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Catalytic Epoxidation of Propylene with tert-Butyl Hydroperoxide in the Presence of Modified Carboxy Cation-Exchange Resin "Amberlite" IRC-50

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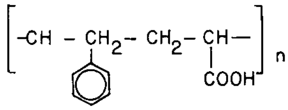
Catalytic epoxidation of propylene with tert-butyl hydroperoxide in the presence of a modified weakly acidic cation-exchange resin, Amberlite IRC-50, is carried out. The order of reaction with respect to the hydroperoxide and the catalyst is studied, as well as the effect of temperature and the solvent, and an assumption is made for the formation of an intermediate complex between the olefine, the catalyst, and the hydroperoxide.

INTRODUCTION

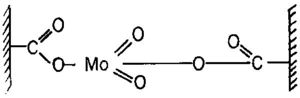
Recently, there has been much interest in the epoxidation of olefines with organic hydroperoxides in the presence of compounds of vanadium, titanium, chromium, and molybdenum as catalysts. On the basis of this reaction, a method for the combined preparation of propylene oxide and tert-butyl alcohol has been suggested. Most of the work on this method has used as catalysts molybdenum and vanadium oleates, stearates, or naphthenates, which are soluble in hydrocarbons, but a disadvantage is their irreversible loss at the end of the reaction (*1–4*).

The purpose of this paper is to describe the preparation of an epoxidation catalyst by bonding a catalytically active substance to the surface of a cation-exchange support and to report on a study of its activity and selectivity as well as to suggest some considerations on the mechanism of the reaction. Recently, reports on similar "heterogenization" of homogeneous catalysts have appeared in the literature (*5–7*), e.g., the modification of the weakly basic anion-exchange resin Amberlite IRA-45 with $Mo(CO)_5$, whose catalytic activity was reported in our previous work (*8*). The suggested catalysts possess high activity and selectivity, which allow their repeated use.

In this paper we present results from the epoxidation of propylene with tert-butyl hydroperoxide in the presence of the modified cation exchange resin Amberlite IRC-50 (molybdenyl-AMB), a copolymer of styrene with acrylic acid possessing the following elementary unit.



The copolymer was treated with an alcohol solution of molybdenyl chloride obtained by evaporation of an acid–salt solution of ammonium molybdate, resulting in the formation of the following modified resin.



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EXPERIMENTAL

tert-Butyl hydroperoxide (Merck-Schuchard) was purified by vacuum distillation at 13 Torr and 28°C. The solvents were purified by standard methods described in Ref. (*9*). Propylene was utilized as the propane–propylene fraction, 95% concentration, which was passed through a column with aluminum oxide immediately before use.

The carboxy cation-exchange resin Amberlite IRC-50 was modified at 70°C for 4 hr with an alcohol solution of $(MoO_2)_nCl_m$ obtained by evaporation of an acid–salt solution of $(NH_4)_6Mo_7O_{24}$. As described in our previous work (*10*), the catalyst obtained in this manner represents heterogenized MoO_2Cl_2 upon weak acidic cation exchange whereby both Cl^- ions are replaced with $-COO^-$ ions from the exchange resin. After a fivefold use of the catalyst barely a 7% decrease in catalytic activity is observed, while over the third, fourth, and fifth use this decrease is only 2% (Fig. 1).

The kinetic study of the epoxidation of propylene with tert-butyl hydroperoxide was carried out in an autoclave for the oxidation of gaseous and liquid hydrocarbons in a manner similar to that described by Emanuel *et al.* (*11*). The catalyst and the solvent were mixed in the reactor, propylene was introduced under a pressure of 30 atm, and the mixture was heated to the desired temperature. Butyl hydroperoxide was injected after 15 min under 35 atm of pressure and that moment was taken as the beginning of the reaction. The products of epoxidation were analyzed for tert-butyl hydroperoxide according to methods given in Ref. (*12*), and for propylene oxide, by nonaqueous titration with $HClO_4$, similar to the method in Ref. (*13*), using the more easily accessible KBr instead of tetraethylammonium bromide.

