Chemically Induced Dynamic Nuclear Polarization. Sign Reversal of the Polarization in the Reaction of Isobutyryl Peroxide with Bromotrichloromethane

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Summary Sign reversal of chloroform polarization at 0·1M-CCl₃Br, added as a scavenger for isopropyl radicals is indicative of long-time spin correlation effects of radical pairs in solution.

CIDNP makes possible the study of the problem of spin-correlation in radical pairs.[1,2] It is of interest to know how long a pair of freely diffusing radicals, formed in a single event, retains its identity as a pair. With regard to observable CIDNP effects, meaningful conditions for this are: (i) there must still be some chance of geminate recombination, and (ii) the electron spins of the pair have not yet lost their phase relationship. The thermal decomposition of isobutyryl peroxide (I) in the presence of bromotrichloromethane allowed us to investigate this problem. The CIDNP spectrum of the decomposition of (I) in hexachloroacetone was reported previously.[3] It is consistent with formation and subsequent reactions of a pair of isopropyl radicals; apart from ionic pathways, which do not give rise to CIDNP effects, this is in accord with other studies.[4]

The reactions of (I) in the presence of bromotrichloromethane are given in the Scheme. R· is the isopropyl

$$(RCO_2)_2 \xrightarrow{} 2R^\bullet \xrightarrow{\quad S \quad} R-R, RH, R(-H)$$

$$(I) \quad CCl_3Br \downarrow$$

$$RBr + \overline{R^\bullet + CCl_3^\bullet} \xrightarrow{\quad S \quad} R-CCl_3, \\ CHCl_3, R(-H)$$

$$CCl_3Br \downarrow$$

$$RBr + 2CCl_3^\bullet$$

$$\tag{1}$$

$$R^\bullet + CCl_3^\bullet \xrightleftharpoons{} \overline{R^\bullet + CCl_3^\bullet} \xrightarrow{\quad F \quad} R-CCl_3, \quad (2) \\ CHCl_3, R(-H)$$

SCHEME

radical and S and F denote pairs from a singlet precursor and from free radical encounters, respectively. Products from S and F pairs give opposite polarization.[2b] The 100 MHz n.m.r. spectrum taken during decomposition at 80° of a 0·2M-solution of (I) in hexachlorobutadiene, containing 5M-CCl₃Br, is shown in Figure 1. Enhanced absorption (A) and emission (E) occur for the products chloroform (δ 7·27 p.p.m., A), propene (methine δ 5·70,

E + E/A; methylene δ 4·90, A + E/A), isopropyl bromide (methine δ 4·19, A + A/E; methyl δ 1·69, E + A/E), 2-trichloromethylpropane (methine δ 2·70, E; methyl δ 1·27, A), propane and 2,3-dimethylbutane (methyl δ 0·85 p.p.m., E/A), and some unidentified products. These polarization patterns are completely in accord with reactions (1) of the Scheme (coupling and disproportionation of and escape from both S-pairs), showing that CCl₃Br interferes with geminate recombination of isopropyl radicals
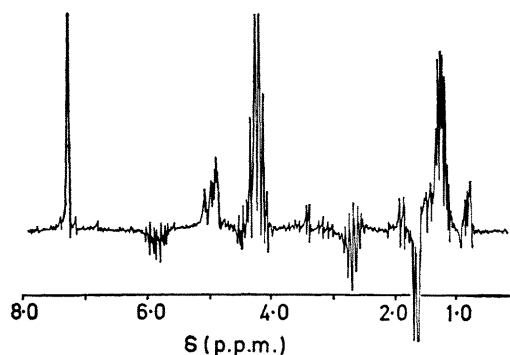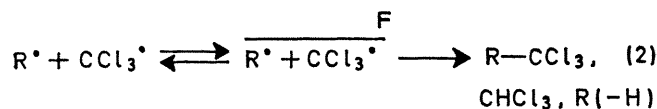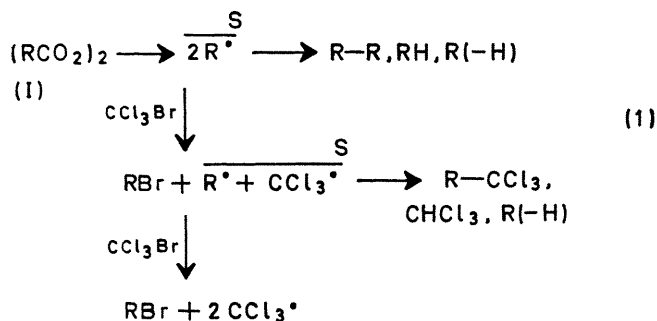

