

## CIDNP in the Photolysis of Coenzyme B<sub>12</sub> Model Compounds Suggesting That C–Co Bond Homolysis Occurs from the Singlet State

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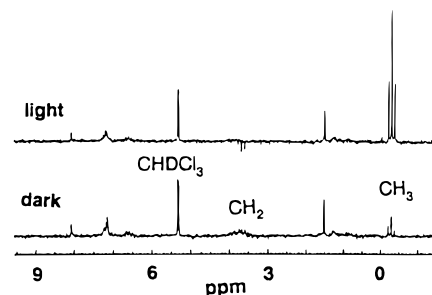
Received May 16, 1996

The photochemistry of coenzyme B<sub>12</sub> and its analogues has received detailed study by laser-flash<sup>1–3</sup> and continuous-wave (CW) photolysis methods, as well as by kinetic magnetic field effect (MFE) studies<sup>2,4–6</sup> and chemically-induced dynamic electron polarization (CIDEP) methods.<sup>7,8</sup> Although these studies clearly indicate the formation of a photochemically-generated radical pair (RP) that partitions between recombination and diffusive separation, CIDEP and MFE studies have led to conflicting conclusions about the electronic spin state of the primary organometallic RP. The photochemical quantum yield of adenosylcob(III)alamin and methylcob(III)alamin decreases as the magnetic field is increased from 0 to 0.7 T.<sup>2,5,6</sup> This is consistent with the organometallic RP being formed in the singlet spin state.<sup>6</sup> In contrast, the results of CIDEP studies of methylaquocobaloxime<sup>7</sup> and methylcob(III)alamin<sup>8</sup> suggest the RP is formed in the triplet spin state.

Herein, we report the results of another spin-chemistry technique: <sup>1</sup>H chemically-induced dynamic nuclear polarization (CIDNP). During CW irradiation of ethyl[*N,N'*-ethylenebis(salicylideneaminato)]cobalt(III) [hereafter EtCo<sup>III</sup>(salen)] and benzyloxycobaloxime [hereafter BzCo<sup>III</sup>(H<sub>2</sub>O)(dmgH<sub>2</sub>)], net emission and enhanced absorption signals are observed in the <sup>1</sup>H NMR spectrum. The polarization of these signals is only consistent with singlet RP formation.

Samples of BzCo<sup>III</sup>(H<sub>2</sub>O)(dmgH<sub>2</sub>) (in CD<sub>2</sub>Cl<sub>2</sub> and CD<sub>3</sub>OD) and EtCo<sup>III</sup>(salen) (in CD<sub>2</sub>Cl<sub>2</sub>) were prepared at a final concentration of 1 mM. Aerobic samples were prepared at atmospheric equilibrium, whereas anaerobic samples were sparged with Ar for 15 min prior to the experiment. The polarized NMR spectrum was acquired at 90 MHz following 10 s irradiation with a 500 W high-pressure mercury lamp with a thermal filter and a 300–400 nm bandpass filter. Time-resolved CIDNP measurements that were synchronized with intense pulsed irradiation proved to be uninformative because of the high concentration of unrecombined paramagnetic Co<sup>II</sup> that causes line broadening of the <sup>1</sup>H NMR signals.

Figure 1 shows the CIDNP spectrum produced by photolysis of an aerated solution of EtCo<sup>III</sup>(salen). The protons of the ethyl group clearly indicate polarization: emission, (E) for CH<sub>2</sub>; absorption (A) for CH<sub>3</sub>. Polarization arises in the ethyl radical (the primary photolysis product) prior to geminate recombination with Co<sup>II</sup>(salen). The same CIDNP signal can also be observed



**Figure 1.** <sup>1</sup>H NMR spectra for 1 mM CH<sub>3</sub>CH<sub>2</sub>Co<sup>III</sup>(salen) in aerated CD<sub>2</sub>Cl<sub>2</sub> acquired without irradiation, as well as after 10 s irradiation with 300–400 nm light.

under deaerated conditions, but with greatly diminished intensity.

