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Radiation induced free radicals in γ-irradiated cristalline ortho—toluenesulphonic acid

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Chimica. — *Radiation induced free radicals in γ-irradiated cristalline* ortho-*toluenesulphonic acid.* Nota di GABRIELLA POGGI (*) e GIAN CARLO MARCONI (**), presentata (***) dal Socio G. SEMERANO.

RIASSUNTO. — L'irradiamento di cristalli di acido *o*-Toluenesolfonico a temperatura ambiente produce per lo meno tre diverse specî paramagnetiche. Di queste, la specie termicamente instabile sembra essere $SO_3^{\bullet -}$, mentre le due termicamente stabili sono state identificate come un radicale cicloesadienile disostituito e un radicale *o*-tolile.

INTRODUCTION

In a previous study the hyperfine tensor analysis of ortho protons in a σ aromatic radical was carried out [1], utilizing the angular dependence of the spectra of γ-irradiated and thermally treated single *p*-toluenesulphonic acid crystals. In that case, the presence of two almost magnetically equivalent protons did not allow the resolution of a single tensor, and only the average of the two tensors involved was obtained. In principle, the study of similarly treated single *o*-toluenesulphonic acid (*o*-TSA) crystals could allow the determination of a single ortho proton tensor. Actually, in this system a more complicated situation arises in that 1) more than one paramagnetic species is present even after annealing and 2) the resolution of the spectra is generally very low, possibly due to the presence of magnetic inequivalent sites within the elementary cell. Therefore, the present note deals essentially with the identification of the species observed after annealing of the irradiated samples of *o*-TSA.

EXPERIMENTAL

The apparatus and technique were the same as described in ref. [1]. Crystals of reagent grade *o*-TSA$\cdot 2\,H_2O$ by Schuchardt (München) were obtained by repeated crystallization from solutions in triply distilled H_2O. The crystals show two well characterized axes perpendicular to each other, henceforth called *b* and *c*. Although the crystal structure of this compound is not known, it is believed that the type of angular dependence exhibited by the ESR spectra is a strong indication that the samples utilized are single crystals. A set of reference axes a^*, b and c, with a^* perpendicular to both other axes, was chosen for the angular variation study.

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Results and discussion

Two typical spectra are shown in fig. 1, where the top trace refers to samples not thermally treated, the lower one to samples heated at 48 °C for a few hours. The intense peak in the middle of the former is characterized by an isotropic g-value of 2.0036. The spectra of the thermally stable species, however, are structured and orientation dependent. Unfortunately they do

