

One of us (TKD) wishes to acknowledge financial support from the Council of Scientific and Industrial Research, India. He further wishes to thank Prof. B. Bhattacharya for making it possible for him to work as a pool officer at Jadavpur University.

Physics Department,
Jadavpur University,
Calcutta 700 032, India,
April 23, 1977.

TAPAN K. DAS*,
UTPAL K. DE.

* Present address: Physics Department, The University of Burdwan, Burdwan, West Bengal, India.

1. Volterra, V., *J. Conseil Permanent Intern. Exploration Mer III*, 1928, 1; translated in *Animal Ecology* by R. N. Chapman (McGraw-Hill, New York), 1931.
2. Geel, N. S., Maitra, S. C. and Montroll, E. W., *Rev. Mod. Phys.*, 1971, 43, 231.
3. Rosen, R., *Dynamical System Theory in Biology* (Wiley-Interscience, New York), 1970.

RELAXATION TIMES AND ACTIVATION ENERGIES OF SOME SUBSTITUTED PHENOLS

RELAXATION times of four polar substituted phenols namely (A) 3, 5 dimethyl phenol, (B) 2, 3, 5 trimethyl phenol, (C) 2, 4, 6 trimethyl phenol and (D) 2, 4, 6 trichlorophenol have been measured in the dilute solution of benzene at 20, 25, 30 and 35°C at S-band. The free energies of activation for the process of dipole orientation and viscons flow have been calculated using Eyring's theory¹ of

rate process. The results have been analysed in the light of molecular motions of the system and it is concluded that dipole orientation is contributed by both molecular as well as intramolecular rotation.

Dielectric studies of polar solutes in the non-polar solvent throw considerable light on various molecular and intramolecular forces. Magee and Walker^{2,3} have investigated the relaxation times of some substituted phenols in a number of non-polar solvents. LeFerve⁴ and Hiremath⁵ have investigated the dielectric behaviour of phenols in the dilute solution of non-polar solvents and concluded that hydroxyl relaxation plays dominant role in the relaxation process of the phenols.

Due to their wide industrial and pharmaceutical applications the present study forms a significant contribution to the existing knowledge of the dielectric behaviour of some di and tri substituted phenols.

The dielectric constant (ϵ') and dielectric loss (ϵ'') have been measured on a S-n and microwave bench⁶ by a technique, due to Roberts and Von Hippel⁷, later modified by Dekin and Works⁸. The relaxation time (τ) has been evaluated using Gopalakrishna fixed frequency method⁹. The compounds obtained from B.D.H., England, were of pure quality. The solvent (A.R.) was distilled before use.

The values of relaxation times and thermodynamic parameters are reported in Table I. It

TABLE I
Relaxation times and activation energies
($\lambda = 9.80$ cm)

| Molecule | Temp. °K | $\tau \times 10^{12}$ sec | ΔF_e Kcal/ mol | ΔH_e Kcal/ mol | ΔS_e Cal/ mol | ΔF_η Kcal/ mol | ΔH_η Kcal/ mol | ΔS_η Cal/ mol |
|-------------------------|-------------|------------------------------|------------------------------|------------------------------|-----------------------------|---------------------------------|---------------------------------|--------------------------------|
| 3, 5 Dimethyl phenol | 293 | 21.2 | 2.83 | 1.90 | -3.17 | 2.90 | 2.52 | -1.29 |
| | 298 | 20.1 | 2.86 | 1.90 | -3.22 | 2.91 | 2.52 | -1.30 |
| | 308 | 17.4 | 2.89 | 1.90 | -3.21 | 2.93 | 2.52 | -1.33 |
| 2, 4, 6 trichlorophenol | 298 | 21.1 | 2.88 | 1.41 | -4.93 | 2.90 | 2.52 | -1.29 |
| | 303 | 19.8 | 2.91 | 1.41 | -4.95 | 2.91 | 2.52 | -1.30 |
| | 308 | 19.0 | 2.94 | 1.41 | -4.96 | 2.93 | 2.52 | -1.33 |
| 2, 4, 6 trimethylphenol | 293 | 11.1 | 2.4 | 1.09 | -4.64 | 2.90 | 2.52 | -1.29 |
| | 298 | 10.6 | 2.5 | 1.09 | -4.75 | 2.91 | 2.52 | -1.30 |
| | 308 | 10.0 | 2.6 | 1.09 | -4.74 | 2.92 | 2.52 | -1.30 |
| 2, 3, 5 trimethylphenol | 293 | 18.0 | 2.73 | 1.63 | -3.75 | 2.90 | 2.52 | -1.29 |
| | 298 | 16.9 | 2.75 | 1.63 | -3.75 | 2.91 | 2.52 | -1.30 |
| | 303 | 15.9 | 2.77 | 1.63 | -3.76 | 2.92 | 2.52 | -1.32 |
| | 308 | 15.3 | 2.88 | 1.63 | -3.83 | 2.93 | 2.52 | -1.33 |

is found that the relaxation times of all the molecules investigated here are found to decrease with increase in temperature. This is due to the decrease in the viscosity of the solvent as the temperature is raised. It is found from Table I that the relaxation time of 2, 4, 6 trichlorophenol is highest and the relaxation time of 2, 4, 6 trimethyl phenol is lowest in the investigated series whereas latter has largest molecular size. It is likely that in the case of 2, 4, 6 trichlorophenol the highly electronegative chloro group forms hydrogen bonding with the -OH group which in turn may hinder the intramolecular rotation of -OH group and increase the relaxation time. Sahni *et al.*¹⁰ have interpreted the high value of relaxation times of many organic molecules as due to intermolecular hydrogen bonding.

