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THE MECHANISM OF EPOXIDATION OF OLEFINS BY PERACIDS

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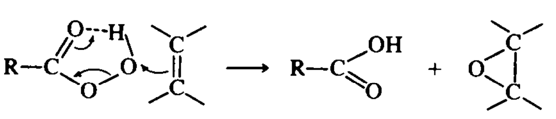
INTRODUCTION

A number of reviews deal with the mechanism of the Prilezhaev reaction (epoxidation of olefins with peracids)[1-3] and the simple mechanism first suggested by Bartlett[4] and by Lynch and Pausacker[5] has become generally accepted. This mechanism involves attack of the intramolecularly H-bonded peracid on the olefin:



A weak point about the proposed mechanism is that it only considers the unsolvated peracid molecule, and does not offer an explanation for a number of experimental observations e.g.: selectivity of epoxidation as a function of the nature of peracid,[2,6,7] specific influence of the solvent,[8,9] induced decomposition of peracids[10] and the formation of rearranged products[11] concurrent with epoxidation.

Most investigators postulate a decrease in the rate and increase of activation energy on increase of the basicity of the medium. As will be shown later the opposite dependence is observed in a number of cases.[12,13]

There are no explanations for contradictory data concerning the influence of additions of acids on reaction rate.[14-16] Thus, trichloroacetic acid catalyses the oxidation of stilbene with perbenzoic acid,[14] but retards the epoxidation of ethyl crotonate.[16]

Conclusions about the influence of hyperconjugation on the kinetics of epoxidation of substituted stilbenes,[17] propenes and butenes,[18] are rendered dubious since solvation effects were ignored. Thus earlier work[6,8] has shown that epoxidation kinetics are dependent on the nature of peracid and solvent.

As regards the structure of peracids, it was shown[19-21] that they form intramolecular H-bonds only in inert solvents (benzene, carbon tetrachloride) and in dilute solutions. In concentrated solutions peracids tend to form dimers, and in weakly basic solvents (ethers, alcohols, amides, ketones, etc.) peracids form mainly intermolecular H-bonds.[20,22-24]

This would be expected on the basis of the theory of acid-base interactions.[25]

In acid media, the intramolecular H-bonded form of peracids is expected to be more important since carboxyl and hydroxyl containing compounds are usually associated as dimers or chains.[26] Some data are available about acid-peracid association.[27]

A suggested mechanism for epoxidation involving a 1,3-dipolar form of the peracid, $R\overset{+}{C}(OH)O\overset{-}{O}$, must be mentioned.[28] It is excluded by the main differences between epoxidation[1,2] and typical 1,3-dipolar addition reactions.[29,30] Firstly the effect of olefin substituents on reaction rate is opposite for the two types of reaction, and secondly 1,3-dipolar additions are characterised by large negative values for the entropy of activation (−45 to −35 e.u.) in contrast to lower values for epoxidation (−30 to −18 e.u.).

There have been some attempts to detect an "Olefin peracid" complex. A complex of stilbazole N-oxide and peroxyacetic acid has been isolated and described as the prototype for the transition state of the Prilezhaev reaction.[31] However its structure may be more complicated because of the ability of the highly polar $N \rightarrow O$ group to coordinate with the percarboxylic acid group. A complex of some sort was detected kinetically[32,33] in that reaction rate reaches a constant value on increase of olefin concentration in certain cases. This was explained in terms of the conversion of all peracid into the complex whose decomposition rate determined that for the formation of oxirane. The question to be settled is the nature of the complex formed.

The above considerations led to the conclusion that further investigations of the epoxidation reaction were needed to provide more information particularly in a wide range of media with proton acceptor properties. Complete analysis of competing reactions was also required, particularly the decomposition of peracid.

New approach to the mechanism of epoxidations. For the investigation of the reaction the following were used: peracids; perbutyric (**1**) perpropionic (**2**), peracetic (**3**), performic (**4**), perbenzoic (**5**), monochloroperacetic (**6**), monoperphthalic (**7**), and monopermaleic (**8**); olefins; allyl derivatives $-(XCH_2CH{=}CH_2)$ where X = −OEt, −OH, −OPh, $-CH_2Ph$, −Br, −Cl, $-CO_2Me$, 1,4-diethoxybut-2-ene, 3,5-dibromocyclopentene, styrene, and phenylcyclohexene.[10-13,34] The peracids (**1–4**) were obtained in concentrations 6.5–7.5 mole/l from the parent anhydrides (formylacetic anhydride in the case of **4**)[13] and concentrated hydrogen peroxide (95–97%) with the addition of catalytic quantities of sulphuric acid. The peracids (**5–8**) were obtained in concentrations: 3.5, 3.5, 7.0 and 8.0 mole/l respectively using small amounts of acetic acid as solvent.

The high concentration of peracids obtained meant that a wide range of concentrations (0.01–5 mole/l) could be obtained by dilution with the chosen solvent. The proton-donor-acceptor properties of the solution were varied over a wide range by mixing N,N-dimethylformamide (DMF), as basic solvent, with acetic acid in different ratios. Various organic solvents containing nitrogenous bases (urea, pyridine, DMF) or inorganic bases (Na_2CO_3, $NaHCO_3$, K_2HPO_4, NaOAc, etc.) were also used.

The reactions were followed by measurement of the consumption of starting materials (peracids and olefin) and formation of products (oxiranes and derivatives). Concentration of peracids were monitored iodometrically[35] while olefin, oxirane and by-products were determined chromatographically. Epoxidations were carried out in the temperature range 0–60°. Kinetic data were calculated by the standard differential method. Blank tests were carried out (without olefin) to allow for the contribution of spontaneous decomposition of peracid to its overall rate of consumption.

Epoxidation of the olefins $XCH_2CH{=}CH_2$ with peracetic (**3**) and permaleic (**8**) acids as well as allyl bromide with all peracids (**1–8**) in acetic acid solution proceeded normally with olefin consumption and oxirane formations obeying second order kinetics. Decomposition of the peracids (**3–8**) were not observed, but allyl bromide induced detectable decomposition of perbutyric (**1**) and perpropionic (**2**) acids (20–25%).

A satisfactory correlation was obtained between epoxidation rate constants and the Taft constants for substituents in peracid and olefin (Fig. 1). It should be noted that the sensitivity of the reaction rate to the olefin substituent decreases as the strength of the peracid as oxidant increases: for peracetic acid $\rho^* = -1.39$ for permaleic acid $\rho^* = -0.56$.

Additions of nitrogen containing organic bases (2–25 mol % with respect to peracid) led to a reduction in rate constant (Table 1), but contrary to literature data the activation energy was diminished and the entropy of activation became more negative. Dilution of the peracid solution had a similar effect and in the first stages of dilution (to peracid concentrations 1–2 mole/l) the greater the basicity of the solvent the more the activation energy decreased (Table 1). As will be shown later, further dilution gave an inverse dependence of the activation energy on solvent basicity.

