

**Free Radicals in Reactions of Tetranitromethane as Studied
by Electron Spin Resonance. Part II. Reactions with
Unsaturated Compounds and with Dithionite
in Alkaline Media and in Pyridine**

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Tetranitromethane (TNM) together with unsaturated substances gives free radicals in the presence of strongly alkaline reagents or pyridine. The electron spin resonance spectra of these radicals indicate that at least two radical species are produced: a nitro radical, derived from the unsaturated compound, and a radical derived from trinitromethane. Radicals were also produced from tetranitromethane by reduction with dithionite in a strongly alkaline medium. The spectrum of this radical was identical with that presumed to be derived from trinitromethane.

It has been found (Lagercrantz and Yhland, part I,¹ Lagercrantz²) that free radicals are formed in liquid solutions of tetranitromethane (TNM) and a variety of unsaturated organic compounds upon irradiation by visible light. The electron spin resonance (ESR) spectra of these radicals exhibited a main hyperfine structure due to an interaction of the unpaired electron with one, or in some systems with two, ¹⁴N nuclei derived from TNM. In most of the spectra recorded there was a secondary splitting of the ¹⁴N lines which was attributed to an interaction with protons, derived from the unsaturated organic compound. It was suggested that the reaction involved a photo-induced transfer of one or two nitro groups from TNM to the unsaturated compound inside an electron-donor-acceptor (EDA) complex, built up from the unsaturated compound (donor) and TNM (acceptor).²

When the reaction mixtures containing TNM are kept in contact with a relatively strong aqueous solution of an alkaline hydroxide, or in some cases (β -oxo compounds) when pyridine is added, it has now been observed that free radicals are formed with several unsaturated substances without any irradiation by light. Reduction of TNM by dithionite was also found to produce radicals in a strongly alkaline medium.

EXPERIMENTAL

The ESR-spectra were obtained by a Varian 100 kc spectrometer, with the samples contained in a flat aqueous solution cell. Hyperfine splitting constants were measured by comparison with the splittings of a fresh solution of peroxyamine disulphonate (13.0 gauss). No measurements of g -values were made. In some experiments degassing was carried out by freezing, evacuating and melting, with the sample contained in a small tube fitted to the sample cell. Before the final melting, the space above the sample was filled with nitrogen at atmospheric pressure.

The olefinic substances and the β -oxo compounds were purified by fractional distillation. Cyclohexene- d_{10} and D_2O were obtained from Merck, Sharp and Dohme of Canada Ltd. Tetranitromethane (Fluka) was used as supplied.

RESULTS

I. Radicals obtained with unsaturated substances, or with β -oxo compounds and TNM in the presence of strong alkali

The reaction was performed by dissolving TNM in the unsaturated substance or β -oxo compound (liquid). An equal volume of aqueous potassium or sodium hydroxide (2 N, 6 N, or 10 N) was then added, and the two phases were mixed by shaking for about 5 sec. After the reaction mixture had been kept in the dark for about 5 min, the organic phase was separated from the aqueous layer. When the reaction was performed with a mole ratio of about 1:10 between TNM and the organic substance, there was generally a complete separation of the two phases leaving the aqueous layer coloured red or reddish-brown. The clear organic phase was found to preserve the original colour obtained on addition of TNM to the unsaturated substance.

When the reaction mixtures were made to contain more TNM than those just described, there was a more or less vigorous reaction upon the addition of alkali with production of heat, leaving the aqueous layer coloured dark brown or almost black. At the same time it was noted that the separation of the organic layer was incomplete. With some substances, such as cyclohexene, no organic layer at all separated when the reaction was performed with a mole ratio of 1:3 between TNM and cyclohexene. Cyclohexadiene was found to give a vigorous reaction even with a very small concentration of TNM. In this case no organic phase remained after the reaction was completed.

a. The free radicals of the aqueous phase. Free radicals were found to be present in the separated aqueous phase in the reaction with β -oxo compounds, such as diethyl malonate, ethyl acetoacetate, and acetylacetone, and with olefinic substances, such as allyl alcohol, methyl methacrylate, styrene, d -limonene, cyclohexene, and cyclohexadiene.

