

Light-Induced Free Radicals in Solutions of Some Unsaturated Compounds and Tetranitromethane

CARL LAGERCRANTZ and
MARGARETA YHLAND

Department of Medical Physics, University
of Göteborg, Göteborg, Sweden

It is generally assumed that the coloured products formed in solutions of many unsaturated compounds and tetranitromethane (TNM) are electron-donor-acceptor (EDA) complexes built up from unsaturated compounds which release electrons to TNM¹. We now wish to report that such systems exhibit an electron spin resonance (ESR) absorption when irradiated by light at room temperature. The spectra recorded were found to be more or less characteristic for the molecular structure of the donor substances. Light-induced radicals in solutions of some other EDA-complexes have recently been described².

The ESR-spectra were obtained by a Varian 100 kc spectrometer. The specimens were irradiated *in situ* through the slots of the ESR-cavity. The light source was a mercury lamp equipped with two sets of filters isolating either the lines 365.0/366.5 m μ (source UV) or the lines 405/407 m μ (source Blue). Substances liquid at room temperature were used either undiluted or diluted by an equal volume of chloroform. Solid substances were dissolved in chloroform. The mole ratio of the substances to TNM was made 10:1. The radical spectra were recorded either during irradiation or in the dark immediately after a period of irradiation. If no radicals were observed after an irradiation period of 10 min, the reaction was considered as negative. No radicals could be observed in a reaction mixture composed of a substance and TNM which had been irradiated separately before mixing.

The results obtained can be divided into four groups as follows.

I. The ESR-spectra of this group exhibited a triplet structure, the lines of which are equally spaced, and are of equal intensity. The width of the individual lines is rather narrow. A characteristic feature is a large splitting amounting to between 26 and 30 gauss for different substances. Some of the spectra exhibited a very narrow secondary splitting of the three

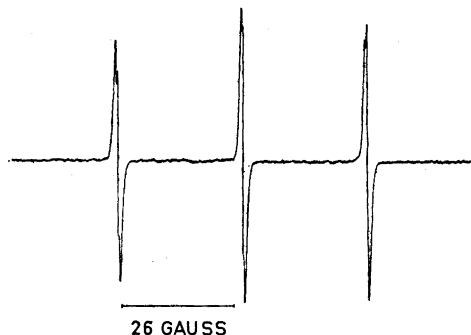


Fig. 1. ESR-spectrum of the light-induced free radicals in a solution of benzoylacetone (1 M) and TNM (1 M) in chloroform. Light source: Blue.

main lines. The following substances were found to belong to this group:

(a) β -oxo compounds: acetylacetone, benzoylacetone (Fig. 1); (b) β -keto esters: ethyl acetoacetate, ethyl benzoylacetate and diethyl acetonedicarboxylate; (c) aliphatic ketones such as methyl nonylketone (reaction mixture: colourless); (d) cyclic ketones: cyclopentanone and cyclohexanone (reaction mixtures: colourless). The spectra of the cyclic ketones exhibited a superposition of two individual spectra. Besides the large-spaced triplet structure of group I, there was another triplet with a closer spacing.

II. The ESR-spectra of this group exhibited also a triplet structure similar to that of group I but the splittings were smaller, and were found to be between 6–13 gauss. Further splittings of the main lines were a common feature of this group.

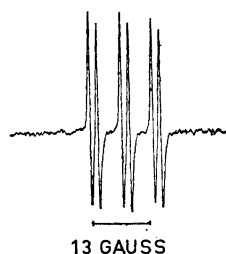


Fig. 2. In mesityl oxide + TNM. Light source: Blue.

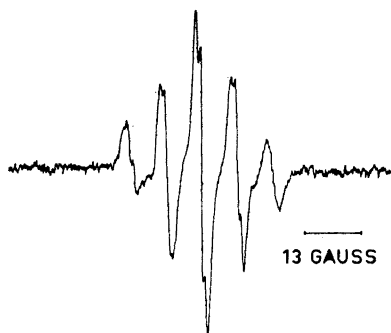


Fig. 3. In cyclohexene + TNM. Light source: Blue.

Included into group II were the following substances:

(a) α,β -unsaturated esters: methyl methacrylate, methyl acrylate and ethyl crotonate (reaction mixtures: colourless); (b) mesityl oxide (Fig. 2); (c) elaidic acid; (d) cyclic ketones, see I (d).

III. The ESR-spectra of this group exhibited a more or less symmetrical five-line structure. The following substances were found to belong to this group:

(a) cyclohexene. The five-line structure exhibited a partially resolved secondary splitting into three lines (Fig. 3); (b) methyl oleate and Δ^{10} -undecylenic acid.

IV. In this group are included substances which give rise to rather complicated spectra such as styrene (Fig. 4) and limonene. When irradiated by light no radicals could be detected in the highly coloured reaction mixtures of benzene, hexamethyl benzene and dimethyl sulphide.

In some of the systems investigated the wavelength of the exciting light (source Blue) is outside the region of absorption of both TNM and the substances but inside the absorption of the reaction mixtures.

