ON THE ABSORPTION OF 3.18 CM MICROWAVES IN SOME SUBSTITUTED PHENOLS IN THE LIQUID STATE*

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ABSTRACT. The absorption of 3.18 cm microwaves in o-bromophenol, 2,4,6-trichlorophenol, o-methoxy phenol, p-cresol and diphenyl ether have been studied for different temperatures of the liquids in continuation of previous investigations. Maximum absorption of 3.18 cm microwaves has been exhibited by o-methoxy phenol at 100°C and p-cresol at 90°C and the values of the radii of the rotors calculated from Debye's theory indicate that those absorption maxima are due to rotation of the substituent OH group about the C-O bond. o-Bromophenol, 2,4,6-trichlorophenol and diphenyl ether did not show any absorption in the 3.18 cm microwave region when the temperature of the liquids were changed from the freezing points to the boiling points. It is pointed out that these three molecules do not show absorption in this region owing to restriction of the rotational freedom of the OH group in the first two cases and absence of such small group as a substituent in the case of diphenyl ether.

INTRODUCTION

From a study of the values of dielectric loss observed in the solution of some substituted benzenes in the metre wave length region Fischer (1949) inferred that orientation of some substituent groups having rotational freedom contributes to dielectric loss in this region. Recently, it was actually observed (Ghosh, 1954a, 1954b, 1955a) that some substituted benzenes such as benzyl chloride, benzyl amine, benzyl alcohol, phenol, cresols etc., show absorption maxima in the microwave region corresponding to rotation of the substituent group about the diameter of the benzene ring passing through the point of substitution. It has also been shown that such molecules exhibit three different discrete values of time of relaxation corresponding to orientation of the single molecule, dimer and the substituent group, and the occurrence of 'effective time of relaxation' postulated by previous workers has been corroborated by these results. Some of the molecules containing OH group as a substituent exhibit absorption peaks in the 3.18 cm microwave

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region at suitable temperatures, showing the freedom of rotation of the OH group about the C-O bond.

It was observed recently (Ghosh, 1955b) however, that in the case of ortho chlorophenol there is no absorption of 3.18 cm waves throughout the temperature range from the freezing point upto the boiling point of the liquid. There are many molecules in which there may be such restriction of rotation of the OH group. The absorption of 3.18 cm microwaves in a few such liquids the molecules of which have other substituents besides the OH group has been investigated at different temperatures to find out whether the rotation of the OH group is restricted in these cases. Again, according to Debye's theory (Debye, 1929) the radius of the rotor depends on τ, the time of relaxation and η, the viscosity of the liquid, and if the same substituent group having a freedom of rotation be present in different molecules, the ratio $\tau T/\eta$ should be constant, T being the absolute temperature of the liquid. It would also be interesting to find out whether the above relation is satisfied in the case of molecules having OH as a substituent. It was thought worthwhile, therefore, to study the absorption of 3.18 cm microwaves in some substituted phenols in order to find out whether the results indicate any hydrogen bonding postulated by Pauling (1939) in some of these molecules.

EXPERIMENTAL

In the present investigation the absorption of 3.18 cm microwaves in o-bromophenol, o-methoxy pehnol, 2, 4, 6-trichlorophenol, p-cresol and diphenyl ether have been studied at different temperatures. o-Bromophenol and o-methoxy phenol were supplied by E. Merck, 2,4,6-trichlorophenol supplied by Scherring -Kahlbaum, and p-cresol and diphenyl ether were supplied by B.D.H. The liquids studied were all of chemically pure quality. They were all distilled in vacuum after proper dehydration. The experimental arrangement in the present investigation was the same as that reported previously (Ghosh, 1953, 1954a).

