

SOLVENT-EFFECTS IN THE EPOXIDATION OF CYCLOHEXENE

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Epoxidation of cyclohexene with peroxy and *p*-substituted peroxybenzoic acids has been studied kinetically in methanol at 30°, 40°, and 50°C ($\pm 0.5^\circ$) and with peroxybenzoic acid in ethanol, acetone and *n*-propanol at 40° ($\pm 0.5^\circ$). A ρ value of +1.30 has been calculated by the Hammett treatment. Energies of activation, entropies of activation and frequency factors have also been calculated. The differences in rate constants have not been found to be significantly dependent either on differences in energies or entropies of activation. However, the rate constants have been observed to be inversely proportional to the dielectric constants of the solvents employed. The addition of corresponding non-peroxybenzoic acids has been shown to cause no catalytic effects on the rate of this reaction.

Oxidation of cyclohexene to afford an epoxide has been known for a long time now.¹ This general reaction of the cyclic olefin with different oxidants has been the subject of various investigations.²⁻⁷ However, Medvedev and Blokh⁸ first reported the kinetics of the oxidation of cyclohexene using *p*-methoxy- and *p*-nitroperoxybenzoic acid in benzene and xylene. They found that in these aprotic solvents the oxidation is a bimolecular process. From these studies, the authors worked out various kinetic parameters and calculated a ρ value of +0.94. Later, Stuurman⁹ studied this oxidation with peracetic acid and also showed that this is a bimolecular reaction.

In connection with another study, it was desired to know the behaviour of polar solvents when olefins were oxidised with *p*-substituted peroxybenzoic acids. Since Medvedev and Blokh had determined the ρ value of this oxidation by using only two *p*-substituted peroxybenzoic acids, we decided to extend this work in polar solvents to employ more than two substituted peroxybenzoic acids. Thus, the present study describes the effects of polar solvents in the oxidation of cyclohexene with peroxy- and *p*-substituted peroxybenzoic acids ($p\text{-RC}_6\text{H}_4\text{O}_3\text{H}$ where $\text{R}=\text{NO}_2$, Cl , CH_3 and OCH_3).

Results and Discussion

The rate constants for the oxidation of cyclohexene with peroxy- and four *p*-substituted peroxybenzoic acids were determined in methanol at 30°, 40° and 50°C ($\pm 0.5^\circ$) and with peroxybenzoic acid in ethanol, acetone and *n*-propanol at 40°C ($\pm 0.5^\circ$). In all these cases strict adherence to second order kinetics was noted. The rate constants obtained with varying concentration of

cyclohexene and unsubstituted/*p*-substituted peroxybenzoic acids in the presence of corresponding acids, also, followed the same order of the reaction. The activation energies and physical factors were calculated from the Arrhenius plots shown in Fig. 1. The entropy of activation, ΔS^\ddagger , was determined from frequency factors,¹⁰ "A". The various physical constants as obtained in these studies are given in Table 1. It is obvious from the plot of E versus $T\Delta S^\ddagger$, depicted in Fig. 2, that there is a linear increase of ΔS^\ddagger with increasing activation energies. Generally the rate constants show their dependency on the difference of both energies and entropies of activation.¹¹⁻¹² However, in the present studies there appears no regular trend as regards this dependency.

Effect of Acids.—The addition of corresponding benzoic acids in the systems concerned did not show any catalytic effect on the rate of reaction. As a result of the addition of these acids only slight differences in rate constants were observed which fall within the limits of experimental errors (Tables 1 and 2). This confirms that respective acids, formed as products, do not catalyse the reaction.

Solvent Effect.—The nature of the solvent, generally affects the rate of reaction. In order to investigate this aspect, the epoxidation of cyclohexene with peroxybenzoic acid was carried out in methanol, ethanol, acetone and *n*-propanol (arranged in the ascending order of their dielectric constants).¹³ The rate constants obtained in these solvents at 40°C $\pm 0.5^\circ$ along with their dielectric constants are recorded in Table 2. A plot of rate constants versus the reciprocal of dielectric constants of the solvents employed gives a straight line as shown in Fig. 3. It is, therefore, apparent that the rate constants are inversely proportional

TABLE I.—SPECIFIC RATE CONSTANTS, ACTIVATION, FREQUENCY FACTORS AND ACTIVATION ENTHALPIES FOR THE OXIDATION OF CYCLOHEXENE WITH PERACIDS IN METHANOL.

