

Kinetics of Epoxidation of Alkyl Esters of Undecylenic Acid: Comparison of Traditional Routes vs. Ishii-Venturello Chemistry

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ABSTRACT: Epoxidation of undecylenic acid and its methyl and ethyl esters with aqueous H_2O_2 was carried out by using different traditional routes, ion exchange resin, and the newly developed synergistic usage of heteropoly acids and phase transfer catalysis in a biphasic system. The so-called Ishii-Venturello chemistry was employed to develop a kinetic model. Interesting selectivities are obtained. *JAOCS* 74, 397-497 (1997).

KEY WORDS: Catalysis, epoxidation, ethyl undecylenate, heteropoly acids, Ishii-Venturello chemistry, kinetics, methyl undecylenate, peroxyacetic acid, phase transfer catalysis, undecylenic acid.

Epoxidation of olefinic compounds leads to products that are commercially important and find application in several fields. Epoxides are raw materials for a wide variety of chemicals, such as glycols, alcohols, carbonyl compounds, alkanolamines, olefinic compounds and polymers like polyesters, polyurethanes, and epoxy resins. Epoxides undergo a variety of reactions of industrial relevance. These processes will undoubtedly become more important as new uses for epoxy plasticizers, stabilizers, elastomers, and surface-coating and curing agents are developed. Epoxides of long-chain olefins, oils, and esters have been commercially used as plasticizers and stabilizers for PVC resins to improve flexibility, elasticity, and toughness and also to impart stability of the polymer on exposure to heat and light.

The unsaturation present in fatty acids and their esters can be epoxidized to prepare a gamut of compounds that are both academically and industrially relevant. Epoxidation of different α - β unsaturated acids, such as maleic, fumaric and crotonic acids, has been carried out by using peroxyacids (1). Epoxides of various fatty acids, such as oleic acid, ricinoleic acid and their vinyl and alkyl esters, which have been used in plastic and resin industry, are prepared by using peroxyacetic acids or hydroperoxides. Derivatives of undecylenic acid find extensive uses; for instance, undecylenic epoxide polymers are used in the coating industry, while chloride, silicon, and sulfur derivatives are used as additives in the lubricant industry and bromo derivatives in the herbicide industry. Nonylic aldehyde, derived from undecylenic acid, is a constituent of

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rose and orange oil (2). A large number of derivatives are used extensively in perfumery. Undecanaldehyde is used in the modification of floral odors (3,4).

Undecylenic acid, with its ethylenic double bond at the terminal position, has different reactivity from other α - β -unsaturated acids. Published work has shown that epoxidation of α - β -unsaturated acids has found greater attention than the terminally unsaturated acids, such as undecylenic acid and its ester. Among the numerous approaches available for epoxidation, the processes involving organic peroxyacids and hydroperoxides, such as cumene hydroperoxide (CHP), *t*-butyl hydroperoxide (TBHP) and ethyl benzene hydroperoxide (EBHP), are by far the most important (5).

In light of these facts, epoxidation of undecylenic acid and its esters would definitely be interesting from the angle of selectivity engineering. The processes that have been used involve peroxy-carboxylic acids; the selectivities offered by them are low and also involve effluent problems. The kinetic and mechanistic aspects of newer routes of epoxidation of undecylenic acid and its esters have not been addressed in the literature.

The current investigation was therefore undertaken to study different traditional routes for epoxidation of undecylenic acid and its methyl and ethyl esters and their comparison with new routes, such as combination of phase transfer catalysis (PTC) and heteropolyacids (HPA), including mechanistic and kinetic interpretation. Instead of sulfuric acid, ion exchange resin was also used in a few experiments. Epoxidation with PTC/HPA and hydrogen peroxide is now called Ishii-Venturello synthesis. More emphasis was laid on the kinetic and mechanistic aspects of the PTC-catalyzed reactions.

LITERATURE REVIEW

There are several methods to prepare epoxy compounds, starting from (i) olefins, (ii) α -halocarbonyl compounds, (iii) carbonyl compounds, (iv) epichlorohydrin, and (v) substituted hydroxyl compounds, which are epoxidized by a number of agents. Excellent reviews are available in the literature: for instance, Swern (6) and Wilkinson (7). Recently, studies have been conducted with phase transfer-catalyzed epoxidation in the presence of heteropoly acids for α -olefins, such as 1-octene, by Duncan *et al.* (8).

Although the epoxidation process with peroxyacids has been extensively studied and often is the method of choice for laboratory-scale work, it has not been widely applied on a commercial scale. This may be partly due to the hazards associated with handling peroxyacids on an industrial scale. In these processes, the yield of epoxides is poor, especially when unreactive α -olefins are employed, and thus their scope is rather limited. On the other hand, catalytic epoxidation by organic hydroperoxides, such as CHP, TBHP and EBHP, possesses many advantages. Alkyl hydroperoxides are relatively easier to handle than organic peroxyacids. A wide variety of olefinic compounds has been epoxidized, including relatively unreactive α -olefin, by hydroperoxides. Moreover, acid-labile epoxides, such as epoxides of styrene, α -methyl styrene and α -pinene, which cannot be prepared satisfactorily with peroxyacids, have been prepared in excellent yields with hydroperoxides (9).

Of all methods, the following three were considered under the purview of this study: (i) preformed peroxyacetic acid as epoxidizing agent, (ii) *in situ*-generated peroxyacetic acid as epoxidizing agent, and (iii) phase transfer-catalyzed epoxidation with hydrogen peroxide and heteropoly acids. The reason for the above choices was as follows:

Industrially, various peroxyacids are available, such as peroxyacetic acid, peroxybenzoic acid, peroxyfluoroacetic acid, *m*-chloroperoxybenzoic acid and *m*-nitroperoxybenzoic acid, from which peroxyacetic acid was selected due to its easy availability, low price, high epoxidation efficiency, and reasonable stability at ordinary temperatures. Besides, epoxidation with peroxyacetic acid can be conducted in aqueous, nonaqueous, homogeneous, and heterogeneous media. However, the peroxyacetic acid has to be prepared separately and stored at low temperature to avoid hazards of its decomposition.

Using the *in situ*-generated peroxyacetic acid has certain advantages, such as minimum amounts of reactants are needed to prepare the epoxidizing reagent and convenient safe preparation and handling of peroxyacetic acid. Homogeneous acids, such as sulfuric acid and *p*-toluene sulfonic acid, can be avoided by using heterogeneous catalysts, such as ion exchange resins, which would avoid disposal of strong acids. The catalyst can be recycled, shows better selectivity, and avoids side reactions.

PTC epoxidations have caught attention due to excellent conversions and yields associated with the process. The reactions are conducted in a two-phase system (8,10–12). Phase transfer catalysts can be heterogenized, to make them reusable and to avoid disposal and effluent problems completely. Higher temperatures can be employed because all catalysts are stable at higher temperatures, resulting in higher conversions in less time and making the process commercially viable. The method has been reported to be excellent for unreactive α -olefins, which are difficult to epoxidize owing to heterogeneity of the reaction medium. However, the PTC method has not yet been studied for terminally unsaturated acids, such as undecylenic acid and its esters.

EXPERIMENTAL PROCEDURES

Chemicals and catalysts. Tricapryl methyl ammonium chloride (Aliquat 336) (AR grade) was obtained from SISCO Laboratories (Mumbai, India). Dodecatungstophosphoric acid (AR grade), 50% aqueous hydrogen peroxide (AR grade), and chloroform (AR grade) were obtained from s.d.Fine Chem (Mumbai, India). Glacial acetic acid was a laboratory-grade reagent. Undecylenic acid (98% pure) was obtained from M/s Jayant Oil Mills Ltd. (Bombay, India). HBr in acetic acid was obtained from S. Merck and diluted with acetic acid to prepare 0.1 N HBr. All other chemicals were obtained from reputed firms. Indion 130, a cation exchange resin catalyst, was obtained from Ion Exchange (India) (Mumbai, India).

