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# Study of Dielectric Relaxation Mechanism in Some Substituted Pyridines

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The relaxation times of 2-chloro-, 2-bromo-, 3-bromo-, 2-methyl-, 2-acetyl- and 2-hydroxypyridines have been determined in the 3 cm microwave region at 20°C using benzene as solvent. It has been concluded from the relaxation times of 2-chloro-, 2-bromo-, 3-bromo- and 2-methylpyridines that these rigid molecules relax predominantly by the process of over-all molecular rotation. The comparatively small relaxation times of 2-acetyl- and 2-hydroxypyridines suggest that these non-rigid molecules relax by both molecular as well as intramolecular rotations. The free energies of activation for dipole orientation for the compounds investigated are always found to be smaller than those for viscous flow, because the process of dipole orientation involves only rotation, while the process of viscous flow involves both rotation and translation.

Rampolla and Smyth[1] have determined the critical wavelengths of 2, 4- and 2, 6-dimethylpyridines. The relaxation times of pyridine, quinoline and isoquinoline in pure liquid state have been reported by Holland and Smyth[2] Muller and Smyth[3] have investigated 2, 4, 6-trimethylpyridine for the study of its dielectric dispersion. However it has been observed that many of the substituted pyridines containing different dipole bearing groups have not been investigated for their dispersion behaviour. The purpose of the present investigation is to extend the dispersion studies in a systematic way to the halogeno-, methyl-, acetyl- and hydroxypyridines.

Also the potential barrier heights for dipole orientation and viscous flow have been calculated at one temperature using Eyring's[4] relation and his estimated values of the frequency factor A and B.

## Theory

Relaxation times have been determined by the fixed frequency method of Krishna[5] for dilute solutions using the relation

$$\tau = \frac{\lambda}{2\pi c}\left(\frac{dy}{dn}\right)$$

where $\lambda$ is free space wavelength and the factor $X$ and $Y$ are given by:

$$X = \frac{\varepsilon'^2+\varepsilon''^2+\varepsilon'-2}{(\varepsilon'+2)^2+\varepsilon''^2}$$

$$Y = \frac{3\varepsilon''}{(\varepsilon'+2)^2+\varepsilon''^2}$$

where $\varepsilon'$ = dielectric constant

and $\varepsilon''$ = loss factor.

## Experimental

The dielectric constant ($\varepsilon'$) and the loss factor ($\varepsilon''$) of solutions required for the calculation of the relaxation time ($\tau$) are determined by the standing wave technique of Von Hippel and Roberts[6] discussed in an earlier paper.[7]

**Meterials.** All the substances used are of pure quality (L. R. grade) and are obtained from Messrs British Drug House. Purest quality of benzene obtained from British Drug House has been distilled before use.

## Results

The experimental data for the determination of the relaxation time ($\tau$) in dilute solution of benzene are given in Table 1. The observed values of the relaxation time and free energies of activation for dipole orientation and viscous flow are reported in Table 2.

## Discussion

It is observed from Table 2 that 2-chloropyridine exhibits a smaller relaxation time than 2-bromopyridine which is in accordance with the

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4) H. Eyring, S. Glasstone and K. J. Laider, "The Theory of the Rate Process," McGraw Hill Co., New York (1941), p. 548.
5) K. V. G. Krishna, *Trans. Faraday Soc.*, **53**, 767 (1957).
6) S. Roberts and A. Von Hippel, *J. Appl. Phys.*, **17**, 610 (1946).
7) N. K. Mehrotra, J. P. Shukla and M. C. Saxena, Under Publication in the Indian Journal of Pure and Applied Physics.

TABLE 1. EXPERIMENTAL DATA FOR THE DETERMINTION OF "$\tau$"
($\lambda$=3.13 cm; Temperature=20°C)