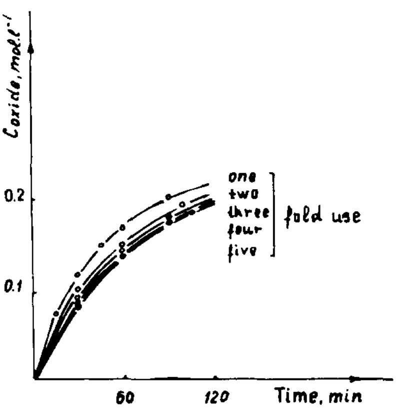

FIG. 1. The repeated epoxidation of propylene with tert-butyl hydroperoxide in the presence of modified Amberlite IRC-50.

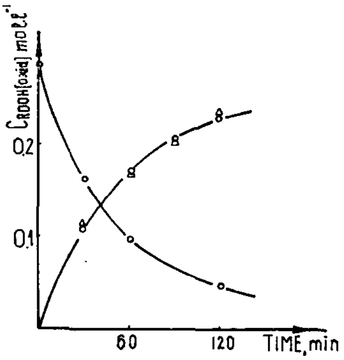

FIG. 2. Accumulation of propylene oxide established (○) by methods described elsewhere (*12*) and (△) by gas–liquid chromatography.

The analytical methods were checked by means of gas–liquid chromatography. The concentrations of propylene oxide measured by the methods reported in Ref. (*12*) as well as by gas–liquid chromatography are shown in Fig. 2.

All experiments were carried out under conditions allowing the reaction to proceed in the kinetic region. In Fig. 3 the dependence between the rate of stirring and the initial rate of the reaction is given. The figure shows the conditions under which the reaction proceeds in the kinetic region.

In Fig. 4a are shown the kinetic curves of the accumulation of propylene oxide and the consumption of the hydroperoxide at 60 to 90°C in the presence of the catalyst. The epoxidation proceeds at a high rate and is characterized by quantitative conversion of propylene into propylene oxide,

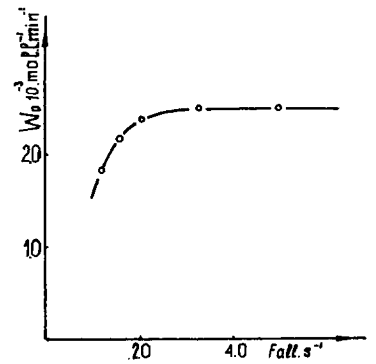

FIG. 3. Transition from a diffusion into a kinetic regime of epoxidation: Solvent, CCl_4 40 ml; C_{ROOH} = 0.164 mol/liter; C_{cat} = 8.7×10^{-3} g-ion/liter; T = 90°C.

which is related to a reacted hydroperoxide selectivity related to tert-butyl hydroperoxide of 90 to 92%.

Analysis of the experimental data shows that conversion of the hydroperoxide does not follow a first-order kinetic equation. There are some literature data (*14*) in support of this fact and it is explained by the inhibiting effect shown by tert-butyl alcohol, which results from decomposition of the hydroperoxide. The kinetic measurements are made on the basis of the initial rates when the final product inhibiting the epoxidation of propylene has not yet accumulated in the system.

The orders of the reaction are determined with respect to the different components by measuring the initial concentrations of the hydroperoxide and the catalyst. In Fig. 5a it is seen that first order with respect to tert-butyl hydroperoxide is observed only within limits. When the initial concentration of the hydroperoxide exceeds 0.35 mol/liter and that of the catalyst is 8.7×10^{-3} g-ion/liter, the linear dependence changes and a tendency for reaching a limiting initial rate of epoxidation, not significantly dependent on the variation in the concentration of the hydroperoxide $-W_\infty$, is observed. The dependence of the initial rate of epoxidation on the concentration of the catalyst is linear also within definite ranges (limits) (Fig. 5b). There is a region (the interval from 3.0 to 15.0) where the initial rate of epoxidation is affected only to a slight extent by a further increase in the concentrations of the catalyst. This means that the order of the reaction with respect to the catalyst is zero. The apparent activation energy is determined from the values of the initial rates of propylene with tert-butyl hydroperoxide when the homogeneous molybdenum resinate is used (*14*).

