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Catalytic Properties of Molybdenum Zeolites in Epoxidation Reactions

II. Oxidation of Cyclohexene

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The liquid-phase catalytic oxidation of cyclohexene with molecular oxygen, using *t*-BuOOH as an initiator, was studied over various molybdenum zeolites. The activities of the MoHY, $MoHY_u$, and MoCoHY catalysts have been compared with the activities of HY, HY_u, and CoY zeolites, and molybdenum supported on NaY, γ-Al_2O_3, and SiO_2–Al_2O_3. Following induction periods ranging from 0 to 12 hr, significant amounts of reaction products, which include cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one, were obtained. Analysis of total hydroperoxides indicated that these were also formed during the course of the reaction, presumably as cyclohexenyl hydroperoxide. The conversion to cyclohexene oxide was ca. 25% after 50% conversion. The rate of epoxidation at 65°C, based on the mass of catalyst, was approximately 7 μmole sec^{-1} g^{-1} for the $Mo_{1.6}Co_{3.5}HY$ zeolite. The importance of acid sites in the hydrogen Y zeolite was found in the decomposition of the initiator and the generation of the peroxy radicals. The catalytic activity for the epoxidation of cyclohexene was shown to result from the heterogeneous molybdenum catalyst; however, a synergistic effect between cobalt and molybdenum was observed with MoCoHY zeolites. For all of the catalysts studied the amount of products confirms that the reaction was catalytic and that the oxygen was largely derived from O_2 rather than the *t*-BuOOH. Many of the mechanistic aspects in the molybdenum zeolite catalysts were found to be similar to those in the homogeneous systems. As catalysts for the epoxidation of cyclohexene, molybdenum-exchanged zeolites are comparable in activity and selectivity to the more active homogeneous catalysts that previously have been investigated.

INTRODUCTION

In recent years, the liquid-phase oxidation of organic substrates using transition metal compounds as catalysts has become a profitable means of obtaining industrially important chemicals. Typical examples of such processes are the Wacker process (*1*) and the Oxirane process (*2*). In the latter process isobutane or ethylbenzene first is oxidized to the corresponding hydroperoxide which then interacts with propylene, yielding propylene oxide and an alcohol byproduct. In the epoxidation step, soluble molybdenum complexes such as naphthenates are used as catalysts. The selective, direct epoxidation of olefins with molecular oxygen or hydrogen peroxide is the subject of intensive industrial research.

The oxidation of cyclohexene has been used as a model reaction by many investigators (*3*–*8*). This reaction, which has been studied using different radical initiators or transition metal complexes, has been discussed in several recent reviews (*9, 10*). Cyclohexene oxidation with O_2 in the presence of Cu, Co, and Mn complexes was found to be a free-radical chain reaction, giving cyclohexenyl hydroperoxide as the intermediate and yielding two major products, 2-cyclohexen-1-one and 2-cyclohexen-1-ol (*9*):

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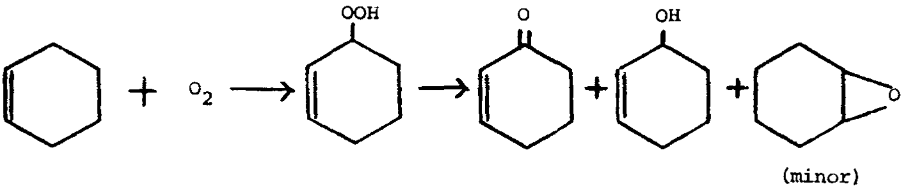
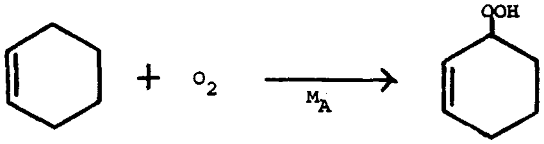
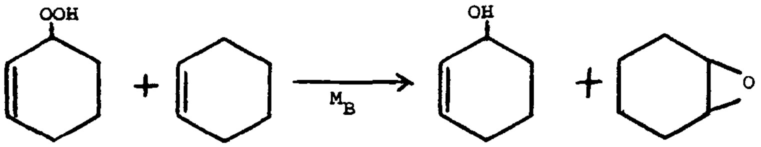


(1)

Mixed catalyst systems (*4*, *11*) have been used to give improved yields of epoxides in the autoxidation of cyclohexene. One metal complex (M_A) is thought to catalyze the formation of hydroperoxide (Eq. (2)), while the second metal complex (M_B) is a catalyst for the epoxidation reaction (Eq. (3)):



(2)



(3)

The M_A metals are complexes of group VIIB, VIIIB, or IB whereas the M_B metals are complexes of group IVB, VB, or VIB. According to this sequence of reactions, the products are roughly 1 : 1 mixtures of the epoxide and the allylic alcohol; however, the product profile is highly dependent on the metal complexes present in the liquid phase and the ratio of M_A to M_B.

