Dielectric Relaxation Mechanism in Some Substituted Phenones

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Dielectric constants and losses at microwave frequency as well as static dielectric constants and refractive indices have been measured for *o*-methylacetophenone, *m*-methylacetophenone, *o*-hydroxybutyrophenone, 2′,4′-dihydroxyacetophenone and 2′,4′-dihydroxypropiophenone in dilute solutions of 1,4-dioxane. These values are used to calculate the dielectric relaxation times, distribution parameters, dipole moments and activation energies of the molecules. The results have been discussed in terms of the molecular motion of the system in the medium. Comparatively higher relaxation times and their variations irrespective of the molecular size, have been attributed to the intermolecular hydrogen bonding between the solvent and solute molecules.

Fong and Smyth[1] investigated the possibility of rotation of the polar acetyl and hydroxyl groups in molecules and the possible effects of the steric hindrance and resonance energy by determining the dielectric relaxation time of a number of organic molecules. Antony and Smyth[2] determined the dielectric relaxation and intramolecular hydrogen bonding in hydroxy- and methoxyacetophenones. In order to investigate the effect of increasing chain length in the case of hydrogen bonded molecules, Makhija *et al.*[3] have studied the dielectric relaxation of 2′-hydroxy-5′-methyl derivatives of phenones and found that whereas the relaxation time and the distribution parameter increase with increasing chain length, the dipole moment does not change significantly. With a view to study the intramolecular rotation of the polar groups and the intramolecular interaction consisting of hydrogen bonding and steric hindrance, the authors have investigated five phenone molecules of different substitutions and chain lengths.

The most probable relaxation time τ_0 and the distribution parameter α have been determined from the measurements of ε' and ε'' at a single frequency using Higasi's[4] equations. The dipole moment μ and the relaxation time τ have been determined for the same compounds by the single frequency method of Gopala Krishna[5] for dilute solutions. A comparison of the τ values obtained by the above two methods has been made.

The values of the free energy of activation for dielectric relaxation and for the viscous flow have been calculated using Eyring's[6] equations by utilising the values of τ obtained by Gopala Krishna's method at varying temperatures.

Experimental

A dipolemeter based on the principle of heterodyne beat method was used for the measurement of the static permittivity at 300 kHz. Refractive indices of all the solutions were measured by Abbe's refractometer, which in turn determined the optical permittivity ($\varepsilon_\infty = n_D^2$). The dielectric constant ε' and loss ε'' were measured at 3 cm wavelength, at four different temperatures by using the standing wave technique of Roberts and von Hippel[7] and its subsequent simplification by Dakin and Works[8]. The estimated accuracies in the measurements of ε' and ε'' are $\pm 1\%$ and $\pm 5\%$ respectively.

All the substances used were of pure quality obtained from Messers British Drug House. The purest 1,4-dioxane was distilled before use.

Results and Discussion

The values of the relaxation time and the distribution parameter, calculated by Higasi's single frequency method are given in Table 1. The τ value for *o*-methylacetophenone is found to be smaller than that of *m*-methylacetophenone, although the two are of the same molecular size. This could, perhaps, be due to the compact shape of the former molecule in contrast with the greater length of the latter molecule.

The relaxation time for *o*-methylacetophenone is less than that obtained by Antony and Smyth[2] for *o*-hydroxyacetophenone ($\tau = 31.0 \times 10^{-12}$ s) in dioxane, the differences in the molecular sizes of the two molecules being negligibly small. This may be due to the fact that the acetyl group in *o*-methylacetophenone has greater freedom of rotation than the acetyl group in *o*-hydroxyacetophenone which behaves almost as a rigid molecule because of the intramolecular hydrogen bonding between the –OH and acetyl groups.[2] The large value of distribution parameter for *o*-methylacetophenone also indicates the presence of an internal mode of relaxation, apart from the overall rotation of the molecule.

The relaxation time value for 2′,4′-dihydroxypropiophenone is greater than that for 2′,4′-dihydroxyacetophenone. This is expected because of the greater chain length of the former molecule. However, the τ value for *o*-hydroxybutyrophenone is found to be less than that of *o*-hydroxyacetophenone.[2] The nearly zero values of distribution parameters for 2′,4′-dihydroxyacetophenone and *o*-hydroxybutyrophenone indicate that the molecules relax largely due to the overall molecular rotations.

