

Chapter IV

Investigations on dielectric studies in isobutyl
halides in the liquid state

1. Introduction :

From the studies of dielectric relaxation in 1,2-dihalo ethane¹, 1-chloro-2-bromopropane², 1,2-dihalopropane and 1,2-propanedithiols³ as described in the last three chapters it was found that the activation energy of dielectric relaxation was almost equal to the electrostatic self-energies of the polar gauche molecules in the liquid state. Further, this electrostatic stabilization energy in all the above liquids was approximately equal to the amount of the lowering of the energy difference between the trans and gauche isomers from the gaseous to the liquid state as was pointed out by Wada⁴. These facts indicate that the activation energy (ΔH_{τ}) due to intermolecular interactions in these liquids is mainly electrostatic in nature. In order to examine this view point further, the dielectric studies have been extended to the case of 1-halo-2-methyl propane (isobutyl halides) where the conformers have moderate dipole moments unlike the case of molecules mentioned above. The results of these investigations are discussed in this chapter.

2. Results :

The values of ϵ_0 , ϵ' , ϵ'' and n^2 at different temperatures for all the liquids are given in Table I. These data were fitted in Cole-Cole arc plots which are shown in Figs. (4.1, 4.2 and 4.3). The most probable relaxation time (τ_0) and the distribution parameter (α) determined from the arc plots are given in Table 2. The activation energies for dielectric relaxation

Table I

Values of static dielectric constant (ϵ_0), dielectric permittivity (ϵ') dielectric loss (ϵ'') and refractive index (n) of these three isobutyl halides at different temperatures

Substance	Temp °C	n^2	$\lambda = 1.62\text{cm}$		$\lambda = 3.17\text{cm}$		$\lambda = 3.49\text{cm}$		ϵ_0
			ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	
Isobutyl chloride	10	1.96	5.80	2.10	6.68	1.40	6.76	1.30	7.19
	30	1.94	5.65	1.85	6.35	1.16	6.45	1.05	6.71
	50	1.91	5.43	1.61	5.99	0.98	6.04	0.90	6.24
Isobutyl bromide	10	2.08	5.30	2.27	6.48	1.78	6.68	1.64	7.53
	30	2.05	5.17	2.09	6.22	1.53	6.42	1.39	6.97
	50	2.01	5.00	1.90	5.93	1.28	6.09	1.10	6.44
	70	1.99	4.96	1.70	5.70	1.10	5.76	0.99	6.04
Isobutyl iodide	10	2.24	4.26	1.80	5.35	1.66	5.52	1.59	6.65
	30	2.22	4.28	1.72	5.24	1.56	5.37	1.48	6.35
	50	2.18	4.30	1.68	5.15	1.38	5.23	1.27	6.02

relaxation ($\Delta H\tau$) and for viscous flow ($\Delta H\eta$) were obtained respectively from the straight line plots of $\log T\tau$ vs $1/T$ Figs. (4.4 and 4.5) $\log \eta$ vs $1/T$ The values of ($\Delta H\tau$) and ($\Delta H\eta$) are given in Table 2. The accuracies in the measurements of ϵ' and ϵ'' are 2% and 4% respectively.