The properties of the heterogenized catalyst obtained from the exchange reaction of the complex $Na_2[Mo_2O_4(OX)_2(H_2O)_2] \cdot 3H_2O$ (OX = oxalato) with anion exchangers were examined in the stoichiometric reaction of cyclohexene with cumene hydroperoxide in trichloroethylene at 85°C (*12*). The best catalyst, Wofatit-AD-41, exhibited about 70% selectivity and 65% yield for cyclohexene oxide.

A resin-bound vanadyl catalyst showed far greater yields of epoxide than the homogeneous analog $VO(acac)_2$ in the reaction of cyclohexene with *tert*-butyl hydroperoxide (*6*). It was also found that the kinetic results for the heterogeneous catalyst were consistent with the mechanism proposed for the homogeneous reaction. Catalytic epoxidation of propylene with *tert*-butyl hydroperoxide in the presence of either a weakly acidic carboxy cation-exchange resin, Amberlite IRC-50, or an Amberlite IRA-45 anion-exchange resin, modified with molybdenum hexacarbonyl, have also been studied (*13*, *14*). For the latter catalyst, the activity was similar to that of $Mo(CO)_6$ used under homogeneous conditions.

In the previous paper, we have reported the preparation and characterization of molybdenum-exchanged Y-type zeolites (*15*). In this paper we describe the role of molybdenum-exchanged zeolites in the selective epoxidation of cyclohexene with molecular oxygen. The catalytic properties of several molybdenum-exchanged HY (MoHY) and molybdenum-exchanged ultrastable Y

($MoHY_u$) zeolites as well as molybdenum- and cobalt-exchanged HY (MoCoHY) zeolites have been determined. In addition, the activities of the molybdenum-exchanged Y zeolites have been compared with the activities of both supported $MoCl_5$ and homogeneous $MoCl_5$ catalysts.

EXPERIMENTAL

Cyclohexene (99% pure), *tert*-butyl hydroperoxide (70% pure), 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and cyclohexene oxide were obtained from the Aldrich Chemical Company. Molybdenum pentachloride was obtained from ICN Pharmaceutical. Dry oxygen from Matheson was 99.6% pure. The preparation of the catalysts was described in the previous paper (*15*).

The liquid-phase catalytic oxidation of cyclohexene was carried out in a batch reactor that consisted of a 50-ml three-necked round flask fitted with a condenser, a gas dispersion tube, and a septum for withdrawing samples. The condenser was kept at −10°C by circulating cooled ethylene glycol. For a typical run, 2.5 ml (18.3 mmole) of *tert*-butyl hydroperoxide (*t*-BuOOH) was added slowly to the reactor that contained 25 ml (247 mmole) of neat cyclohexene and 0.4 g of catalyst. After flushing the gas phase with dry oxygen for 15 min, the temperature of the reactor was rapidly raised to the desired reaction temperature of 65 ± 1°C. During the reaction oxygen was bubbled at a rate of 20 cm^3/min through the slurry, which was stirred rapidly to obtain effective suspension of the catalyst. After completion of a run, the spent catalyst was collected and dried at 25°C.

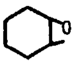
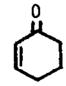
During the course of the reaction 1-μl aliquots of the reaction mixture were analyzed every hour for cyclohexene oxide, 2-cyclohexen-1-one, and 2-cyclohexen-1-ol by gas chromatography. A 9-ft, $\frac{1}{8}$-in.-o.d. stainless-steel column packed with 15% silicone GE × E-60 on Chromosorb W-AW (60 to 80 mesh) was used. The total hydroperoxide concentration was analyzed by a conventional iodometric method immediately after a run was completed. The decomposition of *tert*-butyl hydroperoxide into free radicals over various zeolite catalysts was monitored by means of EPR spectroscopy.

RESULTS

Supported $MoCl_5$ catalysts. The effect of the inorganic support on the catalytic behavior of supported $MoCl_5$ catalysts is shown in Table 1. All of the supported catalysts gave higher initial overall reaction rates than $MoCl_5$ in cyclohexene, which is a homogeneous system. With amorphous SiO_2–Al_2O_3 and an NaY zeolite as sup-

TABLE 1

Effect of Support on the Catalytic Behavior of Supported $MoCl_5$ Catalysts[a]

Support	Induction period (hr)	Overall reaction rate (μmole sec^{-1} μmole Mo^{-1})	Conversion[b] (%)	Selectivity (mole%)		
						
Homogeneous	8	0.018	48.6	32.0	33.0	32.0
Amorphous SiO_2–Al_2O_3	3	0.038	36.7	30.5	41.7	25.0
γ-Al_2O_3	7	0.041	33.0	17.2	39.4	40.3
NaY	10	0.055	52.0	39.7	32.9	24.3

[a] Reaction conditions: cyclohexene, 247 mmole; t-BuO_2H, 18.3 mmole; O_2, 20 cm^3/min.