Methyl undecylenate. Undecylenic acid was esterified with methanol to prepare the ester. Calculated quantities of undecylenic acid and alcohol were placed in an electrically heated three-necked flask, and the esterification was carried out under reflux with 1% *p*-toluene sulfonic acid as the catalyst. The reaction was continued for 3 h. The course of the reaction was followed by analyzing samples that were withdrawn periodically for acid value. At the end of the reaction, the catalyst was neutralized, and the excess alcohol was removed by distillation. The isolated ester was dried over anhydrous sodium sulfate and purified by distillation under reduced pressure.

Ethyl undecylenate. The same procedure as above was followed for the synthesis of ethyl undecylenate, except that the reaction was continued for 6 h.

Preformed peroxyacetic acid. The method reported by Schmitz and Wallace (13) was followed for the synthesis of preformed peroxyacetic acid: 300 g of glacial acetic acid, 3 g of concentrated sulfuric acid, and 34 g (0.5 mole) of 50% aqueous hydrogen peroxide were held at room temperature for 24 h. The solution contained 3.16 g (9.6%) of unreacted hydrogen peroxide and 33.1 g (87.2% conversion) of peroxyacetic acid. After 24 h, the sulfuric acid was neutralized with an equivalent amount of solid sodium acetate. The contents were then filtered to remove sodium sulfate. The peroxyacetic acid thus prepared was used for epoxidation.

Epoxidation with preformed peroxyacetic acid. Undecylenic acid or its esters (0.14 gmol) were put in a reactor, which was allowed to reach the desired temperature. Preformed peroxyacetic acid (70 g) was added to it. Samples were withdrawn periodically and analyzed for oxirane content and for unsaturation by iodine value (14) during the initial part of research. Confirmation was by gas chromatography (GC).

Epoxidation with in-situ preparation of peroxyacetic acid. The method reported by Swern (9) was used. The required amount of undecylenic acid or its esters was placed in the reactor mentioned above. Calculated amounts of acetic acid and H_2SO_4 were added, and the mixture was stirred for 30 min. The 30% aqueous solution of H_2O_2 was added dropwise by means of a dropping funnel for 30 min. After the addition was completed, the reaction was allowed to continue further for 6 h.

Calculated quantities of undecylenic acid or its esters and the acetic acid, containing H_2SO_4 in the mole ratio 1:0.5, were placed in the reactor. Aqueous H_2O_2 (30%) in the mole ratio 1:1.1–2 was added dropwise over 30 min. The reaction was continued further for 6 h. The course of reaction was observed by withdrawing hourly samples, which were extracted with diethyl ether, washed with water, and analyzed for oxirane oxygen by the standard AOCS method (14).

Epoxidation in presence of heteropoly acid and phase transfer catalysts (Ishii–Venturello chemistry). The organic phase, containing olefin, solvent chloroform and phase transfer catalyst, was heated initially to the desired temperature of 60°C . The time of addition of the aqueous phase, containing H_2O_2 and heteropoly acid, was considered zero time. Samples of the organic phase were withdrawn at a definite interval of time and analyzed by GC.

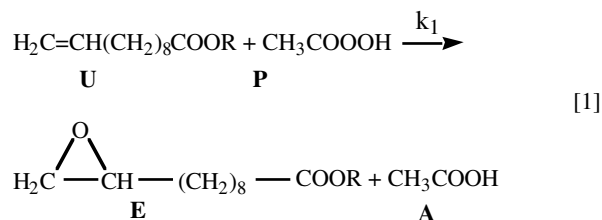
Analysis of the peracetic acid-catalyzed epoxidation. Analysis of the samples was carried out by using the AOCS method for oxirane oxygen (14).

PTC-catalyzed epoxidation. Analysis was performed on a Perkin-Elmer gas chromatograph (Model 8320) (Norwalk, CT) with a 2 m, 1/8" i.d., S.S. column packed with 5% OV-17 on Chromosorb WHP and coupled with a flame-ionization detector. Nitrogen was used as a carrier gas at 30 mL/min. Injector and detector temperatures were maintained at 300°C . Oven temperature was initially maintained at 150°C for 0.5 min and then increased to 300°C at a rate of $30^\circ\text{C}/\text{min}$. Quantitative analysis was done by using a synthetic mixture.

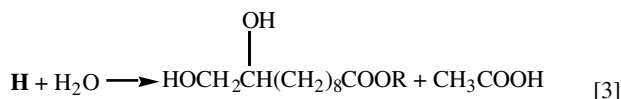
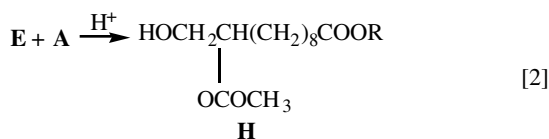
Product identification. Products of the reactions were identified from the retention times on the gas chromatograph by comparing them with corresponding available standards. GC–mass spectrometry was also done for typical reactions to confirm products.

RESULTS AND DISCUSSION

Peroxyacetic acid as epoxidizing species. Depending upon the purity of preformed peroxyacetic acid (dried before use) or the *in situ*-generated peroxyacetic acid, several products are likely to be formed.



The epoxide **E** is the desired product. The products of Reaction 1 are capable of further reaction if there is even a trace of H^+ ions, which might be there owing to the fact that peroxyacetic acid is formed from acetic acid and H_2O_2 with sulfuric acid as a catalyst.



where $\text{R} = \text{H}, \text{CH}_3$ or C_2H_5 .

Reactions 2 and 3 would become significant in the case of *in-situ*-formed peroxyacetic acid because free H^+ and water are available. Other possibilities are: (i) undecylenic acid + hydroxyacetate (**H**) leading to the corresponding ester; (ii) undecylenic acid + dihydroxy (terminal-glycol) undecylenic acid leading to monohydroxy ester; and (iii) dimerization of undecylenic acid, and possibly trimerization.

Depending on the relative rates of formation of the various products, the reaction mixture could contain several components. Reaction 1 produces the desired epoxide. It is apparent that Reactions 2 and 3 are consecutive reactions of the products of Reaction 1 due to acid catalysis and hydrolysis. If the preformed peroxyacetic acid is freed from H^+ ions and water, then the extent of Reactions 2 and 3 will be minimized. On the contrary, *in situ* formation of peroxyacetic acid in the reaction mixture will not be selective owing to the presence of H^+ ions and water of reaction. Published literature indicates that solid acid-catalyzed *in situ* peroxyacetic acid epoxidation (for instance ion exchange resins) would suppress Reactions 2 and 3 to some extent owing to the fact that the rate of formation of peroxyacetic acid, *in situ*, will be much greater than the reaction rate of Reaction 1. In homogeneous acid-catalyzed *in situ* peroxyacetic acid generation, free acid (H^+) is liberated, and also acetic acid is available for Reactions 2 and 3 to proceed. In the presence of solid acid catalysts at lower temperatures, Reactions 2 and 3 will be slower in comparison with the homogeneous sulfuric acid-catalyzed reaction, and hence, better selectivity to the epoxide will be realized.

As said earlier, undecylenic acid, methyl undecylenate, and ethyl undecylenate were epoxidized with peroxyacetic acid as epoxidizing species. The preliminary experiments showed that, with preformed peroxyacetic acid, the conversions and yields were higher than those with the *in situ* formed peroxyacetic acid.

