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CIDNP EVIDENCE FOR RADICAL INTERMEDIATES IN THE THERMAL DECOMPOSITION OF Z-ALKYLARYLDIAZO SULPHIDES

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In solution Z-alkylaryldiazo sulphides[1)] thermally decompose into fragments as well as isomerise, both according to first-order kinetics[2)]. The decomposition is strongly accelerated by polar solvents, indicating a polar mechanism for the rate-determining step. However, the formation of thiol and disulphide as well as of benzene or substituted benzene indicates a radical-reaction mechanism for the product determining step. To account for these experimental facts the mechanism given in Fig. 1 was proposed and radical intermediates were considered to occur in these decomposition reactions[2)].

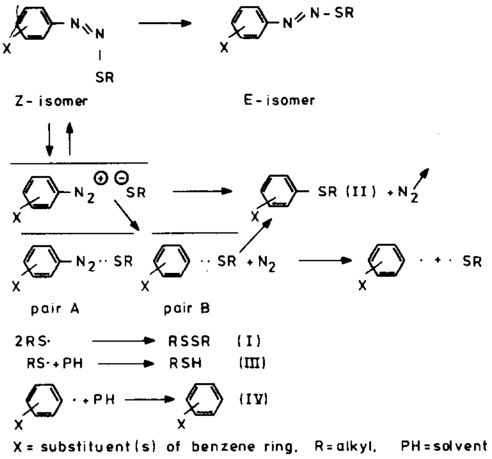
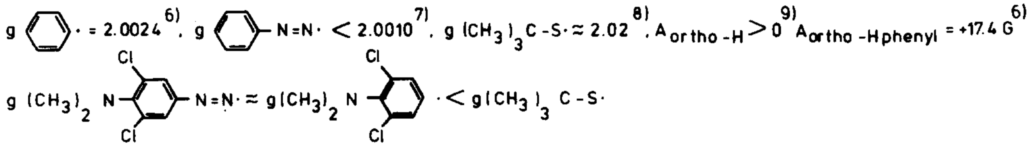


Fig. 1: Mechanism of thermal decomposition and isomerisation of Z-alkylaryldiazo sulphides.

When we heated solutions of Z-3,5-dichloro-4-dimethylaminobenzene diazo tert-butyl sulphide (Z-A) or of Z-benzenediazo tert-butyl sulphide in a Varian A-60 NMR Spectrometer at elevated temperatures (90°C - 135°C) we observed enhanced absorption signals for the phenyl protons of products (II) and emission signals for the phenyl protons of products (IV). The appearance of these Chemically Induced Dynamic Nuclear

Polarisation[3)] (CIDNP) effects proved the occurrence of at leastone radical pair intermediate in the formation of the decomposition products mentioned in Fig.1. It sounds very plausible that these polarisation effects were induced in the radical pair A and/or B of Fig. 1. In this case the qualitative rule of Kaptein[3a)] for net polarisation predicts enhanced absorption for products formed with in the radical pair and emission for products formed outside this radical pair. We proposed in Fig. 1 formation of product (II) within a radical pair and formation of product (IV) outside the radical pair. The observed CIDNP effects are in agreement with this mechanism and at least part of the decomposition products must have been formed via the radical pair A and/or B.

The polarisation determining parameters used in the rule of Kaptein were assigned as:



We determined the thermal decomposition reaction rate of Z-A in several solvents[2)]. Of these, decaline, benzene, dimethyl formamide (DMF) and nitromethane gave rise to CIDNP effects. However, the low boiling points of the other solvents used in our earlier work[2)](dioxane, acetone and acetonitrile) prevented the observation of CIDNP. These polarization effects support the hypothesis of ref.2 that radicals are intermediates in the formation of the decomposition products in apolar as well as polar solvents.

The decomposition of Z-A in DMF-H_7 showed the CIDNP signals of the multiplet of 2,6-dichloro-dimethylaniline in emission (Fig. 2a), but when this reaction was carried out in DMF-D_7 (Fig.2b) the emission signal was changed into a broad singlet by coupling of the ortho protons of the benzene ring with deuterium. Fig.2c reflects the situation at the end of the reaction of Z-A in DMF-H_7 at 130°C after addition of 3,5-dichloro-4-dimethylaminophenyl tert-butyl sulphide and 2,6-dichloro-dimethylaniline to the solution[16)].

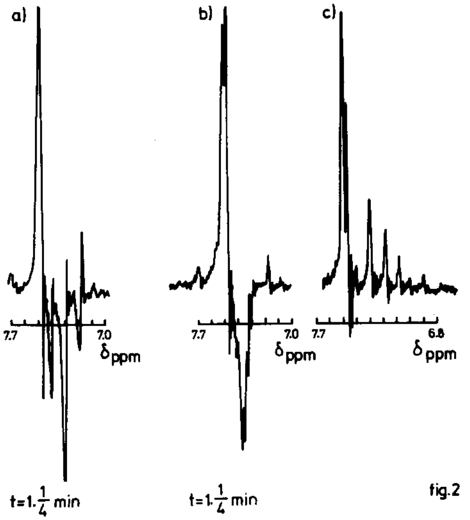


fig.2

Similar results were observed using the undeuterated and deuterated solvents decaline and nitromethane. Hence it is very likely that the formation of product (IV) involves abstraction of a H-atom from the solvent by a phenyl radical (Fig.1).

Careful examination of these spectra showed a small E/A multiplet effect superimposed on the emission signal. These effects were also observed in the photochemical decomposition of dibenzoylperoxides[9].

Emission signals for the phenyl protons of benzene or substituted benzenes were observed by several authors[10,11]. These products were also formed outside the original cage which introduced the CIDNP effects. A maximum enhancement factor for benzene emission of -8.5 at 56.4 MHz[12,13] was observed. We observed maximum enhancement factors[13] of -11 for benzene and -30 for 2,6-dichloro-dimethylaniline signals in $DMF-H_7$. The contribution of the protons meta or para to the radical unpaired electron[9] and of the H-atom abstracted from the solvent[14] was negligible. On including these facts in our calculations the observed enhancement factors for benzene or substituted benzene are almost identical.

No enhanced absorption was observed for the signals of the Z- or E-isomers. Hence, there is no reason to include in Fig.1 reaction steps for the formation of Z- or E-isomers via the radical pair A[15].

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15. Starting with unsymmetric phenyl alkyl azo compounds the E-isomers showed CIDNP effects, indicating a recombination reaction of the diazenyl alkyl radical pair6).
16. Z-A: δ 7.18 (s), E-A: δ 7.49 (s), 3,5-dichloro-4-dimethylaminophenyl tert-butyl sulphide: δ 7.47 (s), 2,6-dichloro-dimethylaniline: δ 7.41, δ 7.31, δ 7.21, δ 7.11, δ 7.04, δ 6.95 (m).

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