Carbon-13 CIDNP in the Reversible Addition of Pentafluorobenzoyloxy Radicals to Chlorobenzene

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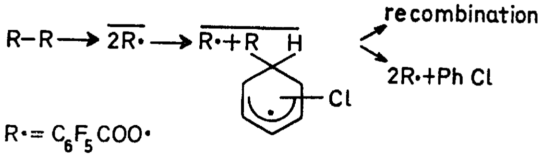
Summary ^{13}C CIDNP observed during photolysis of perfluorobenzoyl peroxide in the presence of chlorobenzene provides evidence for the reversible formation of a σ-complex of the pentafluorobenzoyloxy-radical with chlorobenzene, predominantly *via* attack at the *ortho* and *para* positions.

Chemically induced dynamic nuclear polarization (CIDNP) can be a particularly valuable tool in the study of reversible free-radical reactions where product and reagent are the same. This type of reaction occurs during the decomposition of benzoyl peroxide in the presence of aromatic molecules.[1] Proton CIDNP studies of the decomposition of perfluorobenzoyl peroxide (I), previously reported by Bargon,[2] had indicated that pentafluorobenzoyloxy-radicals reversibly form σ-complexes with a variety of aromatic substrates and that the site of attack is that expected for electrophilic aromatic substitution. In this communication we report the observation of CIDNP of carbon-13 in natural abundance during photolysis of (I) in the presence of chlorobenzene. ^{13}C polarization in this reaction is of interest, since the proton spectra fail to give any information on the type of intermediate σ-radical involved (at 100 MHz chlorobenzene has a single-line ^{1}H n.m.r. spectrum). Furthermore, Oldham and Williams[3] had found that the decomposition of (I) in chloro- and bromo-benzene gives phenyl pentafluorobenzoate in considerable yields, pointing to attack at the 1-position of the solvent. By contrast, the



(I)

Scheme

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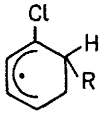
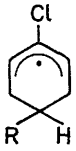
present CIDNP results indicate predominant addition to the carbon atoms in the 2- and 4-positions.

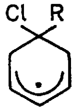
The ^{13}C Fourier transform n.m.r. spectra were recorded on a Varian XL-100 spectrometer, modified such that the sample could be irradiated within the probe with the light of a 1000 W PEK high-pressure mercury arc. The Figure shows the proton-decoupled ^{13}C spectra of a solution of (I) in $CDCl_3$ containing 30% chlorobenzene, both before and during u.v. irradiation. When the light was admitted, the intensities of the carbons in the *ortho* and *para* positions increased, whereas those of the *meta* and quaternary carbons decreased. This polarization pattern can be accounted for by the reactions shown in the Scheme. The bars indicate radical pairs with correlated electron spins. The nature of the "recombination" step is not known; it may be coupling or disproportionation or both. Recombination is, however, a prerequisite for observing polarization in the escape product chlorobenzene. The spectrum suggests that addition occurs predominantly *via* attack at the *ortho* and *para* positions [structures (II) and (III)]. This follows from an analysis of the polarization in terms of the radical-pair theory of CIDNP[4] or, more conveniently, from the qualitative rules[5] which summarize this theory. For instance, application of the rule for net polarization to the emission observed for the quaternary carbon (q) would give



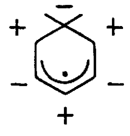
(II)



(III)



(IV)



(V)

$$\Gamma_{ne} = \mu.\epsilon.\Delta g.A_q = - - - + = -$$

[It is known that acyl peroxides decompose photochemically from an excited *singlet* state,[6] $\mu = -$; chlorobenzene is an escape product, $\epsilon = -$; the g-factor of R· is larger than that of the cyclohexadienyl radical, $\Delta g < 0$; structures (II) and (III) account for the positive ^{13}C hyperfine coupling constant A_q required by the observed emission.] Quantum chemical calculations at various levels of sophistication[7] predict alternating signs of the spin densities and, therefore,‡ of $A(^{13}C)$ in the odd alternant cyclohexadienyl radical (V), in accordance with the observed spectra. The *meta*-adduct and species (IV) would yield the opposite polarization. Thus, the present results give no indication of attack at the 1-position of chlorobenzene to yield the σ-complex (IV), which, as has been proposed by Oldham *et al.*,[3] would explain the formation of phenyl pentafluorobenzoate. Either this product is generated *via* a different route or radical (IV) is indeed formed but not reversibly.

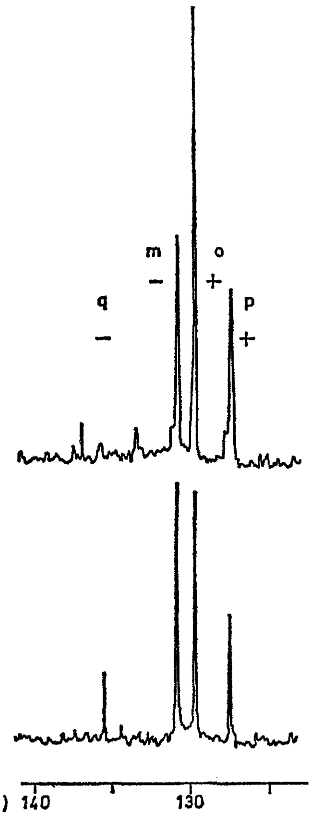


FIGURE. ^{13}C Fourier transform n.m.r. spectra of perfluorobenzoyl peroxide in $CDCl_3$ containing 30% chlorobenzene, before (a) and during (b) u.v. irradiation. For both spectra 16 transients were accumulated; the Overhauser effect was suppressed (see text). The assignment of the chlorobenzene lines is indicated.

The observation of the light-induced intensity differences of the relatively strong solvent lines was greatly facilitated by making use of a technique for the suppression of the Overhauser effect.[8] The ^1H decoupler was gated so that it was "on" only during acquisition of the transients (0·8 s) and "off" during a waiting time (15 s) between the 90° pulses. This procedure results in elimination of the Overhauser enhancement while the ^1H decoupling effect is retained. The effects were qualitatively the same when the decoupler was "on" continuously. Hence, the observed phenomena are not caused by an indirect ^1H–^{13}C relaxation effect due to polarized protons, because the decoupling power is large enough to short-circuit the relaxation transitions.

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‡ In an odd alternant radical the contributions from neighbouring atoms to the hyperfine coupling constant of a carbon nucleus have signs opposite to that of the main carbon atom, thus reinforcing the alternating effect in A (^{13}C).

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