities of these cobalt compounds ($\leq 10^{-2}$ M) limit their use in aqueous systems. We wish to report that the highly water-soluble $[Co(CN)_5(CH_2CO_2^-)]^{-4}$ reacts rapidly with nitroxides according to eq 1, when irradiated in the absence of O_2 with light of 300-400 nm.[5] The relatively long excitation wavelength required, the inertness of the pentacyanocobaltate complexes toward most of the organic functionalities found in phospholipids and proteins,[7] and their nonpermeability through phospholipid membranes make this a highly versatile technique for the specific destruction of nitroxides.[8] It has already been used in this laboratory to measure rates of lateral diffusion in phospholipid bilayers[11] and to determine the number of nitroxide labels (used as antigens in immunochemical experiments[12]) on the outer surface of liposomes.[10]



I

II

III

(1)

I was prepared by the method of Halpern and Maher[13] and purified by fractional recrystallization from aqueous ethanol to give a yellow solid which decomposes and turns green at 180 °C; it is freely soluble in water and slightly soluble in ethanol. A 10^{-2} M solution under argon at 25 °C is stable for several months. Spectral and analytical data are given in the notes.[14]

A solution of I and II (5×10^{-3} M each) is completely stable in normal room light (no reaction after 2 weeks); however, irradiation with a 300-W tungsten bulb causes slow (over 1 h) decrease in the nitroxide paramagnetic resonance signal.[15] Irradiation with a 450-W high-pressure Hg arc lamp abolishes the signal completely in ~45 s. Although kinetics and mechanistic details are still under investigation, the stoichiometry of eq 1 has been verified by quantitative analysis of the nitroxide resonance signal intensity and absorption spectra of the cobalt complexes.[6] No side reactions, such as the abstraction of hydrogen atoms by the alkyl radical or dimerization of the radicals, have been observed.[16] III is stable for at least 24 h at the above concentration, after which there is a slow recovery of the original signal intensity (over about a week.)[17]

The wavelength dependence of the disappearance of nitroxide was observed using a monochromator and mercury source, giving relative pseudo-first-order rate constants (wavelength subscripts in nanometers) $k_{331}/k_{365} = 1.6$ and $k_{331}/k_{312} = 1.2$, indicating a moderate though not pronounced rate maximum at the absorption maximum. This is to be contrasted with the recently reported data of Mok and Endicott[2b] on $Co([14]ane\ N_4)(OH_2)CH_3^{+2}$ for which homolysis quantum yields were wavelength independent from 250 to 520 nm.

We have also begun flash photolysis studies, using a Q-switched doubled ruby laser (340 nm, ~1 mJ/20-ns pulse), and obtained similar results. This approach has been successfully applied to the measurement of membrane lateral diffusion coefficients[11] and may be useful for studies of rapidly relaxing equilibria between two environments separated by a permeability barrier.

Finally it may be noted that, for studies requiring a cobalt concentration $<10^{-2}$ M, vitamin B-12 derivatives and other cobalt macrocycles behave similarly[18] and are particularly suited for use with "leaky" membranes, which pass small ions at an unacceptable rate but not large ones.

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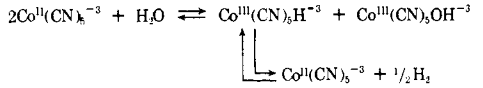
(5) The $Co^{II}(CN)_5^{-3}$ is rapidly converted to $Co^{III}(CN)_5OH_2^{-2}$ (demonstrated by the absorption spectra), presumably through the known reactions[6]



$$2Co^{II}(CN)_5^{-3} + H_2O \rightleftarrows Co^{III}(CN)_5H^{-3} + Co^{III}(CN)_5OH^{-3}$$

$$Co^{III}(CN)_5H^{-3} \rightleftarrows Co^{II}(CN)_5^{-3} + \tfrac{1}{2}H_2$$

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(8) Previously ascorbic acid has been used for this purpose;[9] however, it penetrates lipid bilayer membranes above 0 °C. I does not penetrate bilayer membranes significantly except possibly near phase transition temperatures. The carboxymethyl radical penetrates slowly, presumably in protonated form, but other alkyl ligands have been prepared which are essentially membrane impermeable.[10]

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(14) UV: λ_{max} 333 nm (ϵ 345), 256 (1.16×10^4). IR (KBr pellet): 3000–3500 (s, b, water of crystallization present), 2104 (s, C≡N, lit.[13b] 2106), 1640 cm^{-1} (s, C═O). Nmr: singlet, 2.6 ppm upfield from H_2O (lit.[13b] δ 1.75). Anal. $(Co(CN)_5CH_2CO_2K_4 \cdot 2H_2O)$ Co, H, K. N; C: calcd, 19.13; found, 18.49.

(15) Spectra taken on Varian E-4 or E-12 spectrometer at X-band, room temperature. All reactions carried out at room temperature under argon in sealed 50-μL capillary pipets, or in spectrophotometer cells.

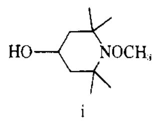
(16) The net negative charge on the radicals is doubtlessly largely responsible for the absence of dimerization; Halpern[13b] found the rate constant for the reaction of $Co(CN)_5^{-3} + ICH_2CO_2^-$ to be 100 times slower than with $ICH_2CO_2CH_3$. Further, the reversibility of the presumed initial step

$$Co^{III}(CN)_5R^{-3} \overset{h\nu}{\rightleftarrows} Co^{II}(CN)_5^{-3} + R\cdot$$

provides a sink, which retards the irreversible loss of alkyl radical. This effect has also been observed with B-12.[2a]

(17) This observation is still being investigated, but probably arises from the hydrolysis of III (perhaps intramolecularly assisted by the basic carboxylate) followed by re-oxidation of the hydroxylamine by $Co^{III}(CN)_5OH_2^{-2}$. A similar compound lacking the carboxylate ($-CH_2C_6H_4N^+(CH_3)_3$) is stable for weeks at pH 7, though rapidly hydrolyzed by base,[10] and that with $-CH_3$ is indefinitely stable.

(18) CH_3-B_{12}, prepared by the method of Dolphin,[19] was photolyzed by light from a 300-W tungsten bulb at a rate similar to i; the product was extracted with ether and identified by gas chromatography/mass spectrometry.



i

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