Preformed peroxyacetic acid. Table 1 shows the data on epoxidation of undecylenic acid with preformed peroxyacetic acid at 25 and 35°C . At 25°C , the conversion was 68% of undecylenic acid after 6 h with an epoxide yield, based on initial undecylenic acid, of 47% and a selectivity of 92%, based on the conversion. At higher temperature, conversion is increased but the selectivity to epoxide suffers. The rate of reaction of undecylenic acid could be correlated by typical second-order kinetics as shown below:

$$\frac{-dC_u}{dt} = k_1 C_u C_p \quad [4]$$

TABLE 1
Epoxidation of Undecylenic Acid with Preformed Peroxyacetic Acid^a

Number	Time (min)	% Conversion by iodine value		% Yield of epoxide		% Selectivity	
		25°C	35°C	25°C	35°C	25°C	35°C
1	0	0	0	0	0	0	0
2	60	31	39	26	36	83	92
3	120	37	53	37	41	100	77
4	180	44	57	38	45	86	79
5	240	53	63	41	46	77	73
6	300	63	72	43	47	68	65
7	360	68	90	47	58	69	64

^aTypical reaction conditions: undecylenic acid: 0.13 mole; peroxyacetic acid: 0.14 mole; volume of reactants: 136 mL; concentration of undecylenic acid: 9.5588×10^{-4} gmol/cm³; concentration of peroxyacetic acid: 1.0294×10^{-3} gmol/cm³. % Conversion: (amount of olefin reacted)/initial amount of olefin) $\times 100$; % yield of epoxide: (amount of epoxide formed)/initial amount of olefin) $\times 100$; % selectivity: (amount of epoxide formed)/(amount of olefin reacted) $\times 100$.

which can be integrated to get

$$\ln \left[\frac{C_p C_{u,0}}{C_{p,0} C_u} \right] = \ln \left[\frac{(M - X_u)}{M(1 - X_u)} \right] = C_{u,0}(M - 1)k_1 t \quad [5]$$

$$= (C_{p,0} - C_{u,0})k_1 t$$

where C_p = concentration of peroxyacetic acid, C_u = concentration of undecylenic acid or its ester, M = the molar ratio $C_{p,0}/C_{u,0}$ at $t = 0$, $X_u = (C_{u,0} - C_u)/C_{u,0}$ = the fractional conversion of undecylenic acid or its ester.

Plots of $\ln[(M - X_u)/M(1 - X_u)]$ against time were made at 25 and 35°C (Fig. 1). The activation energy, calculated from the Arrhenius equation, for these two data points is 20.78 Kcal/gmole for the epoxidation of undecylenic acid. Because only two temperatures were used, this value should only be taken as representative.

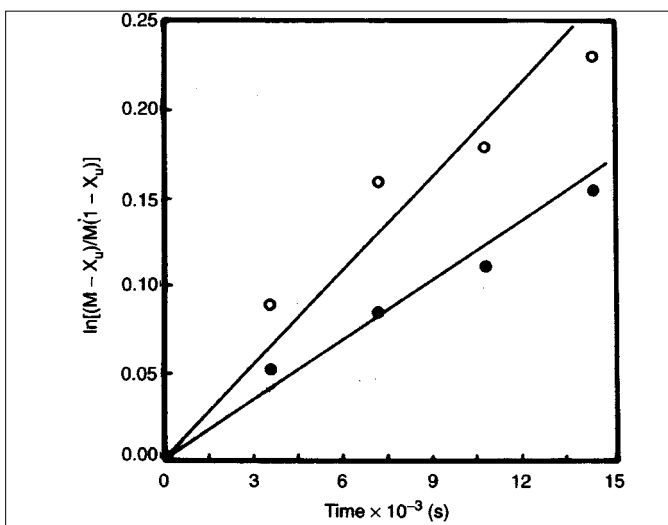


FIG. 1. Second-order kinetic plot for undecylenic acid epoxidation by preformed peroxyacetic acid: ○, 35°C; ●, 25°C.

TABLE 2
Epoxidation of Methyl Undecylenate with Preformed Peroxyacetic Acid^a

Number	Time (min)	% Conversion by iodine value		% Yield of epoxide		% Selectivity	
		25°C	35°C	25°C	35°C	25°C	35°C
1	0	0	0	0	0	0	0
2	60	39	42	28	35	72	83
3	120	46	51	38	50	83	98
4	180	58	61	51	55	88	90
5	240	67	70	65	58	97	83
6	300	79	77	76	60	96	78
7	360	85	82	81	61	95	74

^aTypical reaction conditions: methyl undecylenate: 0.13 mole; peroxyacetic acid: 0.14 mole; volume of reactants: 137 mL; concentration of methyl undecylenate: 9.489×10^{-4} gmol/cm³; concentration of peroxyacetic acid: 1.0218×10^{-3} gmol/cm³.

TABLE 3
Epoxidation of Ethyl Undecylenate with Preformed Peroxyacetic Acid^a

Number	Time (min)	% Conversion by iodine value (%)	% Yield of epoxide	% Selectivity
		0	0	0
2	60	28	21	75
3	120	31	30	96
4	180	37	35	94
5	240	46	45	97
6	300	52	50	96
7	360	55	53	96

^aTypical reaction conditions: ethyl undecylenate: 0.13 mole; peroxyacetic acid: 0.14 mole; volume of reactants: 141 mL; concentration of ethyl undecylenate: 9.219×10^{-4} gmol/cm³; concentration of peroxyacetic acid: 9.929×10^{-4} gmol/cm³.

Tables 2 and 3 contain the data for epoxidation of methyl undecylenate and ethyl undecylenate. Plots of $\ln[(M - X_u)/M(1 - X_u)]$ vs. time for the epoxidation of methyl and ethyl undecylenate are presented in Figures 2 and 3, re-

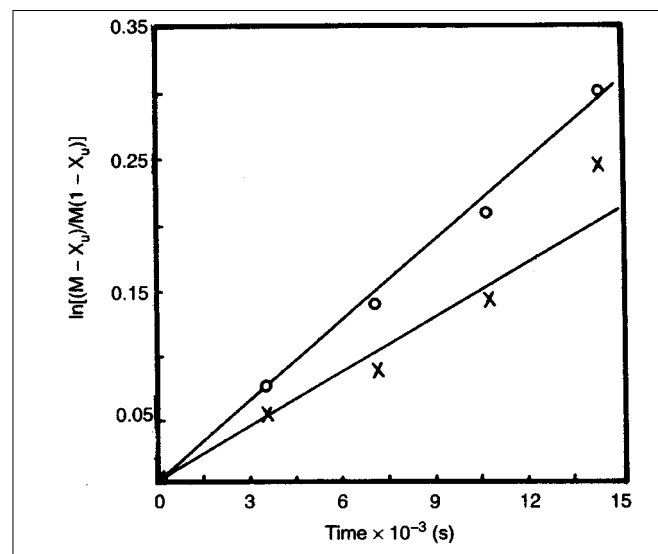


FIG. 2. Second-order kinetic plot for methyl undecylenate epoxide by preformed peroxyacetic acid: ○, 35°C; X, 25°C.

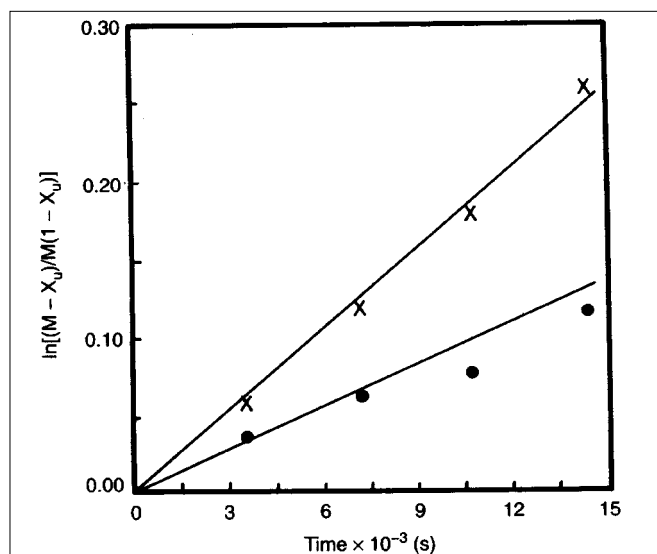


FIG. 3. Second-order kinetic plot for ethyl undecylenate peroxyacetic acid: X, 35°C; ●, 25°C.

