

DIELECTRIC RELAXATION IN SOME HALOGENATED BENZALDEHYDES

THE present communication reports the relaxation times of *p*-fluoro-, *o*-chloro- and *p*-chlorobenzaldehydes in the 3 cm. microwave region at 22° C. in dilute solutions. It has been observed that the molecules are relaxed predominantly by the process of overall molecular rotation.

The relaxation times of some aliphatic aldehydes have been determined by Lal¹ who found that the relaxation time increases as the number of -CH₂ groups in the chain increases. However, it has been observed that many of the halogenated benzaldehydes have not been investigated for their dispersion behaviour.

The values of the relaxation time and free energies of activation are given in Table I.

TABLE I

Values of the relaxation times τ and free energies of activation for dipole orientation and viscous flow

Polar compounds	$\tau \times 10^{12}$ sec.	$H\tau$ (K.Cal./mole)	$H\eta$ (K.Cal./mole)	$H\eta/H\tau$
<i>p</i> -Fluorobenzaldehyde in benzene	5.81	2.10	2.91	1.38
<i>o</i> -Chlorobenzaldehyde in <i>p</i> -xylene	11.2	2.50	3.09	1.24
<i>p</i> -Chlorobenzaldehyde in <i>p</i> -xylene	9.13	2.36	3.09	1.31

The relaxation time of *p*-fluorobenzaldehyde is found to be smaller than those of chlorobenzaldehydes, as is expected from the smaller size of the former molecule. The relaxation time of *o*-chlorobenzaldehyde is found to be higher than that of *p*-chlorobenzaldehyde. This can be explained on the basis of the fact that the former molecule experiences greater steric hindrance to the free rotation than the latter.

The authors express their gratitude to Dr. P. N. Sharma for his interest and encouragement.

Physics Department,
Lucknow University,
Lucknow, June 6, 1966.

N. K. MEHROTRA.
M. C. SAXENA.

1. Lal, K. C., *J. Sci. Instr. Res.*, 1961, 20 B, 181.

THE KINETICS AND MECHANISM OF THE OXIDATION OF ALCOHOLS WITH BROMINE

THE kinetics of the oxidation of simple alcohols with bromine has been studied by a number of workers with a view to formulate the mechanism of the reaction.¹⁻⁷ We considered it desirable to study the effect of structural variation in the alcohols on the rate in order to test the mechanisms proposed. We report in this communication the results of the oxidation of a few typical secondary alcohols, propanol-2, butanol-2, α -phenyl ethyl alcohol and benzhydrol. The oxidations were carried out in solvent mixtures of acetic acid and water with the ionic strength maintained constant with A.R. sodium acetate. It has been found that the bromine oxidation of all these alcohols is of the first order in alcohols and in free bromine. This result is in conformity with the earlier reported kinetic picture. The effect of structure on the course of this oxidation is of the following order:

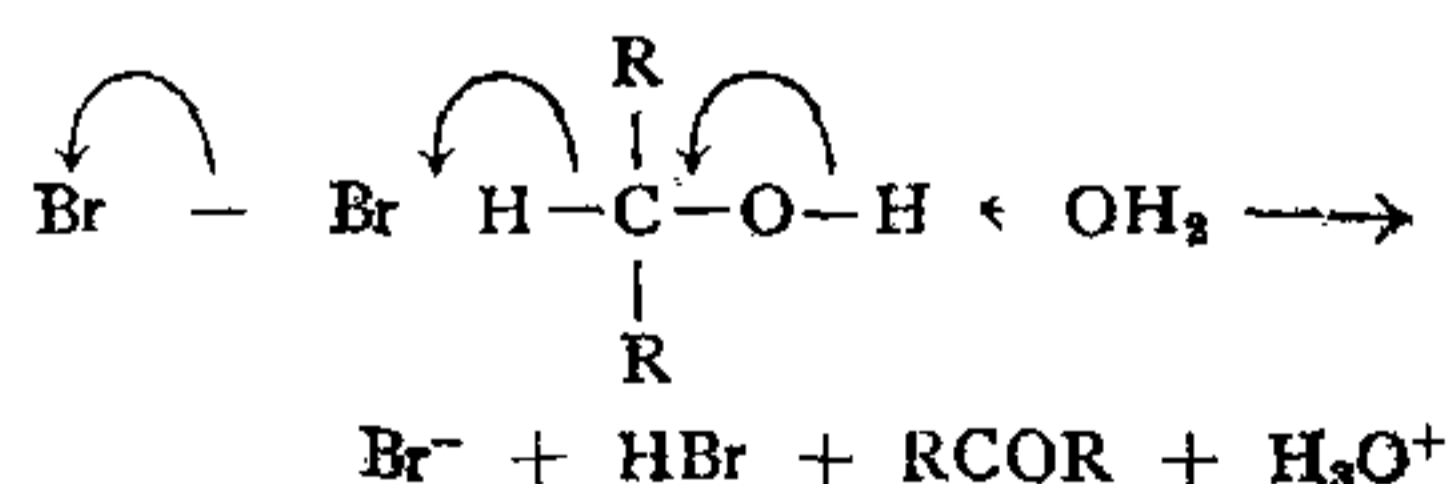
α -phenyl ethyl alcohol > Benzhydrol > propanol-2; butanol-2 > propanol-2.