Figure 6a shows the kinetic analysis of the curves of decomposition of the hydroperoxide in semilogarithmic coordinates. The log C_{ROOH} dependence is linear only in the initial stages, and after conversions from 30 to 40% it deviates from the

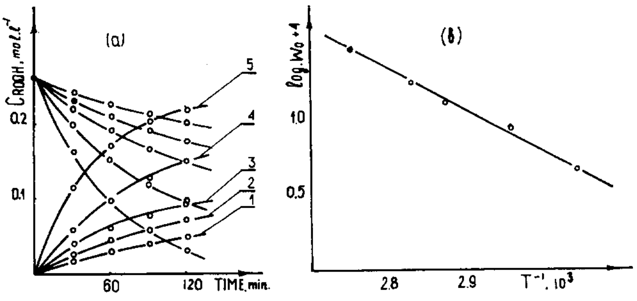

FIG. 4. (a) Epoxidation of propylene with tert-butyl hydroperoxide in the presence of molybdenyl-AMB as catalyst. C_{ROOH} = 0.264 mol/liter; C_{cat} = 5.8×10^{-3} g-mol/liter; solvent, CCl_4, 40 ml; C_{01} = 8 mol/liter. At (1) 60, (2) 70, (3) 75, (4) 80, and (5) 90°C. (b) Arrhenius dependence, log W_0 vs $1/T$, for the epoxidation of propylene under the conditions in (a).

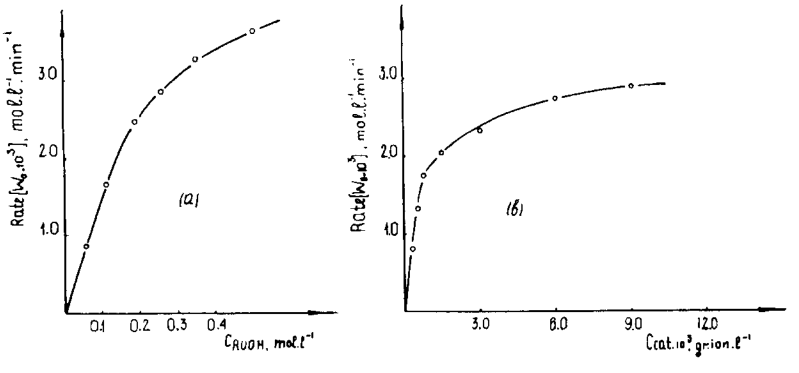

FIG. 5. Determination of the orders of the reaction for $T = 90°C$ (a) with respect to the hydroperoxide when $C_{cat} = 8.7 \times 10^{-3}$ g-ion/liter, $C_{0l} = 8$ mol/liter, and solvent is the same as in Fig. 3; (b) with respect to the catalyst when $C_{ROOH} = 0.35$ mol/liter, $C_{olefine} = 8$ mol/liter, and solvent is the same as in Fig. 3.

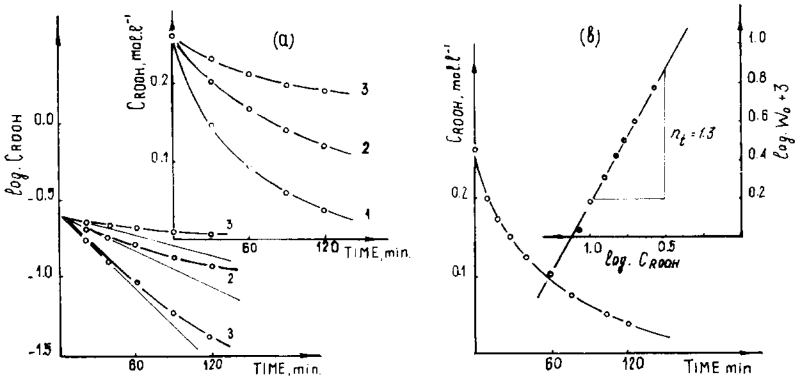

FIG. 6. Kinetic curves of the decomposition of the hydroperoxide in the epoxidation: (a) log $C_{ROOH(\tau)}$ at (1) 90, (2) 80, and (3) 70°C for $C_{ROOH} = 0.264$ mol/liter, $C_{cat} = 8.7 \times 10^{-3}$ g-ion/liter; $C_{olefine}$ and solvent as in Fig. 3. (b) Determination of the order with respect to time under conditions identical to those in (a).