[b] Reaction ran for 24 hr at 65°C.

ports, the product distributions were very similar to that of the homogeneous analog. These results imply that the heterogeneous molybdenum species are more efficiently used, but the reaction mechanisms for the heterogeneous and homogeneous systems are similar. The induction period for the supported catalyst increased in the order SiO_2–Al_2O_3 < γ-Al_2O_3 < NaY. It is known that the total concentration of acid sites follows a reverse trend; therefore, these data suggest that acid sites of the support may participate in the initiation step via acid-assisted homolytic decomposition of *tert*-butyl hydroperoxide.

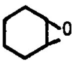
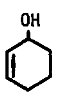
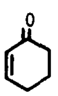
Zeolite catalysts without Mo. For various zeolites that contained no molybdenum, Table 2 shows the activity for the catalytic oxidation of cyclohexene. The most striking feature in this set of catalysts was the relatively low activity of the NaY zeolite. There are two common features among these catalysts. First, comparable amounts of 2-cyclohexen-1-ol and 2-cyclohexen-1-one were formed together with a low selectivity toward cyclohexene oxide. Second, the overall reaction rates were approximately the same for all catalysts except NaY. These results indicate that protons and cobalt ions catalyze the autoxidation of cyclohexene with molecular oxygen.

Molybdenum-exchanged ultrastable Y zeolites ($MoHY_u$). The product profiles for $MoHY_u$ catalysts with various Mo loading, depicted in Table 3, exhibit a gradual change from very low epoxide selectivity for the HY_u catalyst to about 50% selectivity for the $Mo_{3.1}HY_u$ catalyst. For all catalysts, the selectivity to epoxide increased with the reaction time. The products 2-cyclohexen-1-ol and 2-cyclohexen-1-one were predominant at the initial stage of reaction in all of the cases other than $Mo_{3.1}HY_u$. Furthermore, at a given reaction time the selectivity to epoxide increased linearly with an increase in the Mo loading.

The dependencies of the overall reaction rate and the rate of epoxidation on the Mo loading in a series of $MoHY_u$ catalysts are shown in Fig. 1. Both rates increased steadily with Mo loading until reaching maxima at a loading of 1.6 Mo ion per unit cell. Above this exchange level, both rates decreased gradually and approached the values for the homogeneous counterpart, $MoCl_5$ in cyclohexene (Table 5). However, when the rates were expressed on the basis of the molybdenum, the overall reaction rate as well as the rate of epoxidation decreased linearly with increasing Mo loading, as shown in Table 4. Both rates followed the same inverse fractional order dependence on the Mo loading. The

TABLE 2

Catalytic Activities of Various Zeolites for Cyclohexene Oxidation[a]

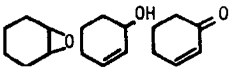
Catalyst	Induction period (hr)	Conversion[b] (%)	Overall reaction rate (μmole sec^{-1} g^{-1} cat)	Product distribution (%)		
						
NaY	11	13.7	1.6	10.2	31.3	41.6
HY_u	0	39.0	3.2	6.4	39.7	49.2
HY	6	30.0	4.1	14.0	35.3	48.3
$Co_{3.5}NaY$	0	49.7	3.6	6.0	39.4	53.0
$Co_{3.5}HY$	6	30.8	4.1	16.0	37.0	45.8

[a] Reaction conditions: cyclohexene, 247 mmole; t-BuO_2H, 18.3 mmole; O_2, 20 cm^3/min.

[b] Reaction ran for 24 hr at 65°C.

TABLE 3

Catalytic Activity and Product Profile of the Cyclohexene Oxidation Catalyzed by the Molybdenum-Exchanged Ultrastable Zeolite Y[a]

Catalyst	Induction period (hr)	Reaction time (hr)	Conversion (%)	Product selectivity (mole%)		
						
HY$_u$	0	11.5	22.3	6.3	44.2	49.5
		21.8	36.5	6.3	43.8	49.9
Mo$_{0.83}$HY$_u$	10	11.3	11.6	4.3	39.7	44.8
		22.0	40.5	24.4	40.7	28.6
Mo$_{1.6}$HY$_u$	10	12.0	21.5	21.8	43.2	28.4
		21.5	42.5	32.1	39.4	30.0
Mo$_{3.1}$HY$_u$	10	11.5	9.0	44.4	30.0	17.8
		22.0	31.0	50.0	29.3	14.8

[a] Reaction conditions: cyclohexene, 247 mmole; t-BuO$_2$H, 18.3 mmole; O$_2$, 20 cm^3/min.

significant change in induction period between the HY$_u$ and MoHY$_u$ catalysts might be ascribed to the substantial loss in strong acid sites of HY$_u$ after the exchange reaction with molybdenum.