Cyclohexene, m-mole/l	Peracid, m-mole/l	Temp. °C	k l-mole ⁻¹ sec ⁻¹	E kcal mole ⁻¹	$\ln A$	ΔS^\ddagger deg ⁻¹ cal mole ⁻¹
<i>p</i> -Nitroperoxybenzoic Acid						
10.0	18.60	30°	0.072			
5.0	9.00	"	0.074			
5.0	9.20 + 20.00 (<i>p</i> -nitrobenzoic acid)	"	0.074			
10.0	18.75	40°	0.160	14.97	22.24	-13.76
5.0	9.20	"	0.164			
5.0	0.10	50°	0.344			
2.5	5.30	"	0.316			
<i>p</i> -Chloroperoxybenzoic Acid						
10.0	19.70	30°	0.0125			
5.0	8.90	"	0.0123			
5.0	8.85	40°	0.0250	14.50	19.67	-18.87
2.5	5.40	"	0.0260			
2.5	4.90	"	0.0240			
10.0	18.00	50°	0.056			
5.0	10.00 + 20.00 (<i>p</i> -chlorobenzoic acid)	"	0.054			
2.5	5.00	"	0.052			
Peroxybenzoic acid						
10.0	15.25	30°	0.0062			
5.0	7.15	"	0.0060			
2.5	3.50	"	0.0064			
10.0	18.45	40°	0.0130	15.99	21.50	-13.90
5.0	9.80	"	0.0140			
2.5	4.10	"	0.0120			
2.5	5.00 + 25.00 (benzoic acid)	"	0.0130			
10.0	19.00	50°	0.030			
2.5	5.30	"	0.032			
2.5	5.20 + 20.00 (benzoic acid)	"	0.032			
<i>p</i> -Methylperoxybenzoic acid						
5.0	8.75	30°	0.0037			
5.0	9.00 + 20.00 (<i>p</i> -toluic acid)	"	0.0036			
2.5	5.20 + 10.00 (<i>p</i> -toluic acid)	"	0.0036			
2.5	4.90	40°	0.0076			
2.5	5.00	50°	0.0160	13.98	17.40	-22.77
<i>p</i> -Methoxyperoxybenzoic Acid						
5.0	10.65	30°	0.0025	14.00	17.23	-23.36
5.0	10.80 + 30.00 (<i>p</i> -anisic acid)	"	0.0024			
5.0	10.80	40°	0.0050			
2.5	5.20	"	0.0050			
5.0	10.30	50°	0.0120			

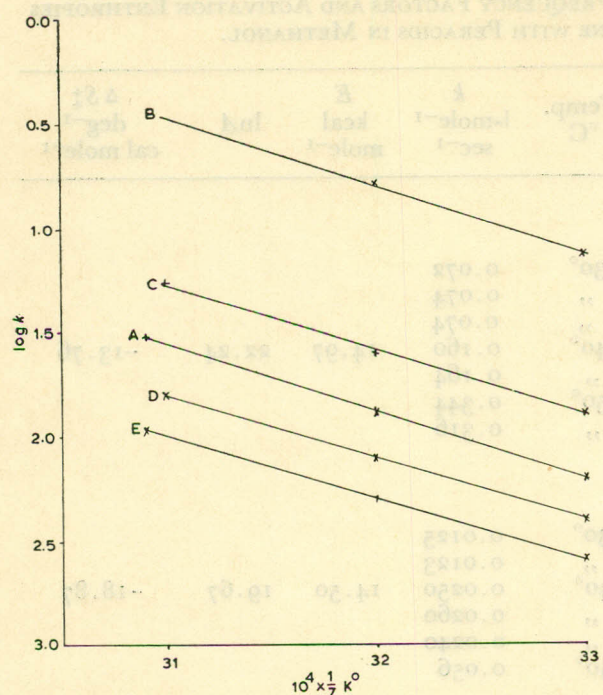


Fig. 1.—Arrhenius plots for peroxybenzoic acids oxidation of cyclohexene in methanol. Points obtained in the oxidation of cyclohexene with A=peroxybenzoic acid, B=*p*-nitroperoxybenzoic acid, C=*p*-chloroperoxybenzoic acid, D=*p*-methylperoxybenzoic and E=*p*-methoxyperoxybenzoic acid.

