Low-field CIDNP Study of the Photolysis of Azomethane

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Summary Low-field CIDNP of ethane formed during photolysis of azomethane in carbon tetrachloride demonstrates that the photodecomposition occurs predominantly from the singlet state.

The photochemistry of aliphatic azo-compounds has been the subject of several investigations.[1,2] In solution the most important process in azomethane is the *trans–cis* isomerization, and photodecomposition occurs with low efficiency. The primary step of this decomposition is assumed to be a concerted nitrogen elimination, yielding two methyl radicals. No consensus seems to exist about the state (singlet or triplet) from which this photodecomposition occurs.

CIDNP[3] has proved itself a valuable tool for the elucidation of radical reactions, and is observed usually when the reaction is performed in the probe of an n.m.r. spectrometer. Photolysis of azomethane presents an example where, in a high magnetic field, no information can be obtained, and so one has to use the less well known low-field CIDNP techniques. Low-field CIDNP[4] can be studied by performing the reaction in an external magnetic field, after which the sample is transferred rapidly into the probe of the n.m.r. spectrometer where the polarization is observed.

A classical system which has been studied extensively by CIDNP is the thermal decomposition of acetyl peroxide.[5] The emission observed for the recombination product, ethane, during the decomposition of this peroxide in a high magnetic field can be accounted for by pair substitution effects[6] in which the acetoxy radical is the intermediate. When the reaction is carried out in low magnetic fields an emission is likewise observed (with a maximum at *ca.* 40 G) for the recombination product, ethane. This emission has a different origin however, namely the mixing of the singlet state of the radical pair with all three triplet levels.

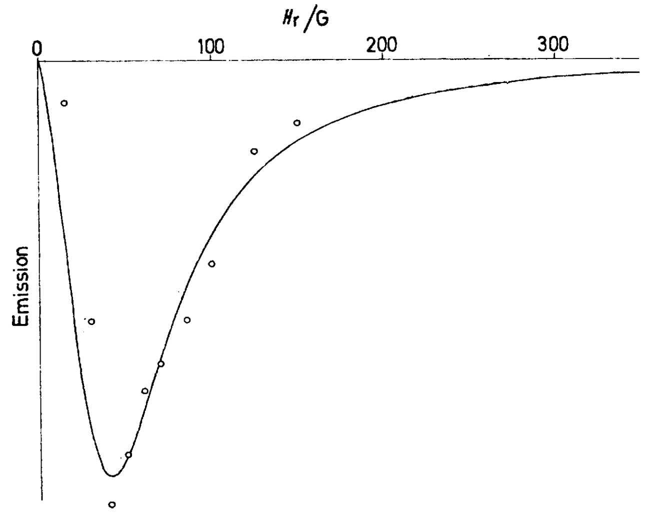
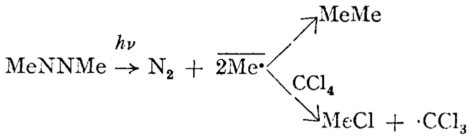


FIGURE. Magnetic field dependence of CIDNP for ethane formed during photolysis of azomethane: ○ experimental points; the line represents calculations for a methyl–methyl radical pair.

We have studied CIDNP during the photolysis of azomethane in CCl_4. In this solvent the major products are the recombination product, ethane and the scavenging product, methyl chloride (Scheme). When the reaction was carried out in high magnetic field no polarization could be detected for ethane. This is to be expected for a methyl–methyl radical pair, since S–T_0 mixing in a symmetrical radical pair cannot give rise to net CIDNP effects,[7] thus confirming that the possible intermediate radical (MeNN•) is too short lived to affect the reactions.[1] However, we have found a low-field CIDNP for ethane formed during the photolysis of azomethane which is analogous to that for ethane formed during the thermal decomposition of acetyl peroxide (Figure). This similar behaviour is to be expected since, in the two systems, the methyl–methyl radical pair is the key intermediate. From these observations in low magnetic fields, we conclude that the photodecomposition of azomethane occurs predominantly from the singlet state. Moreover the emission is predicted by a complete calculation[4] for a singlet-generated methyl–methyl radical pair.



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