Tetrahedron Letters No.46, pp. 4773-4775, 1968. Pergamon Press. Printed in Great Britain.

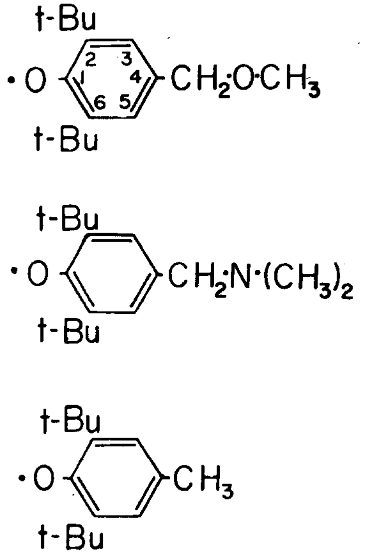
SOLVENT EFFECT ON THE ESR HYPERFINE SPLITTING CONSTANTS OF SOME PHENOXYL RADICALS

Y. Ōishi,* K. Mukai, H. Nishiguchi, Y. Deguchi and H. Takaki

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, Japan

(Received in Japan 22 July 1968; received in UK for publication 12 August 1968)

We have studied the solvent effect on the ESR hyperfine splitting constants of some neutral radicals. One of the authors (YD) has shown that the nitrogen splitting constant of diphenyl nitric oxide depends on the dielectric constants of solvents.(1) Recently it has also been reported(2) that a linear relation holds between the splitting constants of the radicals and dipole moments of solvents except for the case where the hydrogen-bond between a radical and a solvent would be formed. In the course of the study of solvent effect on hyperfine splitting constants of some phenoxyl radicals, we found that the splitting constants did change even in the solvents in which the values of their dielectric constants and dipole moments are nearly zero. In this note, the experimental results will be reported.



(I)

(II)

(III)

FIG. 1

Radicals studied are shown in FIG. 1. They are produced by oxidation of the corresponding phenols with lead peroxide in well degassed solvents. The corresponding phenols commercially obtained were used after recrystallizing several times. Solvents used are n-hexane, methyl-cyclohexane, benzene,

---

* Present address: Shionogi Research Laboratory, Shionogi & Co., Ltd., Sagisu, Fukushima-ku, Osaka, Japan.

toluene, o-xylene, m-xylene, p-xylene and mesitylene. They are the reagents with special grades and were used after thorough dehydration. All measurements were carried out using the JES- 3B type ESR spectrometer equipped with 100 Kc/sec field modulation.

TABLE I

Solvent	Ionization** potential (eV)	a_H value of the para substituent in gauss Radical (I)	Radical (II)	Radical (III)
n-Hexane	9.59	11.68		
Methyl-cyclohexane		11.88		
Benzene	9.21	12.01	10.85	11.08
Toluene	8.88	12.27	10.95	11.07
o-Xylene	8.58	12.58	10.98	
m-Xylene	8.58	12.54		
p-Xylene	8.48	12.55		11.08
Mesitylene	8.10	12.70		

** These values are cited from the reference 3.

The experimental results are shown in TABLE I. In the radical (I), the splitting constant of the para methylene proton in different solvents increases up to ten percent of the value observed in n-hexane. Thus, in FIG. 2, the splitting constant of the radical (I) is tentatively plotted against the inverse of the ionization potential of the solvents. The experimental points fall remarkably close to a straight line. In the radical (II), the a_H of the para methylene proton also increases although its change is fairly small. On the other hand, in the radical (III), the variation of the splitting constant with solvents was never recognized. The a_H of the meta position in a benzene ring, however, was constant in every radical within the experimental error. Since in 2,6-di-t-butyl-4-R-substituted phenoxyl radicals,

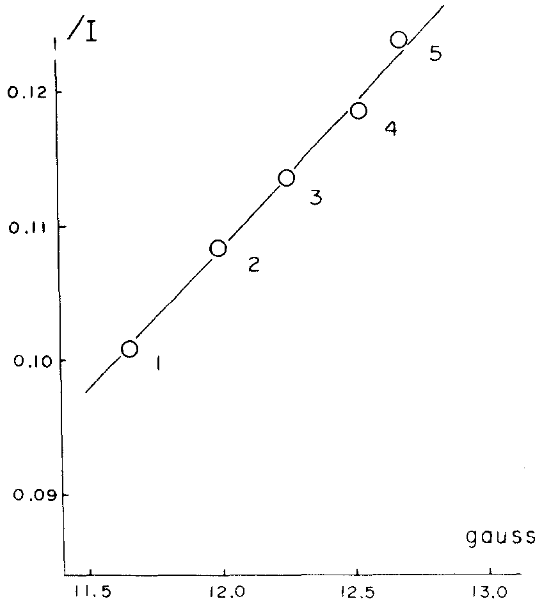


FIG. 2. Methylene proton splitting constant versus ionization potential I, in 1. n-hexane, 2. benzene, 3. toluene, 4. xylene and 5. mesitylene.

the oxygen atom at the position (1) is masked by the two tertiary Buthyl groups at 2 and 6 positions, the interaction with solvent will be very weak at this position (1). Perhaps, methyl groups of the solvent molecules will not play a role because in methyl-cyclohexane, the splitting constant a_H is almost same as that in n-hexane. Thus, the interaction with a solvent molecule should occur at either the benzene ring or the substituent of a radical molecule. The π-π type interaction between the radical and the solvent can be excluded because the methyl proton splitting constant of the radical (III) does not vary with changing the solvent. Comparing these radicals, (I) and (II) have the atom with lone-paired electrons in the para substituent but (III) has not. Thus, one may conclude that the interaction will occur between the atom with lone-paired electrons of the radical and the solvent molecule. These findings might be interpreted in terms of the charge transfer mechanism. Details will be submitted elsewhere.

REFERENCES

1. Y. Deguchi, Bull. Chem. Soc. Japan 35, 260 (1960).
2. K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi, and H. Takagi, Bull. Chem. Soc. Japan 40, 2731 (1967).
3. S. H. Hastings, J. L. Franklin, et al., J. Am. Chem. Soc. 75, 2900 (1953).