TABLE 4
Kinetic Parameters for Epoxidation with Preformed Peroxyacetic Acid

Compound	Temp. (°C)	Slope (s ⁻¹)	k ₁ (cm ³ /gmol/s)	E _{act} (Kcal/gmol)
Undecylenic acid	25	6.282 × 10 ⁻⁴	0.06119	20.78
	35	9.166 × 10 ⁻⁴	0.08928	
Methyl undecylenate	25	9.772 × 10 ⁻⁴	0.09591	6.95
	35	1.231 × 10 ⁻³	0.12079	
Ethyl undecylenate	25	4.561 × 10 ⁻⁴	0.04607	15.34
	35	1.066 × 10 ⁻³	0.10771	
Butyl undecylenate	25	3.6342 × 10 ⁻⁴	0.03776	

spectively. The slopes of the above plots, rate constants, and the energy of activation are shown in Table 4, which also includes the rate constant for *n*-butyl undecylenate. The energy of activation values for Reaction 2 were calculated as 20.78, 6.95, and 15.34 Kcal/gmol for undecylenic acid, methyl undecylenate, and ethyl undecylenate, respectively.

The other important equations are:

$$\frac{dC_E}{dt} = k_1 C_u C_p - k_2 C_E C_A \quad [6]$$

$$\frac{dC_H}{dt} = k_2 C_E C_A - k_3 C_H C_W \quad [7]$$

$$\frac{dC_G}{dt} = k_3 C_H C_W \quad [8]$$

where k_1 , k_2 , k_3 = rate constants for formation of epoxide, hydroxyacetate, and 1,2-glycol, respectively.

From Equations 4 and 6, the concentration profile of the epoxide could be calculated:

$$\frac{dC_E}{-dC_u} = 1 - (k_2/k_1) \frac{C_E C_A}{C_u C_p} \quad [9]$$

Equation 9 requires a numerical solution. However, it is possible to use the rate data to calculate the value of k_2 . For instance, at 25°C, the k_2 value is 2.45 times k_1 for undecylenic acid, where k_2 incorporates the proton concentration (i.e., $k_2 = k_2^1 C_H^+$).

In situ peroxyacetic acid epoxidation. The *in situ*-generated peroxyacetic acid in the presence of sulfuric acid as catalyst was not as selective as the preformed peroxyacetic acid method for the epoxidation of undecylenic acid, methyl undecylenate, and ethyl undecylenate. Tables 5, 6, and 7 present the data. The conversions were obviously low for the reason already given before.

Peroxyacetic acid formation *in situ* is a bimolecular reaction whose mechanism is given by Swern (6).

Peroxyacetic acid preparation is represented by the mechanism shown in Scheme 1.

The rate constants for peroxyacetic acid formation are given by Swern (6). The concentration of peroxyacetic acid generated *in situ* cannot be built up due to the epoxidation reaction. Therefore, the peroxyacetic acid concentration is always lower than that of the preformed peroxyacetic acid method. This results in lowering the epoxidation reaction rate represented by Reaction 1. There is a substantial drop in selectivity of the epoxide due to the formation of by-products.

As delineated earlier, ion exchange resin-catalyzed *in situ*

TABLE 5
Epoxidation of Undecylenic Acid with *in situ* Peroxyacetic Acid^a

Number	Time (min)	% Conversion by iodine value			% Yield of epoxide			% Selectivity		
		35°C	40°C	60°C	35°C	40°C	60°C	35°C	40°C	60°C
1	0	0	0	0	0	0	0	0	0	0
2	60	16	21	23	4	6	8	25	28	32
3	120	27	33	37	7	12	11	26	36	30
4	180	33	44	45	8	13	13	24	29	29
5	240	39	48	50	9	15	16	23	31	32
6	300	44	56	58	10	17	18	23	30	31
7	360	48	60	72	11	19	21	23	31	35

^aTypical reaction conditions: undecylenic acid: 0.217 mole; acetic acid: 0.106 mole; sulfuric acid: 0.0037 mole; 30% aqueous hydrogen peroxide: 0.267 mole; volume of reactants: 44 mL.

TABLE 6
Epoxidation of Methyl Undecylenate with *in situ* Peroxyacetic Acid^a

Number	Time (min)	% Conversion by iodine value			% Yield of epoxide			% Selectivity		
		35°C	40°C	60°C	35°C	40°C	60°C	35°C	40°C	60°C
1	0	0	0	0	0	0	0	0	0	0
2	60	12	21	23	7	7	12	58	33	52
3	120	21	35	35	8	11	13	38	31	37
4	180	28	46	47	9	12	16	32	26	34
5	240	31	53	51	9	14	18	29	26	35
6	300	32	58	59	12	15	19	38	26	32
7	360	35	62	76	14	16	20	40	26	26

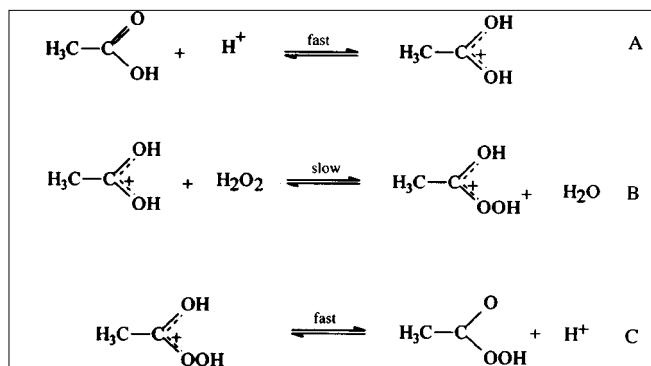
^aTypical reaction conditions: methyl undecylenate: 0.217 mole; acetic acid: 0.106 mole; sulfuric acid: 0.0037 mole; 30% aqueous hydrogen peroxide: 0.267 mole; volume of reactants: 45 mL.

epoxidation was also conducted at 60°C (Table 8). Conversions and selectivities of undecylenic acid and its methyl and ethyl esters were then 53, 42, 48, 43, 71, and 97%, respectively. The resin catalyst required higher temperatures for quantitative conversions in comparison with the homogeneous catalysts.

Synergism of HPA and PTC: Ishii–Venturello chemistry of epoxidation. PTC reactions have pervaded all sectors of synthetic chemistry. Synergism of phase transfer catalysis and tungstate and phosphate (arsenate) ions under acidic conditions for the oxidation of olefins, alcohols, and diols with dilute H₂O₂ has been achieved in the laboratories of Venturello *et al.* (10) and Venturello and Ricci (11) and Ishii *et al.* (16). Venturello and coworkers (10,11,15) demonstrated that olefins can be epoxidized with dilute H₂O₂ (<10%) with high selectivity to epoxide (80–90%) in short times under mild conditions.

We report here on the genesis of Ishii–Venturello chemistry that involves the use of HPA, H₂O₂ and PTC, which was useful in the interpretation of rate data in the present studies.

The highly selective epoxidation of terminal alkenes by the complex W^{VI}/P^V/H₂O₂/CHCl₃/PTC, which is called Ishii–Venturello chemistry, has been extensively investigated by several groups and was recently commercialized. There are contradictory reports about the basic mechanism, and two schools of thought have emerged. According to the general



SCHEME 1

concept of PTC, various steps in this system are given in Scheme 2 as proposed by Ishii's group.