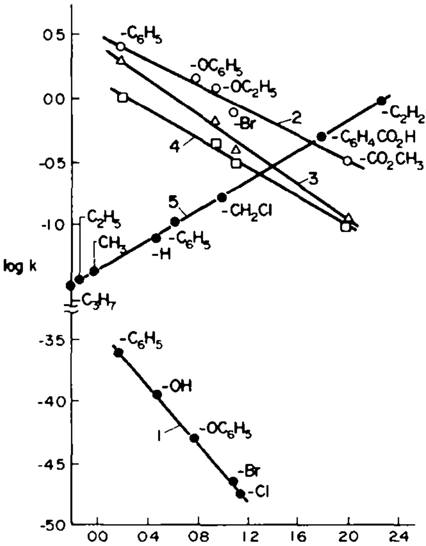
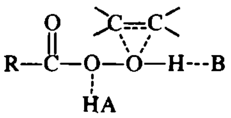


Fig. 1. Correlation of effective rate constants of epoxidation and peracid decomposition with Taft σ^* for the substituents X in olefins $XCH_2CH{:}CH_2$ and peracids X′COOOH. (1) epoxidation $XCH_2CH{:}CH_2$ with peracetic acid (30°, $\rho^* = -1.39$); (2) and (3) epoxidation of the olefins with permaleic acid (40°): (2) in acetic acid ($\rho^* = -0.56$), (3) in acetic acid with 4.6 mol. l^{-1} of DMF ($\rho^* = -0.74$); (4) decomposition of permaleic acid induced by the olefins ($\rho^* = -0.59$); (5) epoxidation of allylbromide with X′COOOH (HOAc, 40°, $\rho^* = 0.054$).

The decrease in reaction rate caused by addition of a proton acceptor (B) may be explained by the fractional negative charge on the oxygen in the H-bonded complex: $R\overset{O}{C}\text{–O–}\overset{\delta-}{O}\cdots H\cdots\overset{\delta+}{B}$. It is to be expected that some degree of freedom of the peracid molecule will be lost resulting in the more negative entropy of activation. Since the peracid molecule is broken in the course of the reaction into three fragments (RCO_2^-, O and H^+) the proton and anion acceptors (B and HA) will be included in the transition state.



Stabilisation of the anion is particularly important, nucleophilic substitution is known not to occur without solvation (protonation) of the leaving anions.[36]

The overall decrease in peracid activity on increase in basicity of the medium is shown in the correlation analysis whereby the reaction constant (ρ^*) for epoxidation with permaleic acid becomes more negative on addition of DMF (Fig. 1).

Further evidence for a base-peracid complex and bifunctional catalysis in the Prilezhaev reaction was provided by investigation of the following points:

(1) Inhibition of the spontaneous decomposition of peracids by olefins.

(2) Decomposition of peracids induced by olefins.

(3) Influence of the solvent on the reaction.

(4) Nature of the olefin-peracid complex and its mode of further transformation.

Influence of the olefin on the decomposition of peracids. Peracids are comparatively stable in acetic acid solution and in slightly acidified organic solvents, but dilution with basic solvents or addition of bases leads to appreciable decomposition which affects the kinetics of epoxidation. If the rate of epoxidation is relatively high the contribution from peracid decomposition is negligably small but in some cases it was observed that peracid decomposition occurred without epoxide formation. The mechanism of peracid decomposition has to be understood in order to interpret correctly the olefin-peracid interactions.

The rate of peracid decomposition increases as the basicity of the medium increases.[37–39] Two modes of decomposition are envisaged, the one involving general base-general acid catalysed formation of a cyclic diperoxide followed by collapse to two molecules of carboxylic acid and oxygen (Scheme 1) and the other unit rated by attack of peracid on peracid-base H-complex (Scheme 2)

In acetic acid–DMF mixtures we found that the decomposition of peracids is affected by the presence of olefins. Thus an olefin leads to substantial suppression of the spontaneous decomposition of the comparatively weak peracids (**1–6**) in acetic acid containing DMF (2.3 mole/l) (Fig. 2), i.e.

$$\frac{d[RCO_3H]blank}{dt} > \frac{d[RCO_3H]}{dt} - \frac{d[oxiran]}{dt}.$$

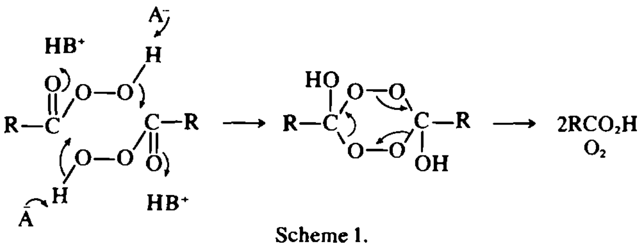
Table 1. Influence of the addition of bases on the kinetics of epoxidation in acetic acid

Peracid	Olefin	Addition[a]	$k.10^5$ $l.mol^{-1}.sec^{-1}$ 30°C	E_a $kcal.mol^{-1}$	$\Delta S^{‡}$ e.u.
CH_3CO_3H	$H_2C{:}CHCH_2Cl$	-	0.47	15.5	32.2
		DMF	0.28	12.3	42.8
	$H_2C{:}CHCH_2Br$	-	0.57	17.1	3.1
		DMF	0.42	14.1	38.2
		urea	0.60	14.4	35.9
	$H_2C{:}CHCH_2OC_6H_5$	-	1.45	17.8	29.8
		DMFA	1.10	13.2	31.4
	$H_2C{:}CHCH_2OH$	-	4.42	18.3	16.1
		DMF	2.60	15.6	27.6
		urea	3.36	16.2	2.5
$C_2H_5CO_3H$	$H_2C{:}CHCH_2Br$	-	0.52	17.8	
		DMF	0.30	16.4	
HCO_3H	$H_2C{:}CHCH_2Br$	-	0.97	17.4	
		DMF	0.64	15.5	
$C_6H_5CO_3H$	$H_2C{:}CHCH_2Br$	-	1.11	17.6	
		DMF	0.80	13.3	
$ClCH_2CO_3H$	$H_2C{:}CHCH_2Br$	-	2.78	12.1	
		DMF	2.19	9.0	
$HO_2CC_6H_4CO_3H$	$H_2C{:}CHCH_2Br$	-	4.87	18.3	
		DMF	3.48	14.9	
	$H_2C{:}CHCH_2Br$	-	8.87	18.3	
		DMF	5.95	12.2	
	$H_2C{:}CHC\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OCH_3}$ †	-	17.80	17.9	21.5
		DMF‡	0.925	10.7	47.7

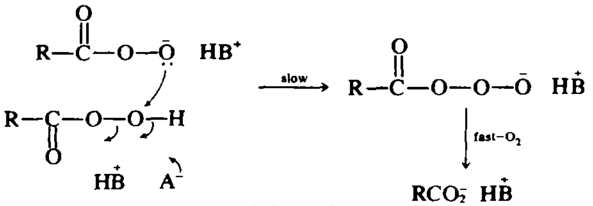
[a] Concentration of DMF 2.3 $mol.l^{-1}$, urea 1.5 $mol.l^{-1}$

† 50°C

‡ 7.6 $mol.l^{-1}$



Scheme 1.



