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A NEW TECHNIQUE FOR SPIN LABELING: NITROSO LABELING OR INITIATOR SPIN TRAPPING

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For the study of short-lived free radicals created by UV irradiation Terabe and Konaka[1] proposed 2,4,5-tri-t-butylnitrosobenzene as a spin trap, which proved to be insensitive under UV irradiation. We found that different 2,6-halogen substituted nitrosobenzenes (2,6-dichloro-, 2,6-dibromo-, 2,4,6-tribromo-) have similar properties, with the additional advantage that their synthesis is very simple[2]. We applied these spin traps to study the photochemical reactions of anthraquinone with hydrocarbons[3] and thermal decomposition of azo-bis-1-phenylethane[4]. These investigations, however, led to the observation that a side reaction also takes place: even in the absence of radical source nitroxide radicals are formed at slightly elevated temperatures. Fig.1 shows a characteristic spectrum obtained with an ortho-xylene solution of 2,6-dichloronitrosobenzene at 50°. The spectrum can be assigned to a trapped 2-methyl-benzyl radical[5], where the primary nitrogen triplet splits into a secondary triplet due to the two alkyl protons, and a tertiary 1:3:3:1 quadruplet due to the equivalent meta- and paraprotons of the phenyl group. This rather unusual equivalence of meta- and paraprotons is due to the strong twist of the phenyl ring related to the CNO plane.[6]

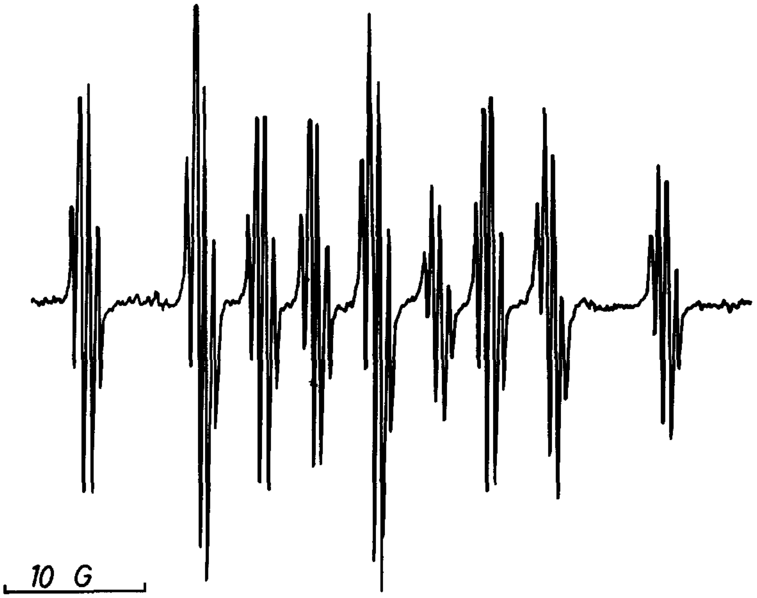

Fig.1. ESR spectrum of saturated 2,6-dichloronitrosobenzene on ortho-xylene at 50°.

The formation of this radical may be explained by a similar mechanism established by Ayscough et al.[7], who studied the effect of UV irradiation on nitrosobenzene in different organic solvents: decomposition of the nitroso compound produces phenyl radicals which abstract hydrogen from the solvents, and the short-lived solvent radicals formed by hydrogen abstraction are trapped by the nitroso compound. The 2,6-halogen substitution, however, has the following consequences: (i) decomposition can take place without irradiation at mildly enhanced temperature owing to the loss of conjugation energy, (ii) self-trapping[7,8] which leads to formation of diphenylnitroxides is prevented due to a strong repulsion between the halogenic atoms, (iii) no formation of monophenylnitroxide radicals[7,8] can be observed.

Owing to the above features 2,6-halogen substituted nitrosobenzene derivatives can be applied not only as good spin traps, but as spin label materials, too. This application is, however, markedly different from the classical labeling procedure being the nitroso label a non--paramagnetic material. The nitroso compound first initiates radical formation in the substance studied and subsequently traps the short-lived primary radicals. We have named our method nitroso labeling, or initiator spin trapping to emphasize the actual mechanisms.

Although nitroso labeling is not as selective as the usual labeling technique[9], where a variety of different spin labels can be combined; our method is advantageous if more direct information is required on the substance under investigation. While, e.g. the position of lines in the spectra of classical spin labels is practically independent of the nature of labeled material, in our case the spectra depend characteristically on the trapped primary radicals. Work is in progress in our laboratory to exploit this property, when the formation of crosslinks in polyethylene samples is studied by the method of initiator spin trapping.

The main purpose of spin labeling studies is generally to derive dynamic information on the material. Bullock et al.[10], who studied the different forms of motion in polystyrene samples, pointed out that the rotation of the non-rigidly linked spin label group may make distinction between the various motions difficult. In case of nitroso labeling the NO group is rigidly linked to the main chain, which may afford more intimate dynamic information. Such experiments with polystyrene samples are in progress in our laboratory, too.

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