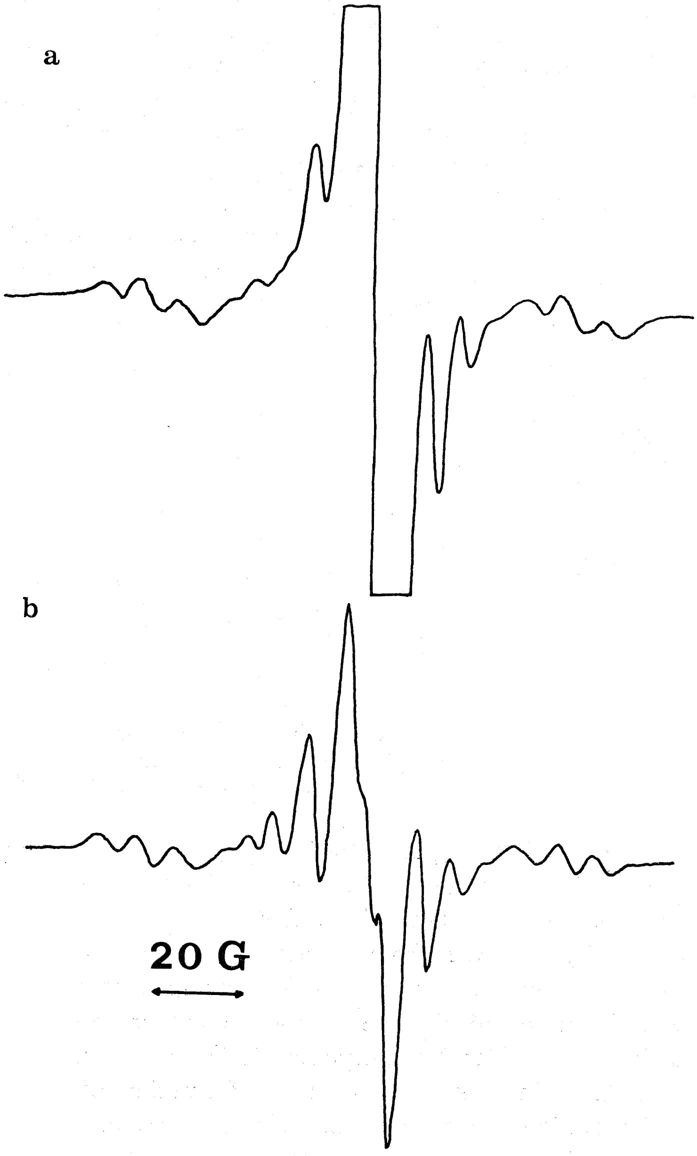


Fig. 1. – ESR spectra of γ-irradiated *o*-TSA; *a*) at room temperature before annealing *b*) at room temperature after annealing for a few hours at 48 °C. Magnetic field normal to the *b* axis, at 0° from the c^* axis. Power level approximately 20 mW.

not lend themselves to a detailed study of *g*-tensors or hyperfine splitting tensors of the different species involved. While the singlet disappearing at 48 °C could be identified with the $SO_3^{\cdot -}$ species observed by Chantry *et al.* [3], an interpretation of the rest of the spectrum in terms of two species, R_1 and R_2, has been attempted as explained below.

R_1 is the species responsible for the outer triplets of low intensity clearly visible in fig. 1, and is characterized by a fairly isotropic *g*-value of circa 2.0025. R_2 is the species mainly contributing to the central part of the spectrum, and the relative *g*-value oscillates around 2.0040 although a marked asymmetry makes a precise determination impossible.

The angular dependence of the hyperfine splitting within the R_1 outer triplets is shown in fig. 2. It is seen that along one plane the anisotropic part of the splitting is as high as 50 %, of the isotropic value. Also, according to the semiquantitative reasoning of Morton [2], the plane where almost no anisotropy is observed could be identified, if the splitting is a ring hydrogen splitting within a π-type radical, with the plane of the aromatic ring. In contrast with this marked angular variation in the secondary hyperfine coupling, a very minor variation of the separation between the centers of the triplets is observed in all planes, i.e. a few percent. The average value is 93 G, and this could come either from a doublet pattern characterized by this value of the hyperfine coupling constant or from a triplet pattern characterized by a coupling constant of 46.5 G, the central component of which is hidden under the R_2 spectrum. The latter hypothesis is considered most likely on the basis of the following considerations: 1) formation of cyclohexadienyl radicals upon irradiation of benzene and related compounds, as a result of H attachment following the primary damage event, has often been observed both in solution [4], [5], [6], and in the solid state [7], [8], [9], [10], [11], [12]; 2) in all cases in which ESR studies were carried out [6], [7], [8],

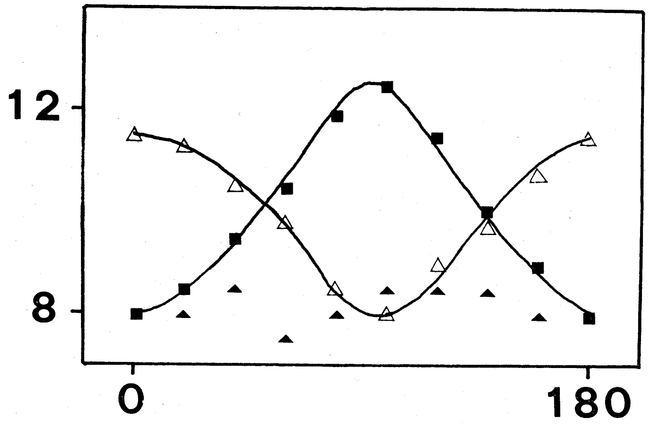
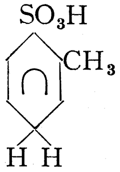


Fig. 2. – Angular dependence of the minor triplet splitting of radical R_1; full square, plane *c* a*, triangle, plane *ab*, full triangle, plane *bc**.