Scheme 2.

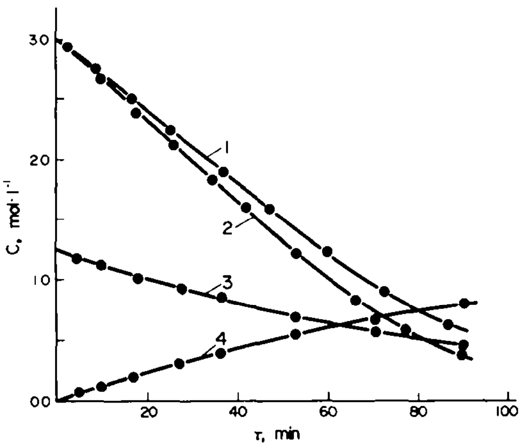


Fig. 2. Inhibition effect. Epoxidation of allyl bromide with peracetic acid in HOAc with addition of DMF (60°). (1) decomposition of the peracetic acid (blank), (2) peracid, (3) allyl bromide, (4) epibromohydrin.

The activation energies for decomposition of the peracids (1–3) are the same (within experimental error) in the presence or absence of allyl bromide and do not depend on the nature of the olefin present (Table 2). The peracids are thus decomposed in either case by a mechanism excluding olefin participation. The activation energies for decomposition were calculated using the difference in initial rates for peracid consumption and oxirane formation at four temperatures.

Table 2. Initial rate (Wo) and activation energy for the decomposition of peracetic acid in acetic acid with addition of DMF in the presence of olefins (40°)

Olefin	$W_o \cdot 10^4$ mol.l^{-1}.sec^{-1}	E_a kcal.mol^{-1}
CH_2:$CHCH_2Br$	0.33	23.3
CH_2:$CHCH_2OC_6H_5$	0.27	21.9
CH_2:$CHCH_2OC_2H_5$	0.17	22.5
Blank test	1.11	22.8

Initial concentrations: peracid-3, olefin-1.25

DMF - 2.3 mol.l^{-1}

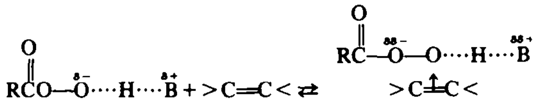
It can be seen (Table 2) that a decrease in the rate of decomposition of peracid (3) occurs as the reactivity of the olefin is increased, and in the case of allyl alcohol and allylbenzene peracid is only consumed by epoxidation.

How does the olefin retard the decomposition of the peracid? If the peracid and base are in equilibrium with an H-bonded complex: $R\cdot CO_3H + B \rightleftarrows RC\overset{\sigma-}{O}_3\cdots H\cdots \overset{\delta+}{B}$ (I) the influence of the olefin may be explained in two ways: (a) olefin coordinates with peracid, shifts the above equilibrium to the left and thereby reduces the importance of the catalyed decomposition of the H-bonded complex; (b) olefin associates according to its nucleophilicity with both free and complexed peracid thus preventing the "peracid-peracid" interaction.

On the basis of the first explanation (a) the reduction in epoxidation rate should not depend on the nature of the olefin when DMF is present in the reaction medium because the equilibrium (I) is rapidly established. But it was detected that the more effective inhibition of peracid decomposition by olefin, the more the epoxidation rate (k_{eff}) is reduced and consequently the more complete the association with complexed peracid.[12] For example, in the epoxidation of allyl chloride the rate (k_{eff}) is reduced on addition of DMF (2.3 mole/l at 20°) from 0.19×10^{-5} to 0.15×10^{-5} while for allyl benzene k_{eff} is reduced from 4.1×10^{-5} to 2.39×10^{-5} l mole^{-1} sec.$^{-1}$

So the olefin can associate with peracid in any form and generate some sort of labile complex in a concentration comparable to the initial reagents otherwise the decomposition process would not be so strongly effected. This complex may be considered as an electron-donor-acceptor complex (EDAC) (see below).

It is expected that attack of olefin on the peracid-base complex should be influenced by steric and electronic factors, and it seems to occur as a nucleophilic substitution of base by olefin.



$$R\overset{O}{\overset{\|}{C}}O-\overset{\delta-}{O}\cdots H\cdots\overset{\delta+}{B} + {>}C{=}C{<} \rightleftarrows \begin{matrix} R\overset{O}{\overset{\|}{C}}-\overset{\delta\delta-}{O}-O\cdots H\cdots\overset{\delta\delta+}{B} \\ {>}C\overset{\uparrow}{=}C{<} \end{matrix}$$

EDAC†

Autocatalysis by developing oxirane in the presence of nitrogenous bases is evidence for the olefin base competition. In this case the equilibrium concentration of the EDAC is apparently produced at a rate which limits the overall process.

In the presence of base it is considered that all peracid is complexed, and it is likely that a variety of species involving various degrees of proton transfer are present:

$$R\overset{\delta-}{C}O_3\overset{\delta+}{H}B;\quad R\overset{\delta\delta-}{C}O_3\cdots H\cdots\overset{\delta\delta+}{B};\quad R\overset{\delta\delta\delta-}{C}O_3-H\cdots\overset{\delta\delta\delta+}{B}$$

If an acid (AH) stronger than the peracid is in solution the following kinds of associations can be considered:[25]

$$RCO_3H\cdots A^-HB^+;\quad RCO_3H\cdots AH(A^-HB^+), \text{etc.}$$

Under such conditions the free peracid molecule would be a limiting structure.

In contrast to epoxidation with the peracids (1–6), epoxidation with permaleic acid containing DMF (2.2–3.8 mole/l) is accompanied by more pronounced decomposition of peracid than in the blank test (Fig. 3). The extent of peracid (VIII) decomposition increases as DMF concentration increases (Fig. 4) while in the absence of DMF, peracid (8) as well as (3–7) are consumed exclusively by epoxidation. As shown in Fig. 4, over the concentration ranges indicated the rate of decomposition of peracid (VIII) is first order in olefin concentration. Thus both olefin and DMF are included in the step responsible for peracid decomposition. Probably the olefin associated with peracid promotes the attack of a second peracid molecule (Scheme 2).

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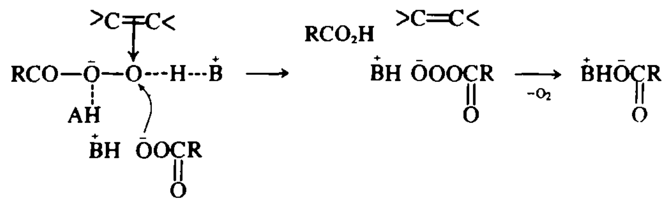
†We represent the complex as a π-complex although at the moment its precise structure is unknown.



