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Preliminary communication

ELECTRON SPIN RESONANCE STUDY OF LASER INDUCED ANAEROBIC Co^{III}—C HOMOLYSIS OF $C_6H_5Co^{III}$BAE* IN THE SOLID STATE

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Summary

The title compound has been subjected to anaerobic photolysis using He-Ne laser irradiation at wavelength 632.8 nm. Electron spin resonance spectra were recorded at 9.1 and 35.1 GHz frequencies as functions of irradiation time, temperature and crystalline versus solution state, for the purpose of studying the incipient homolysis of the Co—C bond. The presence of an exchange coupled Co^{II}-free radical pair was detected in the solid, which is interesting in comparison to the Co^{II}-free radical pairs which have recently been observed and analyzed in coenzyme B_{12} systems.

Photochemistry of coenzyme B_{12}, its derivatives, and model compounds for B_{12} has been of continuing interest [1,2]. There have been numerous electron spin resonance (ESR) studies, coupled with photochemistry, in this area as well [3—5]. Up to now, most of the photochemical studies which have been carried out were concerned with reactions in solution, in which solvent and other reactive molecules (e.g. O_2) affect the successive steps of chemical reaction after the initial photochemical event. We report here an initial photochemical study of the model compound C_6H_5CoBAE, in the solid state, using a low power (2 mW) laser as the source of photochemical energy. Our results are interesting, especially in comparison to solution studies, and suggest that this may be a fruitful line of research.

C_6H_5CoBAE was synthesized by the method described by Costa et al. [6]. The purity of the complex was checked by elemental analysis and melting point determination. The optical spectrum was completely analogous to the literature reported spectrum [6]. An important reason for choosing the pentacoordinated complex for study is that it is more stable, in comparison to the hexacoordinated analogues having a water molecule *trans* to the alkyl group

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*BAE = Dianion of *N,N'*-ethylenebis(acetylaceteoneimine).

[6]. The samples of C_6H_5CoBAE in the solid state were prepared in conventional quartz EPR tubes and evacuated on a vacuum line to pressure of 10^{-6} torr for 48 hours. Samples in benzene solution (0.001 molar) were prepared in sealed quartz sample tubes which had been subjected to at least six freeze pump-thaw cycles obtaining 10^{-6} torr final pressure while immersed in liquid nitrogen. The degassed solid samples were irradiated in the microwave cavity at –160°C. Some solution samples were irradiated at room temperature, while some were irradiated at –160°C. The effects of exposure to air were also studied, but the obvious results are not pertinent to our present conclusions. The low temperatures were obtained with either of two Varian variable temperature controllers (one for X-band, the other for Q-band, each using liquid nitrogen coolant). Two optical sources were used in this study: the laser source was a Spectra-Physics model 133 CW helium-neon gas laser (λ = 632.8 nm), and a source of white light was an Oriel optics light source (equipped with a Fiber-optics accessory) using a 100 watt quartz tungsten halogen lamp (Oriel model 6333), emitting between 400 nm and 1800 nm.

Photolysis of alkyl corrinoids and model compounds results in the homolytic cleavage of the cobalt to carbon bond [3,7,8]. This result is generally believed to be significant, in that the initial step in enzyme mechanisms requiring the B_{12} coenzyme also involves the (radiationless) homolytic cleavage of the same bond [9,10]. In general, the reaction rate and the final products of these photochemical reactions depend upon the presence or absence of oxygen and/or solvent, as well as the time of irradiation, power and frequency of the radiation source, and the temperature at which the sample is irradiated [11—14]. In planning the experiments which we report here, we decided to select those variables which will emphasize the initial events of photolysis, rather than the chemistry of the photolytic products. In addition, we believe the nature of the threshold energy for photolysis (and its associated distribution function) to be an important object of study as well [15—17]. For this purpose we have chosen a compound having BAE as an equatorial ligand, since such compounds are well known as models in vitamin B_{12} chemistry [18].

The C_6H_5CoBAE complex used in this study is pentacoordinated and diamagnetic. Its structure is not precisely known, but the crystal structure of the hexacoordinated aquo-complex has been determined [19]. The optical spectrum of C_6H_5CoBAE in benzene solution exhibits an absorption band in the vicinity of 630—660 nm, and other bands at shorter wavelengths [6]. For this reason, we thought it worthwhile to study the photolysis using a He-Ne laser which lases at about 630 nm. Similar studies (using longer wavelengths, but not laser irradiation) by other workers [14,20,21] indicate that this should be a good tactic, especially since we wish to concentrate on irradiation with a wavelength as near as possible to the threshold energy for obtaining photolytic breaking of the cobalt-to-carbon σ-bond.

