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A note on the dielectric absorption of microwaves in 1, 2-dibromopropane in the liquid state

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The dipolar activation energy ΔH_{τ} in 1,2-dibromopropane in the liquid state obtained from dielectric relaxation studies, is found to have a close parallelism with electrostatic potential energy difference of the trans and gauche isomers in the liquid state The energy difference of the trans and gauche isomers of the molecule obtained from temperature dependence of the mean dipole moment agrees well with that obtained from spectroscopic studies.

INTRODUCTION

Recent investigations on the absorption of microwaves by some rotational isomeric molecules (Hasan *et al* 1971, Ghatak *et al* 1972, Das *et al* 1972 and Hasan *et al* 1972) in the liquid state have shown that the activation energy of dielectric relaxation (ΔH_{τ}) in each case has got a close parallelism with the difference in the values of electrostatic potential energies of the polar isomers in the liquid state, the latter being found to be almost equal to the amount of lowering of the energy difference ($\Delta E_{vap}-\Delta E_{liq}$) between the trans and gauche isomers from the vapour to the liquid state as was pointed out by Wada (1954) from spectroscopic studies. Similar investigations in the case of 1,2-dibromopropane in 1·62, 3·17 and 3·49 cm microwave region were made and the results are discussed in this paper

EXPERIMENTAL

The sample procured from Schuchardt (Germany) was distilled before use Experimental methods for the measurements of complex dielectric constant, static dielectric constant, viscosity, refractive index and density were the same as described earlier (Hasan *et al* 1971).

RESULTS AND DISCUSSION

The dielectric permittivity (ϵ'), dielectric loss (ϵ''), static dielectric constant (ϵ_0) and square of the refractive index n^2 obtained experimentally (table 1) were fitted in Cole-Cole arc plot (figure 1) and the distribution parameter α and the

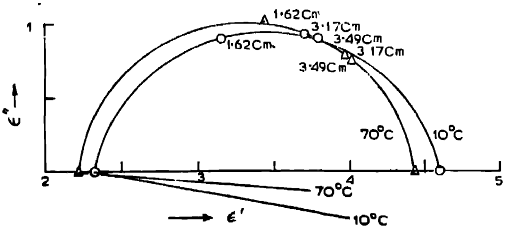

Fig. 1.

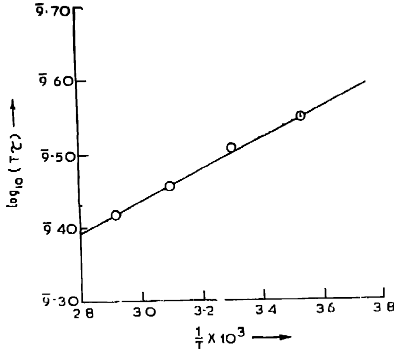

Fig. 2.

relaxation time τ were determined as usual. The values of the activation energy for dielectric relaxation ΔH_τ and that for viscous flow ΔH_τ were determined respectively from the straight line plots of log τT vs $1/T$ and log η vs $1/T$ The values of α, τ, ΔH_τ and ΔH_η are given in table 2.

Table 1. Values of n^2, ϵ', ϵ'', ϵ_0, d and η of 1,2-dibromopropane at different temperatures

$\lambda = 1{\cdot}62$ cm $\lambda = 3{\cdot}17$ cm, $\lambda = 3{\cdot}49$ cm

		$\lambda = 1{\cdot}62$ cm		$\lambda = 3{\cdot}17$ cm		$\lambda = 3{\cdot}49$ cm				
'emp. C	n^2	ϵ'	ϵ''	ϵ'	ϵ''	c'	ϵ''	ϵ_0	$d_{gm/cc}$	η_{cp}
10	2.33	3 16	0.90	3 71	0 93	3.80	0 90	4.60	1.93	1.265
30	2.29	3.22	0.96	3 80	0.90	3 87	0 88	4 53	1 89	1.023
50	2 25	3.34	1.01	3 91	0.87	3 99	0 82	4.49	1.85	0 81$_6$
70	2 22	3.45	1 02	3.98	0 79	4.02	0.76	4 43	1.82	0.697

Table 2. Values of α, m, τ, ΔH_τ, ΔH_η, Electrostatic potential energy difference and energy difference of 1,2-dibromopropane

Temp. °C	α	Mean moment (m) in D	$\tau \times 10^{12}$ Sec	$\Delta H\tau$ k.cal/mole	$\Delta H\eta$ k cal/mole	Electro-static energy diff. k.cal/mole	Energy diff. in liq from dipole moment k cal/mole
10	12	1 23	12 45	0 98	2.04	1 01	1 02
30	.09	1 27	10 61				
50	.07	1 34	8 85				
70	06	1 39	7 63				

The τ-value of 10·6 psec in 1,2-dibromopropane at 30°C (table 1) is larger than τ-value of 8·8 psec in 1,2-dichloropropane (Hasan *et al* 1972) at the same temperature, which is consistent with the sizes of the molecules The ΔH_η-value of 2·04 kcal/mole is as generally observed in polar liquids larger than the ΔH_τ-value of 0·98 kcal/mole In the case of 1,2-dibromopropane three isomeric forms—one trans and two gauche, are possible as in 1,2-dichloropropane (Mizushima 1954). The second gauche form, being of much higher energy due to steric repulsion between two large Br atoms, is expected to be present in negligible amount The energy difference between the trans and gauche 1 isomers in the vapour and liquid states respectively are 1·7 and 1·0 kcal/mole (Mizushima *et al* 1961) Hence the amount of lowering of the energy difference ($\Delta E_{vap} - \Delta E_{liq}$) is 0·7 kcal/mole which agrees fairly well with the dipolar activation energy of 0 98 cal/mole The small difference in ΔH_τ may be due to intermolecular forces other than electrostatic forces as was pointed out in the case of 1,2-dibromoethane (Hasan *et al*, 1971) It may be noted there that the energy difference between the trans and gauche isomer in the liquid state obtained from the measurements of the temperature dependence of the mean dipole moment Mizushima (1954) in the present investigation is about 1 kcal/mole which agrees well with that obtained from the spectroscopic studies as mentioned above

The difference in electrostatic potential energies of the trans and gauche isomers in 1,2-dibromorpropane, obtained from the relation

$$\Delta E = \frac{\epsilon - 1}{2\epsilon + 1} \left(\frac{\mu_g^2}{a_g^3} - \frac{\mu_t^2}{a_t^3} \right),$$

(Mizushima 1954) was about 1 kcal/mole which agrees fairly with the dipolar activation energy of 0·98 kcal/mole. The value of dipole moment of trans ($\mu_t = 0{\cdot}4$ D) and gauche ($\mu_g = 3{\cdot}4$ D) isomers were calculated from geometrical structure using known bond moments and bond angles. This result is similar to those observed in the cases mentioned in the introduction.

It may therefore, be concluded that the dipolar activation energy in the present case is mostly electrostatic in nature, as was pointed out by Mizushima (1954) in 1,2-dihaloethane in the liquid state

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