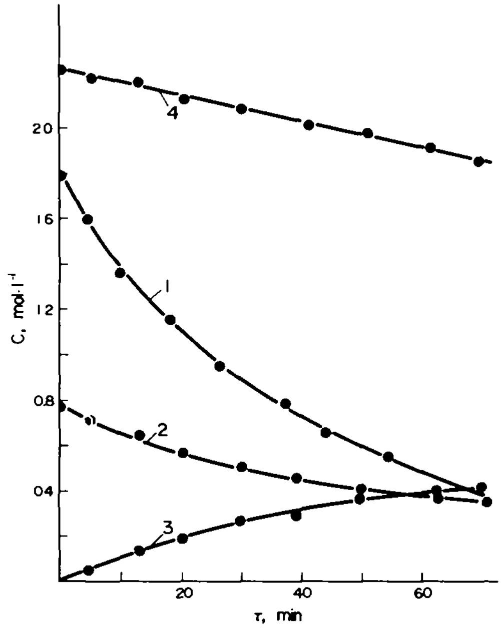


Fig. 3. Decomposition of permaleic acid induced by allyl bromide in acetic acid with addition of 2.3 mol. l^{-1} of DMF (50°). (1) peracid, (2) allyl bromide, (3) epibromohydrin, (4) peracid (blank).

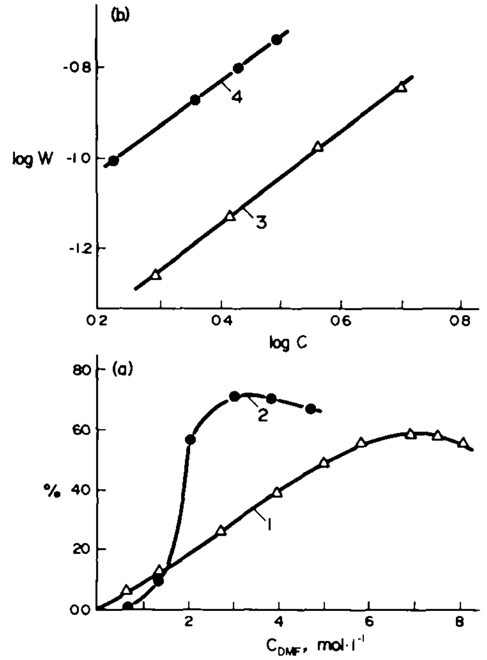


Fig. 4. (a) Dependence of permaleic acid decomposition on the DMF concentration in epoxidation of allyl bromide (1) and methyl methacrylate (2) at 30 and 40° respectively. (b) Order of decomposition of the peracid with respect to allyl bromide (3) and methyl methacrylate (4) in the same reaction.

However the olefin-peracid complex leads not only to peracid decomposition but also to oxirane formation since the yield of the latter does not equal zero when the DMF concentration tends to a maximum (Fig. 4).

Decomposition of the peracid (**8**) is observed only over a definite range of DMF concentration, and characterised by a maximum (Fig. 5) which indicates bifunctional catalysis of the reaction. The apparent rate constant for peracid (**8**) decomposition (k decomp) increases with increase in olefin nucleophilicity and correlates well with σ^* for the substituents (Fig. 1, $\rho^* = -0.592$, $r = 0.995$). This is an argument in favour of olefin participation in the paracid decomposition step. k_{dec} was determined according to the equation

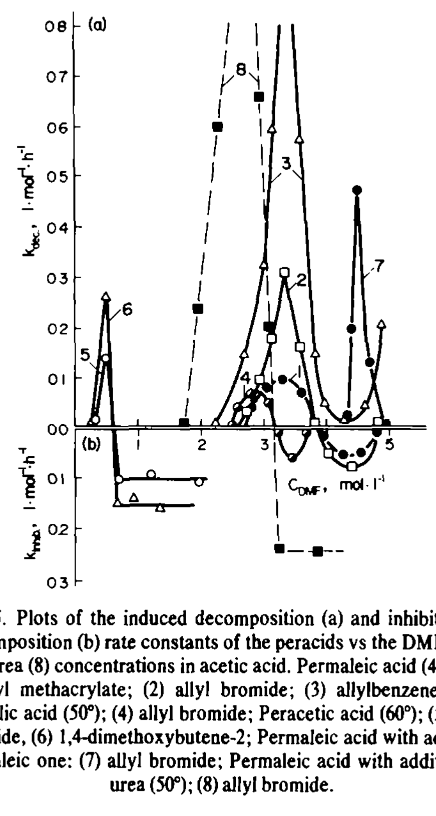


Fig. 5. Plots of the induced decomposition (a) and inhibition of decomposition (b) rate constants of the peracids vs the DMF (1–7) and urea (8) concentrations in acetic acid. Permaleic acid (40°): (1) methyl methacrylate; (2) allyl bromide; (3) allylbenzene; Perphthalic acid (50°); (4) allyl bromide; Peracetic acid (60°); (5) allyl bromide, (6) 1,4-dimethoxybutene-2; Permaleic acid with addition of maleic one: (7) allyl bromide; Permaleic acid with addition of urea (50°); (8) allyl bromide.

$$W_{\text{ind.dec}} = \frac{d[RCO_3H]\text{epoxid.}^{*}}{dt} - \frac{d[\text{oxirane}]}{dt} - \frac{d[RCO_3H]\text{blank}}{dt} = k_{\text{dec.}}\cdot[RCO_3H]\cdot[\text{olefin}].$$

If the DMF concentration is further increased (in the range 3.8–4.8 mole/l) the loss of active oxygen by peracid (**8**) is less than in the blank test, as is also the case for peracids (**1**–**6**). Apparent k inhibition was calculated in the same manner as induced decomposition:

$$W_{\text{inhibition}} = \frac{d[\mathrm{RCO_3H}]_{\text{blank}}}{dt} + \frac{d[\text{oxirane}]}{dt} - \frac{d[\mathrm{RCO_3H}]_{\text{epoxid}^{\text{n}}}}{dt}$$

$$= k_{\text{inhibition}}[\text{olefin}][\mathrm{RCO_3H}].$$

The region of inhibition of peracid (8) decomposition is also characterised by a maximum (Fig. 5) probably indicative of the most favourable conditions for decomposition of "olefin-peracid" complex with formation of oxirane because the rate constant for epoxidation is appreciably increased, for example in the case of allylbenzene from 1,6 (in the max of decomposition) to 2.25 l. $\mathrm{mol^{-1}\,hr^{-1}}$ (in the max of inhibition).

A correlation of the rate constants for epoxidation with σ^* for olefin substituents in both the maximum for decomposition ($\rho^* = -0.74$, $r = 0.971$) and inhibition ($\rho^* = -0.75$, $r = 0.989$). This points to a close connection between the two concurrent processes: epoxidation and induced decomposition of peracids.

