Tetrahedron Letters No.7, pp. 527-530, 1969. Pergamon Press. Printed in Great Britain.

CIDNP EVIDENCE FOR IODINE ATOM ABSTRACTION FROM ALKYL IODIDES

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(Received in USA 21 November 1968; received in UK for publication 1 January 1969)

The observation of emission or enhanced absorption (or both) in a high resolution pmr spectrum taken of a reacting system is indicative of free radical intermediates leading to the products whose protons show the effects of polarization (1). We have observed this phenomenon (called Chemically Induced Dynamic Nuclear Polarization; CIDNP) in spectra taken during the thermal decomposition of acyl peroxides in the presence of alkyl iodides.

The spectrum shown in Figure 1 was taken during the reaction of benzoyl peroxide (0.61 M) and isopropyl iodide (1.48 M) in *o*-dichlorobenzene at 112°. The methine septuplet of isopropyl iodide (δ = 4.34) shows both emission and enhanced absorption. The vinyl methylene protons of propene (δ = 5.14) show only enhanced absorption and the vinyl methine proton (δ = 6.0) only emission. Polarization also is observed in the *ortho* protons of iodobenzene and the methyl protons of propane. Analysis of the solution by gas chromatography after peroxide decomposition was complete showed iodobenzene (50%), isopropyl iodide (49% consumed), cumene (24%) and biphenyl (17%), all percentages based on benzoyl peroxide.

The spectrum taken of a solution of lauroyl peroxide (0.46 M) and isopropyl iodide (1.48 M) in *o*-dichlorobenzene at 112° (at this temperature peroxide decomposition is complete in 7 min) is shown in Figure 2. CIDNP can be seen clearly in the terminal methylene protons of *n*-undecyl iodide (δ = 3.2), the methine proton of isopropyl iodide (δ = 4.34), and the vinyl methylene (δ = 5.16) and methine (δ = 6.0) protons of 1-undecene.

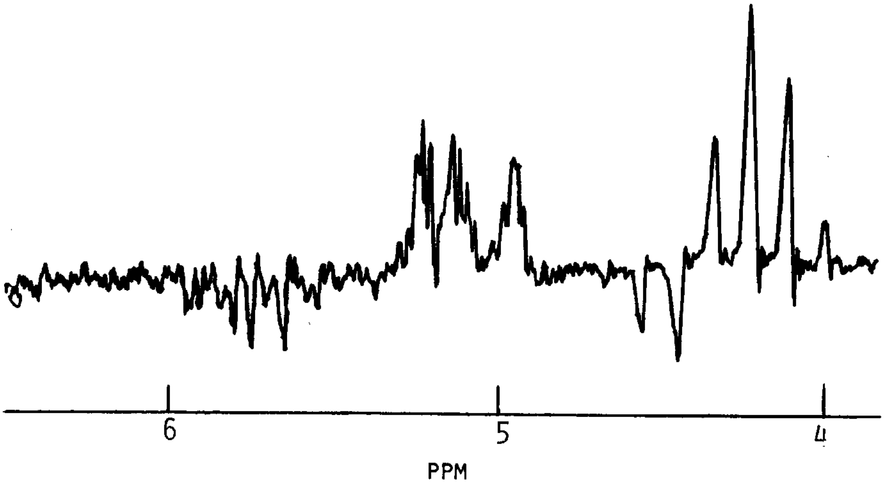

FIGURE 1. PMR SPECTRUM TAKEN DURING THE DECOMPOSITION OF BENZOYL PEROXIDE (112^0) IN A SOLUTION OF ISOPROPYL IODIDE AND O-DICHLOROBENZENE.