Recently, Duncan *et al.* (8) from Hill's group have thoroughly investigated 1-octene conversions and 1,2-epoxyoctane selectivities under biphasic conditions. H₂O₂/1-octene in CHCl₃, with 21 polyoxometalates and cetylpyridinium chloride as the PTC, including the Ishii precursor complex [PW₁₂O₄₀]³⁻, were used to establish that only [PW₁₂O₄₀]³⁻ and [PW₁₁O₃₉]³⁻, which rapidly form the polyperoxometalate {PO₄[WO(O₂)₂]₄}³⁻, are the effective species. Further, the only dominant side reaction is H₂O₂ disproportionation to water and O₂. The structure of this complex polyperoxophosphotungstate (ES) is given in Figure 4. Kinetic and spectroscopic studies have shown that both a PW₄ and a PW₃ species are formed initially, and one PW₂ species subsequently, in the reaction. Here, PW_n (n = 2, 3, 4) stands for PW_nO_x, and these

TABLE 7
Epoxidation of Ethyl Undecylenate with *in situ* Peroxyacetic Acid^a

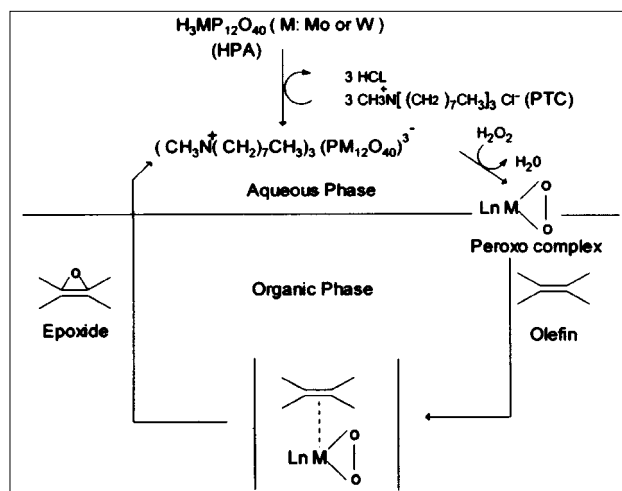
Number	Time (min)	% Conversion	% Yield	% Selectivity
		by iodine value 60°C	of epoxide 60°C	60°C
1	0	0	0	0
2	60	21	10	47
3	120	30	14	46
4	180	35	20	57
5	240	45	21	46
6	300	52	24	46
7	360	55	25	45

^aTypical reaction conditions: ethyl undecylenate: 0.217 mole; acetic acid: 0.106 mole; sulfuric acid: 0.0037 mole; 30% aqueous hydrogen peroxide: 0.267 mole; volume of reactants: 49 mL. Temperature: 60°C.

TABLE 8
Epoxidation with Ion Exchange Resin (Indion 130)^a

Compound	Conversion (%)	Yield (%)	Selectivity (%)
Undecylenic acid	53	23	43
Methyl undecylenate	42	30	71
Ethyl undecylenate	48	47	97

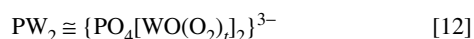
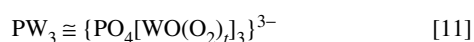
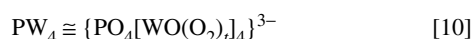
^aTypical reaction conditions: undecylenic or its ester: 0.217 mole; acetic acid: 6.4 g, 0.106 mole; Indion 130: 1% on total weight of reactants; 30% aqueous hydrogen peroxide: 30 g, 0.267 mole; concentration of undecylenic acid or its ester: 4.428 × 10⁻³ mole; time: 6 h.



SCHEME 2

are called subsequent peroxo species (SPS). The reader should refer to the excellent work by Duncan *et al.* (8) to understand the details of this mechanism.

Duncan *et al.* (8) have not given any direct structure of any of the species PW_4 , PW_3 , and PW_2 except the comment that these species are capable of coordinating with quaternary cation Q^+ . Further, in the case of PW_4 , it is expected that three of the tungsten sites remain seven-coordinated and the fourth does not, meaning that the latter must find a ligand in the reaction mixture to obtain coordinate saturation. It is inferred in the current work that the PW_4 , PW_3 , SPS are likely to be:



The value of t is most probably 1. These are all incidentally represented by Duncan *et al.* (8) as $\{P_q W_r O_s (O_2)_t\}^{y-}$.

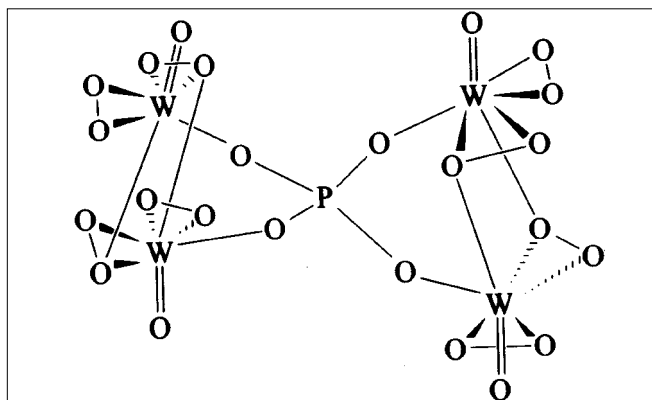


FIG. 4. Molecular structure of active species in Ishii-Venturello epoxidation (Duncan *et al.*, Ref. 8).

The most important inference which can be drawn for the current work is that the quaternary salt of all SPS species is Q_3 SPS and mainly Q_3PW_4 because PW_4 is the dominant species.

The polytungstophosphate formations depend on the ratio $[H_2O_2]/\{H_3[PW_{12}O_{40}]\}$. Addition of H_2O_2 to the HPA solution leads to formation of a number of unidentified species, and at least 50 equivalents of H_2O_2 are required to form the epoxidizing species $\{PO_4[WO(O_2)_2]_4\}^{3-}$, which is designated as ES.

In the epoxidation reaction, the quaternary salt of the epoxidizing species ES requires 1 equivalent of olefin. The quaternary salt Q_3ES contains 8 equivalents of peroxide. The species formed upon transfer of 1 equivalent of active oxygen is likely to be not only epoxidation-competent but also optionally situated to regenerate Q_3ES in the presence of H_2O_2 . The reaction of terminal olefin with Q_3ES produces the epoxide and the quaternary salts of the inorganic species PW_4 , PW_3 , and PW_2 . As said earlier, these are called the "subsequent peroxo species" (SPS) in the form of Q_3SPS . Q_3SPS reacts with 1 equivalent of H_2O_2 to partially regenerate Q_3ES and 50 equivalents of H_2O_2 to completely regenerate Q_3ES .

Duncan *et al.* (8) have also proved that the species Q_3SPS is capable of epoxidation of 1-octene, but the rates are 13% of those with Q_3ES .

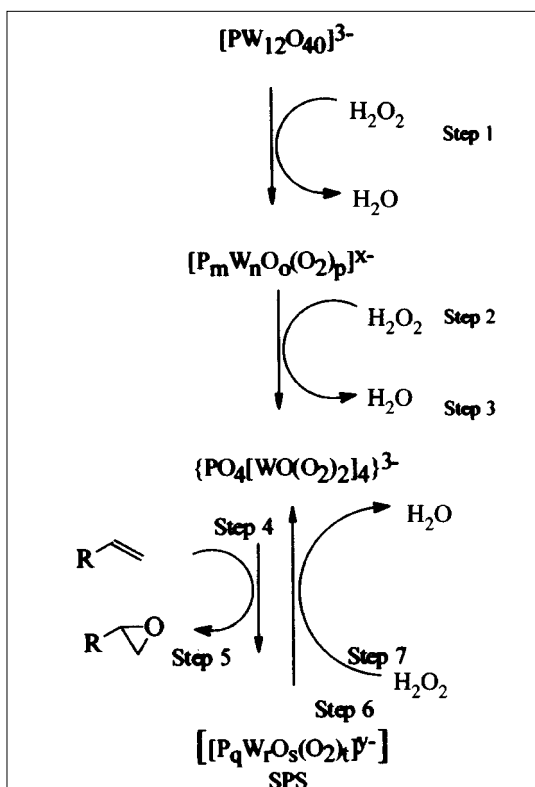
The coordination number of W is 5 (distorted pentagonal bipyramidal) in ES, and also probably in SPS. Both PW_4 and PW_3 species are formed upon transfer of oxygen from ES to olefin. Thus, the value of r in the SPS formula $\{P_q W_r O_s (O_2)_t\}^{y-}$ is primarily 4 or 3 and to a lesser extent 2. Species PW_4 , PW_3 , and PW_2 SPS readily convert back to ES under turnover conditions (i.e., biphasic with aqueous H_2O_2 present), and ES is by far the dominant polytungstophosphate present under such conditions. The necessary implication is that the reoxygenation of PW_4 , PW_3 , and PW_2 by H_2O_2 is faster than epoxidation by ES.