| Polar substance | tan $\delta$ | $X$ | $Y$ |
|---|---|---|---|
| 2-Chloropyridine | 0.01104 | 0.29221 | 0.00412 |
| | 0.01375 | 0.29384 | 0.00514 |
| | 0.02103 | 0.29851 | 0.00765 |
| | 0.02186 | 0.30037 | 0.00816 |
| | 0.02304 | 0.30160 | 0.00860 |
| 2-Bromopyridine | 0.00882 | 0.29078 | 0.00330 |
| | 0.01373 | 0.29405 | 0.00513 |
| | 0.01725 | 0.29556 | 0.00644 |
| | 0.02089 | 0.29758 | 0.00760 |
| | 0.02726 | 0.30235 | 0.01037 |
| 3-Bromopyridine | 0.00710 | 0.28548 | 0.00266 |
| | 0.00909 | 0.28702 | 0.00340 |
| | 0.01116 | 0.28800 | 0.00417 |
| | 0.01199 | 0.28857 | 0.00449 |
| | 0.01373 | 0.28986 | 0.00513 |
| 2-Methylpyridine | 0.00609 | 0.28685 | 0.00228 |
| | 0.00754 | 0.28799 | 0.00282 |
| | 0.00984 | 0.29089 | 0.00368 |
| | 0.01235 | 0.29351 | 0.00462 |
| | 0.01492 | 0.29607 | 0.00557 |
| 2-Acetylpyridine | 0.00772 | 0.28916 | 0.00418 |
| | 0.01329 | 0.29024 | 0.00497 |
| | 0.01671 | 0.29321 | 0.00624 |
| | 0.02162 | 0.29738 | 0.00807 |
| | 0.02448 | 0.29937 | 0.00914 |
| 2-Hydroxypyridine | 0.00780 | 0.28855 | 0.00292 |
| | 0.00973 | 0.29045 | 0.00364 |
| | 0.01199 | 0.29198 | 0.00442 |
| | 0.01359 | 0.29533 | 0.00508 |
| | 0.01509 | 0.29702 | 0.00564 |

TABLE 2. VALUES OF THE RELAXATION TIME ($\tau$) AND FREE ENERGIES OF ACTIVATION FOR DIPOLE ORIENTATION AND VISCOUS FLOW

| Polar substance | $\tau\times10^{12}$ | $H_\tau$ kcal/mol | $H_\eta$ kcal/mol | $H_\eta/H_\tau$ |
|---|---|---|---|---|
| 2-Chloropyridine | 8.30 | 2.29 | 2.90 | 1.27 |
| 2-Bromopyridine | 9.96 | 2.39 | 2.90 | 1.21 |
| 3-Bromopyridine | 7.47 | 2.23 | 2.90 | 1.30 |
| 2-Methylpyridine | 6.64 | 2.15 | 2.90 | 1.34 |
| 2-Acetylpyridine | 7.88 | 2.26 | 2.90 | 1.28 |
| 2-Hydroxypyridine | 5.81 | 2.08 | 2.90 | 1.39 |

greater size of the latter molecule. A similar result has earlier been observed by Srivastava[8] who observed that the relaxation times of *o*- and *m*-bromoanilines are greater than the corresponding chloroanilines. The relaxation time of 2-bromopyridene is greater than that of 3-bromopyridine, although the size of the two molecules is the same. This can not be explained by the Debye equation $\tau=4\pi\eta_1a^3/kT$ which shows that different relaxation times are obtained only for molecules having different molecular sizes. However, if instead of the solvent viscosity $\eta_1$, the mutual viscosity $\eta_{12}$ of the solute and the solvent is considered, the observed difference in the relaxation time is explained.

The relaxation time of 2-methylpyridine is found to be smaller than those of chloro and bromopyridines, which is also expected from the smaller size of the former molecule. This observed variation of the relaxation time with the size of the molecules, leads to the conclusion that the molecules relax predominantly by the process of overall molecular rotation.

The smaller value of the relaxation time of 2-acetylpyridine as compared to those of 2-chloro- and 2-bromopyridines can be explained in term of the intramolecular rotation of the acetyl group. Similarily the smaller relaxation time of 2-hydroxypyridine as compared to 2-methylpyridine is due to the intramolecular rotation of the hydroxyl group. This suggests that the 2-acetylpyridine and 2-hydroxypyridine molecules relax by both molecular as well as intramolecular rotations. A comparison of the relaxation time of 2-hydroxypyridine and 2-acetylpyridine, leads to the conclusion that under similar conditions hydroxyl group has greater freedom of rotation than the acetyl group.

The potential barrier height for 2-bromopyridine is found to be greater than that for 3-bromopyridine, suggesting that there is greater inner-friction experienced by the former molecule in rotation. The ratio of the potential barrier heights for dipole orientation and viscous flow approximately approaches unity, which is in conformity with the results earlier reported by Ahmad and Sharma.[9]

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