

## Free Radicals Derived from the Alkali Salts of Nitroform (Trinitromethane)

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Two different radical species, derived from trinitromethane (nitroform) anions have been prepared and their electron spin resonance (ESR) spectra studied.

Reduction with substances such as dithionite or cysteine, or electrolytical reduction of an alkaline solution of potassium nitroform in water, produced free radicals which exhibited a seven-line ESR-spectrum, indicating an interaction of the unpaired electron with three equivalent  $^{14}\text{N}$  nuclei. This radical species is interpreted as a trinitromethane anion radical.

The second radical species was obtained by heating an alkaline solution of potassium nitroform and glucose on a steam-bath. The ESR-spectrum exhibited five main groups, each split into a doublet indicating an interaction with two equivalent  $^{14}\text{N}$  nuclei and one proton. The spectrum was interpreted as due to a dinitromethane anion radical formed by a hydrolytic cleavage of the parent nitroform anion. The uptake of a proton from the solvent water was confirmed by performing the reaction in  $\text{D}_2\text{O}$ . The doublet splitting was now replaced by a triplet, indicating the interaction with a deuterium nucleus.

The spin densities in the radicals concerned are discussed on basis of the measured hyperfine coupling constants.

It has been shown that free radicals were formed when dithionite was added to a solution of tetranitromethane in a strongly alkaline water solution (Lagercrantz <sup>1</sup>). The electron spin (ESR) spectrum of these radicals exhibited seven equally spaced lines with a hyperfine coupling constant of 8.4 gauss. The intensity ratio was close to 1:3:6:7:6:3:1. These findings were consistent with an interaction of the unpaired electron with three equivalent  $^{14}\text{N}$  nuclei. It was suggested that the radicals were formed by an alkaline-induced cleavage of tetranitromethane into a nitrate and a trinitromethane anion followed by an one-electron reduction of the latter compound by dithionite to the trinitromethane anion radical,  $[\text{C}(\text{NO}_2)_3]^{2-}$ .

It has now been found that trinitromethane anion radicals can be formed from potassium nitroform (trinitromethane) as well as from tetranitromethane dissolved in a strongly alkaline solution, by reduction with a number of sub-

stances in addition to dithionite. In some of these reactions other radical species have been produced from nitroform in addition to the trinitromethane radicals, including a dinitromethane anion radical. The present paper will describe some properties of these radicals.

### EXPERIMENTAL

The ESR-spectra were obtained with a Varian 100 kc spectrometer model V-4500 and a 6" magnet. The measurements were taken with the aid of samples contained in a flat aqueous solution cell. Hyperfine splitting constants were measured by comparison with the splittings of a solution of peroxyamine disulphonate (13.0 gauss) by the use of a dual sample cavity (V-4532) and a dual-channel recorder (G-22 A). Electrolytic generation of radicals was performed *in situ* in the ESR-cavity by use of a Varian electrolytic cell (V-4556).

Tetranitromethane (Fluka) was used as supplied. Potassium nitroform,  $\text{KC}(\text{NO}_2)_3$ , was prepared as described by Hantzsch and Rinckenberger.<sup>2</sup>

### RESULTS

*A. Trinitromethane anion radicals.* Tetranitromethane, or the potassium salt of trinitromethane (potassium nitroform), dissolved in an aqueous solution of sodium hydroxide, was easily reduced by a number of substances besides dithionite. Thus, the characteristic seven-line ESR-spectrum described above (Fig. 1), was obtained after addition of substances such as glucose, ascorbic

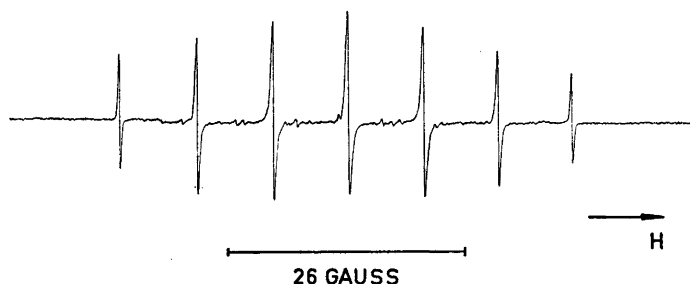


Fig. 1. ESR-spectrum of the free radicals produced by reduction of a 0.05 M solution of potassium nitroform in 2 N NaOH with an equimolar amount of uric acid.

acid, cysteine, glutathione, serum albumin and nucleic acids. The radicals were formed at room temperature, and the spectrum could be observed immediately after dissolving the reducing substances in the alkaline solution of potassium nitroform. Most of the experiments were carried out with 1 N NaOH but radicals were easily observed also in 0.1 N NaOH.\*