For a number of peracids of lower electrophilicity; permaleic > monoperphthalic > peracetic acid the rate of induced decomposition is lower and the concentration interval over which it occurs becomes narrower (Fig. 5). However the range of inhibition of peracid decomposition is substantially expanded. In addition, the ability of induced decomposition of these peracids diminishes in the acetic acid-DMF system more quickly than the electrophilicity with respect to olefins. In accordance with the mechanism proposed (A) the rate equation for decomposition of the peracid is:

$$\text{Rate} = k[\text{olefin}][\mathrm{RCO_3H}\cdots\mathrm{B}][\mathrm{HA}].$$

The concentration of the base-peracid complex ($\mathrm{R{\cdot}CO_3H\cdots B}$) may be expressed as shown below since at least equimolar quantities of the parent acids ($\mathrm{RCO_2H}$) are present in the solutions and p*Ka* $\mathrm{R{\cdot}CO_3H}$–p*Ka* $\mathrm{RCO_2H}$ = 3.5

$$\mathrm{RCO_2H + B \overset{K'}{\rightleftharpoons} RCO_2H\cdots B}$$

$$\mathrm{RCO_3H + B \overset{K''}{\rightleftharpoons} RCO_3H\cdots B}$$

thus

$$[\mathrm{RCO_3H\cdots B}] = K''[\mathrm{RCO_3H}][\mathrm{B}] = \frac{K''}{K'}\cdot\frac{[\mathrm{RCO_3H}]\cdot[\mathrm{RCO_2H\cdots B}]}{[\mathrm{RCO_2H}]}$$

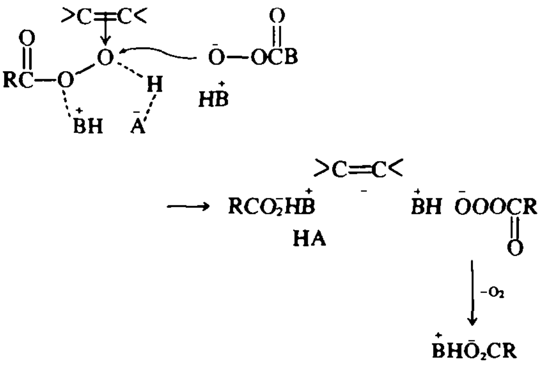
and

$$\text{rate} = k\cdot\frac{K''}{K'}\cdot[\text{olefin}]\cdot[\mathrm{RCO_3H}][\mathrm{RCO_2H\cdots B}].$$

This means that the rate of decomposition of the peracid is determined not only by the nature of the olefin and peracid but also by the concentration of [$\mathrm{RCO_2H\cdots B}$]. This conclusion is supported by the observation that if the reaction mixture is diluted (under conditions of maximum decomposition) by olefin or inert solvent to reduce the association, the extent of decomposition drops significtly (for methyl methacrylate from 78 to 10%). On the other hand, when acid is added to the mixture the decomposition maximum shifts into the region of higher base concentration ([$\mathrm{RCO_2H\cdots B}$] is increased) and decomposition becomes faster.

Addition of urea influences the kinetics of peracid decomposition in a similar way to DMF, but owing to the greater basicity of urea a lower concentration (2.4 mole/l) is needed to achieve the maximum induced decomposition.

On the base of these data it is suggested that the induced decomposition of peracids involves the complex:



Decomposition of the peracid is considered to involve O–O bond clearage at a stage before formation of the transition state leading to oxirane.

Decomposition of permaleic and perphthalic acids in ethyl acetate, t-butanol and dioxan on DMF addition is characterised by similar features to that in acetic acid (Fig. 6) although as the solvent basicity is increased the maximum in the rate of decomposition is reached at a lower DMF concentration and the activation energy of the process is less. It is concluded that the effects of base solvent and DMF addition are additive.

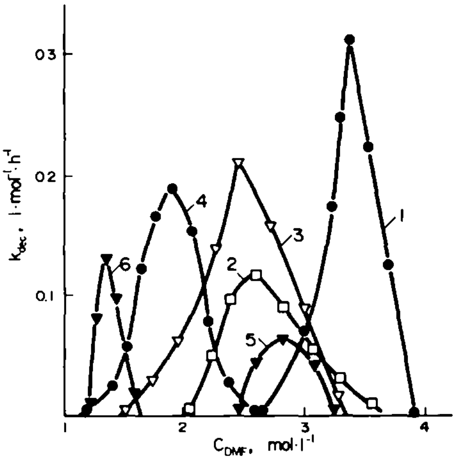


Fig. 6. Influence of solvent and DMF concentration on the decomposition of peracids induced by allyl bromide. Permaleic acid: (1) acetic acid; (2) ethyl acetate; (3) t-butanol; (4) dioxane; Perphthalic acid; (5) acetic acid; (6) t-butanol.

The effective activation energy for the induced peracid decomposition varies over the range 15.8–20 kcal/mole which indicates that the process is heterolytic. The absence of decarboxylation, which characterises the homolytic decomposition of peracids, was shown by a negative test for CO_2.

It is considered that the essential difference in the intensity of induced decomposition of the peracids (3, 7 and 8) is a consequence of specific solvation. The above mentioned decomposition of perbutyric and perpropionic acids induced by allyl bromide supports this view. On the other hand allyl bromide completely suppresses the spontaneous decomposition of permaleic acid induced by tetrahydrofuran. When the epoxidation is over the decomposition of peracid in the blank test is at a level of 25%.

3,5-Dibromocyclopent-1-ene and 1,4-dibromocyclohex-2-ene show a marked ability to initiate the decomposition of the peracids (3, 7 and 8).[40] In contrast to 1,4-dibromobut-2-ene and allyl bromide these cyclic olefins decompose the peracids almost completely (10% of the peracids are consumed by epoxidation). It may be that the orientation of reactants required for efficient orbital overlap in the transition state is more difficult for the cyclic olefins.

Attempts were made to study the behaviour of the peracids in systems containing a heterogenous base.[41] Addition of K_2HPO_4, KH_2PO_4, NaOAc, $NaOAc\cdot3H_2O$, Na_2CO_3, $Na_2CO_3\cdot5H_2O$ or $NaHCO_3$ to a solution of permaleic acid in ethyl acetate led to the expected acceleration in peracid decomposition (Table 4). Addition of allyl bromide to the solutions gave nearly complete inhibition in the peracid decomposition (Table 3). This gives support to the idea that an olefin can complex almost completely with peracid and prevent decomposition. In this case epoxidation rate usually increases or decreases. Thus the olefin does not attack an individual peracid molecule but its complex with the base; otherwise the rate of epoxidation would not depend on the kind of base added.

A marked initiation of decomposition of permaleic acid by olefin was observed in the presence of anhydrous Na_2CO_3. 1,3-Dichlorobut-2-ene also promoted marked decomposition of peracetic acid.

The information obtained about the interaction between peracids and olefins in both homogenous and heteregenous media allows one to conclude that induced decomposition is a feature of all the peracids (1–8) and that it is a function of the reagents and the acid base and solvation properties of the medium.

It is clear from Fig. 6 that a simple relationship between rate of peracid decomposition and solvent polarity is absent (the dielectric constants at 25° for dioxane, t-butanol, ethyl acetate, and acetic acid are 2.2; 12.2, 6.0 and 6.5 respectively).