The exact stoichiometry of transformation of $H_3PW_{12}O_{40}$ into the epoxidizing species ES, $\{PO_4[WO(O_2)_2]_4\}^{3-}$, in the presence of H_2O_2 is not precisely known. However, Duncan *et al.* (8) in their pioneering work mention that the molar ratio of H_2O_2 and $H_3PW_{12}O_{40}$ is very important and that at least 25 equivalents of H_2O_2 are required to form $Q_3^+[ES]^{3-}$ in appreciable quantities, and that beyond 50 equivalents of H_2O_2 , the $Q_3^+[ES]^{3-}$ salt is quantitatively prepared after 1 h reaction. It is therefore necessary to use a large excess of H_2O_2 over $H_3PW_{12}O_{40}$ in reaction with α -olefins. The current work followed the same principle for epoxidation of undecylenic acid esters.

REACTION MECHANISM AND FORMULATION OF KINETIC EQUATION

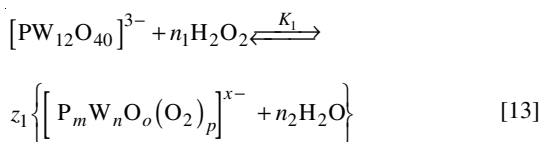
As given in Scheme 3, the following steps are envisaged.

(i) Reaction between dodecatungstophosphoric acid $[H_3PW_{12}O_{40}]$ and H_2O_2 in the aqueous phase to generate an



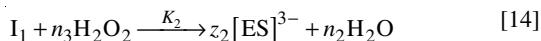
SCHEME 3

intermediate species, I_1 , namely $\{P_m W_n O_o (O_2)_p\}^{x-}$:

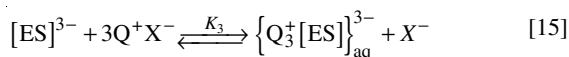


where z_1 , n_1 , and n_2 are stoichiometric coefficients.

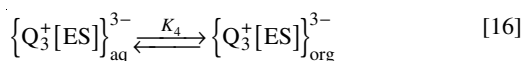
(ii) Reaction of intermediate I_1 with H_2O_2 subsequently to produce the epoxidizing species, ES, namely, $\{PO_4[WO(O_2)_2]_4\}^{3-}$:



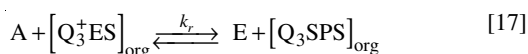
(iii) Ion pair formation of ES with quaternary salt QX present in the aqueous phase:



(iv) Transfer of ion pair $\{Q_3^+[ES]\}_{aq}^{3-}$ to the organic phase:

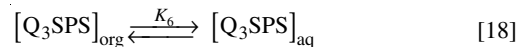


(v) Reaction of $\{Q_3^+[ES]\}_{org}^{3-}$ with the olefin, 1-alkene (A), to give the epoxide (E) and the subsequent peroxy species:

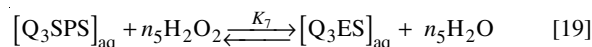


where $[Q_3SPS]$ is the representative of PW_4 (mostly) and, to a lesser extent, of PW_3 and PW_2 .

(vi) Transfer of $[Q_3SPS]_{org}$ to the aqueous phase:



(vii) Reaction of $[Q_3SPS]_{aq}$ with H_2O_2 to regenerate $[Q_3ES]$:



where n_5 is mostly 2. Thus, the catalytic cycle is complete, which is shown pictorially in Scheme 2.

Because the rates of steps 13, 14, 16, 18, and 19 are assumed to be much greater than the reaction of the olefinic compound in the organic phase given by step 17, the overall rate of epoxidation is given by:

$$r_E = \text{rate of epoxidation} = k_r C_{A,org} C_{[Q_3ES]_{org}} \quad [20]$$

It is necessary to find the concentration $C_{[Q_3ES]_{org}}$ from equilibrium considerations. Except step 17, all other steps are in pseudoequilibrium. Thus,

$$K_1 = [I_1]^{z_1} / [HPA][H_2O_2]^{n_1} \quad [21]$$

$$K_2 = [ES]^{z_2} / [I_1][H_2O_2]^{n_3} \quad [22]$$

Now all concentrations are denoted by brackets.

The net rate of formation of $[Q_3ES]_{aq}$ (Equations 15, 16, 19) is:

$$\begin{aligned} r_{[Q_3ES]_{aq}} &= k_3 [ES][QX]^3 - k'_3 [Q_3ES][X^-] - k_4 [Q_3ES]_{aq} \\ &\quad + k_4 [Q_3ES]_{org} + k_7 [Q_3SPS]_{aq} [H_2O_2]^{n_5} - k'_7 [Q_3ES]_{aq} \\ &= 0 \text{ at equilibrium} \end{aligned} \quad [23]$$

The net rate of formation of $(Q_3ES)_{org}$ (Equation 16) is:

$$r_{[Q_3ES]_{org}} = k_4 [Q_3ES]_{aq} - k'_4 [Q_3ES]_{org} = 0 \text{ at equilibrium} \quad [24]$$

Therefore,

$$[Q_3ES]_{org} = k_4 / k'_4 [Q_3ES]_{aq} = K_4 [Q_3ES]_{aq} \quad [25]$$

The net rate of formation of $[Q_3SPS]_{aq}$ (Equations 18 and 19) is:

$$\begin{aligned} r_{[Q_3SPS]_{aq}} &= k_6 [Q_3SPS]_{org} - k'_6 [Q_3SPS]_{aq} \\ &\quad - k_7 [Q_3SPS]_{aq} [H_2O_2]^{n_5} + k'_7 [Q_3ES]_{aq} = 0 \end{aligned} \quad [26]$$

The net rate of formation of $(Q_3SPS)_{org}$ is:

$$r_{[Q_3SPS]_{org}} = -k_6 [Q_3SPS]_{org} + k'_6 [Q_3SPS]_{aq} = 0 \quad [27]$$

Therefore,

$$[Q_3SPS]_{org} = [Q_3SPS]_{aq} / K_6 \quad [28]$$

From Equation 26, the following is obtained by substituting for $[Q_3SPS]_{org}$ from Equation 28:

$$(k_6[Q_3SPS]_{aq}/K_6) - k'_6[Q_3SPS]_{aq} - k_7[Q_3SPS]_{aq}[H_2O_2]^{n_5} + k'_7[Q_3ES]_{aq} = 0$$

and

$$[Q_3ES]_{aq} = k_7[Q_3SPS]_{aq}[H_2O_2]^{n_5} \quad [29]$$

From addition of Equations 23 and 24, 26 and 27, the following is obtained:

$$k_3[ES][QX]^3 - k'_3[Q_3ES]_{aq}[X^-] = 0 \quad [30]$$

i.e.,

$$[Q_3ES]_{aq} = k_3[ES][QX]^3/k'_3[X^-] = K_3[ES][QX]^3 \quad [31]$$

But

$$[Q_3ES]_{org} = K_3K_4[Q_3ES]_{aq} = K_3K_4[ES][QX]^3 \quad [32]$$

$$[ES]^{Z_2} = k_2[I_1][H_2O_2]^{n_3} \quad [33]$$

$$[ES]^{Z_2} = k_2\{k_1[HPA][H_2O_2]^{1/Z_1}[H_2O_2]^{n_3}\} \quad [34]$$

Because from Equation 21,

$$[I_1]^{Z_1} = K_1[HPA][H_2O_2]^{n_1} \quad [35]$$

Thus,

$$[ES] = [K_2\{K_1[HPA][H_2O_2]^{n_1}\}^{1/Z_1}[H_2O_2]^{n_3}]^{1/Z_2} \quad [36]$$

Substituting for ES in Equation 32, we find:

$$\begin{aligned} [Q_3ES]_{org} &= K_3K_4[QX]^3\{K_1K_2[HPA][H_2O_2]^{n_1}\}^{1/Z_1}[H_2O_2]^{n_3}]^{1/Z_2} \\ &= K_{eqbm}[QX]^3[HPA]^{1/Z_1Z_2}[H_2O_2]^{(n_1/Z_1+n_3/Z_2)} \\ &= K_{eqbm}[QX]^3[HPA]^\alpha[H_2O_2]^\beta \end{aligned} \quad [37]$$

where $\alpha = 1/Z_1Z_2$ and $\beta = n_1/Z_1 + n_3/Z_2$.