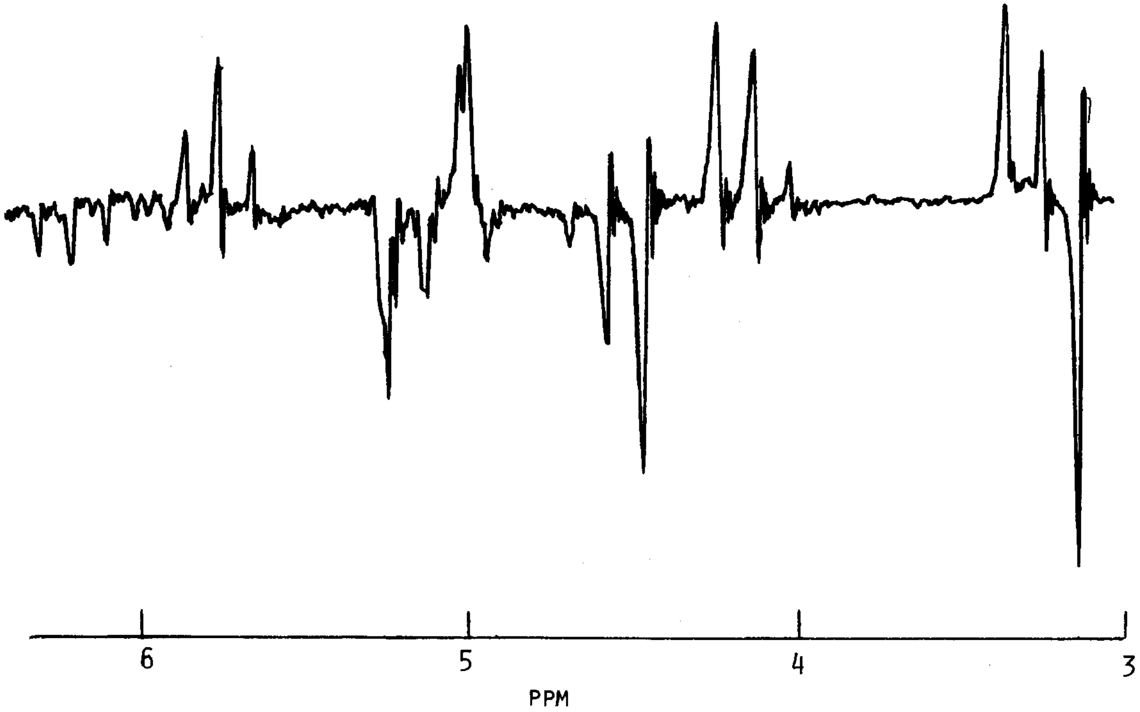

FIGURE 2. PMR SPECTRUM TAKEN DURING THE DECOMPOSITION OF LAUROYL PEROXIDE (112^0) IN A SOLUTION OF ISOPROPYL IODIDE AND O-DICHLOROBENZENE.

The observation of CIDNP from the protons of isopropyl iodide strongly indicates that an iodine atom transfer occurs by a free-radical chain mechanism. The products and proton polarization are consistent with the following reaction scheme:

peroxide $\rightarrow$ $2R\cdot^{*}$ + $2CO_2$ A
$R\cdot^{*}$ + PrI $\rightarrow$ $R^{*}I$ + $Pr\cdot^{*}$ B
$Pr\cdot^{*}$ + PrI $\rightarrow$ $Pr^{*}I$ + $Pr\cdot^{*}$ C
$R\cdot^{*}$ + $Pr\cdot^{*}$ $\rightarrow$ coupling, cross coupling, and disproportionation products D

(* indicates proton polarization; Pr = isopropyl)

Thermal decomposition of benzoyl peroxide (A) gives phenyl radicals in which the protons are dynamically polarized. Abstraction of an iodine atom from isopropyl iodide by these radicals (B) gives iodobenzene, in which some proton polarization is maintained. Reaction (B) also forms an isopropyl radical in which proton polarization can occur and this polarization may be returned to the protons of isopropyl iodide via (C). Although (C) is expected to be a chain process, each step in the chain should not be equally effective in producing proton polarization inasmuch as the latter steps may well involve free radicals with the distribution of electron spin level populations close to equilibrium. The source of the iodine atom donated to the isopropyl radical must be isopropyl iodide and not iodobenzene, since 1-undecyl iodide is not formed in the decomposition of lauroyl peroxide in the presence of iodobenzene and polarization of the iodobenzene protons is not observed. This is consistent with the expected endothermicity of a transfer of iodine from an aryl to an alkyl group. A similar chain mechanism has been proposed by Lepley (2) in the reaction of alkyl iodides with alkyllithium compounds (2,3). The termination reactions (D) give propane and propene, in which the proton polarization is expected and observed.

A chain transfer of iodine has been proposed by Kaplan as an explanation for the isomerization of cyclobutylcarbinyl iodide to 5-iodo-1-pentene during peroxide decomposition (4). Kaplan has also observed iodine atom abstraction by phenyl and *t*-butoxy radicals from a number of alkyl iodides (5). As far as we are aware, however, the present report constitutes the first direct evidence for an iodine atom transfer between identical alkyl moieties (*e.g.* iodine atom transfer from isopropyl iodide to isopropyl radical). Iodine atom transfers between phenyl radicals and aromatic iodides have been reported by Bunnett and Wamser (6) and by Bryden (7). Both groups found no transfer of bromine from bromobenzene, and we have seen no polarization of protons in alkyl bromides when acyl peroxides were decomposed in their presence, even though polarization is observed in disproportionation products of the radicals formed from lauroyl peroxide.

Confirmation of the iodine atom transfer in the alkyl systems may also be found in the observation made by Noyes (8), that optically active *sec*-butyl iodide, when heated in the presence of radioactive iodine, racemized more rapidly than labeled iodine was incorporated. An iodine atom transfer between alkyl radical and alkyl iodide which competes with the reaction of alkyl radicals with iodine would produce the observed results. The latter reaction is known to be rapid, however, and CIDNP can be observed in the protons of the iodides produced by the decomposition of peroxides in the presence of iodine.

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