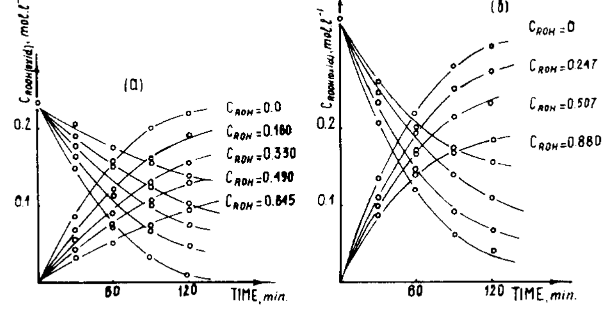

FIG. 7. Study of the inhibiting effect of initial additives of tert-butyl alcohol in epoxidation of propylene with tert-butyl hydroperoxide for $C_{ROOH} = 0.232$ mol/liter and $C_{ROH} = 0.344$ mol/liter. Conditions are the same as those in Fig. 3.

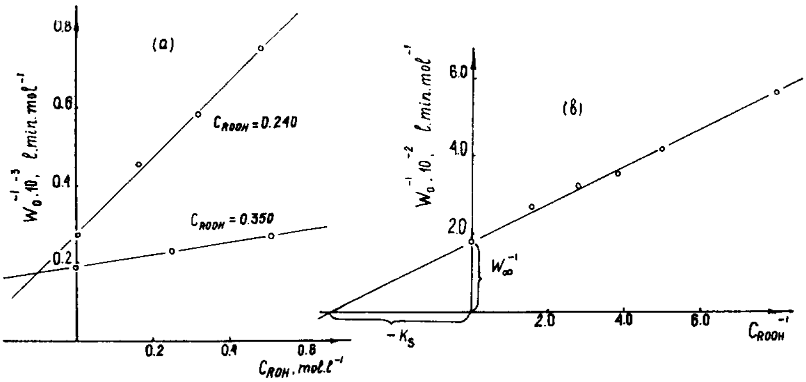

FIG. 8. (a) Determination of the equilibrium constant K_i of the (olefine ... cat ... ROH) complex according to Dickson's method and in accordance with expression (8). Conditions are the same as those in Fig. 7. (b) Graphical determination of the equilibrium constant K_s and the limiting rate of epoxidation according to expression (5). Conditions similar to those in Fig. 5a.

dependence observed for a first-order reaction. The degree of deviation increases with decreasing temperature. A similar effect is described in enzyme kinetics (*15*) and is known as the effect of competitive inhibition shown by the final products. Along with the concentration order, we also determined the order with respect to time upon epoxidation of propylene at 90°C, $C_{\mathrm{ROOH}} = 0.263$ mol/liter, $C_{\mathrm{cat}} = 8.7 \times 10^{-3}$ g-ion/liter (Fig. 6b). The value obtained, 1.3, is also indicative of an autoinhibition reaction. Since tert-butyl alcohol is the only product of the decomposition of the hydroperoxide, it can be assumed that the latter is responsible for the retardation in the rate of epoxidation in the more advanced stages of the reaction. Epoxidation was carried out employing different initial amounts of butyl alcohol and two different initial concentrations of the hydroperoxide (Figs. 7a and b). It is seen from the figure that additions of tert-butyl alcohol in concentrations commensurable with the concentrations of the hydroperoxide lead to a significant decrease both in the initial rate of accumulation of propylene oxide and in the rate of decomposition of the hydroperoxide. Figure 8a shows a linear dependence between the reciprocal value of the initial rate of accumulation of propylene oxide and the concentration of the initially added tert-butyl alcohol as inhibitor.