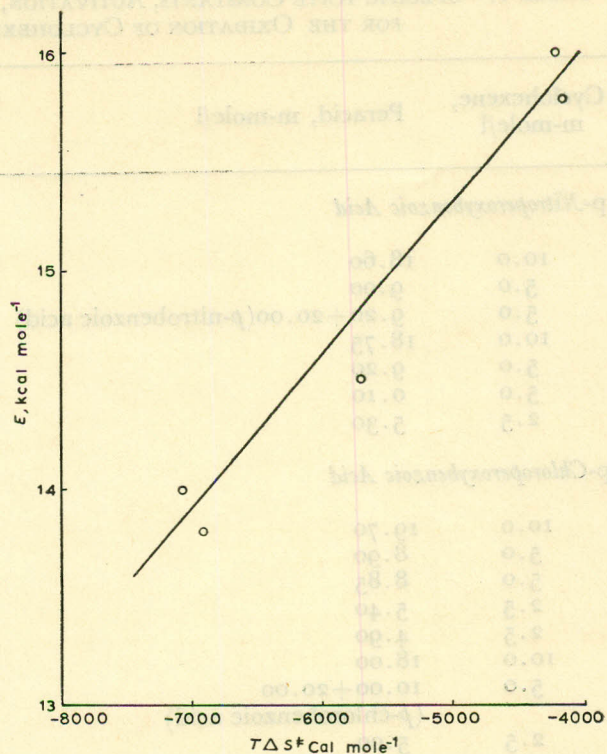


Fig. 2.—Plot E vs. $T\Delta S$ peroxybenzoic acids oxidation of cyclohexene in methanol at $30^\circ\text{C} + 0.5^\circ$.

TABLE 2.—SOLVENT EFFECT IN THE OXIDATION OF CYCLOHEXENE WITH PEROXYBENZOIC ACID AT 40°C .

Solvent	Dielectric constant	Concentration in m-moles/l		Rate constants	
		Cyclohexene	Peroxybenzoic acid	Benzoic acid	k l mole ⁻¹ sec ⁻¹
n-Propanol	20.1	10.0	17.65		0.026
		5.0	8.40		0.024
			8.00	20.0	0.024
Acetone	20.7	10.0	16.80		0.022
		5.0	8.50		0.020
			2.5	5.00	10.0
Ethanol	24.3	10.0	18.20		0.018
		5.0	9.00		0.018
			2.5	4.90	10.0
Methanol	32.63	5.0	8.90		0.014
		2.5	5.00		0.012
			4.80	5.0	0.013

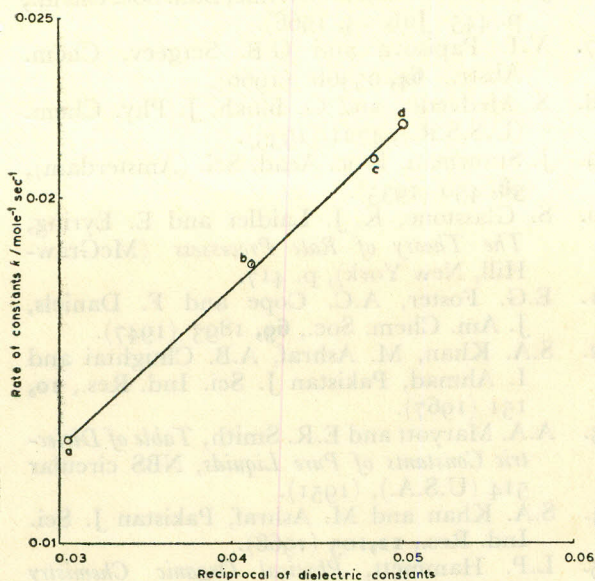


Fig. 3.—Plot of rate constants versus reciprocal of dielectric constants. Points obtained in the oxidation of cyclohexene with peroxybenzoic acid in, A=methanol, b=ethanol, C=acetone and D=n-propranol, at $40^\circ + 0.5^\circ$.

to the dielectric constants of the solvents. Therefore, the electrostatic interactions are more important than the nonelectrostatic ones. Incidentally, the results obtained in these studies are in line with those obtained in the oxidation of sulphoxide to sulphone.¹⁴

