CIDNP Study of Homolytic Substitution (S_H2) Reactions at Metal Centres

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Summary Pair substitution CIDNP effects have been utilized to study S_H2 reactions of benzoyloxyl radicals at the metal centres of group IV (Pb and Sn) and transition-metal alkyls.

Currently, there is much interest in homolytic reactions of organometallic compounds, and their S_H2 reactions have recently been reviewed.[1,2] Whereas mechanistic studies of these reactions have mainly centred on main-group III and IV metals, transition-metal compounds have remained largely unexplored. One recent example is the reaction of t-butoxyl radicals with some Pt alkyls.[3]

We show here that CIDNP can be a useful tool for the study of this type of reaction, which plays an important role in the autoxidation of organometallic compounds.

When heated in the probe of an n.m.r. spectrometer a variety of metal alkyls dissolved in [$^2H_4$]-*o*-dichlorobenzene or C_6D_5Br containing dibenzoyl peroxide (BPO) show emission (E) and enhanced absorption (A) signals for the corresponding alkyl benzoate and alkylbenzene. For tetraethyl-lead (TEL) this is shown in the Figure. The observed polarizations of ethyl benzoate (CH_2, δ 4·10, E; CH_3, δ 1·08, A), ethylbenzene (CH_2, δ 2·60, E), and ethene (δ 5·2, A) are in accordance with a pair substitution sequence[4,5] starting with an S_H2 reaction of the benzoyloxyl radical at the Pb atom, as shown in the Scheme.

$$(PhCO_2)_2 \rightarrow \overline{2PhCO_2\cdot} \qquad (1)$$

$$\overline{2PhCO_2\cdot} + Pb(Et)_4 \rightarrow PhCO_2Pb(Et)_3 + \overline{PhCO_2\cdot + Et\cdot} \qquad (2)$$

$$\overline{PhCO_2\cdot + Et\cdot} \rightarrow CO_2 + \overline{Ph\cdot + Et\cdot} \rightarrow PhEt^* \qquad (3)$$

$$\searrow PhCO_2Et^*,\ C_2H_4^*$$

Scheme

As the rate of decomposition of BPO is not altered upon addition of TEL, the benzoyloxyl–ethyl radical pair is not formed in a direct reaction of BPO with TEL. This contrasts with the reaction of TEL with chlorinated hydrocarbons.[6] Pair substitution CIDNP is based on the fact that spin correlation is preserved in a substitution reaction such as (2), so that the electron spin state of the emerging radical pair is exactly the same as that in the preceding pair. The polarizing pair is the same as in the decomposition of benzoyl propionyl peroxide and in the reaction of BPO with ethyl iodide,[4] and the polarization is accordingly similar.

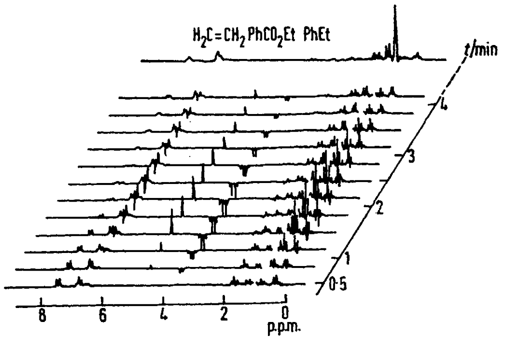

Figure. Series of 90 MHz ^1H Fourier transform n.m.r. spectra obtained during the decomposition of dibenzoyl peroxide in C_6D_5Br in the presence of $Pb(Et)_4$ at 125 °C. Single r.f. pulse transients were stored on disk every 20 s starting 30 s after insertion of the sample in the preheated probe. The strong line of $Pb(Et)_4$ has been suppressed during plotting.

The reaction of BPO with $PbMe_3Cl$ yielded polarized methyl benzoate and toluene. With alkyltin compounds

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($SnEt_4$,$SnMe_3Cl$, $SnBu_3Br$) the polarizations were generally weaker than for the corresponding lead alkyls. This may be due to induced decomposition by radical-chain processes, or, more likely, to a slower rate of reaction (2) in the case of the Sn compounds. No polarization was found in the reaction with alkylsilicon compounds.

In a series of transition-metal alkyls a striking difference was observed between platinum and gold alkyls. In the reaction of BPO with LAuMe (L = PPh_3) strongly polarized lines were found for methyl benzoate and toluene, whereas *cis*-L_2PtMe_2 displayed only weak effects. This shows that LAuMe is much more prone to S_H2 reactions than the platinum compounds.

The observation of pair substitution in the case of TEL allows us to calculate the rate of reaction (2) to be at least 10^8 l mol^{-1} s^{-1} at 125 °C. Precise values for the rates of reactions (2) should be obtainable from an analysis of quantitative measurements of the polarizations using the method derived from the theory of pair-substitution CIDNP.[5,7]

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