COLE-COLE PLOTS AT DIFFERENT TEMPERATURE OF
ISOBUTYL CHLORIDE

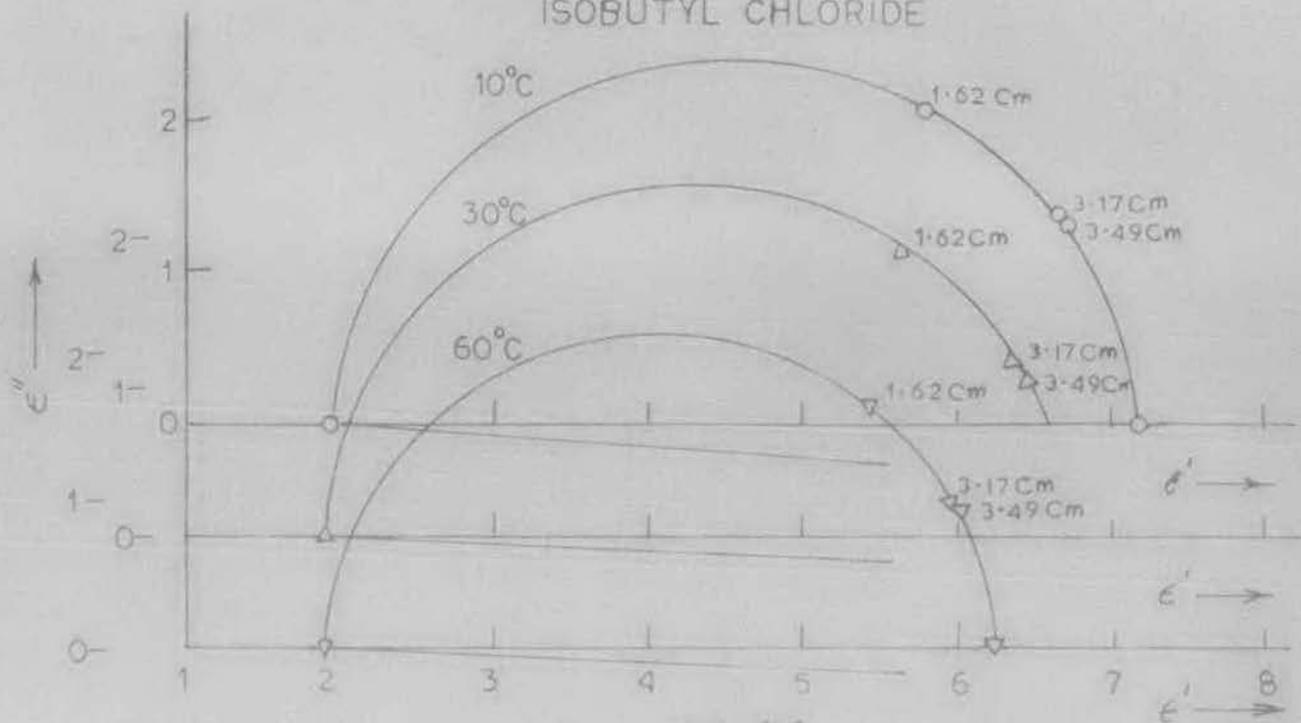


FIG. 4.1