Thus, the rate of epoxidation after substitution in Equation 20 becomes

$$r_E = k_r K_{eqbm} C_{A,org} [QX]_{aq}^3 [HPA]^\alpha [H_2O_2]_{aq}^\beta \quad [38]$$

The total quantity of PTC added to Q_0 is distributed between the aqueous and organic phases:

$$\begin{aligned} Q_0 &= Q_{org} + Q_{aq} = [Q_3ES]_{aq} V_{aq} + [Q_3ES]_{org} V_{org} + [Q^+X^-]_{org} V_{org} \\ &\quad + [Q_3SPS]_{org} V_{org} + [Q_3SPS]_{aq} V_{aq} + [Q^+X^-]_{aq} V_{aq} \end{aligned} \quad [39]$$

$$\begin{aligned} Q_0 &= \{[Q_3ES]_{aq} + [Q_3SPS]_{aq} + [Q^+X^-]_{aq}\} V_{aq} \\ &\quad + \{[Q_3ES]_{org} + [Q_3SPS]_{org} + [Q^+X^-]_{org}\} V_{org} \end{aligned} \quad [40]$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively.

The distribution of the quaternary is mostly in the form of $(Q_3ES)_{org}$ in the organic phase and $(Q_3SPS)_{aq}$ in the aqueous phase. The appropriate equilibria govern the rate greatly.

Thus, the rate of epoxidation from Equation 38 can be written as:

$$r_E = k_{app} C_{A,org} [Q_{aq}]^\gamma [HPA]^\alpha [H_2O_2]_{aq}^\beta \quad [41]$$

where γ is another constant, and Q_{aq} = the total quantity of quaternary added initially to the aqueous phase:

$$\begin{aligned} [Q^+X^-]_{aq} &= [Q]_{aq} = V_{org}/V_{aq} \{Q_0/V_{org} \\ &\quad - ([Q_3ES]_{org} + [Q_3SPS]_{org} + [Q^+X^-]_{org}) \\ &\quad - ([Q_3ES]_{aq} + [Q_3SPS]_{aq}) V_{aq}/V_{org}\} \end{aligned} \quad [42]$$

Equation 41 suggests the following: (i) The rate is proportional to the alkene concentration in the organic phase. For a fixed value of catalyst, HPA and H_2O_2 , it is a pseudo first-order equation: $-\ln(1 - X_A)$ vs. t will give a slope equal to k_p , a pseudo-first-order constant (Fig. 5). (ii) The rate is proportional to $[HPA]^\alpha$. Hence, the initial rate can be obtained, and (r_{Ei}) against $[HPA]$ concentration in the aqueous phase on a log-log plot will give α as the slope (Fig. 6). (iii) If the $[H_2O_2]/[HPA]$ ratio is high, say greater than 100, and if $[H_2O_2]$ is taken in high molar excess over α -olefin, the rate will become independent of H_2O_2 concentration (Fig. 7). (iv) The plot of $\ln(\text{initial rate})$ against $\ln(Q_{aq})$ (Fig. 8) gives the value of γ , which needs to be ascertained. A value of 3 is likely to be found.

Interpretation of data. The experiments were done with Aliquat 336 (tricapryl methyl ammonium chloride) as PTC, and the typical data for undecylenic acid and methyl undecylenate are given in Tables 9 and 10. The reactions were conducted with chloroform as solvent at 60°C. The mole ratio of $[H_2O_2]/[HPA]$ was greater than 492 in all experiments, and $[H_2O_2]$ -to-substrate mole ratio was 6.4.

The selectivity to epoxide is $\gg 85\%$ and large in comparison with that found by the preformed or *in situ* peroxy epoxidation.

To validate the model proposed earlier, the plots of $-\ln(1 - X_A)$ vs. t were made for each concentration of HPA and catalyst for methyl undecylenate (Fig. 5).

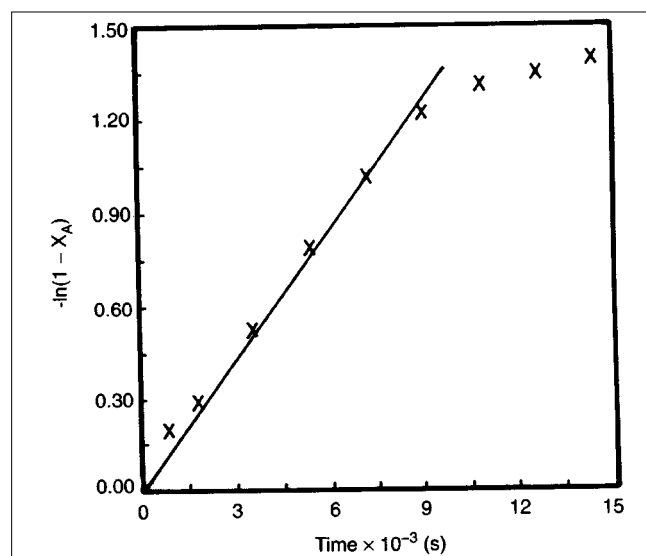


FIG. 5. Typical first-order kinetic plot for the epoxidation of methyl undecylenate at 60°C by the Ishii–Venturello–Hill mechanism. Fixed heteropoly acid concentration.

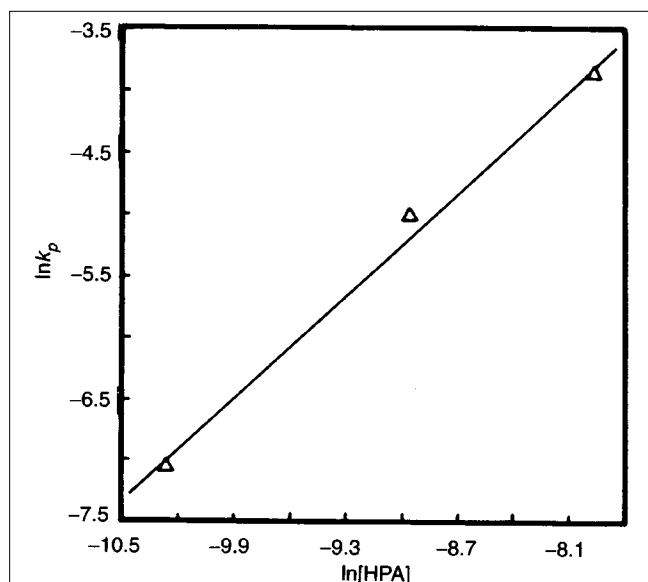


FIG. 6. Plot of $\ln k_p$ vs. $\ln [\text{HPA}]$ for Ishii-Venturello-Hill mechanism (k_p is the pseudo rate constant $= k_{\text{app}}[\text{HPA}]$). HPA: heteropoly acid.