TABLE I

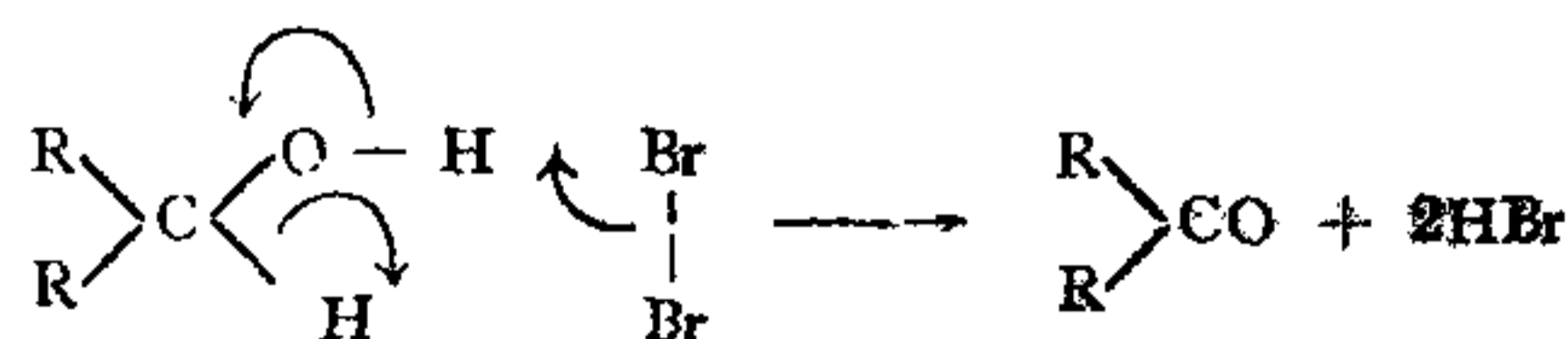
Second order constants for the oxidation of alcohols by bromine in 70% HoAc-H₂O (V/V) at 45° C.

Alcohol	$k_2 \times 10^2$ litre mol. ⁻¹ sec. ⁻¹
Propanol-2	1.562
Butanol-2	2.800
α -Phenyl ethyl alcohol	10.570
Benzhydrol	5.122

The general trend noticed in the above sequence is justifiable on the basis of both the Swain⁴ and the Barker⁷ mechanisms proposed for the oxidation. The former mechanism is represented thus:

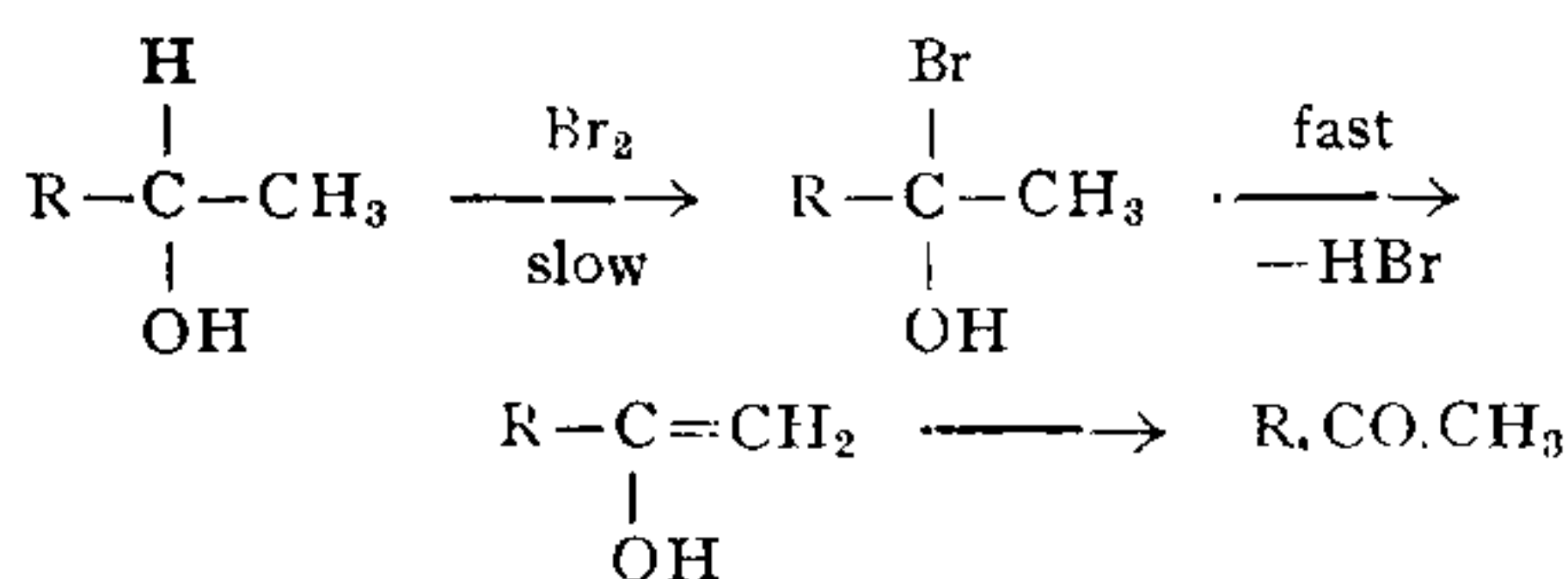


and the latter mechanism is a cyclic one



The increase in the rate of oxidation of butanol-2 over propanol-2 is obviously due to the +I effect of the β -methyl group facilitating hydride abstraction and also due to the hyperconjugative stabilisation of the positive charge

on the carbinol carbon atom in the transition state. This stabilisation would be by a mesomeric shift of electrons in the case of α -phenyl ethyl alcohol resulting in a higher rate benefit.* But the decreased rate of benzhydrol over α -phenyl ethyl alcohol is surprising. While two phenyl rings should stabilise the carbonium ion-like transition state to a larger extent than one, the considerable constriction of the C-H bond (because of the three strong-I substituents attached to the α -carbon atom) would oppose a rate-determining breakage of the -C-H bond resulting in reduced rate. An alternative and attractive possibility is that while for α -phenyl ethyl alcohol (or in general for a secondary alcohol with a β hydrogen atom) an alternative or parallel mechanism is available, which is totally absent for benzhydrol.



This type of oxidation route has been suggested for the N-Bromosuccinimide oxidation of primary and secondary aromatic alcohols having the -OH group on the carbon adjacent to the aromatic nucleus.⁸⁻¹⁰

Preliminary investigations on the effect of solvents on the rate of oxidation indicate that the rate of the reaction falls with increasing proportions of acetic acid in solvent mixtures of acetic acid and water. This points to the fact that the reaction is essentially one of the dipole-dipole type.

Dept. of Chemistry, V. THIAGARAJAN.
Vivekananda College, N. VENKATASUBRAMANIAN.
Madras-4, July 19, 1966.

* The acid catalysed bromination of acetophenone is negligibly slow under the conditions of the experiment.

1. Bugarzky, S., *Z. Phys. Chem.*, 1903, 42, 545.
2. Farkas, L., Perlmutter, B. and Schacher, O., *J. Amer. Chem. Soc.*, 1949, 71, 2827.
3. Kaplan, L., *Ibid.*, 1958, 80, 2039.
4. Swain, C. G., Wiles, R. A. and Bader, R. F. W., *Ibid.*, 1961, 83, 1945.
5. Perlmutter-Hayman, B. and Weissmann, Y., *Ibid.*, 1962, 84, 2323.
6. — and Persky, *Ibid.*, 1960, 82, 276.
7. Barker, K. R. L., Overend, W. G. and Rees, C. W., *J. Chem. Soc.*, 1964, p. 3263.
8. Leconte, J.* and Defour, C., *Compt. rend.*, 1952, 234, 1887.
9. — and Gault, H., *Ibid.*, 1954, 238, 2538.
10. Filler, R., *Chem. Revs.*, 1963, 63, 21.

SYNTHESIS OF SOME NEW C-, AND N-BIS (BENZOQUINONES)

THE isolation of vilangin and its synthesis¹ has initiated this further study of the reactivity of various dihydroxybenzoquinones in undergoing ready condensation with both aldehydes and nitroso compounds. Rapanone (I) isolated from *Ardisia macrocarpa* Wall² in these laboratories has now been condensed with various aldehydes to give new methylene-bis-benzoquinones of types II and III while with nitroso compounds, the corresponding N-bis (anhydrobenzoquinones) (IV) are obtained. They are further characterized by the preparation of the acetates of their reduction products thus confirming our earlier proposals with regard to the nature of these condensations using embelin³ and 2, 5-dihydroxybenzoquinone.⁴ Tables I and II give a summary of the condensations carried out.