Results obtained on the olefin induced decomposition of di- and tri-halogenoperacetic acids,[42] are also in full accord with suggestions made above.

Influence of solvent on the epoxidation reaction. The effect of solvent (nitromethane, nitrobenzene, benzene, acetonitrile, ethyl acetate, acetic acid -t-butanol, methanol, dioxane, DMF and tetrahydrofuran) on the rate of epoxidation of a number of olefins with permaleic, perphthalic and peracetic acids was investigated.[43] Solutions of the peracids were prepared by dilutions of the acetic acid solutions (5–6M) with the appropriate solvent in the ratio 1:1 and second order rate constants for epoxidation of allyl bromide were determined.

As the basicity of the solvent is increased the effective rate constant decreased in agreement with earlier observations on the effect of addition of N-containing bases (Table 1). The activation entropy also tends to a lower value. A satisfactory correlation between log k for epoxidation and p*Ka* of the solvent was observed (for peracetic acid $r = 0.951$, for permaleic and perphthalic ones $r = 0.952$).

The sensitivity of the reaction to medium basicity was observed to increase with the activity of the peracid: for 3, $\rho = -0.042$; 7, $\rho = -0.049$ and for 8, $\rho = -0.058$. Since the acidity of the peracids increases in this sequence, the effect of basic solvents in reducing epoxidation rate is thus caused by H-complex formation. If the rate decrease had been due to a lowering in the concentration of free peracid the correlation lines would have been parallel.

It was established that the effect of dilution with basic solvents is essential on the kinetics of epoxidation. Thus, epoxidation of allyl bromide with permaleic acid occurs almost instantaneously at 20° and is accompanied by a marked induced decomposition when the peracid concentration is greater than 5 mole/l. Dilution of peracid with nitromethane which is unable to solvate the peracid

Table 3. Effect of the buffer on the initial rate of decomposition of permaleic acid in the blank test (Wo) and rate constant of epoxidation of allyl bromide (k_o)

Buffer	W_o mol.l^{-1}.hour^{-1}	k_o l.mol^{-1}.hour^{-1}	Influence of the olefin on the peracid decomposition
-	-	1.61	-
K_2HPO_4	0.84	1.80	inhibition
NaOAc	14.40	0.69	"
$NaOAc.3H_2O$	0.14	0.25	"
KH_2PO_4	0.11	2.16	"
Na_2CO_3	0.33	0.38	initiation
$Na_2CO_3.5H_2O$	0. 1	1.87	inhibition
Na_2HCO_3	0.11	2.90	"
$Na_4B_xO_7.10H_2O$	-	2.80	"

40°C, solvent-ethylacetate ; initial concentrations: peracid -2, olefin -1 mol.l^{-1}; buffer - 1 mol per mol of the olefin.

effectively[25] leads to a reduction in the rate constant of epoxidation (Table 4) which tends to a constant value at high dilution (Fig. 7). The dilution effect is probably due to destruction of associations typical of hydroxylic compounds, and it indicates a relay mechanism for proton transfer to the leaving carboxylate ion.

Table 4. Effect of dilution on the kinetics of the epoxidation of allyl bromide with permaleic acid

Solvent	Peracid concentration mol.l^{-1}	k.10^4 l.mol^{-1}sec.$^{-1}$ 40°C	Ea kcal.mol^{-1}	$-\Delta S^{\ddagger}$ e.u
nitromethane	4.1	6.06	19	12.2
	2.8	4.20	16	22.6
	0.1	3.34	13.7	30.1
dioxane	4.6	3.12†	16.2	21.4
	2.9	1.05	15.5	26.8
	1.0	0.31	13.7	35.6

† 30°C

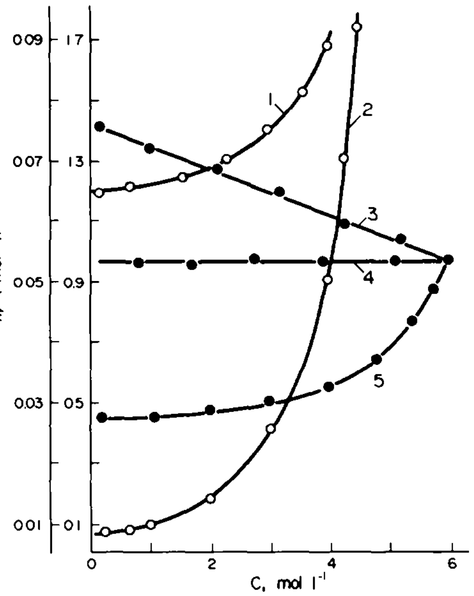
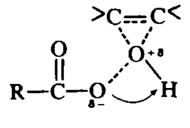


Fig. 7. Dependence of the rate constants for allyl bromide epoxidation on the peracid concentration (70°). Permaleic acid: (1) nitromethane; (2) dioxane; Peracetic acid (left scale): (3) benzene; (4) acetic acid; (5) DMF.

The epoxidation rate constant is reduced much more on dilution of permaleic acid solution with the basic solvent dioxan which is able to solvate the peracid.

Dilution of peracetic acid has an effect similar to that found for permaleic acid (Fig. 7) but dilution with the insert solvent benzene resulted in an increase in rate constant.

Extrapolation of the rate constants to infinite dilutions shows the effectiveness of the peracids under complete solvation. In an inert solvent the individual molecules of peracid can be considered as epoxidising agent as in the Bartlett mechanism, though it is also reasonable to assume proton transfer to the adjacent oxygen:



In the epoxidation of methyl methacrylate with peracetic acid an extreme dependance of the rate constant on DMF concentration is observed,[34] and is considered as evidence in favour of bifunctional catalysis of the reaction. A reaction which fails to proceed at significant rate under 40° in acetic acid is accelerated to a reasonable value on addition of DMF (2.3 mole/l). Addition of further DMF results in a reduction in rate.

The epoxidation of a polar double bond by a weak peracid (CH_3CO_3H) can be regarded as an intermediate case between typical epoxidation by peracids (electrophilic attack) and the epoxidation of α,β-unsaturated carbonyl compounds with hydrogen peroxide in the presence of bases (nucleophilic attack).[44]

On diluting the reaction mixture with solvent, the activation parameters are changed in the same way as for increase in medium basicity (Table 4). Apparently the destruction of the solvated aggregates lowers the probability of proton transfer to the leaving anion.

As it can be seen for example in the epoxidation of methylmethacrylate under high dilution conditions (0.2–0.4 mole/l), activation energy decreases with decrease in solvent basicity-dioxane, 19.2; ethyl acetate, 18.8; acetonitrile, 15.7; benzene 14.9 (kcal·mol^{-1}).[41] This dependence is in agreement with the earlier literature,[1,2] and is thus true only at relatively low reagent concentrations. In this region, second order kinetics for reactions of permaleic acid with relatively unreactive olefins (methyl methacrylate and allyl bromide) was only observed in the inert solvent (benzene). Other solvents which are capable of solvating the peracid lead to an autocatalytic consumption of reagents as in the case of base addition. It is considered that the formation of the olefin-peracid EDAC is in competition with specific solvation of the reagents and it occurs at a rate comparable with that of the overall process. It can be expected that the formation in the course of reaction of the parent acid reduces the solvation of peracid and shifts the equilibrium of EDAC formation to the right.