Molybdenum, cobalt-exchanged hydrogen Y zeolites (MoCoHY). The catalytic properties of various combinations of molybdenum, cobalt-exchanged HY zeolites for the epoxidation of cyclohexene were studied in an attempt to test the reaction mechanisms proposed for dual-metal catalyst systems (*4, 11*). In this set of catalysts, the exchange level of cobalt ions was kept constant at about 3.5 Co^{2+}/u.c., while the Mo loading was varied from 0.75 to 3.7 Mo ion/u.c. The dependencies of the overall reaction rate and the rate of epoxidation on the Mo loading are shown in Fig. 2 and Table 5. Initially, the rate of epoxidation increased rapidly with increasing Mo loading until it reached a maximum at 1.6 Mo ion/u.c. Then the rate decreased linearly with increasing Mo loading. The overall reaction rate followed a similar trend up to 1.6 Mo ion/u.c., but beyond this loading the overall reaction rate decreased more rapidly, and approached the limiting value

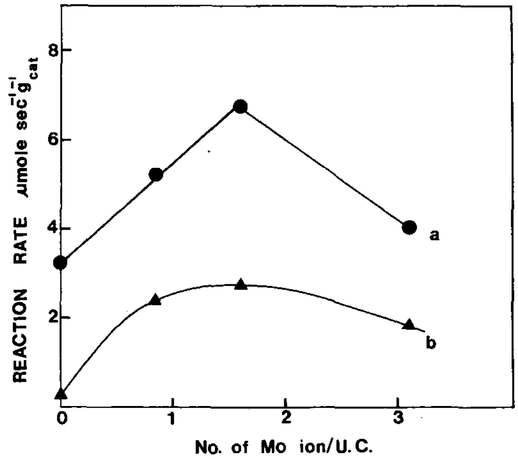


FIG. 1. The dependence of reaction rate on the Mo loading in a series of MoHY$_u$ catalysts. (a) Overall reaction rate and (b) rate of epoxidation.

TABLE 4

Dependence of Catalytic Activity on Molybdenum Loading in Ultrastable Zeolite Y[a]

Catalyst	Rate (μmole sec^{-1} μmole Mo^{-1})	
	Overall reaction	Epoxidation
Mo$_{0.83}$HY$_u$	0.106	0.049
Mo$_{1.6}$HY$_u$	0.071	0.031
Mo$_{3.1}$HY$_u$	0.022	0.010

[a] Reaction conditions: cyclohexene, 247 mmole; t-BuO$_2$H, 18.3 mmole; O$_2$, 20 cm^3/min; reaction temperature, 65°C.

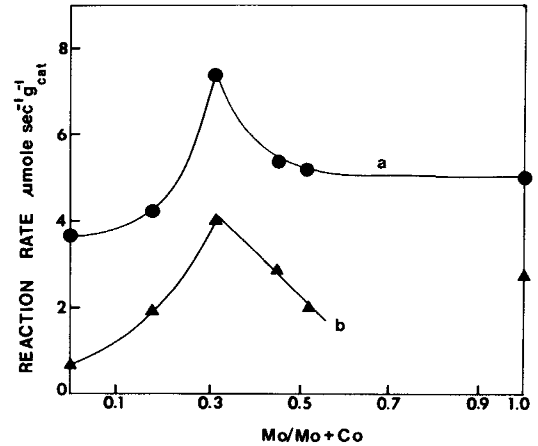


FIG. 2. The dependence of reaction rate on the ratio of Mo/(Mo + Co) in a series of MoCoHY catalysts. (a) Overall reaction rate and (b) rate of epoxidation.

of 5.0 μmole sec^{-1} g^{-1} cat for the $Mo_{1.2}HY$ catalyst. It is of interest to note that the maxima occurred at a ratio of Co to Mo of about two, which is in contrast with the corresponding homogeneous catalyst $Co(acac)_2/MoO_2(acac)_2$ where a maximum in activity was reached at a Co to Mo ratio of one (*4*).

Upon comparing the rate of epoxidation for $Mo_{1.6}Co_{3.5}HY$ with $Co_{3.5}HY$ and $Mo_{1.2}HY$ catalysts, it is apparent that the two transition metal ions act in a synergistic manner. The best catalyst, $Mo_{1.6}Co_{3.5}HY$, gave a fivefold greater specific activity than the homogeneous $MoCl_5$ and $Mo(CO)_6$ catalysts. Moreover, its catalytic activity is comparable to the homogeneous $Co(acac)_2/MoO_2(acac)_2$ catalyst (*4*).

TABLE 5

Dependence of Catalytic Activity on the Molybdenum Loading[a]

Catalyst	Mo/Co + Mo	Rate (μmole sec^{-1} μmole Mo^{-1})	
		Overall reaction	Epoxidation
$Mo_{0.75}Co_{3.6}HY$	0.172	0.094	0.043
$Mo_{1.6}Co_{3.5}HY$	0.308	0.104	0.060
$Mo_{2.9}Co_{3.9}HY$	0.426	0.031	0.017
$Mo_{3.7}Co_{3.5}HY$	0.513	0.023	0.009
$MoCl_5$ (Homog)		0.018	0.003
$Mo(CO)_6$ (Homog)		0.019	0.011
$Mo_{1.2}HY$		0.074	0.040

[a] Reaction conditions: cyclohexene, 247 mmole; *t*-BuO_2H, 18.3 mmole; O_2, 20 cm^3/min; reaction temperature, 65°C.