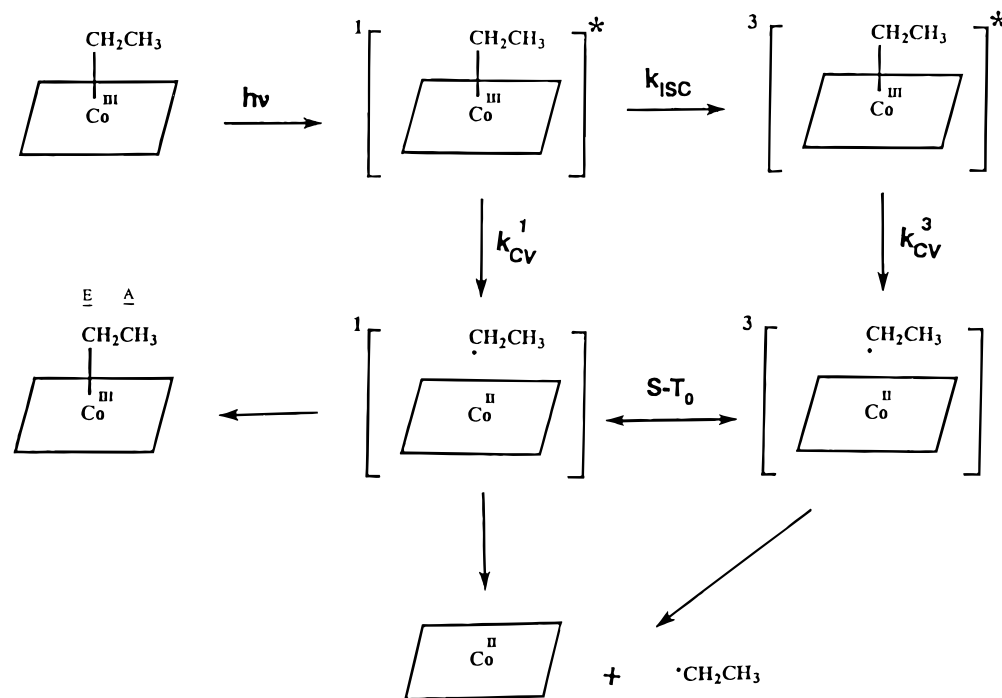
Diminished CIDNP signal intensity in the presence of oxygen is generally assumed to result from relaxation of a triplet excited state. However, this cannot be the case with alkylcobalt complexes, where excited state lifetimes are less than 6–30 ps.<sup>1,2</sup> Recombination in the *geminate* RP is at least 70% efficient and occurs with a unimolecular rate constant of  $1 \times 10^9 \text{ s}^{-1}$ . O<sub>2</sub> is not likely to react with CH<sub>3</sub>CH<sub>2</sub><sup>•</sup> or Co<sup>II</sup> in the short-lived *geminate* radical pair. However, oxygen can still react with the solvent-separated RP to trap either CH<sub>3</sub>CH<sub>2</sub><sup>•</sup> or Co<sup>II</sup> and thereby preclude recombination between ethyl radical and Co<sup>II</sup>(salen) in the bulk solution. Thus, in the presence of oxygen, formation of the recombination product is possible only from the initial *geminate* RP. In the absence of oxygen, the recombination product will be formed from both the *geminate* RP, as well as from the randomly-diffusing radical pairs (F-pairs). F-pairs are statistically 75% triplet and 25% singlet, and the polarization effect of triplet RP is more pronounced on the polarization of the F-pair recombination product. If the *geminate* RP is in the singlet state, then the F-pair recombination will decrease the magnitude of the CIDNP signal.

The expected CIDNP intensity for the protons of the ethyl group of EtCo<sup>III</sup>(salen) can be calculated by using the S–T<sub>0</sub> approximation of the RP diffusion model (Table 1).<sup>9</sup> The sign of the ethyl group polarization indicates the RP is formed in the singlet electronic spin state. The calculations also predict a slight difference in polarization intensity if the precursor multiplicity is changed from singlet to triplet (*cf.*  $-7.24 \times 10^{-5}$  vs  $+9.90 \times 10^{-5}$ ), as expected for long-lived radical pairs.<sup>9</sup> Thus, the experimentally-observed polarization of the ethyl protons in EtCo<sup>III</sup>(salen) clearly originates from recombination of a *singlet* *geminate* RP and is consistent with MFE studies of RP recombination in alkylcob(III)alamin photolysis.

In the case of BzCo<sup>III</sup>(H<sub>2</sub>O)(dmgH<sub>2</sub>) irradiation, net emission of the benzyl protons is observed in the <sup>1</sup>H NMR spectrum,

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Scheme 1. Photolysis of Alkylcobalt Model Systems<sup>a</sup>

<sup>a</sup> Legend: E indicates net emission, A indicates enhanced absorption.

