BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1354—1356 (1973)

Dielectric Studies on Isobutyl Halides in the Liquid State

Arati DAS, Alpana GHATAK, and Abul HASAN
Optics Department, Indian Association for the Cultivation of Science, Calcutta-32, India

(Received July 25, 1972)

The activation energies of dielectric relaxation ΔH_τ in three isobutyl halides in the liquid state are found to be almost equal to the mean value of the electrostatic self energies of the *trans* and *gauche* isomers in the corresponding compounds. The energy difference between the two isomers in the liquid state obtained from the dipole moment measurements agree well with those obtained by the spectroscopic method.

From studies of dielectric relaxation of 1,2-dihaloethanes,[1] 1-chloro-2-bromoethane,[2] 1,2-ethane- and 1,2-propane dithiols and 1,2-dichloropropane,[3] it was observed that the activation energy of dielectric relaxation ΔH_τ was almost equal to the electrostatic self energies of polar *gauche* molecules in the liquid state. The electrostatic stabilization energy in all the above liquids was approximately equal to the amount of lowering of the energy difference between the *trans* and *gauche* isomers from the gaseous to the liquid state as pointed out by Wada.[4] 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 viewpoint further, the dielectric studies have been extended to the case of three isobutyl halides where the conformers have moderate dipole moments unlike the case of the molecules mentioned above. The results of these investigations are discussed in this paper.

Experimental

Pure samples of 1-chloro-2-methylpropane, 1-bromo-2-methylpropane and 1-iodo-2-methylpropane (Schuchardt, Germany) were distilled under reduced pressure before use. The dielectric permittivities ε' and dielectric losses ε'' of the liquids at different temperatures were measured by Surber's method at 1.62, 3.17 and 3.49 cm microwave regions. The static dielectric constant ε_0 was measured at 1 MHz and the refractive index n was obtained with an Abbe refractometer. The density d was measured with a picnometer and the viscosities η were determined with an Ostwald viscometer. The temperatures in all the experiments were controlled within ±1°C by a thermostat.

Results

The values of ε_0, ε', ε'', and n^2 at different temperatures for all the liquids are given in Table 1. These data were fitted in Cole-Cole arc plots, some of which

TABLE 2. VALUES OF α, τ, η, ΔH_τ, ΔH_η, AND MEAN ELECTROSTATIC ENERGY $(E_g+E_t)/2$ IN kcal/mol

Temp °C	α	τ psec	η c. poise	Mean E $(E_g/+E_t)/2$	ΔH_τ kcal/mol	ΔH_η kcal/mol
	Isobutyl chloride					
10	0.04	4.88	0.41	0.51	0.40	1.29
30	0.03	4.35	0.36			
50	0.01	3.92	0.32			
	Isobutyl bromide					
10	0.09	6.55	0.57	0.39	0.33	1.32
30	0.07	5.88	0.49			
50	0.04	5.38	0.42			
70	0.01	4.74	0.38			
	Isobutyl iodide					
10	0.11	9.37	0.81	0.3	0.26	1.63
30	0.10	8.69	0.64			
50	0.09	7.77	0.55			

TABLE 1. VALUES OF n^2, ε', ε'', AND ε_0

Temp °C	n_2	λ=1.62 cm		λ=3.17 cm		λ=3.49 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	1.34	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

---

1) A. Hasan, A. Das, and A. Ghatak, This Bulletin, **44**, 322 (1971).

2) A. Ghatak, A. Das, and A. Hasan, *J. Chem. Phys.*, (in press).

3) A. Hasan, A. Das, and A. Ghatak, *ibid.*, (in press).

4) A. Wada, *ibid.*, **22**, 198 (1954).

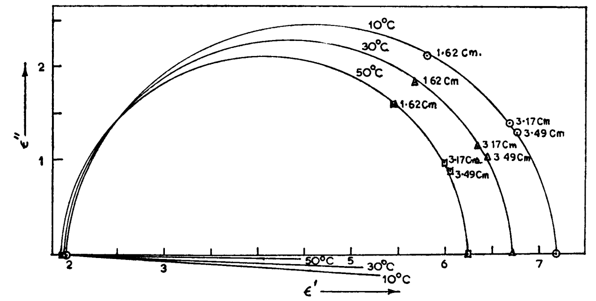

Fig. 1(a). Cole-Cole arc plots of isobutyl chloride at different temperature.