The kinetic curves for the formation of the three major products from cyclohexene epoxidation at 65°C in the presence of $Mo_{1.6}Co_{3.5}HY$ catalyst are shown in Fig. 3. For 10 hr after the induction period the overall reaction rate and the rate of epoxidation were 7.5 and 4.0 μmole sec^{-1} g^{-1} cat, respectively. The turnover frequency for the overall reaction was 0.02 molecule sec^{-1} ion^{-1}. Later in the course of the reaction a decline in the specific activity was observed.

The product distributions of the cyclohexene epoxidation catalyzed by various MoCoHY catalysts are listed in Table 6. The selectivity toward cyclohexene oxide was about 50% for all of the MoHY and MoCoHY catalysts. The total amount of products was 138.3 mmole when the reaction ran for 21.5 hr at 65°C in the presence of 0.4 g $Mo_{1.6}Co_{3.5}HY$ catalyst; thus it is clear that the reaction was catalytic with respect to the initial hydroperoxide and the metal in the zeolite.

Temperature effect. The influence of temperature on the catalytic behavior of

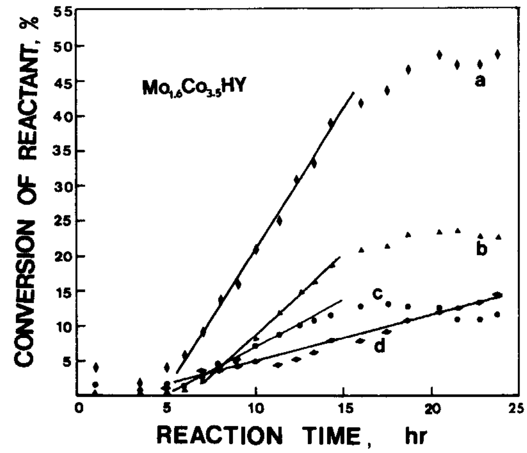
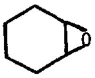
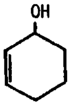
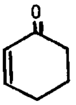


FIG. 3. Conversion of cyclohexene as a function of time. (a) Overall oxidation; (b) oxidation to cyclohexene oxide; (c) oxidation to 2-cyclohexen-1-ol; and (d) oxidation to 2-cyclohexen-1-one.

TABLE 6

Catalytic Activity and Product Distribution of the Cyclohexene Oxidation Catalyzed by the Molybdenum, Cobalt-Exchanged HY[a]

Catalyst	Induction period (hr)	Rate of epoxidation (μmole sec^{-1} g^{-1} cat)	Conversion[b] (%)	Product distribution (mole%)		
						
$Co_{3.5}HY$	6	0.59	29.5	12.3	32.7	44.1
$Mo_{1.2}HY$	5	2.71	38.0	50.0	25.0	16.0
$Mo_{0.75}Co_{3.6}HY$	5	1.90	48.4	48.9	30.9	20.3
$Mo_{1.6}Co_{3.5}HY$	5	4.00	56.0	47.7	23.8	26.7
$Mo_{2.9}Co_{3.9}HY$	5	2.88	36.6	46.2	25.4	21.3
$Mo_{3.7}Co_{3.5}HY$	5	2.00	45.6	49.1	22.8	23.2

[a] Reaction conditions: cyclohexene, 247 mmole; t-BuO_2H, 18.3 mmole; O_2, 20 cm^3/min; ca. 0.4 g catalyst.

[b] Reaction ran for 21.5 hr at 65°C.

$Mo_{1.6}Co_{3.5}HY$ catalyst for the oxidation reactions is shown in Fig. 4 and Table 7. The maximum rate of epoxidation, as well as the overall reaction rate, was obtained at 65°C. The epoxidation rate decreased slightly with increasing reaction temperature beyond 65°C, yet the overall reaction rate decreased markedly. The apparent activation energy estimated for the overall reaction in the temperature range from 45 to 65°C was 11 kcal/mole, which is in good agreement with those reported for metal oxide catalysts (*5*, *16*).

At temperatures below 65°C, the three major products were evident in nearly equal amounts at lower conversions. The selectivity to cyclohexene oxide increased to ca. 50% at high conversions. At 65°C and above greater selectivity to the epoxide was observed, even at lower conversion. In general, temperature had no pronounced effect on the product distribution for prolonged reaction times.

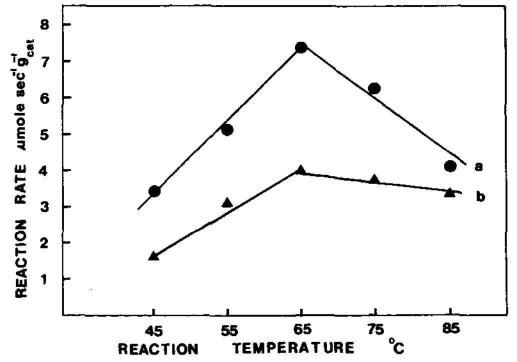


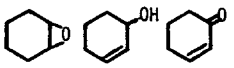
FIG. 4. The dependence of reaction rate on the temperature for the $Mo_{1.6}Co_{3.5}HY$ catalyst. (a) Overall reaction rate and (b) rate of epoxidation.