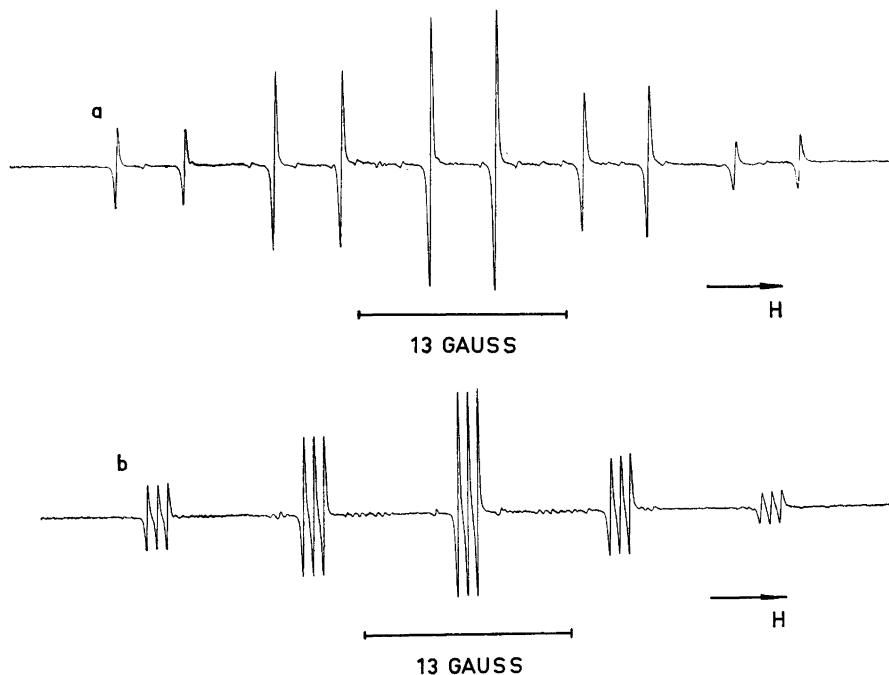
Radicals appeared from potassium nitroform dissolved in aqueous NaOH by electrolytic reduction *in situ* in the ESR-cavity. The spectra of the radicals were identical with those obtained by chemical reduction. The appearance potential of the radicals was about  $-0.30$  V when the negative electrode was

\* When the temperature was decreased to about  $+5^\circ\text{C}$  the ESR-spectrum of these radicals exhibited a very pronounced alternation of the line-widths. (Lagercrantz, C. *To be published*).

a platinum grid and a saturated KCl-calomel electrode was used as the reference electrode. The radicals were rather stable and the spectrum could be observed for several hours after disconnecting the power supply.

*B. Unidentified radicals giving rise to overlap spectra.* In some of the systems investigated other radical species were present in addition to the trinitromethane anion radicals which gave rise to the seven-line spectrum. The concentration of these radicals increased, whereas the concentration of the trinitromethane radicals diminished slowly with time, creating complicated overlap spectra, showing a varying proportion between the components. Mixtures of radical species, giving rise to overlap spectra and apparently identical with those just described, have also been found to be present in the separated aqueous layer after the alkali-induced reaction between tetrani-tromethane and a variety of olefinic substances.<sup>1</sup> The nature of these additional radicals is not understood.

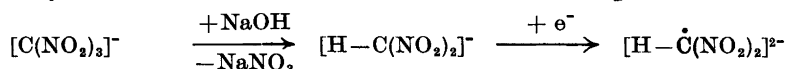
*C. Dinitro radicals.* In experiments, performed at room temperature with glucose as the reducing substance, one more radical species was sometimes observed to be produced from the alkali salts of nitroform in addition to those giving rise to the seven-line spectrum (*A*) and the overlap structures described above (*B*). Thus, it was found that a spectrum dominated by the overlap structures suddenly changed to a completely new pattern. However,



*Fig. 2.* ESR-spectrum of the free radicals produced when heating a solution of equimolar amounts of potassium nitroform and glucose in 1 N sodium hydroxide on a steam-bath for 1 min. *a.* in  $H_2O$ ; *b.* in  $D_2O$ .

the most convenient method of producing the radical species concerned was to heat a solution of equimolar amounts of glucose and potassium nitroform (0.05 M) in 1 N NaOH on a steam-bath for about 1 min. The spectrum of these radicals (Fig. 2a) exhibited ten narrow lines distributed in five equally spaced groups with a hyperfine coupling constant of 9.6 gauss. Each of the five groups was split into a doublet with a coupling constant of 4.1 gauss. The intensity ratio of the ten lines was close to 1:1:2:2:3:3:2:2:1:1. These findings are consistent with the interaction of the unpaired electron with two equivalent  $^{14}\text{N}$  nuclei and one proton.