The relaxation time of 2, 3, 5 trimethyl phenol is greater than 2, 4, 6 trimethyl phenol though both the molecules have almost similar molecular size. Also the relaxation time of 3, 5 dimethyl phenol is larger than the relaxation time of 2, 3, 5 trimethyl phenol and 2, 4, 6 trimethyl phenol though the former molecule is smaller than both the latter molecules in molecular size. This indicates that the molecule having irregular arrangement of the substituted groups experience greater hindrance in dipolar rotation.

The free energies of activation for the process of dielectric relaxation and viscous flow increase with temperature. Similar results have been observed earlier¹¹. The entropies of activation are found to be negative indicating that activated state is more ordered than the normal one. Further the heats of activation and energies of activation for viscous flow are greater than those for dipole relaxation, since the former involves both rotation and translation, while the latter only rotation.

The authors express their sincere thanks to Prof. B. G. Gokhale for his interest and encouragement.

Microwave and E.P.R.
Research, Laboratory,
Physics Department,
Lucknow University,
Lucknow, April 14, 1977.

C. K. MISRA.
A. MATHUR.
M. C. SAXENA.

5. Hiremath, G. C. *et al.*, *Bull. Nat. Inst. Sci.*, India, 1965, 30, 113.
6. Gupta, K. C. and Pradhan, B. P., *Proc. Nat. Inst. Sci.*, India, 1959, 25 (A), 184.
7. Roberts, S. and Von Hippel, A., *J. Appl. Phys.*, 1946, 17, 610.
8. Dakin, T. W. and Works, C. N., *Ibid.*, 1947, 18, 610.
9. Gopalakrishna, K. V., *Trans. Faraday Soc.*, 1957, 53, 767.
10. Sahni, N. *et al.*, *Bull. Chem. Soc.*, Japan, 1976, 41, 973.
11. Dhar, R. L., Shukla, J. P. and Saxena, M. C., *Ind. J. Pure and Appl. Phys.*, 1972, 10, 530.

KINETICS OF OXIDATION OF DIMETHYL SULPHOXIDE BY CHLORAMINE-T

THE reaction $\text{DMSO}-\text{Mn}^{3+}$ has been employed as a redox initiator for vinyl polymerisation¹. We have recently reported a kinetic study of DMSO oxidation by Cr (VI) and Ce (IV)². We report in this communication kinetics of oxidation of DMSO by Chloramine-T (CAT) in acid medium and OsO_4 -catalysed oxidation of DMSO by alkaline CAT.

Oxidation of DMSO by CAT in acid medium

The reactions are first order in $[\text{DMSO}]$, $[\text{CAT}]$ and independent of $[\text{HClO}_4]$ in the range studied. First order rate constants ($k_1 \text{ min}^{-1}$) at varying $[\text{DMSO}]$ are reported in Table I. The enhancement of the values of k_1 is due to the increase in the concentration of the DMSO.

TABLE I

Dependence on $[\text{DMSO}]$ Temp.: 35°C
CAT = $5.0 \times 10^{-4} \text{ M}$, $\text{HClO}_4 = 0.05 \text{ M}$,
 $\text{NaClO}_4 = 0.025 \text{ M}$.

| Aqueous medium | | 20% aqueous HOAc | |
|----------------------|-------------------|----------------------|-------------------|
| $10^3 [\text{DMSO}]$ | $10^3 k_1$ | $10^3 [\text{DMSO}]$ | $10^3 k_1$ |
| M | min ⁻¹ | M | min ⁻¹ |
| 2.1 | 14.8 | 3.0 | 11.7 |
| 4.3 | 31.2 | 4.3 | 18.7 |
| 6.6 | 42.2 | 7.1 | 23.8 |
| 11.0 | 69.1 | 11.7 | 37.0 |

Variation of acidity (with respect to HClO_4) in the range 0.01 to 0.1 M in aqueous medium and in 20% aqueous HOAc leads to the same value of k_1 proving insensitivity to acidity. Second order rate constants ($1 \cdot \text{m}^{-1} \text{ min}^{-1}$) in aqueous medium and in 20% aqueous HOAc are 7.3 and 4.0 respectively. This is at variance to the acidity dependence in the Cr(VI) and Ce(IV) oxidation of DMSO², where there is definite acid dependence. Ionic strength has been varied (NaClO_4 , 0.025 to 0.1 M) and the effect is marginal. Added *p*-toluene sulphonamide has no effect on the

1. Eyring, H., Glasstone, S. and Laidler, K. J., *The Theory of the Rate Process*, McGraw-Hill Co., New York, 1941, p. 548.
2. Magee, M. D. and Walker, S., *J. Chem. Phys.*, 1971, 55, 3068.
3. — and —, *Canadian J. Chem.*, 1972, 50, 2799.
4. LeFerve, R. J. W. *et al.*, *Aust. J. Chem.*, 1967, 20, 623.