Effect of initial t-BuOOH concentration and purity. The influence of initial t-BuOOH concentration on the catalytic activity was investigated by carrying out the epoxidation of cyclohexene at 65°C with a fixed amount of $Mo_{1.6}Co_{3.5}HY$ and various initial concentrations of *t*-BuOOH. From the results given in Table 8 it is clear that the epoxidation did not take place in the complete absence of *t*-BuOOH. With 3.6 to 9.8 mmole of *t*-BuOOH, the overall reaction was zero order with respect to the initial concentration of *t*-BuOOH. A maximum rate was observed with 18.3 mmole of *t*-BuOOH in solution. Upon comparing the activity obtained with 1 ml 70% pure *t*-BuOOH (7.3 mmole) with that achieved using 1 ml 94% pure *t*-BuOOH (9.8 mmole), it appears that the purity of *t*-BuOOH has no effect on the activity of $Mo_{1.6}Co_{3.5}HY$ catalyst.

Effect of catalyst pretreatment. The im-

TABLE 7

Effect of Temperature on the Product Distribution of Cyclohexene Oxidation Catalyzed by $Mo_{1.6}Co_{3.5}HY$[a]

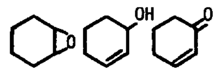
Temperature (°C)	Reaction time (hr)	Conversion (%)	Product distribution (mole%)		
					
45	11.0	17.0	30.0	33.2	36.8
	21.0	33.0	46.2	38.3	15.5
55	11.3	26.0	33.2	34.9	31.9
	22.5	54.0	49.4	29.0	23.7
65	11.3	27.0	48.2	36.7	15.1
	21.5	56.0	47.7	23.8	26.7
75	10.5	31.4	44.3	31.8	23.9
	20.7	56.3	46.7	30.0	23.3
85	10.5	23.2	50.4	32.3	17.2
	21.5	36.0	50.3	33.3	16.3

[a] Reaction conditions: catalyst, ca. 0.4 g $Mo_{1.6}CO_{3.5}HY$; cyclohexene, 247 mmole (25 ml); O_2, 20 cm^3/min; *t*-BuOOH, 18.3 mmole.

portance of Mo(V) in the catalyst was revealed by studying the effect of pretreatment on the catalytic activities of $Mo_{1.6}HY_u$ and $Mo_{1.6}Co_{3.5}HY$ as shown in Table 9. The $Mo_{1.6}HY_u$ catalyst, which was allowed to stand in the air at 25°C for 1 week after preparation, exhibited a slightly greater specific activity than the freshly prepared catalyst. Upon reduction of $Mo_{1.6}HY_u$ in flowing CO at 500°C for 3 hr, a large increase in Mo(V) concentration was detected using the EPR technique. A significant decrease in the overall reaction rate, as well as a somewhat shorter induction period, was observed for this reduced catalyst. Upon oxidation in the air at 100°C for 9 hr, the $Mo_{1.6}HY_u$ catalyst exhibited a lower activity and longer induction period than was observed for the catalyst that was in the air at 25°C for 1 week. Likewise, EPR spectra revealed that there was a considerable decrease in the intensity of the Mo(V)

TABLE 8

Effect of *t*-BuO_2H Concentration on the Overall Reaction Rate and Product Distribution[a]

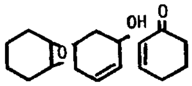
t-BuO_2H (mmole)	Overall reaction rate (μmole sec^{-1} g^{-1} cat)	Reaction time (hr)	Conversion (%)	Product distribution (mole%)		
						
0	0	24	1.1			100
3.6	1.4	33	14.0	53.0	35.0	12.0
7.3	1.5	24	13.7	56.2	32.8	11.0
9.8[b]	1.6	24	13.4	57.5	32.0	10.5
18.3	7.4	24	54.7	49.3	23.3	26.4
25.6	5.2	24	38.2	55.0	27.3	17.7
36.5	2.2	24	23.4	40.2	31.2	25.6

[a] Reaction conditions: catalyst, ca. 0.4 g $Mo_{1.6}Co_{3.5}HY$; cyclohexene, 247 mmole (25 ml); O_2, 20 cm^3/min; reaction temperature, 65°C.

[b] 1 ml *t*-BuOOH of purity above 94% was used.