The effect of solvents, such as benzene, tetrachloromethane, ethylbenzene, chlorobenzene, *n*-decane, *n*-hexane, and nitrobenzene, was also studied. High rates of epoxidation and high selectivity were established for obtaining propylene oxide when the reaction was carried out in tetrachloromethane and benzene. The conversion with respect to propylene oxide decreases in the

TABLE 1

Conversion with respect to Propylene Oxide

	Solvent						
	Benzene	CCl_4	Ethylbenzene	Chlorobenzene	*n*-Decane	*n*-Hexane	Nitrobenzene
Conversion (%)	90.5	90.0	82.6	68.5	36.6	28.5	26.7
$W_0 \times 10^3$	2.5	2.4	1.94	1.58	1.26	1.10	0.92

following order: benzene, tetrachloromethane, ethylbenzene, chlorobenzene, n-decane, n-hexane, nitrobenzene (Table 1).

DISCUSSION

The effects observed resemble greatly the Michaelis-Menten kinetics familiar in enzyme catalysis. The minimum concentrations of the catalyst, the limiting rate of epoxidation obtained with definite concentration of one of the reactants, namely, the hydroperoxide, and the inhibition effect shown by the final products can be explained by formation of an intermediate complex between the catalyst and the hydroperoxide as well as between the catalyst and the olefine. Results confirming the existence of such an intermediate complex were obtained by two independent methods. The kinetics of adsorption of the hydroperoxide on the surface of the catalyst were studied. It was preliminarily established that no selective adsorption of the hydroperoxide occurs on the support (Fig. 9a, curves 1 and 2). The effect seen in Fig. 9a, curve 2, is ascribed to adsorption of the hydroperoxide on the catalyst and not to decomposition at the listed temperatures. The latter is supported by the data given in Fig. 9a, curve 3, which show that with increasing temperature up to 30°C, relaxation effects of adsorption are observed on the hydroperoxide adsorbed initially at lower temperature (20°C). The effects show that under these conditions decomposition is not accomplished to a significant extent and the variation in the concentration of the hydroperoxide is due to its adsorption on the surface of the catalyst. About 85% of the initially free hydroperoxide is bonded to the surface molybdenum centers at 30°C and 35 atm, and the initial concentration of the hydroperoxide is 0.196 mol/liter (Fig. 9a, curve 2). On the other hand, catalytic decomposition of the hydroperoxide was carried out in the absence of propylene at 90°C and at an initial hydroperoxide concentration of 0.164 mol/liter (Fig. 9b, curve 1), establishing an initial rate of decomposition of 1.47×10^3 mol/liter min. This value is 4.5 times higher than that of a decomposition inhibited by a stoichiometric amount of tert-butyl alcohol (Fig. 9b, curve 2). These data give us grounds to assume a competitive complex formation between the tert-butyl alcohol and molybdenum, which reduces the active concentration of the molybdenum–hydroperoxide complex.

When the catalyst was treated with

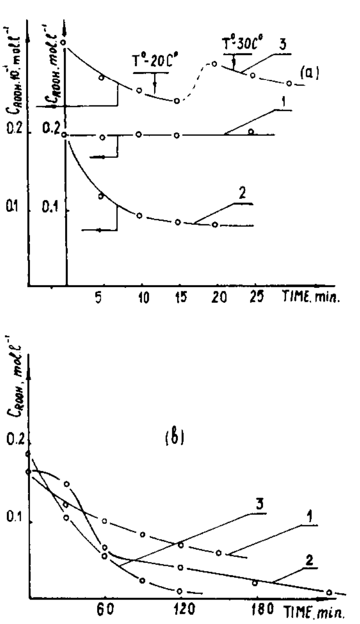

FIG. 9. (a) Study of the formation of the complex between the catalyst and the hydroperoxide. (1) Adsorption on the support Amberlite IRC-50: T = 30°C, P_{N_2} = 35 atm; C_{ROOH} = 0.195 mol/liter; solvent is CCl_4, 40 ml; C_{resin} = 5 g. (2) Adsorption of ROOH on molybdenyl-AMB. Conditions are the same as in Fig. 8a. C_{cat} = 0.146 g-ion/liter. (3) Relaxation effect due to the adsorption and desorption of the hydroperoxide. C_{cat} = 0.073 g-ion/liter.

