

Short Communications

On the Interpretation of the Electron Spin Resonance Spectrum of the Light-Induced Radicals from *s*-Trinitrobenzene Dissolved in Tetrahydrofuran

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We have recently described the generation of free radicals when a solution of *s*-trinitrobenzene in tetrahydrofuran was irradiated by light¹. It was believed that the radiant energy absorbed promoted a charge transfer in an electron-donor-acceptor complex built up from tetrahydrofuran (donor) and *s*-trinitrobenzene (acceptor) leading to an unpairing of the electrons involved. The electron spin resonance (ESR) spectrum exhibited a 12-lines structure with four lines of the intensity ratio 1:3:3:1 distributed into three equal groups. This spectrum is consistent with the interaction of the unpaired electron with one nitrogen atom and three equivalent protons.

In the note¹ the spectrum was tentatively connected with the formation of a negative radical ion derived from *s*-trinitrobenzene in spite of the presence of only one nitrogen hyperfine interaction. The suggestion was made that this single interaction was dependent on a splitting common to the three nitrogen nuclei due to the high symmetry of the molecule. The three protons, however, were assumed to interact in a conventional way. This explanation can of course be questioned, and other interpretations can be suggested.

A radical which is formed by the transfer of an electron to *s*-trinitrobenzene would be expected to give rise to a splitting into seven energy levels by the interaction

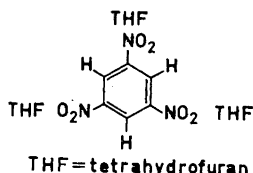
of the three equivalent nitrogen nuclei. The three equivalent protons would split each of these levels into four, giving rise to $4 \times 7 = 28$ lines, if no overlapping is present. The intensity ratio of these lines should be: 1:3:3:1:3:9:9:3:6:18:18:6:7:21:21:7:6:18:18:6:3:9:9:3:1:3:3:1. It is obvious that the spectrum described by us is not consistent with this hypothetical spectrum. Consequently, the structure of the radicals giving rise to the recorded spectrum has to be explained in other terms than those of a negative radical ion derived directly from *s*-trinitrobenzene.

A situation very similar to the one discussed has been encountered by Ward² in a study of the ESR-spectra of radicals produced by the action of alkali metals on nitro-substituted derivatives of benzene dissolved in dimethoxyethane and tetrahydrofuran. In agreement with our results one single nitrogen hyperfine interaction was found for *m*-dinitrobenzene, *p*-dinitrobenzene, *s*-trinitrobenzene and trinitromesitylene. In *s*-trinitrobenzene the single nitrogen hyperfine interaction was combined with the interaction of three equivalent protons. The spectra of the chemically prepared negative radical ions described by Ward were found to be different from those prepared by electrogeneration³. The spectra of the dinitrobenzenes obtained by the last method exhibit the interaction of two nitrogen nuclei. The difference in the spectra of the electrogenerated and the chemically produced dinitrobenzene negative ions was tentatively explained by Ward to be due to the existence of a tight complex between the alkali metal and the nitro-substituted hydrocarbon. Through the formation of this complex the equivalence of the three nitrogen atoms would be completely removed.

No spectrum of *s*-trinitrobenzene radicals obtained by electrogeneration seems to have been reported. The chemically obtained radicals of *s*-trinitrobenzene reported by Ward were produced in dimethoxy-

ethane, and the spectrum was recorded with a relatively low resolution. A direct comparison between this spectrum and that reported by us is therefore rather difficult.

In view of the findings described by Ward, it is not impossible, however, to still assign our spectrum to negative ions derived from *s*-trinitrobenzene. The peculiar single nitrogen interaction of our system in which no alkali metals were present, is perhaps connected with some kind of interaction with the tetrahydrofuran molecules. It may be suggested that the complex between tetrahydrofuran and *s*-trinitrobenzene involves three molecules of tetrahydrofuran and one molecule of *s*-trinitrobenzene according to the formula given below. The presence of three simultaneous spin systems each enclosing the aromatic nucleus with the three protons and one nitro-group with the attached tetrahydrofuran molecule, could possibly explain the obtained spectrum.



1. Lagercrantz, C. and Yhland, M. *Acta Chem. Scand.* **16** (1962) 1043.
2. Ward, R. L. *J. Am. Chem. Soc.* **83** (1961) 1296.
3. Maki, A. H. and Geske, D. H. *J. Chem. Phys.* **33** (1960) 825.

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Interconversion of 1-Phenyl-5-mercapto-1,2,3-triazole and 5-Phenylamino-1,2,3-thiadiazole

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From the reaction between 1-phenyl-5-chloro-1,2,3-triazole (I) and sodium hydrogen sulphide one would expect to get 1-phenyl-5-mercapto-1,2,3-triazole (II).

Hess has, however, shown¹ that this reaction produces a mixture of two compounds one of which is a sulphide with the structure (VIII). The other product, with melting point 173°, has the composition corresponding to (II) but since it shows no acidic properties it cannot be a mercaptotriazole and Hess proposed that it has the structure (III). Hess, furthermore, found that this compound would dissolve in hot, aqueous sodium hydroxide; acidification of the alkaline solution gave a new, isomeric compound with m.p. 65° for which the structure (II) was proposed. The lower melting isomer, when heated in ligroin, rearranged to the higher melting isomer.

Since the structures (II) and (III) are tautomeric it is unlikely that they should represent two different compounds and it has now been shown that the higher melting isomer is identical with the known 5-phenylamino-1,2,3-thiadiazole (IV) which is easily prepared from phenyl isothiocyanate and diazomethane².

The lower melting isomer was prepared from authentic 5-phenylamino-1,2,3-thiadiazole (IV) by heating with sodium hydroxide according to Hess¹. That it is 1-phenyl-5-mercapto-1,2,3-triazole (II), as proposed by Hess, was shown by convert-