The production of these radicals seems to involve a hydrolytic cleavage of trinitromethane (nitroform) anions into nitrate and dinitromethane anions, followed by an one-electron reduction of the latter compound.



Alternatively, the mechanism may involve a hydrolytic cleavage of the initially produced trinitromethane radicals and a direct formation of the observed radicals. The first alternative is supported by the observation of the unknown radical species (*B*) dominating the ESR-spectrum, and of the intensity of the seven-line spectrum being very low or almost zero just prior to the appearance of the  $2 \times 5$  line spectrum.

A cleavage with an uptake of a hydrogen atom from the solvent water was confirmed by the spectrum obtained when the reaction was produced in 1 N NaOD in  $\text{D}_2\text{O}$  (Fig. 2b). Each of the five main groups was now split into a triplet in place of the doublet splitting obtained in  $\text{H}_2\text{O}$ . The hyperfine coupling constant of the triplet splitting was 0.61 gauss. These findings were consistent with the interaction of the unpaired electron with two equivalent  $^{14}\text{N}$  nuclei and a deuterium nucleus ( $I = 1$ ), and the formation of a radical containing a deuterium nucleus. The ratio between the doublet and the triplet splitting, *i. e.*  $a_{\text{H}}:a_{\text{D}}$ , was 6.71 in satisfactory agreement with the expected ratio of 6.51.<sup>3</sup>

The radicals concerned were very stable. Kept in stoppered sample cells at room temperature, the intensity of the radicals was only reduced by a factor of about 2 after a week.

The spectra shown in Figs. 2a and b exhibit an asymmetric linewidth variation. The lines of the low field side of the spectra are narrower than those of the high field side. This phenomenon seems probably to provide an example of the line-width variation due to anisotropy in the electronic *g* and nuclear hyperfine tensors, combined with the random tumbling motions of the molecules in solution as predicted by Carrington and Longuet-Higgins,<sup>4</sup> and observed in respect of several radical species.

## DISCUSSION

On the basis of the measured hyperfine coupling constants, it might be possible to estimate the spin densities of the radicals here considered. As no information is available about the conformation and the steric arrangement of the dinitromethane and trinitromethane anion radicals, such considerations

must be uncertain, however. From the spectrum of the dinitromethane anion radical, it is evident that the molecular orbital containing the unpaired electron extends over both the carbon and the nitrogen atoms. Let us assume that the dinitromethane radical has a  $sp^2$  hybridization on the central carbon atom and a  $\pi$ -orbital available for the unpaired electron in analogy with the methyl radical.<sup>5</sup>

The proton splitting constant,  $a_H$ , in a  $\pi$ -electron radical is related to the unpaired electron density,  $\rho_C$ , at the adjacent carbon atom by the expression  $a_H = Q_H \rho_C$  where  $Q_H$  is the spin polarization parameter. On using the value for the methyl radical,  $Q_H = -22.5$  gauss, together with  $|a_H| = 4.1$  gauss, the spin density on the carbon atom of the dinitromethane anion radical becomes equal to  $|0.18|$ .

I. On assuming the spin density on the carbon atom of the dinitromethane anion radical to be positive, the density on each of the two equivalent nitro groups will be equal to 0.41. From this value and from the observed nitrogen splitting constant,  $|a_N| = 9.6$  gauss, it is possible to evaluate a spin polarization parameter for the entire nitro group,  $Q_{NO_2}$ , being equal to 23.4 gauss. If we assume that this value of  $Q_{NO_2}$  is valid also for the trinitromethane anion radical, we may find the spin density on each of the three equivalent nitro groups in this radical to be equal to 0.36 by the use of the observed nitrogen splitting constant,  $|a_N| = 8.4$  gauss, indicating a small negative spin density on the carbon atom of about 0.08.

II. Assuming the algebraic sum of the densities to be unity, a negative spin density on the carbon atom of the dinitromethane anion radical, *i.e.*  $\rho_C = -0.18$ , produces a spin density equal to 0.59 on each of the two nitro groups. From  $\rho_C = 0.59$  we obtain  $Q_{NO_2} = 16.3$  gauss. This value gives  $\rho_{NO_2} = 0.52$  for the trinitromethane anion radical, with a total density equal to 1.55 on the nitro groups and a negative density of 0.55 on the carbon atom.

It would be possible to determine the sign of the spin density on the carbon atom of the dinitromethane anion radical by comparing the magnitude of  $^{13}C$ -splittings in the two radicals, since alternative II implies a density in the trinitromethane anion radical nearly seven times as large as that of alternative I, and about three times the density on the carbon atom of the dinitromethane anion radical. Due to the presence of a small amount of the radical species described in *B* in the spectra of both the dinitromethane (Figs. 2a and b) and the trinitromethane anion radicals (Fig. 1), the observation of any  $^{13}C$ -splittings has so far been seriously hampered.

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