[9], [10], [11], [12] a hyperfine splitting constant of circa 50 G has been observed for the methylenic protons, in good agreement with the theoretical results derived by Colpa and de Boer, for the unsubstituted cyclohexadienyl species [13], oddly at variance with the more sophisticated INDO results of Pople, Beveridge, and Dobosh [14], from which a value twice as large as the experimental one is derived. As far as the ring hydrogen hyperfine splittings are concerned, they were found to be in the unsubstituted species: 9.06 G (ortho), 2.69 G (meta), and 13.15 G (para) [6]. They were also found to be fairly insensitive to substitution [6]. Accordingly, the hyperfine pattern presently observed would be consistent with the one due to a cyclohexadienyl radical having either both ortho positions free from substituents or one ortho and one para. The remaining meta hydrogen splitting would only contribute to the line width. The choice between the two alternatives mentioned is not clear-cut. However, the regularity of the triplet pattern observed at all orientations could be interpreted in terms of a near chemical equivalence of the two protons involved with respect to the CH_2 group, that is in terms of the first structure proposed. Next, one might want to consider the relative position of the CH_3 and SO_3H groups with respect to the ring CH_2. In this respect, it can be mentioned that, although the effect of the sulphonic group has not to our knowledge been investigated, the COOH group has been found to direct preferentially to the para position [10]. This, if transferable to the SO_3H group, would also be in keeping with the result that no cyclohexadienyl type radical was produced irradiating the *p*-toluenesulphonic acid [1]. In that case, the position in which addition would have been favored was occupied. It is felt therefore that the most likely structure for radical R_1 is as follows:



It might be added that it was not considered worthwhile to check the attribution theoretically by calculating the hyperfine splitting constants of the structure proposed, and for two reasons, i.e. first, the difficulty of adequately treating second row atoms within an INDO calculation, and also because of the disagreement found by Pople *et al.* in their study of the unsubstituted species [14].

The interpretation of R_2 has been based on analogy with the behavior of the *p*-TSA [1]. Since in both cases the same thermally unstable species was formed, it seems logical that in both systems a tolyl radical should be formed. Due to the difficulty of determining a set of hyperfine splitting constants from the fairly unresolved spectra, a theoretical calculation of their

TABLE I

INDO *spin densities and hyperfine splitting constants for protons*, a_H, *in the* o-*tolyl radical, averaged over rotation of the methyl group. Results obtained by means of the* 141 QCPE *Computer Program.*

Position with respect to the radical centre	ρ	a_H
ortho	.0313	16.92
meta	.0123	6.62
para	.0085	4.58
meta	.0088	4.74
methyl	—.0050	— 2.75