The ESR-spectra were identical in all the systems investigated, and exhibited seven equally spaced lines, with a hyperfine coupling constant of 8.4 gauss (Fig. 1). The intensity ratio was close to 1:3:6:7:6:3:1, consistent with the interaction of the unpaired electron with three equivalent ^{14}N nuclei.

In most of the systems investigated the aqueous phase was found to contain mainly radicals exhibiting the seven-line spectrum. In the reaction with some

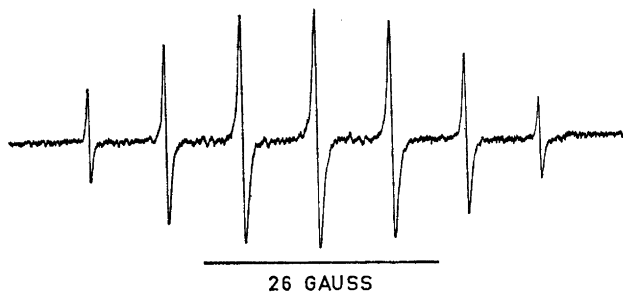


Fig. 1. ESR-spectrum of free radicals collected in the aqueous layer separated after the reaction between TNM and ethyl acetoacetate in the presence of 6 N KOH. A very small amount of the structures giving rise to the superposition spectra shown in Fig. 2, is also present in this spectrum.

substances, however, especially with cyclohexene and cyclohexadiene, the aqueous phase was found to contain other radicals in addition to those giving rise to the seven-line spectrum. These systems were found to create complicated overlap spectra with a varying proportion between the components (Fig. 2a and b). Spectra identical with those shown in Fig. 2 were obtained with both *d*-limonene, cyclohexene and cyclohexadiene, indicating that these radicals are obviously not of a type specific for the organic substance reacting with

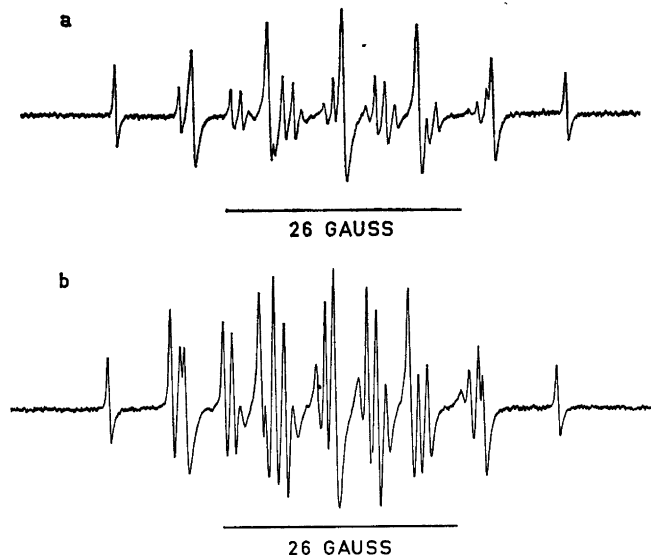


Fig. 2. ESR-spectrum of radicals collected in the aqueous layer separated after the reaction between TNM and cyclohexene (mole ratio 1:3) in the presence of 6 N KOH. *Fig. 2a* shows the spectrum about fifteen minutes subsequent to the addition of alkali. *Fig. 2b* after about an hour.

TNM. In an experiment performed with cyclohexene- d_{10} , TNM and 6 N potassium hydroxide dissolved in D_2O (H:D ratio equal to about 3:55), a spectrum identical with that shown in Fig. 2b was also obtained, indicating that the structures concerned are not due to an interaction with protons derived from unsaturated compounds.