(b) Catalytic decomposition of ROOH in the presence of AMB. (1) $C_{cat} = 2.7 \times 10^{-3}$ g-ion/liter; T = 90°C, absence of olefine; solvent = CCl_4; C_{ROOH} = 0.160 mol/liter. (2) Decomposition of the hydroperoxide inhibited with 0.184 mol/liter tert-butyl alcohol under the conditions given for curve 1 in (b). (3) Decomposition of the ROOH under conditions of epoxidation similar to those for curve 1 in (b), but in the presence of 6 mol/liter olefine.

propylene under a pressure of 30 atm in the absence of the hydroperoxide, a change in color of the initially introduced catalyst from light yellow to bluish green was observed, which shows the presence of four- and five-valent molybdenum on direct interaction with the olefine. When hydroperoxide was added, the catalyst regained its former yellow color. This shows that alternation of lower and higher valence states of molybdenum is possible in the course of the epoxidation, which is accompanied by a transfer of electrons.

The presence of a stage of complex formation between the catalyst and the olefine is also supported by the strong effect olefine has on the rate of decomposition of the hydroperoxide (Fig. 9b, curve 3). Olefine produces a strong activating effect on the decomposition of the hydroperoxide. The epoxidation of propylene may be represented by the following scheme:

$$\text{cat} + \text{olefine} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \text{cat} \ldots \text{olefine}, \qquad (1)$$

$$\text{olefine} \ldots \text{cat} + \text{ROOH} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \text{ROOH} \ldots \text{cat} \ldots \text{olefine}, \qquad (2)$$

$$\text{ROOH} \ldots \text{cat} \ldots \text{olefine} \xrightarrow{K_3} \text{cat} + \text{ROH} + \text{oxide}. \qquad (3)$$

If we assume k_3 Reaction 3 as the rate-determining step (taking into account the fact that equilibrium between the catalyst and the hydroperoxide is readily established, Fig. 9a, curve 2) as well as the experimentally proved catalytic reduction during the first several minutes on treatment of the catalyst with propylene, the rate of the reaction according to the Michaelis–Menten equation (*15*) may be expressed as follows:

$$W_0 = \frac{K_3(\text{cat})_0(\text{olefine})_0(\text{ROOH})_0}{K_S + (\text{ROOH})_0 K_T + (\text{olefine})_0}. \qquad (4)$$

$$\frac{1}{W_0} = \frac{K_s K_T + (\text{olefine})_0}{K_3(\text{cat})_0(\text{olefine})_0} \times \frac{1}{S_0} + \frac{K_T + (\text{olefine})_0}{K_3(\text{cat})_0(\text{olefine})_0}. \qquad (5)$$

$K_T = K'_2/K_1$ is the equilibrium constant of the (olefine) ... (cat) complex.

$K_S = K_2/K_1$ is the equilibrium constant of the (olefine) ... (cat) ... (ROOH) complex.

K_S and $K_3(\text{cat})_0(\text{olefine})_0/K_T + (\text{olefine})_0$ may be obtained from expression (5), by plotting $1/W_0$ versus $1/S_0$.

We obtained values of 0.285 mol/liter for K_S and 5.5×10^{-3} mol/liter/min for

$$\frac{K_3(\text{cat})_0(\text{olefine})_0}{K_T + (\text{olefine})}.$$

On the other hand, considering the high excess of olefine, it can be assumed that (olefine) $\gg K_T$. In the latter case the expression for W_∞ (with respect to ROOH) is rewritten as $W_\infty = K_3(\text{cat})_0$, from which $K_3 = 0.63\ \text{min}^{-1}$ is obtained.