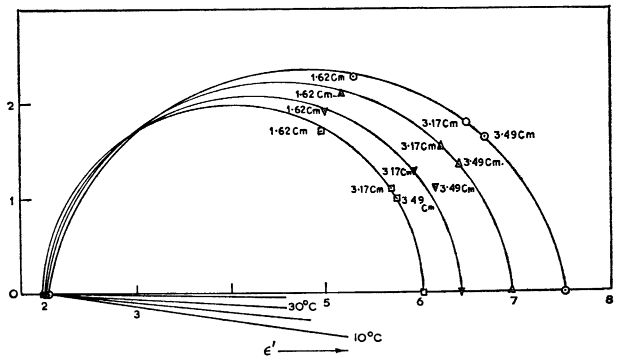

Fig. 1(b). Cole-Cole are plots of isobutyl bromide at different temperature.

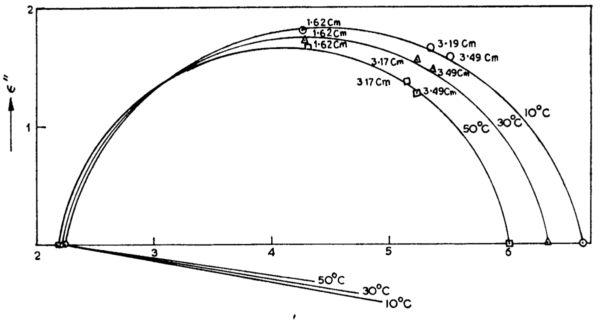

Fig. 1(c). Cole-Cole arc plots of isobutyl iodide at different temperature.

are shown in figures 1 (a, b, c). The most probable relaxation time τ and the distribution parameter α determined from the arc plots are given in Table 2. The activation energies for dielectric relaxation ΔH_τ and for viscous flow ΔH_η were obtained respectively from the straight line plots of log $T\,\tau$ *vs.* $1/T$ and log η *vs.* $1/T$ (Fig. 2). The values of ΔH_τ and ΔH_η are given in Table 2. The accuracies in the measurements of ε' and ε'' are 2 and 4% respectively.

Discussion

It can be seen from Table 2 that the most probable relaxation time τ of 6.55 psec at 10°C in isobutyl bromide is larger than 4.55 psec in isobutyl chloride but smaller than 9.37 psec in isobutyl iodide at the same temperature. This is consistent with the sizes of the molecules. The relaxation time τ and the distribution parameter α in all the liquids are seen to decrease with increase of temperature as is generally observed in polar liquids.

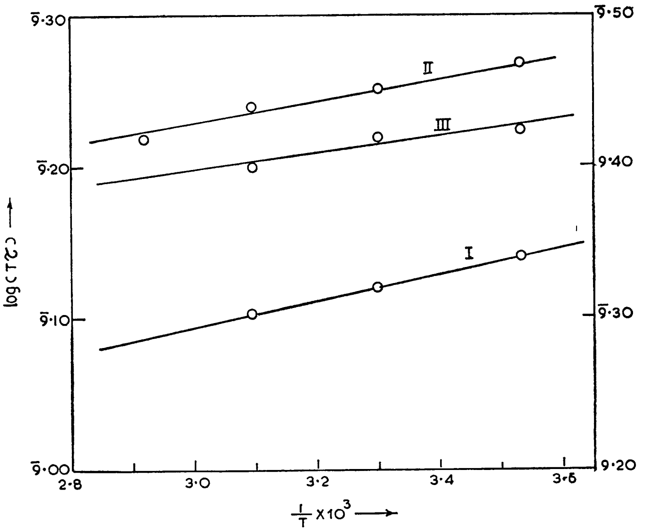

Fig. 2. Plots of log $T\tau$ *vs.* $1/T$.
Curve I: Isobutyl chloride (ordinate left),
Curve II: Isobutyl bromide (ordinate left),
Curve III: Isobutyl iodide (ordinate right).