FIGURE 1. 100 MHz n.m.r. spectrum during thermolysis of 0·2M-isobutyryl peroxide in hexachlorobutadiene with 5M-CCl₃Br at 80°.

in this high concentration range. At lower CCl₃Br concentrations the propene and isopropyl bromide lines acquire more E/A and A/E character, i.e., polarization becomes determined by reactions of the first pair (cf. ref. 3).

The chloroform signal is shown in Figure 2; it changed sign at 0·11M-CCl₃Br, indicating that effects of reactions (1) and (2) just cancel at this concentration. Below 0·11M, reaction (2) predominates (F-pairs). At first sight it
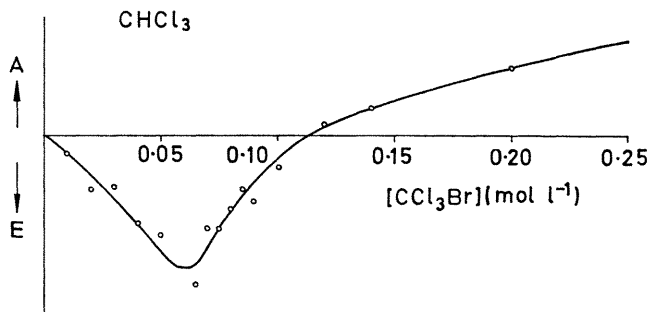

FIGURE 2. Maximum polarization of CHCl₃ versus concentration of CCl₃Br during thermolysis of 0·2M-isobutyryl peroxide in hexachlorobutadiene.

appears unlikely that the transfer reaction with CCl_3Br in *ca.* 0·1M-solution is fast enough to yield a pair with appreciable probability of geminate recombination. This process is usually thought to occur within a time of 10^{-10}—10^{-9} s; to compete on this time scale the transfer reaction should have a rate constant k_{tr} in the range 10^9—10^{10} l mol^{-1} s^{-1} (close to diffusion controlled) which is unreasonably large for this reaction.[5] Indeed, for a somewhat similar radical ($CCl_3CH_2\dot{C}HOAc$), k_{tr} for this reaction has been measured[6] and would have a value of $2·2 \times 10^4$ l mol^{-1} s^{-1} at 80°.

By applying a quantitative theory of CIDNP based on a random walk model for the diffusive motion of radical pairs, it can be shown[7] that even at 0·1M-CCl_3Br chloroform formed in (1) would still give an observable enhancement for k_{tr} = 5×10^6—5×10^7 l mol^{-1} s^{-1}, giving life times for R· of

the order of microseconds (a larger value of k_{tr} for the isopropyl radical than for the vinyl acetate derived radical does not seem to be unrealistic). Essentially this longer time scale for polarization in the diffusion model is due to the dependence of both product formation and polarization on $\sqrt{k_{tr}[S]}$, where [S] is the concentration of scavenger. A more detailed discussion will be given elsewhere.[7] Although calculations are tentative because of lack of information on rate constants, the present work seems to show that spin-correlation effects of radical pairs in solution can be of rather long duration (microseconds). This observation would support our view that CIDNP arises from S–T mixing in freely diffusing radical pairs.

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