The radicals of the aqueous phase were found to be stable for hours at room temperature once this layer had been separated from the organic phase. In the reaction with β -oxo compounds it was found that a too long mixing time of the two phases by shaking completely destroyed the radicals of the aqueous layer. At the same time it was noted that the red colour of the aqueous layer faded.

b. The free radicals of the organic phase. In many of the systems investigated the organic phase separated after the reaction was found to contain radicals, the ESR-spectra of which were different from those present in the aqueous layer. Thus, the organic layer, separated after the reaction with β -oxo compounds, such as ethyl acetoacetate,* contained radicals which gave rise to an ESR-spectrum consisting of a triplet structure, with a splitting constant of about 28 gauss (Fig. 3). The spectrum of the radicals present in the organic phase separated in the reaction with cyclohexene is shown in Fig. 4. The main structure of this spectrum consisted of five lines with an intensity ratio close to 1:2:3:2:1, consistent with an interaction of the unpaired electron with two

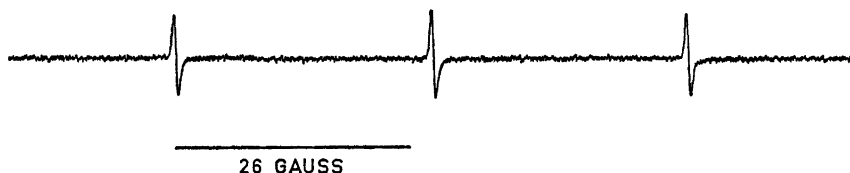


Fig. 3. ESR-spectrum of radicals collected in the organic layer after the reaction between TNM and ethyl acetoacetate (mole ratio 1:10) in the presence of a small amount of 10 N NaOH.

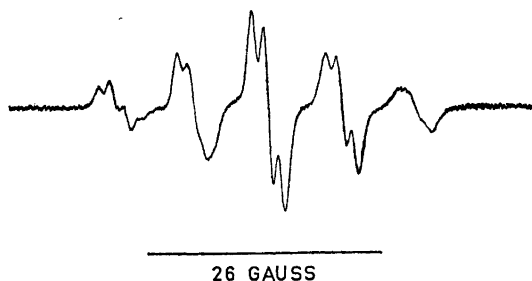


Fig. 4. ESR-spectrum of the radicals collected in the organic layer after the reaction between TNM and cyclohexene (mole ratio 1:10) in the presence of 6 N KOH.

* In order to get a separable organic phase in this case, a small amount of alkali (10 N) only had to be added due to the high solubility of ethyl acetoacetate in this solution.

equivalent ^{14}N nuclei derived from TNM. The partially resolved secondary splittings into three lines seem to be due to an interaction with two protons derived from cyclohexene. The spectra now described (Figs. 3 and 4), are almost identical with those obtained with TNM and ethyl acetoacetate and cyclohexene, respectively, upon irradiation with visible light.^{1,2}

II. Radicals obtained with β -oxo compounds and TNM in the presence of pyridine

When pyridine was added to a mixture of TNM and β -oxo compounds, such as acetylacetone, ethyl acetoacetate and ethyl benzoylacetate, free radicals were obtained. The ESR-spectra of these radicals exhibited a large triplet splitting, very similar to that obtained from the radicals present in the organic layer of a reaction with β -oxo compounds and TNM subsequent to the addition of a strongly alkaline solution (Fig. 3). No radicals were observed with diethyl malonate, or with olefinic substances, such as cyclohexene.

III. Radicals derived from TNM by reduction with dithionite in an alkaline medium

Free radicals were found to be formed after addition of TNM to a solution of sodium dithionite in 6 N KOH or after addition of dithionite to a solution of TNM in KOH. The ESR-spectrum of these radicals exhibited a seven-line structure identical with that obtained with ethyl acetoacetate (Fig. 1) and other unsaturated substances in the presence of a strongly alkaline solution. No radicals could be observed without the presence of dithionite. The colour of the radical-containing solutions in reaction with dithionite was pale yellow.

