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Preliminary communication

CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION (CIDNP) STUDIES OF REACTIONS OF ALKYLLEAD COMPOUNDS WITH HEXACHLOROACETONE AND HEXACHLOROCYCLOPENTADIENE

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Summary

CIDNP studies show that alkyllead compounds when reacting with reactive organic halides produce lead chlorides and a radical pair in a singlet state.

Since the advent of CIDNP, there have been several observations of nuclear polarization during reactions of alkyl derivatives of alkali and alkaline-earth metals with organic halides [1]. The known examples of bimolecular reactions of alkylmetals and alkyl halides producing radical pairs all involve the reactive alkyls of the lighter metals (Li, Na, Mg). It has been known [2] for some time that tetraethyllead reacts with organic halides, but no CIDNP or other mechanistic data have been reported. We describe below our observation of CIDNP during the reaction of alkyllead compounds with reactive organohalides.

At 140 °C a fast reaction takes place between tetraethyllead (0.5 mol l^{-1}) and hexachlorocyclopentadiene (solvent); the products (reaction 1) displaying CIDNP (Fig. 1) are summarized in Table 1.

$$(C_2H_5)_4Pb + C_5Cl_6 \rightarrow (C_2H_5)_3PbCl, C_2H_5Cl, C_2H_5C_5Cl_5, C_5Cl_5H, C_2H_4, (C_5Cl_5)_2 \quad (1)$$

Similar polarizations are observed when hexachloroacetone is used as the solvent (Table 1). Essentially the same spectra are found in both solvents with diethyllead diacetate or triethyllead acetate at 120 °C.

The occurrence of CIDNP rules out ionic mechanisms as the sole reaction path to these products; radical reactions must be involved. Homolysis of the lead—carbon bond (reaction 2) can be ruled out in view of the fact that the

$$\geqslant Pb{-}C_2H_5 \rightarrow \geqslant Pb^{\bullet} + {}^{\bullet}C_2H_5 \quad (2)$$

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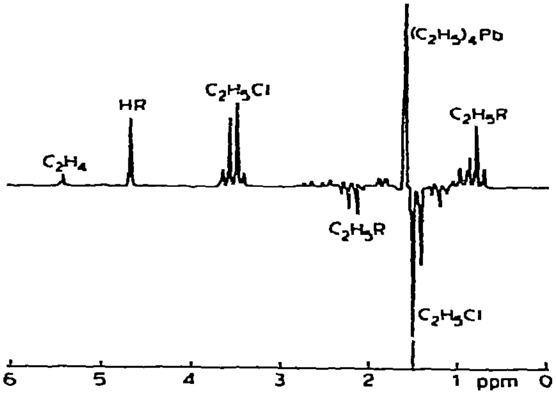

Fig. 1. ^1H Fourier transform CIDNP spectrum of $(C_2H_5)_4Pb$ in hexachlorocyclopentadiene at 140 °C (at 90 MHz, Bruker WH-90).

TABLE I

CIDNP DATA FOR THE REACTION OF TETRAETHYLLEAD WITH RCl

		Chemical shift (δ)		Polarization [6]
Product [a]	Nucleus	R = $Cl_3CCOCCl_2$	R = C_5Cl_5	
C_2H_5Cl	CH_2	3.52	3.53	A quartet
	CH_3	1.48	1.52	E triplet
C_2H_4		5.38	5.50	A
C_2H_5R	CH_2	2.67 [c]	2.25	E quartet
	CH_3	—	0.86	A triplet
	CH_2	4.22 [d]		E quartet
	CH_3	1.28 [d]		A triplet
HR		6.79	4.67	A

[a] All products except c have been identified by comparing their spectra with those of authentic samples. [b] A = enhanced absorption, E = emission. [c] 1,1,1,3,3-Pentachloropentanone-2. [d] 2-Ethoxypentachloropropene.

decomposition rate of tetraethyllead is dependent on the nature of the solvent; for example in inert solvents such as decaline or bromobenzene no decomposition can be observed at 120-140 °C after ten minutes. Two mechanisms (a) and (b) can be put forward (R = C_5Cl_5 or $Cl_3CCOCCl_2$):

(a) Chain process involving Pb^{III} radicals:

$$RCl + (C_2H_5)_3Pb^{\bullet} \rightarrow R^{\bullet} + (C_2H_5)_3PbCl \qquad (3)$$

$$R^{\bullet} + (C_2H_5)_4Pb \rightarrow C_2H_5R + (C_2H_5)_3Pb^{\bullet} \qquad (4)$$

$$R^{\bullet} + (C_2H_5)_4Pb \rightarrow HR + C_2H_4 + (C_2H_5)_3Pb^{\bullet} \qquad (5)$$

(b) Bimolecular reaction producing a radical pair

$$(C_2H_5)_4Pb + RCl \rightarrow (C_2H_5)_3PbCl + R^{\bullet} + C_2H_5^{\bullet} \qquad (6)$$

The signs of the polarizations indicate [3] that the observed CIDNP arises from singlet pairs of $R^{\bullet}$ and $C_2H_5^{\bullet}$. Reactions 3-5 would lead only to free-encounter pairs of $R^{\bullet}$ and $C_2H_5^{\bullet}$, giving polarizations opposite to those observed. Therefore the main radical reaction occurring in this system is reaction 6. The radical pair $\overline{R^{\bullet}, C_2H_5^{\bullet}}^{\,S}$ [1] accounts for all the polarizations, viz. the electron-pair recombination products RH, C_2H_4, and RC_2H_5, and the "escape" product C_2H_5Cl.

Reaction 6 could formally be regarded as an electron-transfer step. However, it is not known whether an actual electron transfer, giving a radical cation and a radical anion, occurs as the initial step, as in the reaction [4] of tetraethyllead with $IrCl_6^{2-}$.

$$(C_2H_5)_4Pb + RCl \rightarrow (C_2H_5)_4Pb^+ + RCl^-$$

References

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