The olefin-peracid complex and its transformations. An investigation of the kinetics of epoxidation of methylmethacrylate, allyl bromide and allylbenzene with permaleic acid has been carried out over a wide range of concentration of olefin.[33,34,41] As was expected, for a large excess of olefin the rate of oxirane formation reached a constant value and was unaffected by further increase in olefin concentration (Fig. 8). It is considered that all per peracid is converted to olefin-peracid complex in the constant rate region and the overall reaction rate is then determined by the rate of transformation of complex (k).

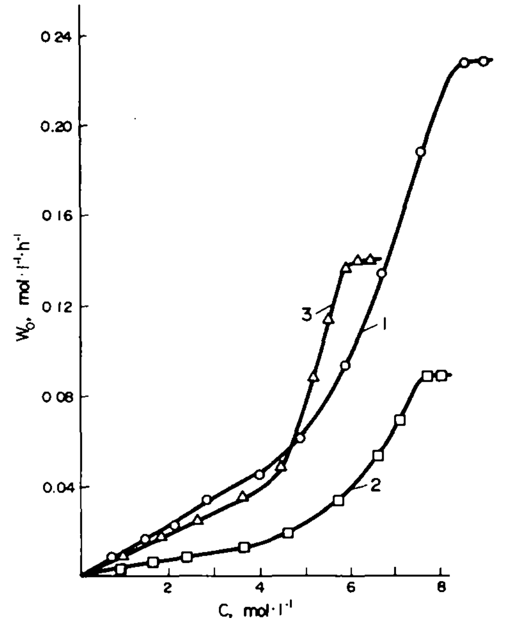
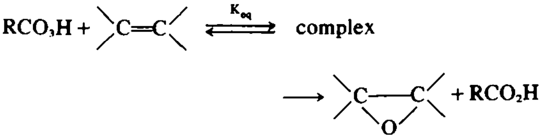
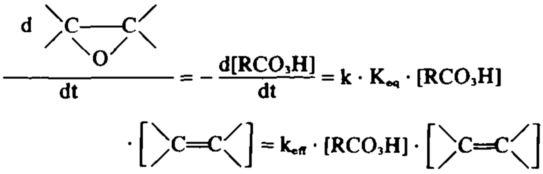


Fig. 8. Influence of the olefin concentration on the epoxidation rate with permaleic acid. (1) methyl methacrylate, 50°; (2) allyl bromide, 30°; (3) allylbenzene, 20°. Peracid concentration for every olefin is constant and consists 0.12, 0.07, 0.04 mol. l^{-1} respectively.

Further calculations were made on the basis that the rate of establishment of equilibrium (K_{eq}) is much greater than that of further transformation (k).



then



Knowing k_{eff} from experiments in which the reagent concentrations were of the same order K_{eq} was calculated (Table 5).

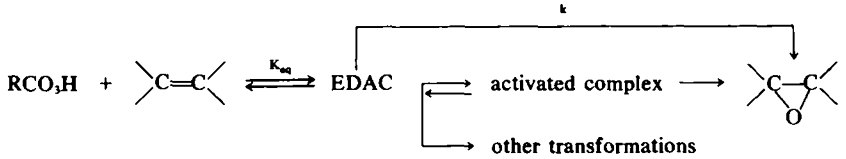
As shown in Fig. 8 the first order dependence on olefin is observed only up to 4–4.2 mole/l and then increases several fold. This indicates a non-stoichiometric solvation of the peracid by the olefin. The solvation is considered to lead to formation of an electron-donor-acceptor complex of the charge transfer type.[45] The low value of the activation energy for complex formation (3–5 kcal/mol^{-1}) supports its associative nature.

The activation energy for transformation of the EDAC to the final products is close to or even greater than E_{eff} (Table 5) confirming that it precedes the rate determining step. The scheme for expoidation can thus be presented in

Table 5. Kinetic and activated parameters of the formation of olefin-peracid EDAC (20–60°C)

Olefin	Solvent	Concentration of olefin (peracid) mol.l^{-1}	$k_{eff}.10^4$ l.mol^{-1} sec^{-1}	k.10^4 sec^{-1}	$K_{eq}.10^2$ EDAC l.mol^{-1}	E_a, kcal.mol^{-1}		
						eff.	eff. EDAC transf.	EDAC formation
methyl-metacry-late	ethylacetate	0.9 (0.9)	0.14			23.7		
		9.1 (0.11)		1.6	8.7		18.3	5.4
		0.31	0.031			18.8		
	dioxane	0.31	0.017			19.2		
	acetonitryl	0.31	0.70			15.7		
	benzene	0.31	4.21			14.9		
allyl-bromide	ethylace-tate	1.19 (1.06)	0.41			16.6		
		7.8 (0.065)		3.58	8.8		12.3	4.3
allyl-benzene	ethylace-tate	0.76 (0.66)	6.14			15.5		
		6.0 (0.05)		11.0	10.6		11.9	3.6

the following way:



Summarising the data about the influence of nucleophilicity of the olefin and nature of the proton donor–acceptor system on activation parameters, it can be concluded that variations of E_a are mostly determined by the EDAC formation step. The more intense and mobile the system of proton donor-acceptor bonds, the greater its sensitivity to temperature variations, and consequently the higher E_a. The highest E_a values are characteristic of concentrated peracid solutions. Dilution of the solution reduces H-bonding and in the case of basic solvents makes it "harder"—E_a is decreased. Under a high dilution E_a is greater for a basic solvent than for an inert one because of more intense H-bonding.

As the solvation shell of the reagents becomes more labile or partially destroyed, with temperature increase, the change of K_{eq} is often less marked in a higher temperature range so that the overall temperature coefficient of the reaction tends to reduce and a deviation from the Arrhenius low is observed.

Attempts were made to clarify the factors which control the course of the oxidation of olefins by peracids.[11,41] Carbonyl containing compounds and products of oxirane opening are often in the Prilezhaev reaction, and the former are the main products in oxidation of the phenyl substituted olefins.[46] It is not clear whether these carbonyl compounds are formed concurrently with the oxirane[47] or as a result of oxirane rearrangement.[48] We have studied a range of olefin (cyclohexene, 1-methylcyclohexene, 1-phenylcyclohexene, styrene, 1,4-dimethoxybut-2-ene, 1,3-dichlorobut-2-ene and 3,5-dibromocyclopent-1-ene) under conditions where such by-products are formed.

