

process, accompanied by a rapid evolution of hydrogen, when water was added to the coloured absolute alcoholic solutions.

The properties of these systems are being investigated and we hope to publish full details in the future.

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¹ Platzman, R. L., and Franck, J., "Farkas Memorial Volume", 21 (1952). Platzman, R. L., "Basic Mechanisms in Radiobiology" (Nat. Acad. Sci. Pub. 305, 1, and discussion, 1953). Magee, J. L. *ibid.*, 51. Dewhurst, H. A., Samuel, A. H., and Magee, J. L., *Radiation Res.*, 1, 62 (1954). Stein, G., *Farad. Soc. Discuss.*, 12, 227, 239 (1952). Magee, J. L., *ibid.*, 238.

² Wolthorn, H. J., and Fernelius, W. C., *J. Amer. Chem. Soc.*, 56, 1551 (1934).

The Hydrogen Atoms in Alpha-Resorcinol

As the first example of the location of hydrogen atoms in aromatic molecules by single-crystal neutron diffraction methods, we have studied α -resorcinol, $C_6H_4(OH)_2$. This substance was examined with X-rays in 1936 by Robertson¹, who located the carbon and oxygen atoms in the structure, concluding that there were O—H—O bonds of lengths 2.66 and 2.75 Å. which formed infinite helices throughout the crystal.

Our preliminary Fourier projection of the neutron scattering density on the (001) plane is given in Fig. 1, which shows a resorcinol molecule, inclined at 61° to the plane of the projection, together with the hydroxyl groups of neighbouring molecules. All the hydrogen atoms, which have a negative scattering amplitude for neutrons, are clearly defined. Those which are attached to the benzene ring have a C—H distance of approximately 1.1 Å. The hydrogen bonds which link the molecule to its neighbours are non-symmetrical, with the proton about 1 Å. away from the nearer oxygen atom.

We are at present refining the structure by difference syntheses in order to determine these bond-lengths accurately, and full details of this work will be published in due course.

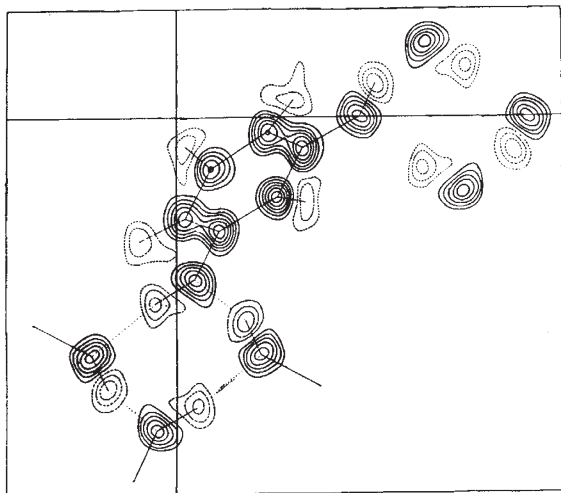


Fig. 1. A projection on the (001) plane of the neutron scattering density for α -resorcinol. The full lines are positive contours (carbon, oxygen); the dotted lines are negative contours (hydrogen)

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¹ Robertson, J. M., *Proc. Roy. Soc., A*, 157, 79 (1936).

Detection of Free Radicals in Polyacrylonitrile by Paramagnetic Resonance

EVIDENCE has been presented¹ that, during the polymerization of vinyl monomers under conditions such that precipitation of the polymer occurs, the propagating free radicals become occluded by the polymer with a resulting decrease in their accessibility for reaction. The effective rate-coefficients for the free radical reactions, particularly that of chain termination, are thus reduced, giving rise to the characteristic kinetic features observed in heterogeneous vinyl polymerizations. In the case of acrylonitrile, extreme degrees of occlusion may be reached, leading to the presence in the polymer of trapped radicals for which the propagation and termination coefficients are practically zero. The concentration of these radicals has been estimated by reaction with α -diphenyl β -picryl hydrazyl². We now wish to report the detection and estimation of trapped radicals by observation of the paramagnetic resonance absorption spectrum of the polymer. This method has already been employed to detect radicals in activated carbon and other carbonaceous solids^{3,4}, and also in gel systems prepared from cross-linked vinyl polymers⁵.

Acrylonitrile was polymerized photochemically in a tube of $\frac{1}{4}$ in. diameter with di-*tert*-butyl peroxide (10 per cent v/v) as catalyst. The rate was 7×10^{-3} mol.lit.⁻¹sec.⁻¹. After 20 per cent conversion the unchanged monomer and catalyst were distilled off in vacuum and the tube sealed. The paramagnetic resonance absorption spectrum of the polymer was observed at room temperature at a wave-length of 3 cm., and also at 90° K. and 20° K. at 1.25 cm. The tube containing the polymer was first inserted into an H_{012} 3 cm. wave-length rectangular resonant cavity, when an absorption line with a width of about 20 gauss and a spectroscopic splitting factor of 2.00 ± 0.01 was observed, using a normal crystal-video system of detection. Comparison of the integrated intensity of the signal with that obtained from low-temperature carbon samples calibrated directly against diphenyl picryl hydrazyl⁴ indicated that the concentration of unpaired electrons present in the polyacrylonitrile was about 10^{17} per ml. (based on the initial monomer volume). The concentration of free radicals determined by the chemical method using diphenyl picryl hydrazyl may be seen from a short extrapolation of the line in Fig. 3 of ref. 2 to be approximately 8×10^{-5} mol.lit.⁻¹ or 5×10^{16} radicals per ml. The agreement between the two completely independent methods of radical counting is highly satisfactory. Even under the favourable conditions used in these experiments, only about 1–2 per cent of the total number of radicals generated become trapped; hence it is clear that no kinetic treatment of the polymerization which embodies termination predominantly by radical occlusion is valid.

The effect of admitting air to the polyacrylonitrile sample was also studied by breaking off the tip of