Adgonker and Kher[9] have determined the value of τ to be 38.73×10^{-12} s for 2′-hydroxy-4′-methylacetophenone in solutions of carbon tetrachloride. This value is considerably smaller than that of 2′,4′-dihydroxyacetophenone in dioxane. This may be partly due to the higher viscosity of dioxane than that of carbon tetrachloride and also because of the hydrogen bonding due to the solvent solute interaction at *para* position of the latter molecule. On comparing the τ value for 2′,4′-dihydroxypropiophenone with that obtained by Dhar *et al.*[10] of *p*-hydroxypropiophenone ($\tau = 25.4 \times 10^{-12}$ s in dioxane), it is found that the former value is more than 2½ times greater than the latter value.

TABLE 1. SLOPES OF PLOTS OF DIELECTRIC PERMITTIVITY AGAINST CONCENTRATION, VALUES OF RELAXATION TIME AND DISTRIBUTION PARAMETER (22 °C)

Compound	a_0	a'	a''	a_∞	τ_0	α
o-Methylacetophenone	4.81	2.12	1.49	0.32	23.1	0.240
m-Methylacetophenone	6.60	1.81	2.62	0.26	29.1	0.025
o-Hydroxybutyrophenone	6.82	2.05	2.88	0.27	26.0	0.002
2′,4′-Dihydroxyacetophenone	8.01	1.30	2.31	0.44	46.8	0.018
2′,4′-Dihydroxypropiophenone	8.73	1.29	1.90	0.36	66.4	0.139

TABLE 2. RELAXATION TIMES, DIPOLE MOMENTS AND THERMODYNAMICAL PARAMETERS ($\lambda = 3$ cm)

Compound	T K	$\tau \times 10^{12}$ s	μ D	ΔF_ε kcal/mol	ΔH_ε kcal/mol	ΔS_ε cal/mol	ΔF_η kcal/mol	ΔH_η kcal/mol	ΔS_η cal/mol
o-Methylacetophenone	287	14.6	—	2.55	1.10	−5.07	4.61	3.27	−4.67
	295	13.5	2.03	2.59	1.10	−5.07	4.66	3.27	−4.71
	303	12.2	—	2.62	1.10	−5.01	4.70	3.27	−4.71
	311	11.7	—	2.67	1.10	−5.07	4.75	3.27	−4.75
m-Methylacetophenone	287	19.9	—	2.73	1.24	−5.19	4.61	3.27	−4.67
	295	18.6	2.35	2.78	1.24	−5.23	4.66	3.27	−4.71
	303	17.0	—	2.82	1.24	−5.22	4.70	3.27	−4.71
	311	15.8	—	2.86	1.24	−5.22	4.75	3.27	−4.75
o-Hydroxybutyrophenone	295	16.4	2.18	2.71	0.73	−6.70	4.66	3.27	−4.71
	303	15.9	—	2.78	0.73	−6.75	4.70	3.27	−4.71
	311	15.1	—	2.84	0.73	−6.76	4.75	3.27	−4.75
2′,4′-Dihydroxyacetophenone	287	19.0	—	2.70	1.19	−5.27	4.61	3.27	−4.67
	295	18.1	2.19	2.77	1.19	−5.33	4.66	3.27	−4.71
	303	16.6	—	2.80	1.19	−5.32	4.70	3.27	−4.71
	311	15.4	—	2.85	1.19	−5.33	4.75	3.27	−4.75
2′,4′-Dihydroxypropiophenone	287	21.6	—	2.78	0.87	−6.64	4.61	3.27	−4.67
	295	19.1	2.68	2.80	0.87	−6.52	4.66	3.27	−4.71
	303	17.8	—	2.85	0.87	−6.52	4.70	3.27	−4.71
	311	16.7	—	2.90	0.87	−6.52	4.75	3.27	−4.75

Apart from the greater size of the molecule, the unusually high relaxation time of 2′,4′-dihydroxypropiophenone can be explained as due to the hydrogen bonding between the solvent and the solute molecules, at various positions of the benzene ring.

It is significant from Table 2 that the values of relaxation times obtained by Gopala Krishna's method are invariably lower than those obtained by Higasi's method (Table 1). This may be due to the fact that unlike Higasi's method, Gopala Krishna's method is based on Debye's model of single relaxation process in which the distribution parameter is zero. Similar results were reported by Krishnaji for esters in solutions.[11]

It is evident from Table 2 that while the relaxation time decreases with increasing temperature, the free energy of activation increases. This is in line with the observation of other workers.[12] The free energy of activation ΔF_η is greater than ΔF_ε, which is quite natural because the viscosity process consists of rotational as well as translational motion of the molecule, while the dielectric relaxation is only due to rotation.

For all the molecules, the free energy of activation is greater than the molar enthalpy of activation, with the result that the entropy of activation is negative. This shows that the activated state is more ordered than the normal state.

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