Aldehydes and ketones were only detected as primary reaction products in the case of the phenyl substituted olefins styrene and 1-phenylcyclohexene (Table 6). Kinetic plots for formation of products corresponded to a reaction first order in both olefin and peracid. The ratio of the rate of appearance of oxirane to that for the related carbonyl compound does not tend to zero at zero time (Fig. 9). This shows that both products are formed in parallel. In agreement, addition of styrene epoxide to the

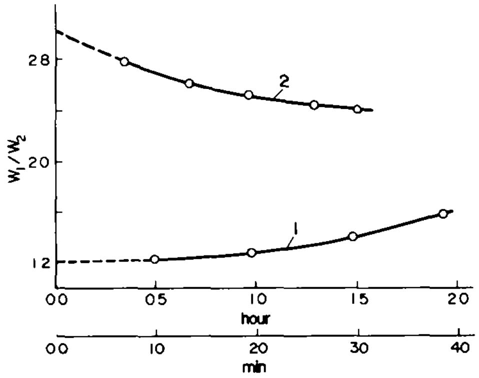


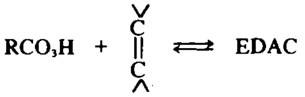
Fig. 9. Time dependence of ratio of the rates of oxirane (W_1) and oxo compound (Wo) formation in the oxidation of: (1) styrene, (2) (lower scale) 1-phenylcyclohexene.

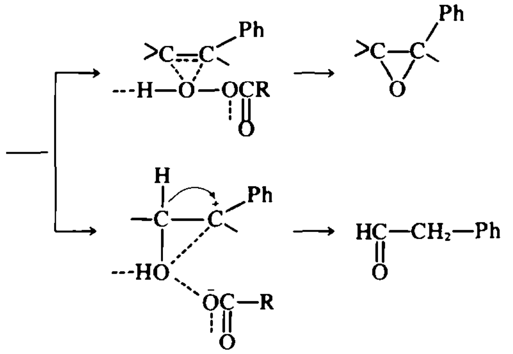
Table 6. Kinetic data for the oxidation of styrene and 1-phenylcyclohexene with peracids

Olefin	Peracid	Solvent	Reaction product	$k.10^4$ $l.mol^{-1}sec^{-1}$ 20°C	E_a $kcal.mol^{-1}$	$-\Delta S^{\ddagger}$ e.u.
styrene	peracetic	diethylether	phenylepoxyethan	1.53	13	31.5
			phenylacetaldehyde	1.0	21	5.0
	permaleic	diethylether	phenylepoxyethan	3.55	12.7	30.8
			phenylacetaldehyde	2.71	8.7	45.0
1-phenylcyclohexene	peracetic	ethylacetate†	1-phenyl-1,2-epoxycyclohexane	3.7	9.2	42.7
			1-phenyl-2-cyclohexanone	0.56	19.9	9.65
		DMF	1-phenyl-1,2-epoxycyclohexane	0.51		
			1-phenyl-2-cyclohexanone	0.38		
		diethylether	1-phenyl-1,2-epoxycyclohexane	4.45		
		tetrahydro furane	1-phenyl-1,2-epoxycyclohexane	3.47		
		ethylacetate	1-phenyl-1,2-cyclohexandiol	7.67		
	permaleic	ethylacetate	1-phenyl-1,2-epoxycyclohexane	27.4	7	41.6
			1-phenyl-2-cyclohexanon	7.9	14.8	14.0

† with addition of NaOAc

reaction mixture in the oxidation of styrene did not affect the initial rate of aldehyde formation. Because the activation parameters for the two parallel reactions are different, it is concluded that the oxirane and carbonyl compound are formed from different activated complexes which both arise from the olefin-peracid EDAC:


$$RCO_3H + >C{=}C< \rightleftharpoons EDAC$$



The extent of oxo compound formation is much less for the phenylcyclohexene reaction than for styrene (Table 6). Possibly the phenyl group and a double bond can less readily achieve coplanarity for the cyclic olefin, thus raising the activation energy for the carbonium ion like transition state leading to a ketone.

The data also indicate an influence of specific solvation on the course of the reaction. Thus the overall rate of oxidation of phenylcyclohexene is lower in tetrahydrofuran than in diethylether owing to the greater basicity of the former, but in contrast to ether, tetrahydrofuran promotes diol formation.

Oxiranes are the only products from the oxidation of cyclohexene and 1-methylcyclohexene with peracids (**3**, **7** and **8**). Additions of sulphuric acid promotes the formation of ring opening products but rearranged carbonyl compounds were absent. The dependence of the oxirane concentration with time does not show the maximum characteristic of an intermediate product in a consecutive process. In addition the initial rate of consumption of cyclohexene is much greater than that for epoxycyclohexane formation. Thus ring opened products can be produced not only by way of oxirane but also by direct attack on the peracid-olefin complex.

In a similar way the peculiarities of the oxidation of 3,5-dibromocyclopent-1-ene and 1,4-dibromocyclohex-2-ene[40] can be explained. The corresponding oxiranes are formed using peracetic acid in acetic acid (yields 35 and 20% respectively) or permaleic acid in ethyl acetate (50% yield). Dilution of the peracid solutions with diethyl ether, dioxan or THF etc accelerates the rate of overall reaction and leads mainly to the formation of ring opening products.

Since added oxiranes are quite stable to the reaction conditions it is considered that the products are obtained directly from the peracid-olefin complex.

Addition of trichloracetic acid accelerates the oxidation of dibromocyclopentene by peracetic acid but retards the reaction with permaleic one.

It may be concluded that the reaction of olefins with peracids in a number of cases is very sensitive (a) to the solvating properties of the medium and (b) to the ratio of acidic and basic components involved in bifunctional catalysis.

On oxidation of 1,3-dichlorobut-2-ene, 1,4-dimethoxybut-2-ene and allyl bromide with the peracids (**3** and **8**) oxiranes were the primary products of the reaction and they underwent further transformations in the presence of acid catalysts.

CONCLUSIONS

The epoxidation of olefins can be accompanied by two processes (i) the induced decomposition of the peracids and (ii) direct formation of rearranged products bypassing oxirane. These reactions depend on the nature of the olefin and the medium and are characterised by a polycentric mechanism: the reactants are associated in a donor-acceptor system leading to bifunctional catalysis which can influence the course of the reaction.

Dilution of the reaction mixture leads to destruction of the associations thus reducing the rate constant for oxidation.

Coordination of an olefin and peracid can lead to an electron donor-acceptor complex in concentrations comparable to that of the components. The olefin-peracid complex formation ("soft" interaction) is in competition with the formation of H-bonded complexes by peracid ("hard" interaction) and the balance is influenced by solvation effects. In certain circumstances the attainment of the equilibrium concentration of the olefin peracid complex is the rate determining process.

In a number of cases the olefin peracid coordination may either promote the oxidation of one peracid molecule by another (induced decomposition) or even inhibit this process (inhibition of peracid decomposition).

The olefin-peracid complex can, depending on the nature of the reagents and the medium, lead to more than one product determining transition state thus forming in competition with oxirane products of rearrangement and ring clearage.

The nature of the donor-acceptor bonding in the system has an important influence on the activation parameters for the pre-equilibrium step of olefin-peracid complex formation and on the overall process.

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