FURTHER OBSERVATIONS ON SOLVENT EFFECTS IN THE EPOXIDATION OF CYCLOHEXENE

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Abstract. Epoxidation of cyclohexene with peroxybenzoic acid (PBA) in 2-methoxy-ethanol, n-propanol, acetone, ethanol, methanol, dimethylformamide, acetonitrile, carbon tetrachloride, benzene, *o*-xylene and toluene has been studied at $40°(\pm0.5°C)$. It has been observed that the rate constant is inversely proportional to the dielectric constant of the solvent employed.

In an earlier communication the epoxidation of cyclohexene with peroxybenzoic and *p*-substituted peroxybenzoic acids was described. It was pointed out that this reaction follows second order kinetics, is uncatalysed by the corresponding carboxylic acid and that the observed rate constants were inversely proportional to the dielectric constant of the solvents employed.[1]

A number of other solvents with widely varying dielectric constants have now been studied for this reaction with a view to further substantiate the earlier findings. Presently cyclohexene has been oxidised with peroxybenzoic acid in different solvents at 40°C $(\pm0.5°)$. The following polar as well as nonpolar solvents, arranged in their ascending order of dielectric constants respectively, have been investigated in the present studies:

(a) *Polar Solvents.* 2-Methoxy-ethanol, n-propanol, acetone, ethanol, methanol, dimethylformamide and acetonitrile.

(b) *Nonpolar Solvents.* Carbon tetrachloride, benzene, *o*-xylene and toluene.

The choice of these solvents was necessitated not only because of their considerable differences in the dielectric constants but also for their ready availability.

In the oxidation of an olefin by peroxy acids, two types of mechanisms have been considered by various investigators. In one mechanism it is proposed that there is the nucleophilic attack of an olefin on the electrophilic peroxy acid molecule. This mechanism is also referred to as 1,1-addition mechanisms.[2]
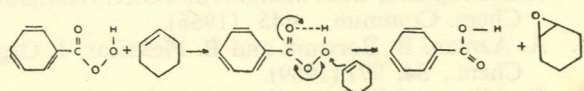
The other mechanism postulates a 1,3-dipolar addition of a hydroxy carbonyl oxide to the double bond of the olefin. This hydroxy carbonyl oxide is supposed to be derived from the intramoleculary hydrogen-bonded peroxy acid molecule.[3]
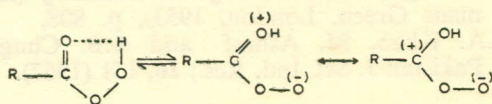

More recently the reaction of an olefin with peroxy acid has been studied, from a molecular orbital point of view.[4] On the basis of molecular orbital study it has been proposed that a 1,3-dipolar addition mechanism is operative in polar, while a 1,1-addition occurs in the nonpolar media. In view of these findings it will be seen that the generation of a 1,3-dipolar species should be favourably enhanced in polar solvents. As a result, higher rate constants should be obtained in such solvents.

The present findings are contrary to this postulate of 1,3-dipolar addition mechanism. However, it is to be pointed out that the reaction rate is higher in nonpolar than in polar solvents as demanded by the 1,1-addition mechanism. One reason for this behaviour can be that the reactants in the ground state are better solvated in polar than in nonpolar solvents. Also in a solvent of low dielectric constant the electrostatic forces would be expected to exercise a small dissociating influence on the peroxy oxygen. As a consequence, therefore, the rate of oxidation will be higher in such solvents. Further in the solvated form the peroxy acid losses many of its degrees of freedom and thus undergoes more restrictions on proceeding from the unreacted to the transition state. This is why the rate of reaction decreases with the increase of the dielectric constant of the solvent. A plot of the rate constant (k) versus the reciprocal of the dielectric constant ($1/D$) of the solvent used would thus indicate a linear relationship and actually that is obtained when the present results are considered. It has thus been confirmed now that the earlier observations were general in character both for polar and nonpolar solvents.

It has previously been reported that this reaction is not catalysed by acid. More evidence supporting this view is also provided as a result of the present study. The rate constant in nonpolar solvents is 10 times faster than in polar solvents (Table 1). This observation is interesting in so far as carboxylic acids are known to exist as dimers in various aprotic or nonpolar solvents.[5]
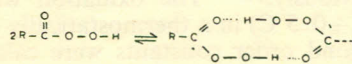
The enhanced reactivity in nonpolar solvents may be attributed to the existence of free monomer in such solvents.

TABLE 1. SPECIFIC RATE CONSTANTS FOR EPOXIDATION OF CYCLOHEXENE FOR NONPOLAR SOLVENTS.