RESULTS

The absorption curves for o-methoxy phenol and p-cresol are given in figures 1 and 2. Ortho bromophenol, 2,4,6-trichlorophenol and diphenyl ether showed no absorption at all in the 3.18 cm microwave region when the temperature of the liquids was changed from the boiling point upto the freezing point. The frequencies of absorption peaks observed for the first two liquids, the corresponding temperatures, the values of a and τ calculated from Debye's theory and the different constants involved in the calculation are shown in Table I. The value of a, the radius of the rotor in the case of o-methoxy pehnol could not be obtained correctly as the value of ϵ_1 could not be measured at different temperatures owing to slight conductivity of the liquid. For approximate calculation the value of
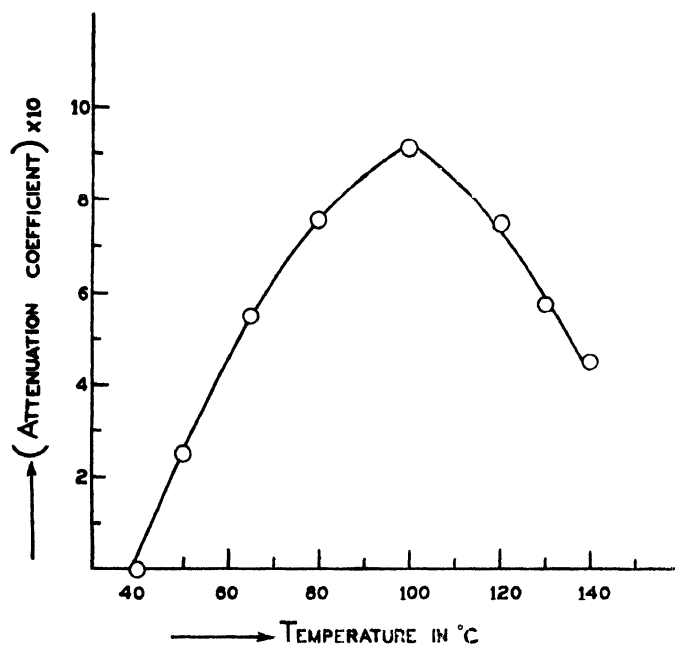
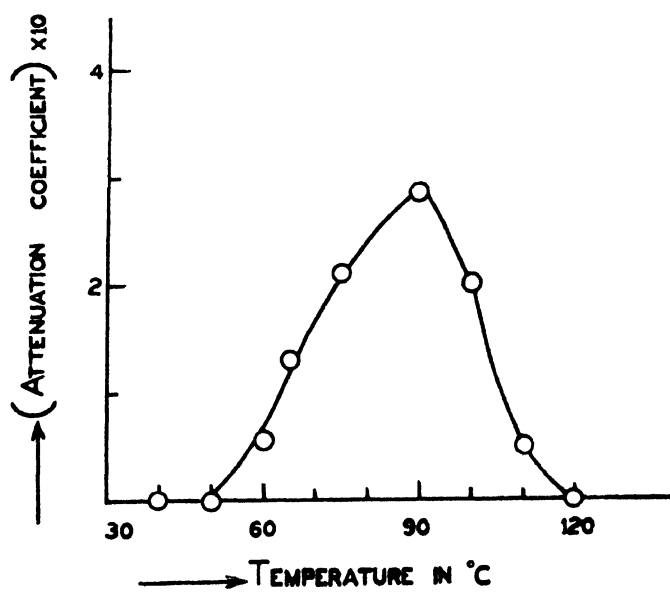Fig. 1. o-Methoxy phenol; $f = 9415$, Mc/sec, thickness of the liquid, 1 cm.

Fig. 2. p-Cresol; $f = 9415$ Mc/sec., thickness of the liquid, 1 cm.

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ϵ_1 has been taken as 8. The values of the constants as well as of a for p-chloro-phenol are included in Table I for comparison.

TABLE I

$$\frac{\omega}{2\pi} = 9415 \text{ Mc/sec.}$$

Liquid	T for max. ab- sorption	ϵ_0	ϵ_1	$\tau \times 10^{11}$	$\eta \times 100$	$a \times 10^8$cm
p-Chlorophenol	358	2.43	7.9	1.361	1.4	1.55
p-Cresol	363	2.37	6	1.469	1.6	1.53
o-Methoxy phenol	373	2.37	8 (rough esti-mation)	1.358 (approx.)	.95	1.7 (approx.)

