

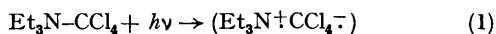
Chemically Induced Dynamic Nuclear Polarization during the Photoreaction of Triethylamine with Carbon Tetrachloride

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Summary Enhanced absorption CIDNP is observed for the chloroform proton and for the terminal olefinic protons of *NN*-diethylvinylamine during photolysis of the triethylamine-carbon tetrachloride charge transfer complex in methanol and acetonitrile; this points to the formation of the singlet radical pair $\text{Et}_2\text{N}\dot{\text{C}}\text{HMe}-\dot{\text{C}}\text{Cl}_3$ as a primary reaction step.

In alkane solvents aliphatic amines and carbon tetrachloride form weak complexes by electron donor-acceptor interaction. The solutions are photochemically unstable and yield amine hydrochlorides, chloroform, hexachloroethane, and imines or vinylamines as products.¹⁻³ Presumably a radical chain reaction is involved which is initiated by excitation of the complex and its dissociation into trichloromethyl and aminyl or aminoalkyl radicals. Kosower³ has suggested that the initial steps of the reaction of triethylamine with CCl_4 follow equations (1) and (2).

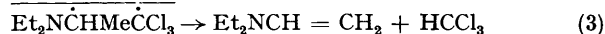


These steps are then followed by further radical-molecule and radical-radical reactions.

We have now obtained evidence for equations (1) and (2) by proton-CIDNP studies during the photolysis of triethylamine- CCl_4 solutions (4 M:1 M—1 M:4 M) in CD_3OD and acetonitrile. We have chosen these solvents because precipitation of the amine hydrochloride renders alkane solvents unsuitable for n.m.r. studies. Also, u.v. studies revealed the formation of an amine-halide complex in more polar solvents by a strong red shift of the first absorption band.¹ Irradiation in the region of the charge transfer absorption ($270 \leq \lambda \leq 330$ nm) in the photo-CIDNP

system described earlier⁴ leads to enhanced absorption (A) for chloroform (δ 7.85 p.p.m. *vs.* Me_4Si in CD_3OD for 4 M:1 M solution) and for the terminal olefinic protons of *NN*-diethylvinylamine⁵ (δ 4.1 p.p.m. in the same solvent). However, line broadening was observed for the α -methylene quartet of the starting amine which made the observation of any CIDNP effect of this group impossible. The line broadening persisted after shutting off the photolytic source. During irradiation the solutions developed a reddish-brown colour but remained transparent. *NN*-Diethylvinylamine was also detected by its characteristic i.r. absorption⁶ at 6.1 μm . When aqueous NaOH was added to the methanol solutions before irradiation, less coloration and no line broadening was observed. The phase of the chloroform CIDNP was not affected and no CIDNP of the starting amine was observed.

The observed CIDNP effects are most easily explained by Kaptein's rules,⁷ and the free radical parameters⁸ $g(\dot{\text{C}}\text{Cl}_3) = 2.0091$, $g(\text{Et}_2\text{N}\dot{\text{C}}\text{HMe}) = 2.0030$ and $a_{\text{Me}}(\text{Et}_2\text{N}\dot{\text{C}}\text{HMe}) = +19.6$ G by the intermediate geminate radical pair $\text{Et}_2\text{N}\dot{\text{C}}\text{HMe}\dot{\text{C}}\text{Cl}_3$ which disproportionates as shown in equation (3), if a singlet multiplicity of the radical pair



precursor is assumed. These findings support reactions (1) and (2). They imply further that the complex decays from an excited singlet state, and that the ion radical pair $(\text{Et}_3\text{N}^+\text{CCl}_4^-)$ transforms to the neutral radical pair by HCl elimination within nanoseconds. The latter is consistent with the known short lifetime of the CCl_4^- radical anion.⁹

The selective and persistent line broadening of the amine cannot be explained by degenerate electron transfer^{5,10} of transient ion radicals $(\text{Et})_3\text{N}^+$ escaping from the ion radical

pair and is due to the formation of triethylamine hydrochloride, which shows additional couplings and slow exchange with the amine.¹¹ Addition of base prevents the formation of the hydrochloride, and consequently the line broadening. The fact that, even for basic solutions, no CIDNP of the amine was observed, points to a nearly irreversible photo-induced electron transfer [equation (1)] and again to rapid formation of the neutral radical pair. The nature of the coloured photoproducts has not yet been

elucidated but they are thought to be secondary products of the vinylamine.

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