It is seen from Figs. 7a and b that the accumulation of tert-butyl alcohol and its stoichiometric amounts lead to a significant decrease in the initial rate of epoxidation. Such a deviation in the rate of the reaction in the later stages can be explained by the inhibiting effect of alcohol, which probably forms a similar inactive complex with the molybdenum center. Therefore, in this case, one more stage should be added to the main two reactions:

$$(\text{olefine} \ldots \text{cat}) + \text{ROH} \underset{K_5}{\overset{K_4}{\rightleftarrows}} (\text{olefine} \ldots \text{cat} \ldots \text{ROH}), \qquad (6)$$

where $K_5/K_4 = K_i$ is the equilibrium constant of the molybdenum–inhibitor complex. It was established that the more active the inhibitor the lower the K_i value. On studying the kinetics of the inhibited epoxidation in connection with the initial rate of the reaction, a correction of the initial concentration of the inhibitor should be made.

$$W_0 = \frac{K_3(\mathrm{cat})_0(\mathrm{ROOH})_0}{(\mathrm{ROOH})_0 + K_s\left(1 + \dfrac{(I)_0}{K_i}\right)} \qquad (7)$$

$$K_3(\mathrm{cat})_0 = W_\infty$$

$$(\mathrm{I})_0 = C_{(\mathrm{ROH})_0}$$

$$W_0^{-1} = W_\infty^{-1} + \frac{K_s}{W_\infty(\mathrm{ROOH})_0}\left[1 + \frac{(I)_0}{K_i}\right] \qquad (8)$$

The experimental data processed by Dickson coordinates W_0^{-1} from (ROH) become linear and, at the point of intersection of the curves for two initial concentrations of the hydroperoxide, show the equilibrium constant of the molybdenum–inhibitor complex (Fig. 8a). The value of K_i thus determined is equal to 0.105 mol/liter and it correlates well with those of Farberow *et al.* (*14*): $K_i(\mathrm{H_2O}) = 0.00675$ mol/liter and K_i (methylphenylcarbinol) = 0.175 mol/liter. The value indicates that tert-butyl alcohol possesses an intermediate inhibiting property in the epoxidation with the catalyst we used.

By means of K_s and K_i values obtained graphically, the concentrations of the (cat ... olefine ... ROOH) and (olefine ... cat ... ROH) complexes can be calculated. Since K_s is defined as a stability constant of the (olefine ... cat ... ROOH) complex, the following equation may be suggested:

$$K_s = \frac{[(\mathrm{ROOH})_0 - (X)_e][(\mathrm{Mo})_0 - (X)_e]}{(X)_e}. \qquad (9)$$

On the basis of the calculations employing $C_{\mathrm{ROOH}} = 0.234$ mol/liter and $C_{\mathrm{cat}} = 8.7 \times 10^{-3}$ g-ion/liter, a value for $(X)_e$ of 4.10^{-3} mol/liter was obtained [where $(X)_e$ is the equilibrium concentration]. In the case of total concentration of $(\mathrm{MoO_2})^{2+} = 8.7 \times 10^{-3}$ g-ion/liter, the degree of complex formation in the epoxidation is 46%.

Analogously, on the basis of the graphically determined stability constant K_1, the concentration of the (olefine ... cat ... ROH) complex can be calculated under conditions of inhibited epoxidation, according to the following expression:

$$K_i = \frac{[(\mathrm{ROH}) - (Y)_e][(M_0) - (Y)_e]}{Y_e}. \qquad (10)$$

After solving Eq. (10) with a concentration for the added inhibitor, C_{ROH}, of 0.33 mol/liter and $C_{\mathrm{cat}} = 8.7 \times 10^{-3}$, we obtain for $(Y)_e$ the value 6.5×10^{-3} g-mol/liter. The result correlates well with the better electro-donor properties of tert-butyl alcohol as compared to tert-butyl hydroperoxide and explains the shifting of hydroperoxide from the preliminary complex formed (olefine ... cat ... ROOH) after introducing an additional amount of the tert-butyl alcohol as inhibitor. Thus the actual concentration of the catalyst is not equal to the total one, since in the case of inhibited epoxidation only 2.2×10^{-3} g-ion/liter molybdenum centers are capable of complex formation with the hydroperoxide. From the dependence between W_0 and C_{cat} (Fig. 5b) for concentrations of the catalyst equal to 8.7×10^{-3} and 2.2×10^{-3} g-ion/liter, we obtain the following initial rates: $W_0 = 2.88 \times 10^{-3}$ mol/liter min, and $W_{0\ \mathrm{inhib.}} = 2.1 \times 10^{-3}$ mol/liter min. Therefore, the introduction of 0.33 mol/liter ROH leads to a decrease of 27.2% in the initial rate of epoxidation.

