Chemically Induced Dynamic Nuclear Polarization Study of the Mechanism of Photodecarboxylation

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Summary The participation of the radicals $PhS\dot{C}H_2$ and $PhS\dot{C}HCO_2H$ in the sensitized photodecarboxylation of (phenylthio)acetic acid is indicated by the results of a CIDNP study of the reaction.

Carboxylic acids of the type $R–X–CH_2CO_2H$ (R = alkyl, Ph or derivatives; X = NH, O, or S) undergo sensitized photodecarboxylation to yield methyl derivatives of the type R–X–Me, and other products.[1] Suitable sensitizers are ketones,[1a–c] quinones,[1d] aromatic hydrocarbons,[1e] nitroderivatives,[1f] and dyes.[1g]

We report the results of a proton-CIDNP[2] study of the photodecarboxylation of (phenylthio)acetic acid (I) (R = Ph, X = S) sensitized by aromatic ketones and quinones and discuss some possible mechanistic conclusions. Typical 90 MHz ^1H n.m.r. spectra measured during and following irradiation are shown in the Figure. Emission (*E*) of the methylene protons of (I) (δ 2·12 in C_6D_6) is observed when the decarboxylation is sensitized by benzophenone (II), anthraquinone (III), duroquinone (IV), fluoren-9-one (V), and phenazine (VI), the solvent being C_6D_6, $CDCl_3$, CD_2Cl_2, CD_3CN, or $[^2H_5]$-pyridine. The emission intensity varies, *e.g.* sensitization by (III) results in a strong negative signal while sensitization by (II) is observable only as a reduction in the methylene proton absorption.

The methyl protons of the product [thioanisole (VII) δ 1·98, in C_6D_6] show emission when the decarboxylation is sensitized by (II), (V), and (VI) in C_6D_6 solution. However, in CD_3CN solutions, sensitization by (II), (V), and (VI) results in enhanced absorption (*A*). Sensitization by quinones (III) and (IV) induces enhanced absorption of the methyl protons both in C_6D_6 and in CD_3CN solutions.

The polarization patterns of the methylene protons of (I) and of the methyl protons of (VII) are best accounted for by the reactions in the Scheme. In the first-step intermediate T, either ^{3}(I) or the exciplex suggested by

$$\text{(I)} + {}^3\text{SEN} \rightarrow \text{T} \tag{1}$$

$$\text{T} \rightarrow {}^3[\text{PhS}\dot{\text{C}}\text{HCO}_2\text{H} \cdots \text{HSEN}\cdot]\ (\text{GP1}) \rightarrow \text{Ph*SCH}_2\text{*-CO}_2\text{H} + \text{SEN*} \tag{2}$$

$$\text{T} \rightarrow {}^3[\text{PhS}\dot{\text{C}}\text{H}_2 \cdots \text{CO}_2\text{H}]\ (\text{GP2}) \rightarrow \text{Ph*SCH}_2\text{*CO}_2\text{H} \tag{3}$$

$$\text{T} \rightarrow {}^3[\text{PhS}\dot{\text{C}}\text{H}_2 \cdots \text{HSEN}\cdot]\ (\text{GP3}) + \text{CO}_2 \rightarrow \text{Ph*SMe*} + \text{SEN*} \tag{4}$$

$$\text{(IX)} \xrightarrow{\text{escape}} \text{Ph*SMe*} \tag{5}$$

Scheme. ^{3}SEN denotes the first excited state of the sensitizer, HSEN· the ketyl radical, and the asterisk (*) spin polarization. Free radicals $PhS\dot{C}HCO_2H$ and $PhSCH_2\cdot$ are denoted as (VIII) and (IX), respectively.

Davidson and Steiner,[1d] $^3[Ph\overset{+\cdot}{S}CH_2CO_2H \cdots \overset{-\cdot}{SEN}]$, is formed (see below). This intermediate transforms into one of the geminate pairs GP1, GP2, or GP3. The effect Γ_{NE} in the methylene protons† of (I), resulting from collapse of pairs GP1 and GP2 is:[3] μ(+ve, triplet radical pairs); ϵ (+ve, collapse products); Δg[+ve in GP1, GP2, and GP3 isotropic g-factor of (VIII) and (IX) *ca.* 2·006,[4] of $CO_2H\cdot$ and HSEN· *ca.* 2·003[2c,5]]; A_1 (−ve, *ca.* −21 G[5]). Hence $\Gamma_{NE} = \mu\epsilon\,\Delta g A_1 = + + + - = -$ (E). EH MO calculations indicate that (VIII) is unlikely to undergo decarboxylation.[6]

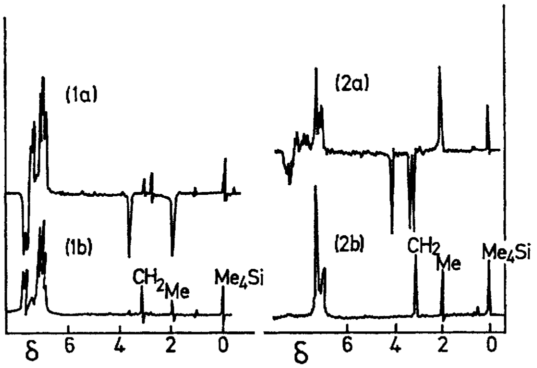

FIGURE. 90 MHz ^1H n.m.r. spectra: (a) During irradiation with a 1000 W Hg–Xe lamp; (b) following irradiation. (1), (Phenylthio)acetic acid and benzophenone, both 0·1 M, in C_6D_6, Me_4Si standard. (2), same as (1), but anthraquinone (saturated solution) used as sensitizer.

The analysis of Γ_{NE} of the methyl protons of (VII) in the case of emission is entirely analogous, this effect being due to polarization within GP3 [step (4), *e.g.* sensitization by (II), (V), and (VI) in C_6D_6 solution]. This collapse process of GP3 is concurrent with the escape process [step (5)]. In the latter case ϵ is −ve, the other factors are as above, and the net effect Γ_{NE} is positive (A). A is also observed in sensitization by (III) and (IV) in C_6D_6 solution and by (II), (V), and (VI) in CD_3CN solution. The observed effect (E or A) is thus the result of the competition between the ketyl radicals and other proton sources, such as solvent molecules. The escape process predominates in the presence of an additional H atoms source. Thus sensitization by (II) in the presence of benzenethiol in C_6D_6 solution results in enhanced absorption of the methyl protons.

The observed E effect on the methylene protons of (I) indicates that the triplet exciplex T is not involved in a polarization step. Otherwise we would have expected enhanced absorption of these protons due to the +ve sign of A_1 (β protons, A_1 *ca.* + 25 G[5]), the signs of the other parameters being unchanged. Thus we may conclude that T can at most be a very short-lived primary precursor giving GP1, GP2, and GP3 as the pairs responsible for the observed polarization. The lack of any significant solvent effect on the polarization of the methylene protons also points to the same conclusion.

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† The polarization pattern of the ring protons of (I) as well as of other transient or stable products will be dealt with elsewhere.

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