The activation energy of dielectric relaxation ΔH_τ is as usual less than the corresponding value for viscous flow ΔH_η in all the liquids. However, while the ΔH_τ-values decrease with increase in size of the molecules, the ΔH_η-values increase in the same order.

Activation Energy and Electrostatic Energy. In the case of some 1,2-disubstituted ethanes[1-3] the dipole activation energy 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 *trans* and *gauche* isomers have moderately large dipole moments, both contributing to the relaxation process, but as they are almost similar in size the τ-values would be almost the same. Thus it was not possible to analyse the dielectric data in terms of two relaxation processes one due to each, and the activation energy ΔH_τ for the isomers could not be obtained separately. The activation energy obtained experimentally has been taken as the average ΔH_τ of the *trans* and *gauche* isomers.

To correlate the 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 and bond angle values: $\mu_{\mathrm{C-Cl}}\approx1.85$ D,[5] $\mu_{\mathrm{C-Br}}\approx1.7$ D,[5] $\mu_{\mathrm{CH_3}}\approx0.4$ D[6] the carbon valence angle $\approx110°$ and the azimuthal angle of rotation $\approx60°$. The value of $\mu_{\mathrm{C-I}}$ was assumed to be ≈1.6 D, a little smaller than that of $\mu_{\mathrm{C-Br}}$. The calculated values of μ_g and μ_t are given in Table 3. The values of a^3 (≈40 Å^3—

---

[5] J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publication (1955), p. 292.

[6] C. P. Smyth, "Dielectric Behaviour and Structure," McGraw Hill Book Company, Inc., (1955), P. 368.

TABLE 3. VALUES OF d, m, μ_t, μ_g, AND ELECTROSTATIC ENERGY E_g AND E_t IN kcal/mol

Temp °C	Density d	Mean moment (m) in D	Dipole moment		Electrostatic energy	
			trans μ_t	*gauche* μ_g	E_{trans}	E_{gauche}
	Isobutyl chloride					
10	0.881	1.92	1.60	2.19	0.68	0.36
30	0.360	1.93				
50	0.316	1.94				
	Isobutyl bromide					
10	1.296	1.91	1.50	2.01	0.51	0.28
30	1.259	1.93				
50	1.230	1.94				
70	1.210	1.95				
	Isobutyl iodide					
10	1.609	1.75	1.38	1.90	0.40	0.20
30	1.580	1.78				
50	1.546	1.81				

50 Å^3) were estimated from a comparison with the molecules of 1,2-dihaloethanes.7) The electrostatic energies of the *trans* and *gauche* isomers of all the compounds calculated from the relation7) $E=(\varepsilon-1)/(2\varepsilon+1)\cdot\mu^2/a^3$ are given in Table 3 and their mean values in Table 2. We see 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.1–3)

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 the mean moments 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 by spectroscopic studies8) (Table 4).

TABLE 4. ENERGY DIFFERENCE ΔE IN kcal/mol

Compound	Liquid (Present work)	Spectroscopic method8)	
		Liquid	Vapour
Isobutyl chloride	0.39	0.37±0.15	0.23±0.09
Isobutyl bromide	0.20	0.26±0.12	0.3 ±0.03
Isobutyl iodide	0.24	—	—

It may be noted from Table 3 that the electrostatic energies of the *trans* isomer in all the molecules are larger than that of the *gauche* isomer. In the gaseous state also 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 (Table 4).

The authors are grateful to Dr. S. B. Roy for his guidance and to Professor G. S. Kastha for his continued interest in the work.

---

7) S. Mizushima, "Structure of Molecule and Internal Rotation," Academic Press Inc., New York (1955), p. 42.

8) E. Wye Jones and W. J. Orville Thomas, *Trans. Faraday Soc.*, **64**, 2911 (1968).