Solvents	Dielectric constants	Concn (m-moles/litre)		Rate constants, k 1 mole^{-1} sec^{-1}
		Cyclohexene	PBA	
Carbon tetrachloride	2·238	9·0	15·0	0·35
		5·0	10·0	0·34
		5·0	9·5	0·35
Benzene	2·284	9·0	15·0	0·32
		9·0	20·0	0·31
		2·5	5·0	0·32
Oxylene	2·374	9·0	15·0	0·30
		5·0	10·0	0·29
		2·5	10·0	0·30
Toluene	2·438	10·0	20·0	0·28
		5·0	85·0	0·27

TABLE 2. SPECIFIC RATE CONSTANTS FOR THE EPOXIDATION OF CYCLOHEXENE FOR POLAR SOLVENTS.

Solvents	Dielectric constants	Concn (m-moles/liter)		Rate constant, k 1 mole^{-1} sec^{-1}
		Cyclohexene	PBIA	
2-Methoxy-ethanol	16·0	2·5	5·0	0·028
		10·0	15·0	0·027
		4·5	9·9	0·028
n-Propanol	20·1	10·0	17·65	0·025
		5·0	8·50	0·024
		2·5	5·00	0·024
Acetone	20·7	10·0	16·80	0·022
		5·0	8·50	0·020
		2·5	5·00	0·022
Ethanol	24·3	10·0	18·20	0·018
		5·0	9·00	0·018
		2·5	4·90	0·017
Methanol	32·63	5·0	8·90	0·014
		2·5	5·00	0·012
		2·5	4·80	0·013
Dimethylformamide	37·6	10·0	19·0	0·012
		5·0	10·0	0·011
		5·0	8·5	0·012
Acetonitrile	46·0	10·0	19·0	0·0069
		10·0	15·0	0·0068
		5·0	9·5	0·0070

Experimental

All the solvents used in the present study were purified by the standard procedures.[6] Preparation of peroxybenzoic acid, purification of cyclohexene and the kinetic measurements were carried out as reported previously.[7,8] The oxidation was carried out at 40°C ($\pm$0.5°C) in a thermostatically controlled bath and second order constants were calculated by the usual method.
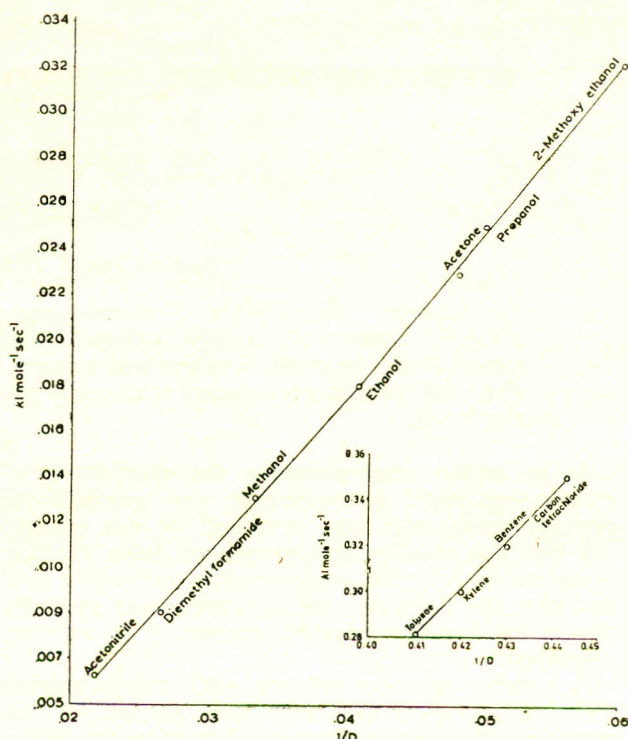

Fig. 1. Graph between rate constants versus reciprocal of dielectric constant of polar solvents. Scale along y-axis=rate constants; Scale along x-axis=reciprocal of dielectric constants.

Concentrations of the reactants, calculated second order rate constants and the dielectric constants of the solvents studied are recorded in Table 1. A graph, as plotted between the rate constant and the reciprocal of the dielectric constant is given in Fig. 1.

References

1. S.A. Khan, M. Ashraf and N.A. Chughtai, Pakistan J. Sci. Ind. Res., **11**, 105 (1968).
2. H. Kwart, P.S. Starcher and S.W. Tinsley, Chem. Commun., 335, (1967).
3. K.D. Bingham, G.D. Meakins and G.H. Whitham, Chem. Commun., 445 (1966).
4. A. Azman, B. Borstnik and B. Plesnicar, J. Org. Chem., **34,** 971 (1969).
5. G. Allen and E.F. Caldin, Quart Rev. (London), **7,** 255 (1953).
6. A Weissberger and S. Proskaue, *Technique of Organic Chemistry* (Interscience, New York, 1955), vol. VII, p. 297
7. A.I. Vogel, *Practical Organic Chemistry* (Longmans Green, London, 1953), p. 808.
8. S.A. Khan, M. Ashraf and A.B. Chughtai, Pakistan J. Sci. Ind. Res., **10,** 151 (1967).