ISOBUTYL BROMIDE

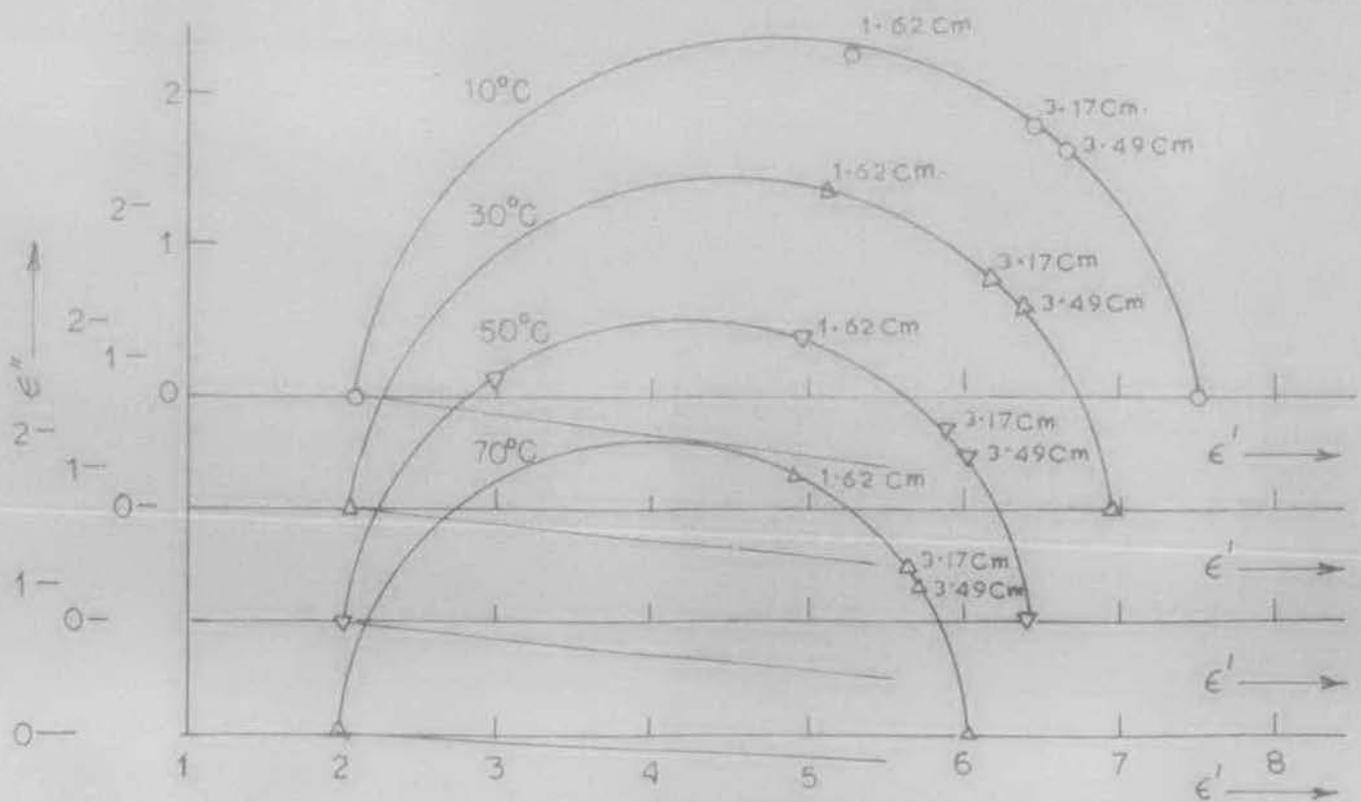


FIG. 4.2

COLE-COLE ARC PLOTS AT DIFFERENT TEMPERATURE