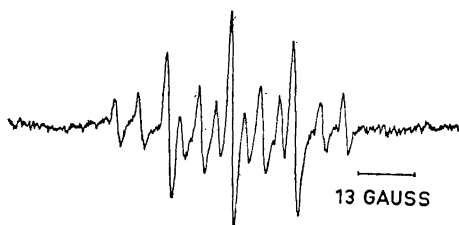


Fig. 4. In styrene + TNM. Light source: Blue.

The excitation of these systems leading to an unpairing of electrons seems to be connected with the absorption of radiant energy by a coloured EDA-complex. In other systems, including several coloured ones, light of a higher energy (source UV) had to be used in order to produce radicals. At present it does not seem possible to decide whether the excitation of the last-mentioned systems depends on the presence of a preformed non-excited complex, or whether the reaction mechanism involves an individual excitation of the donor molecules and/or TNM.

The common feature of the substances which give a positive radical reaction with TNM, is the presence of an olefinic double bond. The β -oxo compound and the ketones very probably react in their enol forms. The superposition spectra obtained with the cyclic ketones do not seem to depend on the presence of impurities but are believed to be due to photo-sensitized secondary reactions.

The triplet structure of groups I and II is very probably caused by the interaction of the unpaired electron with one nitrogen nucleus of TNM. The secondary splittings of the nitrogen levels seem to be due to the interaction with protons of the donor molecules. These findings would indicate that the radicals really are composed of parts both from the presumed donors and TNM. There seems to be a reciprocal relation between the magnitude of the nitrogen couplings and the presence and the magnitude of the proton splittings. The larger the nitrogen couplings, the smaller are the proton splittings and *vice versa*. This observation would indicate that the unpaired electrons of the radicals belonging to group I spend most of their time in the acceptor part of the complex. The sharing of the odd electron between the donor and the acceptor parts would be more pronounced in the radicals of group II.

The origin of the five-line structure of the spectra obtained in group III can be interpreted as due to an interaction of the odd electron with one nitrogen nucleus of TNM and with two equivalent protons of the donor assuming the coupling constants of the nitrogen and the protons to be equal. This interpretation should correspond to an intensity ratio of 1:3:4:3:1. Alternatively, the interaction of two equivalent nitrogen nuclei gives rise to a five-line spectrum with an intensity ratio of 1:2:3:2:1. The difference between the intensity ratios of these two alternatives is too

small to permit a definite decision by comparison with the experimentally obtained ratios.

The colour reaction of TNM with many unsaturated compounds is currently used for detecting the presence of double bonds. The value of the test is somewhat restricted as no colour is obtained with some unsaturated compounds such as α,β -unsaturated acids. Coloured products are also formed with non-olefinic substances such as benzene and alkyl sulphides. It is evident that the light-induced radical reaction here described is sometimes more specific for the presence of olefinic double bonds than are the absorption spectra in the visible and ultraviolet of the complexes formed with TNM.

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2. Lagercrantz, C. and Yhland M. *Acta Chem. Scand.* 16 (1962) 1043.

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Di-(hydroxyalkyl) Diselenides

LARS-BÖRGE AGENÅS

*Chemical Institute, University of Uppsala,
Uppsala, Sweden*

Di-(hydroxyalkyl) sulfides and disulfides have been known and studied over a long period. Thus di-(hydroxyethyl) disulfide was prepared as early as 1862 by F Guthrie¹, while the corresponding sulfide was prepared in 1886 by V Meyer². Considerable attention has since been paid to these compounds and some of their higher homologues have been obtained. By comparison the corresponding selenium compounds have been given much less attention. Only di-(hydroxyethyl) selenide has been prepared by Smedslund^{3,4} and while some

ether derivatives of di-(hydroxyethyl) diselenide have been prepared⁵ the diol itself has never been isolated.

As part of an investigation of di-(hydroxyalkyl) diselenides which is being undertaken in this Institute, the compounds I, II, and III have been prepared by reacting halohydrines with sodium diselenide solution. The reaction is almost immediate and only a slight evolution of heat has been observed.

The lowest reaction rate was found in the preparation of III; this is clearly a consequence of steric hindrance in the hydroxyneopentyl group. Thus the two compounds with a straight carbon chain were obtained after shaking the components for a few minutes, while the hydroxyneopentyl derivative was obtained only after heating the reaction mixture on a water bath for some hours.

The compounds were obtained as red-yellow oils which are almost insoluble in water but which dissolve easily in chloroform and in a proportionately large amount of ether. They have characteristic, more or less unpleasant odours. They tend to decompose when attempts are made to purify them by fractionation. As the substances are very high-boiling, the temperature necessary to distil the substances has obviously reached the temperature known to decompose diselenides. Decomposition can be avoided and thus the yield raised by distilling in high-vacuum.

The products obtained have been identified by selenium analyses and by infra-red spectroscopy. A comparison of the spectra of the starting materials and the products shows that in all three cases the bands in the 3 and 9.5 μ ranges of -OH are unchanged by the reaction. The absorption peaks arising from the carbon chains are not altered to such a degree that rearrangement may be suspected. In the region investigated, the Se-Se bond shows no absorption and in the long-wave region where this bond is expected giving an absorption band, nobody has so far been able to identify it.

A more detailed report on further compounds of this type is planned.