The slopes of these plots are calculated as 8.62×10^{-4} , 6.74×10^{-3} , and $2.01 \times 10^{-2} \text{ s}^{-1}$ at 60°C . Plots of \ln (slope) vs. $\ln [\text{HPA}]$ are shown in Figure 6. This gives the value of α as 1.4. Thus, the order in $[\text{HPA}]$ is 1.4. Because α is $(Z_1 Z_2)^{-1}$, this would suggest that $Z_1 = Z_2 \approx 1$, which would be a fairly good inference.

Initial rates are also plotted against H_2O_2 concentration (Fig. 7) to show that the rates are independent of H_2O_2 concentration.

However, as the reaction proceeds to completion, the order in $[\text{H}_2\text{O}_2]$ concentration may not remain zero. When all

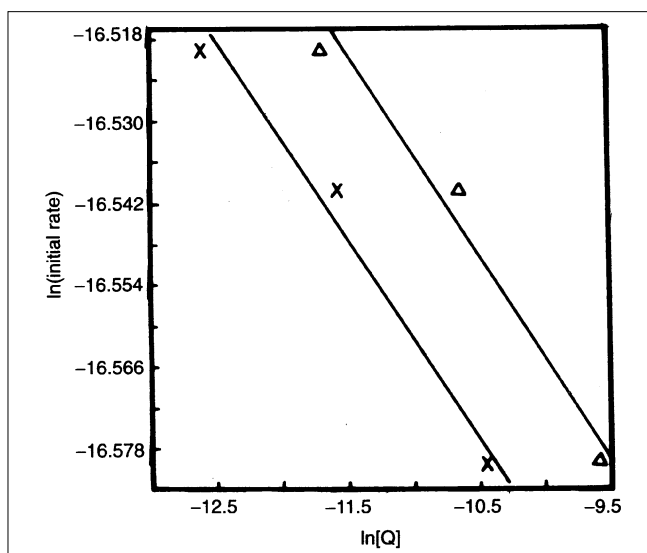


FIG. 7. Effect of H_2O_2 concentration on initial rate of epoxidation of methyl undecylenate for the Ishii-Venturello-Hill mechanism.

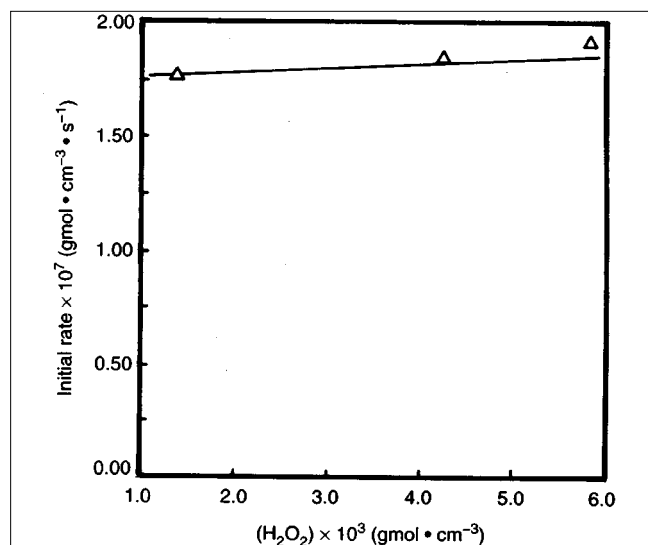


FIG. 8. Plot of \ln (initial rate) vs. $\ln [Q]$ for the epoxidation of methyl undecylenate for the Ishii-Venturello-Hill mechanism: X, Q_{aq} , aqueous phase concentration of Q; Δ , Q_{org} , organic phase concentration of Q.

olefinic substrate is consumed, there is still 0.162 equivalent H_2O_2 (1 mole olefin:1 mole H_2O_2) remaining, which makes $[\text{H}_2\text{O}_2]/[\text{HPA}] = 0.162$.

The plots of \ln (initial rate) against $\ln [Q_{\text{aq}}]$, where Q_{aq} is the initial amount of quaternary divided by the volume of aqueous phase, are shown in Figure 8.

Similar plots are made for \ln (initial rate) against $\ln [Q_{\text{org}}]$, where Q_{org} is the initial amount of catalyst divided by volume of organic phase. This plot is also shown in Figure 8. Because the volume phase ratio was not changed, these lines run parallel to each other.

This analysis shows that the theory presented above represents the data satisfactorily.

In conclusion, the epoxidation of undecylenic acid, methyl and ethyl undecylenate was studied with three different methods. *n*-Butyl undecylenate was also covered. The results show that: (i) Between *in situ* peroxy and preformed epoxidation, the latter gives better conversion and selectivity. The data have been interpreted with a kinetic model. (ii) The ion exchange resin-catalyzed epoxidation is much slower, but it gives better selectivity. (iii) The Ishii-Venturello chemistry with Hill's mechanism was kinetically modeled for the biphasic epoxidation with aqueous hydrogen peroxide, heteropoly acid, and tricaprilmethyl ammonium chloride as PTC for the above esters at 60°C . Selectivity was more than 85% in all cases. The kinetic equation fits the data satisfactorily.

ACKNOWLEDGMENTS

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TABLE 9
Epoxidation of Undecylenic Acid with HPA/PTC/H₂O₂ System^a

HPA (moles)	PTC (moles)	H ₂ O ₂ (moles)	Temp. (°C)	Conv. (%)	Selectivity (%)	Yield (%)
0.00013	0.00037	0.192	65	88	30	51
0.00013	0.00037	0.192	45	79	57	46
0.00013	0.00037	0.192	35	46	61	62
0.00013	0.00025	0.192	65	86	32	47
0.00013	0.0013	0.192	65	78	61	51
0.00013	0.0025	0.192	65	76	31	60
0.000035	0.00037	0.192	65	48	78	21
0.00013	0.00037	0.192	65	88	30	51
0.00035	0.00037	0.192	65	100	45	45
0.00013	0.00037	0.064	65	85	65	27
0.00013	0.00037	0.192	65	88	30	51
0.00013	0.00037	0.250	65	93	32	47

^aTypical reaction conditions: undecylenic acid: 0.03 mole; PTC: 0.00037 mole; HPA: 0.00013 mole; H₂O₂: 0.192 mole; time: 5 h; temperature: 65°C; chloroform: 40 g; conversion = amount of epoxide converted/amount of epoxide taken × 100; yield = gmole of product formed/gmole of reactant converted × 100. HPA: dodecatungstophosphoric acid; PTC (Aliquat 336): tricaprilyl methyl ammonium chloride.

TABLE 10
Epoxidation of methyl undecylenate with HPA/PTC/H₂O₂ System^a

HPA (moles)	PTC (moles)	H ₂ O ₂ (moles)	Temp. (°C)	Conv. (%)	Selectivity (%)	Yield (%)
0.00013	0.00037	0.192	65	75	88	70
0.00013	0.0003	0.192	45	64	82	85
0.00013	0.00037	0.192	35	28	82	85
0.00013	0.00025	0.192	65	81	75	55
0.00013	0.0013	0.192	65	75	82	70
0.00013	0.0025	0.192	65	78	82	69
0.000035	0.00037	0.192	65	22	82	19
0.00013	0.00037	0.192	65	75	88	70
0.00035	0.00037	0.192	65	100	89	99
0.00013	0.00037	0.064	65	71	84	27
0.00013	0.00037	0.192	65	75	88	70
0.00013	0.00037	0.250	65	69	83	53

^aTypical reaction conditions: methyl undecylenate: 0.03 mole; PTC: 0.00037 mole; HPA: 0.00013 mole; H₂O₂: 0.19 mole; time: 5 h; temperature: 65°C; chloroform: 40 g; conversion = amount of epoxide converted/amount of epoxide taken × 100; yield = gmole of product formed/gmole of reactant converted × 100. For abbreviations see Table 9.

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