OF
ISOBUTYL IODIDE

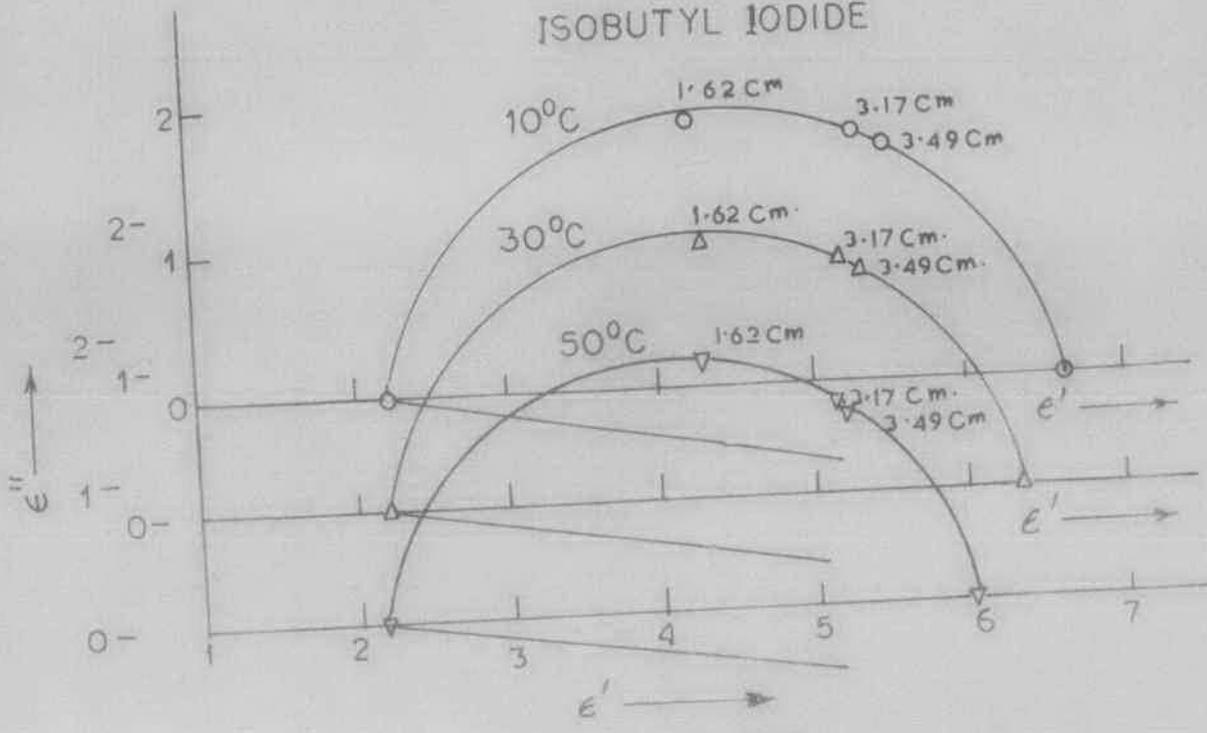
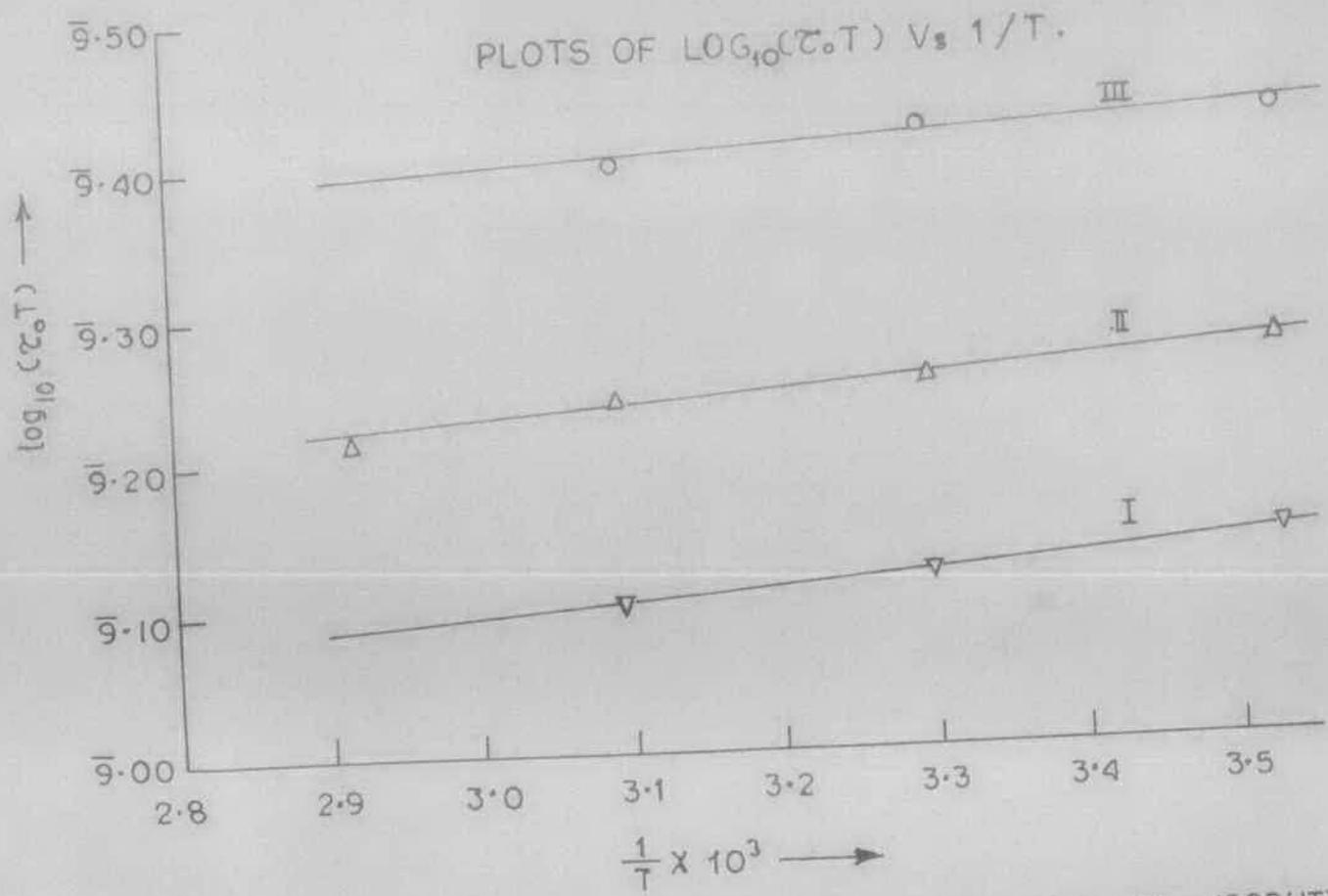