The value of η for p-chlorophenol at 85°C was obtained after Frenkel (1946) from the values of viscosity at two different temperatures given in the International Critical Tables. The value of η for o-methoxy phenol was taken from the data reported by Friend and Hargreaves (1946). The values of ϵ_1 have been obtained from the table of dielectric constants of pure liquids published by the National Bureau of Standards, United States, Department of Commerce and also from the International Critical Tables. The values of ϵ_0 have been assumed to be equal to n^2, n being the refractive index at 20°C for sodium D-line. The value of n for o-methoxy phenol was not available and it was therefore measured with an Abbe refractometer.

DISCUSSIONS

In the case of o-bromophenol no absorption was observed in the 3.18 cm microwave region in the whole temperature range from the melting point to the boiling point. The infrared absorption curves for o-bromophenol is similar to those for o-chlorophenol as reported by Pauling (1939). The absence of absorption of 3.18 cm microwaves in o-bromophenol shows that in this molecule also the hydrogen atom of OH group is attached to the bromine atom as in the case of o-chlorophenol (Ghosh, 1955b). The total absence of absorption further shows that all the molecules in the liquid are of the cis configuration. This further shows that phenol was not present as impurity in the liquid although Rossmy et al (1953) suggested that all samples of o-bromophenol contains phenol as impurity.

In the case of 2,4,6-trichlorophenol no absorption in the 3.18 cm microwave region has been observed. The two configurations of the 2,4,6-trichlorophenol molecule are equivalent as shown in figure 3. In this case also the OH group

has no freedom of rotation about the C-O bond due to cent percent chelation in both the configurations. The absence of absorption in the microwave region thus
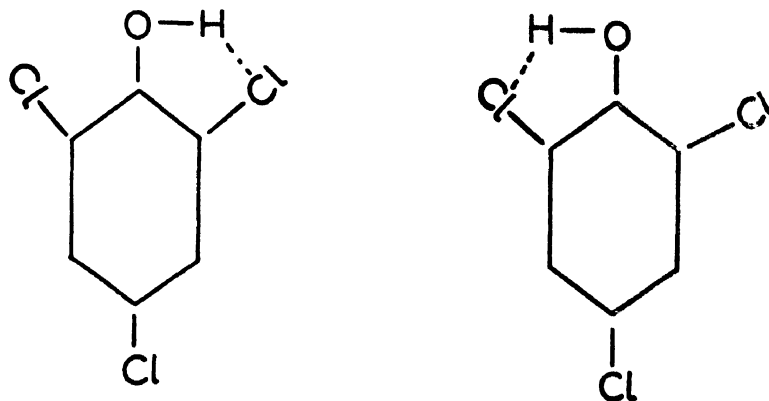

Fig. 3 2,4,6-thrichlorophenol.

confirms the configuration of the molecule given in figure 3. Ortho methoxy phenol showed absorption in whole temperature range from 50° with maximum at 100°C (figure 2). It can be seen from Table 1 that the approximate value of the radius of the rotor in the case of *o*-methoxy phenol comes out as 1.7 A.U. which is much less than the value for the single molecule. Evidently, the substituent OH is the rotor in this case. In the case of *p*-cresol absorption was indicated in the 3.18cm microwave region in the whole temperature range from 60°C to 120°C with a maximum at 90°C, but the intensity of absorption is very low compared to that in the case of ortho-and meta cresol studied previously (Ghosh, 1954b) The value of the radius of the rotor in this case is 1.53 A.U. and evidently, the OH group is responsible for the absorption in this case also.

The absence of absorption of 3.18 cm microwaves in some of the molecules mentioned above confirms the conclusion drawn earlier that all such molecules in which the OH group has freedom of rotation show absorption in this region at suitable temperatures and when the freedom of rotation is restricted the molecules cease to exhibit absorption in this region.

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