

Summary

In Chapter I, the dielectric relaxation times for 1,2-dichloro- and 1,2-dibromoethane in the liquid state have been found to be respectively 6.06 and 8.8 p.sec which are consistent with the sizes of the molecules.

The heat of activation for dielectric relaxation have been found to be 1.30 and 1.09 k.cal/mole respectively in 1,2-dichloro- and 1,2-dibromoethane. These values of activation energy agree fairly well with the corresponding values of electrostatic potential energy of the polar gauche isomers in the liquid state reported by Wada. Mizushima and Wada have shown that the lowering of the energy difference between the trans and gauche isomers of 1,2-dihaloethanes from gaseous to liquid state was almost equal to the electrostatic potential energy of the gauche isomers in the respective cases. So the activation energy of dielectric relaxation in the 1,2-dihaloethanes in the liquid state agree fairly well with the amount of lowering of energy difference between the trans and gauche isomers from the gaseous to liquid state.

In Chapter II, the relaxation time of 1-chloro-2-bromoethane in the liquid state at any temperature has been found to be intermediate between the relaxation times of 1,2-dichloro- and 1,2-dibromoethane in the liquid state at the corresponding temperature. These are consistent with the sizes of the molecules.

The heat of activation for dielectric relaxation in this case is found to be about 1 k.cal/mole which is in good agreement with the calculated values of the difference of electrostatic energies

of 0.9 k.cal/mole between the gauche and trans isomers in the liquid state. This heat of activation energy of 1 k.cal/mole is almost equal to the amount of lowering of the energy difference of 940 cal/mole between the trans and gauche isomers of the 1-chloro-2-bromoethane molecule from vapour to the liquid state reported in literature from spectroscopic studies.

The energy difference of 550 cal/mole between the two rotamers of this molecule in the liquid state calculated from the mean value of dipole moment at different temperatures agree fairly well with the value of 490 cal/mole measured from spectroscopic studies.

In Chapter III the values of dielectric relaxation time of 1,2-dichloropropane and 1,2-dibromopropane in the liquid state at 30°C have been found to be 8.8 p.sec and 10.6 p.sec which are greater than the values of 6.06 and 8 p.sec in 1,2-dichloro- and 1,2-dibromo ethane respectively. These are consistent with the sizes of these molecules.

The heat of activation for dielectric relaxation in 1,2-dichloro and 1,2-dibromopropane in the liquid state have been calculated to be 1.4 and 0.98 k.cal/mole respectively. These activation energy values agree well with the corresponding values of electrostatic potential energy of 1.2 and 1 k.cal/mole.

The heat of activation in the two 1,2-halopropanes also compare favourably well with the lowering of the energy difference between trans and gauche rotamers from the gaseous to the liquid state of the molecules.

The energy difference between the trans and gauche isomers in these two liquids calculated from dipole moment studies at different temperatures agree well with those obtained from spectroscopic methods.

In the case of 1,2-propanedithiol the heat of activation for dielectric relaxation also agree with the electrostatic potential energy in the liquid state as in 1,2-dihalopropanes. But in contrast to all other 1,2-disubstituted ethanes in the case of 1,2-propane dithiol the distribution parameter is found to increase with the increase of temperature. This has been explained as due to the increase in the proportion of the higher energy form of the gauche II isomer with the increase of temperature.

In Chapter IV, the relaxation time of the three isobutyl halides have been determined. These are found to be consistent with their sizes as also with the size of 1,2-dihalopropanes.

The heat of activation for dielectric relaxation in these molecules in the liquid state are found to be almost equal to the mean value of the electrostatic potential energies of the polar trans and gauche isomers in the respective compounds.

The energy difference between the two isomers in the liquid state, obtained from dipole moment measurements, agree well with those reported from spectroscopic methods reported in literatures.

In Chapter V, the relaxation time of 1,2-dimethoxy and 1,2-diethoxy ethane in the liquid state have been found to be about

3.5 p.sec and 5.5 p.sec respectively. These relaxation times are comparable to 3 p.sec and 4 p.sec of the relaxation time of the methoxy and ethoxy group rotation respectively in the cases of anisole and phenetole in the liquid state. It is concluded that in the two dialkoxyethanes the relaxation is mainly due to group rotations.