FIG. 4.3



I — ISOBUTYL CHLORIDE ; II — ISOBUTYL BROMIDE ; III — ISOBUTYL IODIDE

FIG. 4.4

Table 2

Values of distribution parameter (α), viscosity (η), relaxation time (τ_0), activation energy for dielectric relaxation (ΔH_τ) and that for viscous flow (ΔH_η) and mean electrostatic energy ($(E_g + E_t)/2$) in k.cal/mole

Substance	Temp °C	α	η cp	$\tau_0 \times 10^{12}$ sec	ΔH_τ k.cal/ mole	ΔH_η k.cal/ mole	Mean electro- static energy ($E_g + E_t$)/2 k.cal/mole
Isobutyl chloride	10	0.04	0.41	4.88			
	30	0.03	0.36	4.35	0.40	1.29	0.51
	50	0.01	0.32	3.92			

Isobutyl bromide	10	0.09	0.57	6.55			
	30	0.07	0.49	5.88			
	50	0.04	0.42	5.38	0.33	1.32	0.39
	70	0.01	0.38	4.74			

Isobutyl iodide	10	0.11	0.81	9.37			
	30	0.10	0.64	8.69	0.26	1.63	0.30
	50	0.90	0.55	7.77			

3. Discussion :

It can be seen from Table 2 that the most probable relaxation time (τ_0) of 6.55 p.sec at 10°C in isobutyl bromide is larger than 4.55 p.sec in isobutyl chloride but smaller than 9.37 p.sec in isobutyl iodide at the same temperature. This is consistent with the sizes of the molecules. It is also seen from the same