TABLE 9

Effect of Pretreatment on the Catalytic Activities of $Mo_{1.6}HY_u$ and $Mo_{1.6}Co_{3.5}HY$

Catalyst	Induction period (hr)	Conversion (%)	Overall reaction rate (μmole sec^{-1} g^{-1} cat)	Product (mole%) 		
$Mo_{1.6}HY_u$[a]	12	40.7	6.6	39.0	35.0	22.0
$Mo_{1.6}HY_u$[b]	12	57.0	7.3	39.5	36.0	23.7
$Mo_{1.6}HY_{u,red}$[c]	11	28.0	4.2	39.3	37.6	21.5
$Mo_{1.6}HY_{u,ox}$[d]	14	34.6	5.6	36.4	38.7	23.4
$Mo_{1.6}Co_{3.5}HY$[e]	—	54.7	7.4	49.3	23.3	26.4
$Mo_{1.6}Co_{3.5}HY_{ox}$[f]	—	33.5	4.4	47.7	29.5	22.8

[a] Fresh catalyst.
[b] Catalyst *a* in the air at 25°C for 1 week.
[c] Catalyst *a* reduced in 1 atm CO at 500°C for 3 hr.
[d] Catalyst *b* oxidized in the air at 100°C for 9 hr.
[e] Fresh catalyst.
[f] Catalyst *e* oxidized in O_2 stream at 400°C for 4 hr.

signal after air oxidation at 100°C. A decline in the overall reaction rate also was observed for the $Mo_{1.6}Co_{3.5}HY$ catalyst that was oxidized in flowing O_2 at 400°C for 4 hr as compared to the freshly prepared catalyst. For these two catalysts, there was no significant change in the product distributions upon variation in pretreatment.

The formation of hydroperoxide. The formation of hydroperoxides as reaction intermediates has been repeatedly established in the liquid-phase oxidation of olefinic and alkylaromatic compounds (*17*). In the presence of homogeneous $RhCl(PPh_3)_3$ catalyst, for example, autoxidation of cyclohexene gave 76 mole% of cyclohexene hydroperoxide at 20% conversion (*11*). It was important to check the formation of hydroperoxide in our system. The final total concentration of hydroperoxides as determined by iodometric titration of reaction mixtures is listed in Table 10. When only molybdenum was present in the zeolite, the total concentration of hydroperoxide essentially doubled over 24 hr of reaction; however, the presence of cobalt led to a decrease in the hydroperoxide concentration. These results show that hydroperoxides are considerably more stable in the presence of Mo only whereas hydroperoxides are decomposed rapidly by Co ions.

Based on previous studies (*7*, *8*) one may conclude that most of the *t*-BuOOH reacted with cyclohexene to form *tert*-butyl alcohol (*t*-BuOH) and cyclohexene oxide in the presence of a molybdenum catalyst. The amount of *t*-BuOH produced in the reaction as determined by gas chromatography was about 85% of the amount of *t*-BuOOH introduced in our system. This indicates that most of the *t*-BuOOH was consumed

TABLE 10

Hydroperoxide Concentration

Catalyst	Initial [ROOH][a] (*M*)	Final [ROOH][b] (*M*)
$Mo_{1.6}HY_u$	0.67	1.21
$Mo_{1.6}HY_{u,red}$	0.67	1.12
$Mo_{1.2}HY$	0.67	1.28
$Mo_{0.75}Co_{3.6}HY$	0.67	0.57
$Mo_{1.6}Co_{3.5}HY$	0.67	0.61
$Mo_{1.6}Co_{6.6}HY$	0.67	0.31

[a] Initial concentration of *t*-BuOOH.
[b] Final total concentration of hydroperoxides as determined by iodometric titration.

TABLE 11

Determination of Molybdenum in the Cyclohexane Oxidation Reaction Mixture by Colorimetric Method with Ammonium Thiocyanate

Catalyst[a]	Background A	Sample A	ΔA	Mo concentration[b] (μg/ml)
$Mo_{1.6}HY_u$	0.864	0.891	0.027	0.033
$Mo_{1.6}Co_{3.5}HY_l$	0.769	0.793	0.024	0.015
$Mo_{3.7}Co_{3.5}HY_l$	0.755	0.794	0.039	0.099

[a] For each catalyst, ca. 127 μg/ml of Mo was used in the reaction.

[b] The concentration was calculated by the calibration equation $\Delta A = 0.82C + 0.021$, where C is in μg/ml, A = absorbance at 465 nm.

during the reaction. Therefore, the hydroperoxides in the final reaction mixtures were apparently cyclohexenyl hydroperoxides, although no spectroscopic evidence was obtained to confirm their formation.

Mo concentration in the liquid phase. There has been discussion in the literature as to whether epoxidation activity is due to a heterogeneous Mo species (*18*) or to a small amount of dissolved molybdenum, perhaps formed by the reaction of the heterogeneous Mo with a hydroperoxide (*19*). In an effort to demonstrate that our zeolite catalysts were indeed heterogeneous, the reaction mixtures were analyzed for Mo content by a colorimetric method using ammonium thiocyanate (*20*). The data, presented in Table 11, show that in all cases, less than 0.1% of the total Mo was present in the solution. It is difficult to justify that such a small amount of Mo would yield the observed reaction rate; therefore, we conclude that the catalytic activity resulted from the solid phase.