Substituent Effect.—The effect of the substituents on the reactivity of the peroxybenzoic acids was considered with reference to σ and ρ values introduced by Hammett.¹⁵ The Hammett plot (Fig. 4) consisting of $\log k/k_0$ versus the substituent constant gives a straight line with a ρ value of $+1.30$. This is to be contrasted with a ρ value of $+0.94$ obtained by Medvedev and Blokh in the epoxidation of cyclohexene with only two *p*-substituted peroxybenzoic acids.⁸

p-Substituents generally have small influence upon the entropy of activation in the reactions of benzene derivatives.¹⁶ However, the present values of entropies of activation differ from one another in the range of -23.36 to -13.76 . Moreover, the energies of activation in all these observations vary from 13.98 to 15.99 kcal/mole. The rate constants with *p*-chloro- and *p*-nitro-peroxybenzoic acids are approximately 2 and 12 times higher, while with *p*-methyl- and *p*-methoxy-peroxybenzoic acids nearly 2.5 and 1.5 times lower than with unsubstituted peroxybenzoic acid.

It is to be pointed out that present results favour the mechanism put forward by Swern for the

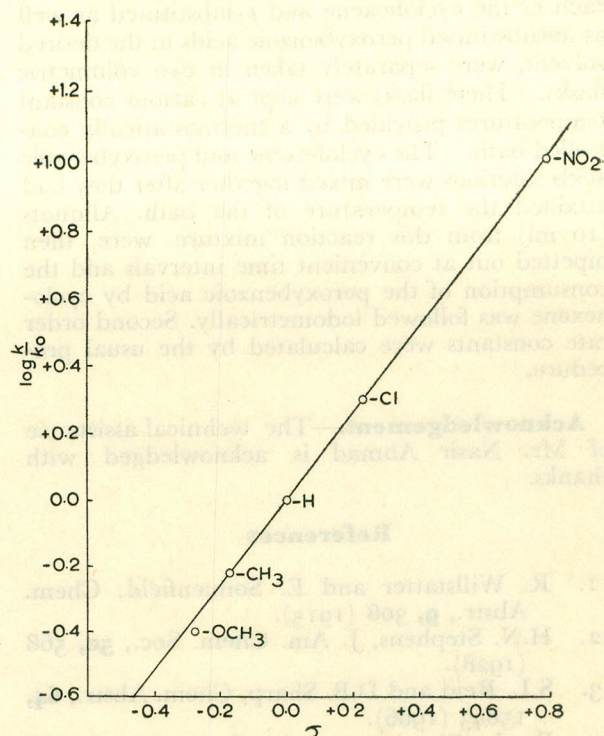


Fig. 4.—The Hammett plot.

oxidation of various substituted/unsubstituted olefins, which involves a nucleophilic attack of the double bond of an ethylenic system on the peroxy-oxygen of the peroxybenzoic acid.¹⁷

Experimental

Absolute methanol, ethanol, acetone and n-propranol used as solvents were purified according to standard procedures.

Peroxybenzoic acid and three *p*-substituted peroxybenzoic acids ($-\text{Cl}$, $-\text{CH}_3$ and $-\text{OCH}_3$) were obtained by Kolthoff, Lee and Mairs modifications¹⁸ of the Braun procedure¹⁹ from benzoyl peroxide and respective *p*, *p'*-disubstituted benzoyl peroxides, which in turn were prepared from the corresponding acid chlorides, whereas, *p*-nitro-peroxybenzoic acid was prepared from *p*-nitrobenzoyl chloride by Michel Vilkas's method.²⁰ These peroxybenzoic acids were prepared just before use in the kinetic runs, dissolved in the desired solvent and stored in a refrigerator (0°). They were iodometrically standardised and the solutions of different concentrations were then prepared by dilution. Cyclohexene, used in these studies, was of the B.D.H. standard. It was purified by fractional distillation and only the middle fraction was used in the kinetic studies.

Kinetic Measurements.—Solutions (50 ml) of each of the cyclohexene and *p*-substituted as well as unsubstituted peroxybenzoic acids in the desired solvent, were separately taken in two volumetric flasks. These flasks were kept at various constant temperatures provided by a thermostatically controlled bath. The cyclohexene and peroxybenzoic acids solutions were mixed together after they had attained the temperature of the bath. Aliquots (10 ml) from this reaction mixture were then pipetted out at convenient time intervals and the consumption of the peroxybenzoic acid by cyclohexene was followed iodometrically. Second order rate constants were calculated by the usual procedure.

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