**Table 1.** Calculated CIDNP Intensities in the RP, {CH<sub>3</sub>CH<sub>2</sub>•,Co<sup>II</sup>(salen)}, with Singlet (S) and Triplet (T) Electron Spin Multiplicities

polarized group of protons	CIDNP intensity <sup>a</sup>		recombination probability	
	S	T	P <sub>S</sub>	P <sub>T</sub>
For Deaerated Solution				
-CH <sub>2</sub> -	-7.24 × 10 <sup>-5</sup>	9.90 × 10 <sup>-5</sup>	0.640	0.160
-CH <sub>3</sub>	1.30 × 10 <sup>-4</sup>	-1.78 × 10 <sup>-4</sup>		
For Aerated Solution <sup>b</sup>				
-CH <sub>2</sub> -	-8.04 × 10 <sup>-5</sup>	1.02 × 10 <sup>-5</sup>	0.621	0.150
-CH <sub>3</sub>	1.45 × 10 <sup>-4</sup>	-1.84 × 10 <sup>-4</sup>		

<sup>a</sup> Parameters used in the calculations:<sup>9</sup>  $H_0 = 2.14$  T; recombination radius " $b$ " = 1 nm;  $k_{\text{rec}} = 2 \times 10^{11}$  s<sup>-1</sup>;  $D = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>; thickness of the reaction layer " $a$ " = 0.015 nm; and initial distance  $r_0 = b$ . <sup>b</sup> The ethyl radical only reacts with oxygen in an aerated medium (rate constant of 10<sup>7</sup> s<sup>-1</sup> is assumed).

and this is consistent with formation of the singlet RP. This complex has a different substituent, (benzyl *vs* methyl), as compared to the methylaquocobaloxime studied by Sakaguchi, et al.<sup>7</sup> If one assumes the photophysical characteristics (rate of intersystem crossing and rate of bond cleavage) of BzCo<sup>III</sup>(H<sub>2</sub>O)(dmgH)<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Co<sup>III</sup>(H<sub>2</sub>O)(dmgH)<sub>2</sub> in (CH<sub>3</sub>)<sub>2</sub>CHOH are not vastly different, it is possible to explain the observation of triplet CIDEP in the photodecomposition<sup>7</sup> of CH<sub>3</sub>Co<sup>III</sup>(H<sub>2</sub>O)(dmgH)<sub>2</sub>, in spite of RP recombination that originates from a singlet precursor.

The contributions to electron polarization, as observed by CIDEP, are described by eq 1, where  $P_{\text{obs}}$  is the observed polarization intensity,  $P_{\text{TM}}$  is the intensity generated through the triplet mechanism,  $P_{\text{RP}}$  is the intensity generated through RP recombination,  $k_{\text{ISC}}$  is the rate of intersystem crossing, and  $k_{\text{CV}}$  is the rate of C-Co bond cleavage.

$$P_{\text{obs}} \approx \{k_{\text{ISC}}/(k_{\text{ISC}} + k_{\text{CV}})\}P_{\text{TM}} + \{k_{\text{CV}}/(k_{\text{ISC}} + k_{\text{CV}})\}P_{\text{RP}} \quad (1)$$

Nonequilibrium populations for CIDEP formed via the RP mechanism ( $P_{\text{RP}}$ ) are usually in the range of 0.01–0.03 (when

the equilibrium electron polarization  $P_{\text{EQ}} \approx 0.001$ ), whereas electron polarization through the triplet mechanism can be much larger.<sup>9</sup>  $P_{\text{TM}}$  depends on the ISC rate, the zero-field splitting parameters, the external magnetic field strength, and the rotational correlation time.<sup>9,10</sup> In complexes with axial symmetry where  $E \approx 0$ , the magnitude of  $P_{\text{TM}}$  can be estimated within the frame of perturbation theory.<sup>10</sup> This approach suggests  $P_{\text{TM}} \approx 0.07$ –0.145. Since polarization through the triplet mechanism is much larger than polarization through the radical pair mechanism, it is not surprising that even a slight fraction of triplet radical pair precursor could dominate the CIDEP signal. Using the data in Table 1, it is possible to estimate the maximum triplet RP fraction as less than 0.3. Furthermore, the substantial kinetic magnetic field effects observed in the photodecomposition of methylcob(III)alamin and adenosylcob(III)alamin suggests a far smaller contribution from triplet radical pairs.

In conclusion, it is possible for the observed CIDEP signal to be dominated by a minor triplet reaction pathway *via* TM, whereas the major singlet reaction pathway will only be apparent in the kinetic MFE and CIDNP experiments. This may explain the apparent contradiction between the assignment of the RP spin state of alkyl-cobalt complexes by different experimental techniques. A comprehensive reaction scheme that accounts for the minor triplet reaction pathway and the major singlet RP reaction pathway is depicted in Scheme 1. The spin-correlated RP is the dominant species undergoing spin-dependent recombination and accounts for the magnetic field dependent chemistry previously reported.

**Supporting Information Available:** <sup>1</sup>H NMR spectrum of benzylaquocobaloxime [BzCo<sup>III</sup>(H<sub>2</sub>O)(dmgH)<sub>2</sub>] in CD<sub>3</sub>OD showing emissive polarization of the benzyl methylene group and text and figures giving a detailed explanation of calculations to estimate expected sign and magnitude of CIDNP (9 pages). Ordering information is given on any current masthead page.

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