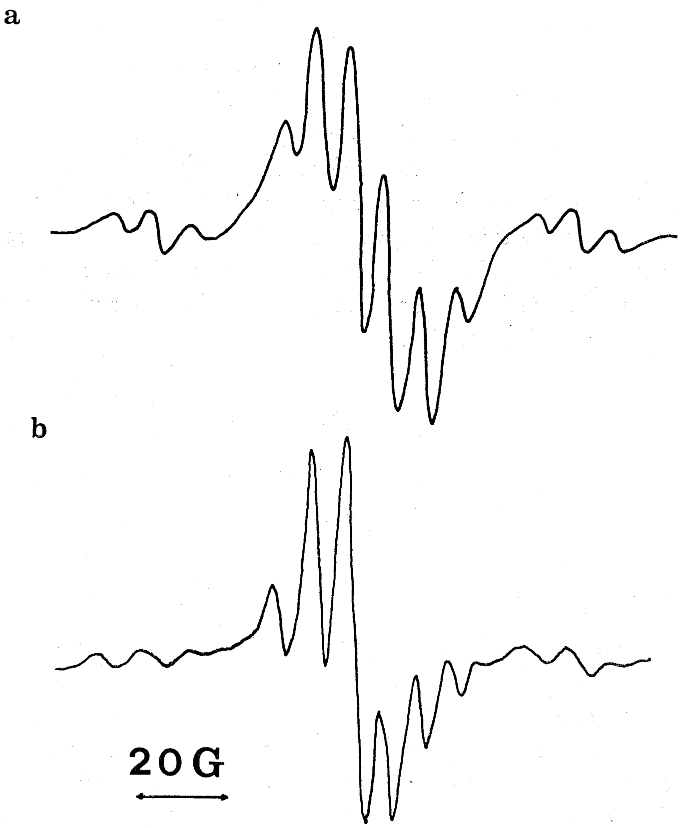


Fig. 3. – Comparison between calculated and experimental spectrum. Magnetic field parallel to the *b* axis at 30° from the *c**. The calculated spectrum contains one triplet of triplets, with hyperfine splittings of 46.5 G and 8.5 G, corresponding to R_1, and one doublet of quadruplets, characterized by a doublet splitting of 15.5 G and a quadruplet splitting of 7.5 G, corresponding to R_2. For both, a linewidth of 4 G was used. The separation between the centers of the two spectra was 5 G and the integrated intensity ratio 0.2/1.

isotropic values was carried out for the *o*-tolyl radical within the INDO frame. The results are reported in Table I. Clearly, they cannot be directly compared with experiment due to the fact that anisotropy can be quite relevant and that the contribution of R_1 to the overall pattern must be taken into account. However, taking the calculated values as indicative, it has been possible to reconstruct fairly closely one of the observed spectra, by computer simulation, introducing the experimentally determined triplet splittings for R_1 and a simplified set of splittings for R_2, as explained under fig. 3, where the comparison between simulated and experimental spectrum is shown. While this is not a demonstration that the structure proposed for R_2 is correct, it is felt that the extent of agreement gives it some credibility. Among other species that could possibily be present, one might perhaps envisage a substituted benzyl radical.

Finally, the fact that the ratio between the concentrations of R_1 and R_2 is approximately 0.2/1 perhaps deserves some attention. This might indicate that the hydrogen attachment reaction is subsequent to the SO_3H detachment reaction leading to the formation of *o*-tolyl, and that the hydrogen atom comes from the sulphonic group.

CONCLUSIONS

It seems to have been established that *o*-TSA belongs to the class of substituted benzenes giving rise to cyclohexadienyl radicals under γ-irradiation. Until now, only a few studies on single crystals have been reported [9, 11]. The present case does not allow for very good measurements of the hyperfine splitting tensor due to the low yield of cyclohexadienyl formation. Also, it would be desirable to study a system for which the crystal structure is known. Nevertheless, it is interesting to note that this type of radical can be formed in the 1,2 disubstituted compound, but not in the 1,4 disubstituted one.

Secondarily, the experimental findings are compatible with the formation of a radical formed by SO_3H group abstraction, in analogy with the clear-cut behavior of the 1,4 isomer.

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REFERENCES

[1] F. BARIGELLETTI, G. POGGI and A. BRECCIA (1974) - « J.C.S. Faraday Trans. », II, 1198.
[2] J. R. MORTON (1964) - « Chem. Rev. », *64*, 453.
[3] G. W. CHANTRY, A. HORSFIELD, J. R. MORTON and D. H. WHIFFEN (1962) - « Mol. Phys. », *5*, 233.

[4] S. GORDON, A. R. VAN DYKEN and T. F. DOUMANI (1958) – « J. Phys. Chem. », *62*, 20.
[5] A. MANTAKA, D. G. MARKETOS and G. STEIN (1971) – « J. Phys. Chem. «, *75*, 3886.
[6] K. EIBEN and R. FESSENDEN (1971) – « J. Phys. Chem. », *75*, 1186.
[7] H. FISCHER (1962) – « Kolloid Z. », *180*, 64.
[8] S. OHNISHI, T. TANEI and I. NITTA (1962) – « J. Chem. Phys. », *37*, 2402.
[9] D. CAMPBELL and D. T. TURNER (1967) – « Cand. J. Chem. », *45*, 881.
[10] D. CAMPBELL, M. C. R. SYMONS and G. S. P. VERMAN (1969) – « J. Chem. Soc., A », 2480.
[11] D. CAMPBELL and M. C. R. SYMONS (1969) – « J. Chem. Soc., A », 2977.
[12] P. J. BAUGH, K. KERSHAW, G. O. PHILLIPS and M. G. WELLER (1973) – « Carbohydr. Res. », *51*, 199.
[13] J. P. COLPA and E. DE BOER (1963) – « Mol. Phys », *7*, 333.
[14] J. A. POPLE, D. L. BEVERIDGE and P. A. DOBOSH (1968) – « J. Am. Chem. Soc. », *90*, 4201.