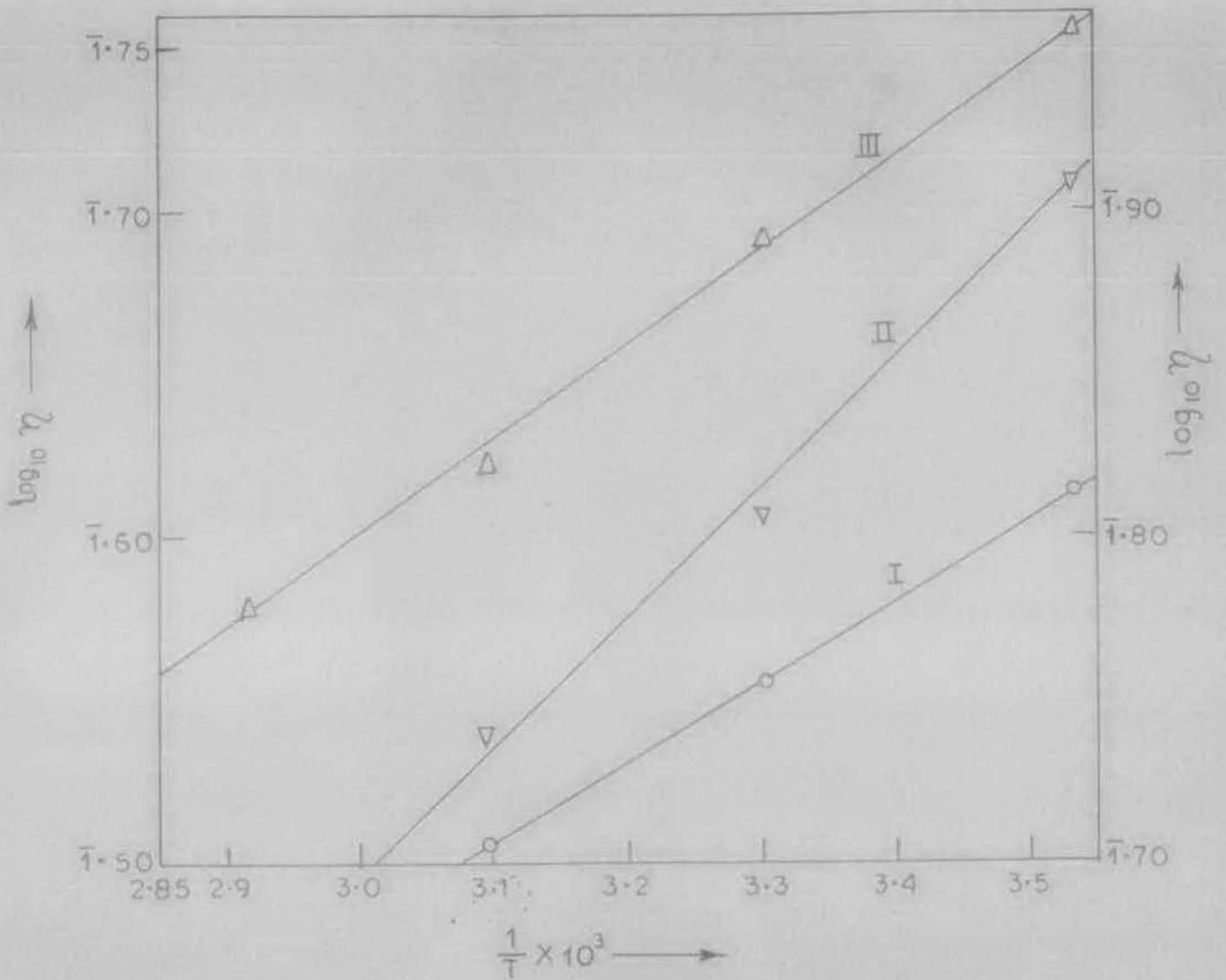
table that the relaxation time (τ) and the distribution parameter (α) in all the liquids decrease with increase of temperature as is generally observed in polar liquids.

The activation energy of dielectric relaxation (ΔH_{τ}) is as usual less than the corresponding values for viscous flow (ΔH_{η}) in all the liquids. However, while the (ΔH_{τ}) value decrease with increase in size of the molecules, the (ΔH_{η})-values increase in the same order.

3.1. Activation energy and electrostatic potential energy :

In the case of some 1,2-disubstituted ethanes^{1,2,3} the dipole activation energy (ΔH_{τ}) was almost equal to the respective values of electrostatic energy of the polar gauche molecules in the liquid state. This is because in all these molecules the dipole moment of trans isomer is negligible compared to that of the gauche isomer. In the present case, however, in all the isobutyl halides both the trans and gauche isomers have moderately large dipole moment and both of them will contribute to the relaxation process. But as the trans and gauche isomers in each compound are of almost similar in size, the τ -values would be almost the same and so it was not possible to analyse the dielectric data in terms of two relaxation processes. For this reason, the activation energy (ΔH_{τ}) for the isomers could not be obtained separately. So the activation energy (ΔH_{τ}) obtained experimentally has been taken to be the average of the activation energies (ΔH_{τ}) of the trans and gauche isomers.