DISCUSSION

TNM is known to be a highly reactive compound.³ In the presence of strong alkali the potassium salt of trinitromethane (nitroform) and potassium nitrate are formed.⁴ It is very interesting to note the ability of TNM to behave as a nitrating agent towards certain olefins. Under appropriate conditions, the coloured EDA-complexes between unsaturated compounds and TNM will decompose. β -Alkoxy-nitro compounds are formed in the presence of alcohol, whereas nitro-olefins are produced in the presence of pyridine.⁵

The radicals here described are evidently associated with the reactions of TNM referred to above. The splitting of TNM into a mono-nitro and a tri-nitro fragment corresponds to the two main radical species observed. Thus, the mono-nitro fragment is recovered as a nitro-radical derivative of the unsaturated compound. In the reactions with β -oxo compounds and unsaturated substances, this radical could be identified in the organic layer of the reaction mixture by the appearance of the ESR-spectra (*cf.* Figs. 3 and 4). Evidently two nitro groups have been introduced into cyclohexene.

The seven-line spectrum (Fig. 1), obtained from the dominating radical species present in the alkaline aqueous phase, indicates the presence of three

equivalent ^{14}N nuclei. Consequently it appears very probable that this radical constitutes the other fragment derived from TNM, *i.e.* a trinitromethyl radical. Any double splitting of the seven lines, indicating the presence of a hydrogen atom in this radical, could not be resolved.

At present it is not clear if the formation of the free radicals considered in this case constitutes a primary or a secondary process. The first alternative will involve a homolytic splitting of TNM bond in an EDA-complex with the unsaturated substance or the enol form of the β -oxo compound by the action of alkali. The mono-nitro radical fragment would then be added to the double bond of the unsaturated substance forming the nitro-radical derivative observed, whereas the trinitromethyl radical is recovered unchanged in the aqueous phase. The second alternative is consistent with a heterolytic splitting of TNM and the formation of a nitro-derivative of the organic substance together with a trinitromethane compound, *i.e.* nitroform, or the potassium salt of this substance. The formation of the two radical species would then involve the transfer of an electron from the nitroderivative to the trinitromethane compound. A secondary formation of free radicals is partly supported by the fact that no radicals could be detected in a solution containing TNM and alkali only, indicating that the simple nitroform splitting of TNM does not involve any radical mechanism. The observation of the seven-line ESR-spectrum in an alkaline solution of sodium dithionite and TNM demonstrates that the alkali splitting is to be followed by an one-electron reduction in order to produce free radicals from the trinitromethane derivative of TNM.

The idea of an one-electron transfer between the nitro-derivative of the unsaturated compound and the trinitromethane derivative is also partly supported by the observation of molecular complexes between these substances.⁵ It may be suggested that a charge transfer will be produced in polar solvents inside this complex, leading to a dissociation into a positive and a negative radical, analogously with the findings described by Isenberg and Baird⁶ for the system tetramethyl-*p*-phenylenediamine and chloranil in solvents of increasing polarity.

If formed by an one-electron transfer to nitroform, $(\text{NO}_2)_3\text{CH}$, or the potassium salt of nitroform, $\text{K}^+[\text{C}(\text{NO}_2)_3]^-$, the radicals giving rise to the seven-line spectrum are probably present in the alkaline solution as the divalent radical ion, $[(\text{NO}_2)_3\text{C}]^{2-}$.

The nature of the radicals present in the aqueous phase (Fig. 2) in addition to the radicals derived from trinitromethane is completely unknown at present, partly because it has not yet been possible to produce a resolved spectrum without a superposition of the seven-line structure. The experiments described above indicate that the ESR-structures considered are not specific for the unsaturated compounds reacted with TNM, and that they do not seem to be dependent on an interaction with protons derived from the unsaturated compounds.

The radical spectra obtained with TNM and β -oxo compounds, or unsaturated substances in the presence of aqueous alkaline hydroxide, are evidently dominated by radicals derived both from TNM after splitting off one nitro group, and radicals derived from the reaction between this nitro-radical and the organic substance. In contrast to these findings, the ESR-spectra, obtained

when solutions of TNM and unsaturated substances or β -oxo compounds, respectively, are irradiated by light, are dominated only by radicals formed by a transfer of nitro groups to the unsaturated substances, whilst no trace of the remaining fragment of TNM could be detected in this case.^{1,2} Evidently, in several cases the radical species present in the organic phase of the alkaline reaction with TNM seem to be identical with those obtained with TNM and the same organic compounds upon irradiation by light.

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