A variety of interesting ESR spectra were obtained, but one type of spectrum in particular appears to be significant. The ESR spectrum of the photolytic product, in the solid state, of evacuated (anaerobic) $C_6H_5Co^{III}$BAE obtained at 9.1 GHz is shown in Fig. 1. This spectrum consists of a narrow, line at $g = 2.002 \pm 0.002$ (with some structure in one shoulder) plus a half-field line at $g = 4.272 \pm 0.005$. The half-field line was found to grow at the

Fig. 1. ESR spectrum of the photolysis products of anaerobic, solid (a powder) C_6H_5CoBAE in an evacuated quartz sample tube. Conditions: T = −160°C, power = 20 mW, gain = 1000, field modulation = 5 Gauss, microwave frequency = 9.070 GHz, nominal field center = 2550 G, Range of sweep = 5000 G, sweep time = 5 minutes. The arrow indicates the half-field line. Most of the structure between g = 2.0 and g = 4.0 is due to cavity background, but some may be due to the sample absorption. Future measurements with a better ESR spectrometer should resolve this portion of the spectrum.

same rate as the narrow line at g = 2.002 upon photolysis at 632.8 nm and −160°C. When the ESR spectrum was recorded at 35 GHz (also in an evacuated ESR tube), the same type of spectrum was obtained, but with clear resolution of a broad structure-less component near g = 2.0, as well as the sharp free-radical-like line at g = 2.002. These characteristics are very similar to those which we have previously calculated for powder spectra of two weakly exchange and dipole-dipole-coupled spin systems, except (contrary to an assumption in our calculational model) the two components of the exchange-split free radical signal have widely different relaxation times. (Similar behaviour is well known in an exchange coupled system arising in xanthine oxidase, which we have also treated [22].) Based on these observations, we tentatively assign this spectrum to a $Co^{II}BAE\text{-}C_6H_5^{\bullet}$ radical pair.

The initial step of homolytic cleavage can be represented by the following equilibrium reaction:

$$RCo^{III}L \underset{}{\overset{h\nu}{\rightleftharpoons}} Co^{II}L + R^{\bullet} \tag{1}$$

When anaerobic photolysis is carried out in solution, the solvent "cage" effect forces the Co^{II} and the free radical to recombine; in the presence of oxygen, on the other hand, the free radical reacts rapidly with oxygen, shifting the equilibrium to the right-hand side, thereby converting $RCo^{III}L$ to photolytic products. Photochemical reactions in the solid state, in contrast, are well known to have low chemical yields [23]. This is due, in part, to the poor penetration of light into the solid, and in part to low quantum yields which result from the rapid recombination of Co^{II} and free radical pairs as a result of the "cage" effect. We found (by double integration of the absorption derivative) that only about 10^{-4} of all C_6H_5CoBAE had been converted to paramagnetic form, and that the strength of the signal increased as more (powder) surface was exposed to laser radiation. So, we conclude that the spectra of

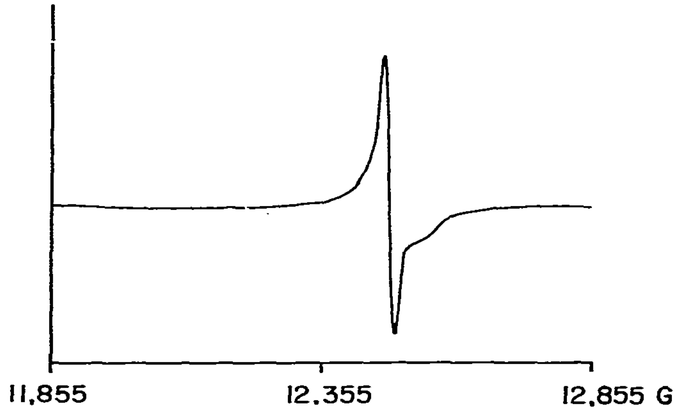

Fig. 2. This sample was similarly prepared as for that shown in Fig. 1, but the sample was in a 2 mm evacuated quartz tube. Temperature = –160°C, power = 20 mW, microwave frequency = 35.1 GHz, gain = 160, field modulation = 25 Gauss (to bring out the broad line), nominal center of scan = 12,355 G, scan range = 1000 G, sweep time = 5 minutes.

Figs. 1 and 2 represent the ESR absorption of a Co^{II}BAE molecule and a $C_6H_5^{\bullet}$ radical trapped in some type of lattice "cage", and that the integrated intensity is of about the expected magnitude for a solid-state photolytic reaction.

The nature of the state of the lattice-stabilized Co^{II}BAE plus radical is interesting. There are two possibilities, depending on the nature of the lattice "cage". The cage may either be related to a nearest-neighbor lattice or surface vacancy (which would physically separate the Co^{II}BAE and free radical, preventing recombination), or the "cage" may be a normal lattice site in which the Co^{II}, free radical pair is stabilized by a reorientation of the free radical (so that the π rather than σ orbitals point towards the Co^{II} bonding orbital), accompanied by a lattice relaxation which "traps" the phenyl radical in a state where normal (i.e. leading to a diamagnetic state) recombination is not possible. We cannot decide, at present, which alternative is correct, but the latter model is certainly more interesting.

In summary, laser irradiation of solid, anaerobic C_6H_5CoBAE at λ = 632.8 nm generates an EPR spectrum characteristic of a caged Co^{II}BAE plus phenyl radical pair. The chemical structure of this pair is interesting and will require further studies to elucidate. Of greatest interest is that we are able to detect and monitor a well defined characteristic of the initial step of photolytic homolysis in a model compound for coenzyme B_{12}, and that it is, in principle, possible to determine both the magnetic geometry [24] and some of the electronic exchange parameters of the associated Co^{II}-radical pair state. In future work, we plan to subject this and other similar systems to more accurate experimental measurements, and the ESR lineshapes and exchange parameters to critical theoretical study. We believe that studies in this direction hold promise of providing some clues to a better understanding of the nature of the electronic factors responsible for cleavage of the Co—C σ-bond in these systems, and this should be of great significance in unravelling the details of the enzyme mechanisms.

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