PLOT OF $\text{LOG}_{10} \eta$ Vs $\frac{1}{T}$



- I- ISOBUTYL CHLORIDE. (ordinate left.)
- II- ISOBUTYL IODIDE (" right)
- III- ISOBUTYL BROMIDE (" left)

FIG. 4-5

Table 3

Values of density (d), mean moment (m), dipole moment of trans (μ_t) and gauche (μ_g) isomers and electrostatic energy

Substance	Temp °C	Density d gm/cc	Mean moment m D	Dipole moment		Electrostatic energy	
				trans isomer μ_t D	gauche isomer μ_g D	trans isomer E_t k.cal/mole	gauche isomer E_g k.cal/mole
Isobutyl chloride	10	0.881	1.92				
	30	0.360	1.93	1.60	2.19	0.68	0.36
	50	0.316	1.94				
Isobutyl bromide	10	1.296	1.91				
	30	1.259	1.93	1.50	2.01	0.51	0.28
	50	1.230	1.94				
	70	1.210	1.95				
Isobutyl iodide	10	1.609	1.75				
	30	1.580	1.78	1.38	1.90	0.40	0.20
	50	1.546	1.81				

To correlate this average activation energy with the corresponding values of the electrostatic energy of the two isomers the dipole moments of the trans and gauche forms for all the molecules were calculated from their geometrical structures using known bond moments ($\mu_{C-Cl} \approx 1.85$ D; $\mu_{C-Br} \approx 1.7$ D⁵ ;

$\mu_{CH_3} \approx 0.4 \text{ D}^6$. The value of μ_{C-I} was assumed to be 1.6 D a little smaller than that of μ_{C-Br}) and bond angles (the carbon valence angle $\approx 110^\circ$ and the azimuthal angle of rotation $\approx 60^\circ$). The calculated values of μ_g and μ_t are given in Table 3. The values of a^3 ($\approx 40^\circ \text{ \AA}^3 - 50^\circ \text{ \AA}^3$) were estimated from a comparison with the molecules of 1,2-dihaloethanes⁷. The electrostatic energies of the trans and gauche isomers of all the compounds calculated from the relation⁷

$$E = \frac{\epsilon_0 - 1}{2\epsilon_0 + 1} \frac{\mu^2}{a^3}$$

are given in Table 3 and their mean values are in Table 2. It is seen from the Table 2 that the activation energy in each case is almost equal to the mean value of the electrostatic energies of the gauche and trans isomers of the respective compounds. This supports the conclusion drawn earlier^{1,2,3}.

3.2. Energy difference between the isomers in the liquid state :

The energy difference between the isomers in all the liquids were obtained by the method given by Mizushima⁷ with the values of mean moment (m) of the molecules in the liquid state at different temperatures and the values of μ_g and μ_t calculated as above. The mean moments were calculated by using Onsager's equation⁵ from the values of ϵ_0 , d and n . The energy differences between the two isomers in all the liquids, thus obtained, are found to agree fairly well with those obtained from spectroscopic studies⁸ given in Table 4.

Table 4

Calculated values of the liquid state energy difference (ΔE_L) between the rotamers and the spectroscopic values of energy difference between the rotamers in the liquid (ΔE_L) and vapour (ΔE_V) state obtained from the literature for three isobutyl halides

Compound	ΔE_L (calculated) k.cal/mole	Spectroscopic values of energy difference in k.cal/mole	
		Liquid phase ΔE_L	Vapour phase ΔE_V
Isobutyl chloride	0.39	0.37 \pm 0.15	0.23 \pm 0.04
Isobutyl bromide	0.20	0.26 \pm 0.12	0.3 \pm 0.03
Isobutyl iodide	0.24		

It may be noted from Table 3 that the electrostatic energies of the trans isomers in all the molecules are larger than that of the gauche isomer. Also in the gaseous state the trans isomer is of lower energy in all the compounds. Hence if the electrostatic energy in the liquids was mainly responsible for the intermolecular potential energy, the energy difference between the two isomers in the liquid state would be greater than that of the gaseous state. This is found to be true in the case of isobutyl chloride given in Table 4.

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