On the other hand, the rate of reaction determined experimentally, when it was carried out under noninhibited and inhibited conditions with 0.33 mol/liter ROH, shows a 32% decrease in W_0. This difference can be explained if we assume that a deactivation of the hydroperoxide, resulting from the association with alcohol in the liquid phase, took place beforehand.

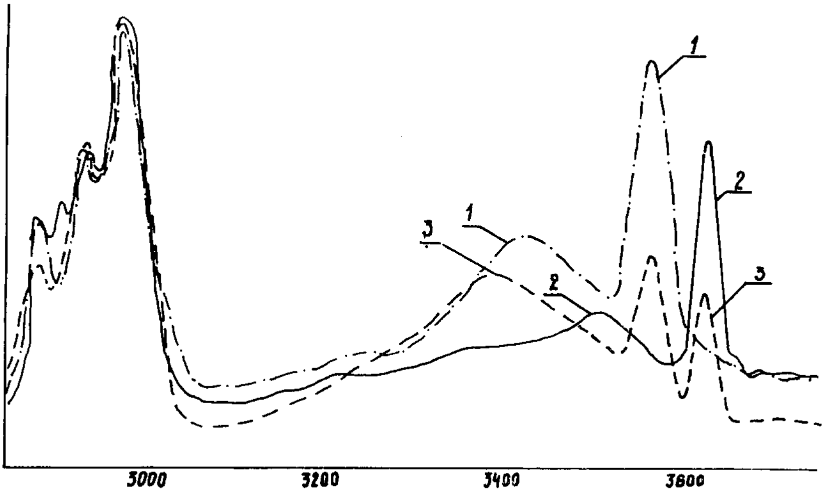

FIG. 10. Infrared spectra of: (1) 1% solution of tert-butyl hydroperoxide in CCl_4; (2) 1% solution of tert-butyl alcohol in CCl_4; (3) 1% solution of the equimolar mixture of the two components in CCl_4.

This assumption is justified if we take into account the infrared spectra of the hydroperoxide, the alcohol, and the equimolar mixture of the two components. Figure 10 shows the appearance of a new band at 3380 cm^{-1}, while the hydrogen bonds in the associates of the pure hydroperoxide and alcohol are observed at 3440 and 3500 cm^{-1}, respectively. Therefore, it can be concluded that in the liquid phase, part of the hydroperoxide is linked in a dimer or trimer with molecules of the inhibitor. In all cases the associates participate in complex formation with the molybdenum center.

The epoxidation of olefines with hydroperoxides in the presence of transition-metal complexes is known in the literature as a process proceeding according to a heterolytic mechanism (*1, 3, 5*). The dependences observed can be explained by formation of an intermediate transition complex with participation of one molecule of the reagents. The catalytic activity of molybdenum in the 6 + state (in accordance with the authors mentioned above) is estimated with the presence of vacant 3*d* orbitals allowing donor–acceptor interaction with the hydroperoxide or the propylene. Delocalization of the electron pair at the oxygen of the hydroperoxide occurs, and the O^- charge at the latter is suitable for a nucleophilic attack by the olefine.

A second scheme is also possible, supported by Markevitsch and Shtivel (*16*) and based on the simultaneous participation of the hydroperoxide and the olefine in the intermediate complex. In this case the role of the catalyst is to facilitate the electron coupling of the two reactants and to participate in the electron transfer.

Furthermore, Mimoun *et al.* (*17*) support the conception that the epoxidation effect of the peroxomolybdates is a last stage in the transformation cycle of the molybdenum–hydroperoxide complex.

Since no data are available referring to the nature of the intermediate complex, no light can be shed on the mechanism of the elementary act of epoxidation. The experimental data obtained by us and, in particular, the complex formation established between the catalytic reduction in the reaction with propylene give us grounds to suggest the scheme summarized in Eqs. (1) to (3) above.

The suggested scheme correlates well with the analysis and the interpretation of the experimental data and satisfactorily explains at present the effects observed.

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