Molecular and Intramolecular Relaxation in Several Biphenyls

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(Received February 7, 1966)

The relaxation times of some biphenyls have been determined in the 3 cm. microwave region at a temperature of 20°C, using benzene as the solvent. It has been concluded from the smaller values of the relaxation time that the molecules are relaxed by both molecular and intramolecular rotations.

DiCarlo and Smyth[1] have determined the relaxation times of diphenyl sulphide, diphenyl methane and triphenyl amine. Kalman and Smyth[2] have investigated 4-bromobiphenyl in making a study of its dielectric dispersion. However, apparently no attempt has yet been made to study the mechanism of intramolecular rotation in the many biphenyls with different dipole-bearing groups. The aim of the present investigation is to get an idea about the nature of the molecular unit responsible for group rotation in *o*-aminobiphenyl, *p*-aminobiphenyl and 3, 5-dinitro-2-hydroxybiphenyl.

The free energies of the activation for dipole orientation and viscous flow have been calculated at the same temperature, using Eyring's[3] relations and estimated values of the constants A and B.

The relaxation times are determined by means of the fixed frequency method of Gopala Krishna.[4] The standing-wave technique of Von Hippel and Roberts[5] has been used for the measurements of the dielectric constant, ε', and the loss factor, ε''.

All the substances used were of pure quality L. R. grade and were obtained from the British Drug House. The purest-quality benzene obtained from the British Drug House was distilled before use.

The observed values of the relaxation time, along with the values of the activation energy, are given in Table I.

It may be seen from Table I that the relaxation time of *o*-aminobiphenyl is greater than that of *p*-aminobiphenyl, although the size of the two molecules is the same. This difference in the relaxation time can be explained by considering intramolecular group rotation. The polar $-NH_2$ group, which is capable of rotation round its bond with the ring, experiences a greater steric hindrance to rotation at the ortho position than at the para position. Further, however, while the molar volumes of the two molecules may be approximately same, the volumes swept out for dipole orientation by the two molecules must be different.

The relaxation time of 3, 5-dinitro-2-hydroxybiphenyl is found to be greater than those of *o*-amino- and *p*-aminobiphenyls. This may be due to the fact that there is a greater steric hindrance to the rotation of the –OH group at the position 2 due to the presence of a $-NO_2$ group at the position 3. Further, the observed larger value of relaxation time is in accordance with the bigger size of the molecule due to the presence of two nitro groups.

It may, therefore, be concluded from the rotations of the $-NH_2$ and –OH groups that the molecules are relaxed predominantly by the process of intramolecular rotations, resulting in a decrease in the observed relaxation time.

The value of the free energy of activation for *o*-aminobiphenyl has been found to be greater than that of *p*-aminobiphenyl, suggesting that the inner friction experienced by the former molecule is greater than that of the latter.

The free energies of activation for a viscous flow (H_η) are always found to be greater than those for the dielectric relaxation (H_τ). This is in conformity with the finding of Franklin and his coworkers[6] that H_τ and H_η are nearly equal only in the case of low viscosity solvents. A similar result was also obtained by Ahmad and Sharma[7] in the case of solutions of nitrotoluenes and *o*-chlorotoluene in cyclohexane.

TABLE I. VALUES OF THE RELAXATION TIME (τ) AND THE FREE ENERGIES OF ACTIVATION FOR DIPOLE ORIENTATION AND VISCOUS FLOW

Compound	$\tau \times 10^{12}$ sec.	H_τ kcal./mol.	H_η kcal./mol.	H_η/H_τ
(1) *o*-Amino-biphenyl	7.47	2.23	2.90	1.30
(2) *p*-Amino-biphenyl	6.64	2.16	2.90	1.34
(3) 3, 5-dinitro-2-hydroxy-biphenyl	9.96	2.39	2.90	1.21

1) E. N. DiCarlo and C. P. Smyth, *J. Am. Chem. Soc.*, **84**, 3638 (1962).
2) O. F. Kalman and C. P. Smyth, ibid., **82**, 783 (1960).
3) H. Eyring, S. Glasstone and K. J. Laider, "The Theory of the Rate Process," McGraw Hill Co, New York (1941), p. 548.
4) K. V. Gopala Krishna, *Trans. Faraday Soc.*, **53**, 767 (1957).
5) S. Roberts and A. Von Hippel, *J. Appl. Phys.*, **17**, 610 (1946).
6) A. D. Franklin, W. H. Heston, E. J. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3447 (1950).
7) S. I. Ahmad and M. N. Sharma, *Indian, J. Phys.* **39**, 149 (1965).