Electron Spin Resonance Spectrum of the Phenyl Radical prepared by Chemical Reaction at 77°K

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THE phenyl radical is one of the most reactive hydrocarbon radicals,[1] but the reasons for its exceptional reactivity are not completely understood. It is not known whether the unpaired electron is localized on one carbon atom or delocalized in the π-electron system of the radical. Information about its structure and thus about its high reactivity should be obtainable from a study of its electron spin resonance (e.s.r.) spectrum.

Previous attempts to prepare and stabilize the phenyl radical at low temperatures have not been very successful. Exposure of benzene or other suitable parent material to high-energy radiation resulted in the formation of cyclohexadienyl-type radicals.[2] Tolkachev, Chkheidze, and Buben[3] have reported the preparation and trapping of the phenyl radical by photolysis of iodobenzene adsorbed on silica gel. Their results were somewhat inconclusive as the resolution and signal/noise ratio of the e.s.r. spectrum were poor. We have attempted previously to prepare the phenyl radical in a matrix of iodobenzene by the reaction between sodium atoms and iodobenzene at 77°K in a rotating cryostat,[4] but the e.s.r. spectrum was too poorly resolved to allow a reliable interpretation to be made.

Our technique has been developed further and we now report the successful preparation and trapping of the phenyl radical in a variety of matrices.

In our original method the halogenohydrocarbon was deposited on the cold surface (77°K) of a drum which was spinning rapidly in a high vacuum. Sodium atoms were deposited very sparsely on the surface of the halogenohydrocarbon and the free radicals, formed by the reaction:

$$\mathrm{Na\cdot} + \mathrm{RX} \rightarrow \mathrm{R\cdot} + \mathrm{NaX},$$

were trapped in a matrix of the halogenohydrocarbon. In the modified method an additional

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[1] W. Fielding and H. O. Pritchard, *J. Phys. Chem.*, 1962, **66**, 821.

[2] H. Fischer, *Kolloid Z.*, 1962, **180**, 64.

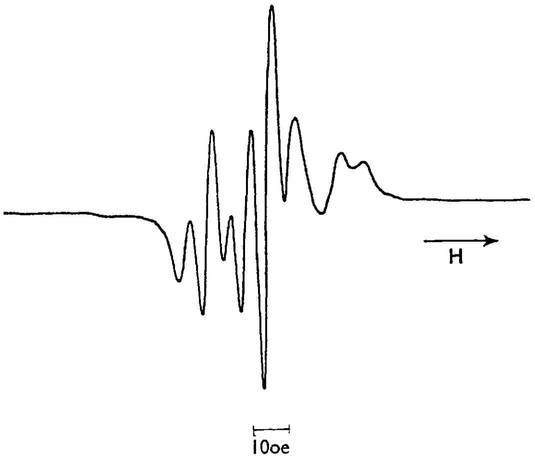
[3] V. A. Tolkachev, I. I. Chkheidze and N. Ya. Buben, *Zhur. strukt. Khim.*, 1962, **3**, 709.

[4] J. E. Bennett and A. Thomas, *Proc. Roy. Soc.*, 1964, **A**, **280**, 123.

material is deposited as a third layer which forms the bulk of the deposit and acts as the matrix for trapping the radicals. The flux of the halogenohydrocarbon is reduced to a value comparable to that of the sodium and thus the radicals are surrounded by the third material instead of by the parent halogenohydrocarbon.

We have examined a wide variety of matrices in our attempt to trap the phenyl radical. In several cases the e.s.r. spectra showed that the phenyl radical (prepared by the reaction between sodium and iodobenzene) had abstracted hydrogen from the matrix. However, we observed the same basic spectrum from the radicals trapped in benzene, hexadeuterobenzene, dodecafluorocyclohexane, and water, showing that the phenyl radical had been trapped in these matrices. The line widths varied with the matrix, the best resolved spectrum being obtained with water (see Figure). The spectrum is similar to that observed by Tolkachev *et al.*[3] and confirms that they had prepared and trapped the phenyl radical.

The spectrum consists of nine lines which can be separated into three equally spaced triplets with intensity ratios of approximately 1 : 2 : 1. The lines within each triplet are also equally spaced and have intensity ratios of 1:2:1. This spectrum can be attributed to a major hyperfine coupling of 18·1 ± 1·0 oersted to two equivalent protons and a smaller coupling of 6·4 ± 0·5 oersted to another pair of equivalent protons. The spectrum of the *o*-dichlorophenyl radical (prepared from 2,6-dichloro-1-iodobenzene) is a poorly resolved triplet (1 : 2 : 1) with a hyperfine coupling constant of 7·0 ± 1·0 oersted, showing that the major coupling is with the *ortho*-protons in the phenyl radical, and the smaller coupling is with the *meta*-protons.



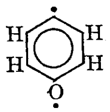
First derivative spectrum of the phenyl radical at 120°K.

Tolkachev *et al.*[3] have interpreted their results by suggesting that the carbon atom at which bond fission occurs becomes bivalent and that the unpaired electron is located in the five π-electron system of the other five carbon atoms. However, this π-electron system is similar to that in the cyclohexadienyl radical, for which the hyperfine coupling to the single *para*-proton is much larger than that to the *meta*-protons.[2] Since the spectrum of the phenyl radical shows coupling only to the *ortho*- and *meta*-protons we think that this bivalent structure is unlikely.

A second possible structure for the phenyl radical is one in which an electron from the π-electron system pairs with the unpaired electron in the carbon sp^2-orbital to give a lone pair. The remaining π-electron system will be similar to that of the benzene positive ion which would be expected to give a spectrum very different from the one observed.

We consider that the results are explained best by assuming that the unpaired electron remains in the sp^2-orbital of the carbon atom to give a σ-type radical. Morokuma, Ohnishi, Masuda, and Fukui[5] have calculated the hyperfine couplings for this structure and obtained values of 12·1 oersted and 6·3 oersted for the *ortho*- and *meta*-protons respectively, which are in reasonable agreement with our experimental values. They predict also that the hyperfine coupling constant of the *para*-proton will be much smaller than these values, which again accords with our results.

Wasserman and Murray[6] obtained the e.s.r. spectrum of the triplet state molecule in which they suggest that one of the unpaired electrons is located in an sp^2 σ-type orbital of the carbon atom. They observe a hyperfine coupling of this electron with the two *ortho*-protons which is similar to the value we have observed in the phenyl radical.



Recently Porter and Ward[7] have reached a similar conclusion about the structure of the

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[5] K. Morokuma, S. Ohnishi, T. Masuda and K. Fukui, *Bull. Chem. Soc. Japan*, 1963, **36**, 1228.
[6] E. Wasserman and R. W. Murray, *J. Amer. Chem. Soc.*, 1964, **86**, 4203.
[7] G. Porter and B. Ward, *Proc. Chem. Soc.*, 1964, 288.

ground state of the phenyl radical from their study of the electronic spectra of the radical in the gas phase.

Thus we conclude that all the evidence favours a σ-type structure for the phenyl radical in which the unpaired electron remains in the sp^2-orbital of the carbon atom at which bond scission occurs. This localized structure helps to explain the very high reactivity of the phenyl radical that we have observed in our experiments at 77°K.

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