DISCUSSION

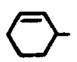
The simplest reaction mechanism that accounts for many of the results is described in the following reaction scheme. This scheme involves acid- and metal-catalyzed decomposition of the initiator *t*-BuOOH, autoxidation of cyclohexene with O_2, and molybdenum-catalyzed epoxidation. In many respects this mechanism combines the accepted reactions for autoxidation and epoxidation reactions that have been proposed previously for homogeneous catalysts.

Initiation. The presence of heterogeneous catalysts, especially metal oxides, has a significant influence on the autoxidation of hydrocarbons in the liquid phase (*5, 21–25*). In the case of autoxidation of cyclohexene over MnO_2 (*5, 21*), the decomposition of cyclohexenyl hydroperoxide is considered to be the initial step of the autoxidation reaction, i.e., the primary source of radicals. Recently the kinetics of liquid-phase decomposition of hydroperoxides by metal oxides have been studied by EPR spectroscopy (*26–29*). The presence of the peroxy radical has been confirmed in the autoxidation of cumene with MnO_2, PbO_2, Ag_2O, etc., by use of EPR (*21, 27, 30*). We therefore studied the decomposition of *t*-BuOOH with several zeolite catalysts. After adding HY_u zeolite powder to the *t*-BuOOH solution, the EPR signal of the *tert*-butyl peroxy radical ($t\text{-}BuO_2\cdot$) was detected, having $g_\parallel = 2.030$ and $g_\perp = 2.001$. It is evident from the EPR result that protons catalyze the decomposition of *t*-BuOOH to generate free radicals that induce the autoxidation of cyclohexene:

$$ROOH + HZ \rightarrow RO\cdot + H_2O + Z\cdot \qquad (4)$$

$$ROOH + Z\cdot \rightarrow RO_2\cdot + HZ \qquad (5)$$

R = *t*-Bu,



It is well known that in the presence of metal ions that can undergo a one-electron redox reaction, the metal-catalyzed decomposition of hydroperoxide follows the Haber–Weiss mechanism as written in reactions (6) and (7):

$$M^n + t\text{-BuOOH} \rightarrow M^{(n+1)+} + OH^- + t\text{-BuO}\cdot$$
$$M^{n+} = \text{Co(II) and Mo(II) to Mo(V)} \qquad (6)$$

$$M^{(n+1)+} + t\text{-BuOOH} + OH^- \rightarrow M^{n+} + H_2O + t\text{-BuOO}\cdot \qquad M^{(n+1)+} = \text{Co(III)}. \quad (7)$$

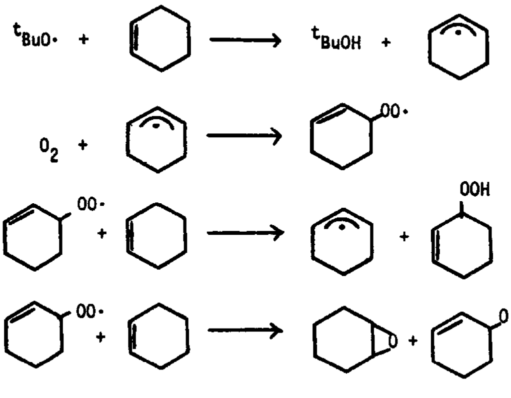
Sheldon (*31*) has shown that the stoichiometric reduction of *t*-BuOOH by Mo(V) complexes was facile, whereas Mo(VI) complexes decomposed *t*-BuOOH slowly. In contrast, both Co(II) and Co(III) are of comparable stability in solution, thus reactions (6) and (7) occur concurrently.

In the zeolite it has been shown that Co(II) is more stable than Co(III), but Co(II) undergoes oxidation to Co(III) in the presence of peroxides (*32*). Nevertheless, the XPS spectra of the used catalysts taken after the cyclohexene oxidation did not indicate the presence of any Co(III) (*15*). The failure to observe the ion is presumably due to a low steady-state concentration of Co(III), which has been noted for cobalt catalysts in solution (*10, 33*). Therefore, the chain initiation with $Co_{3.5}NaY$ catalyst must result from reactions (6) and (7).

For the molybdenum-exchanged zeolites, a significant amount of low-valent Mo ions was oxidized to Mo(VI) upon the reaction with *t*-BuOOH (*15*). However, the reaction of an oxidized $Mo_{1.6}HY_u$ sample with *t*-BuOOH did not yield an EPR signal of Mo(V), but rather a signal of $t\text{-BuO}_2\cdot$ radical. This fact confirms that reaction (7) with Mo(VI) did not occur. Thus, the formation of $t\text{-BuO}_2\cdot$ radical is ascribed to the proton-catalyzed decomposition of *t*-BuOOH with the oxidized $Mo_{1.6}HY_u$ catalyst.

The difference in the induction period between HY and HY_u catalysts can be attributed to the number of strong acid sites required for the decomposition of *t*-BuOOH. Moreover, in the supported $MoCl_5$ catalysts the induction period decreased with the increasing number of acid sites in the support. These phenomena support the acid-assisted homolysis of *t*-BuOOH as described by reactions (4) and (5), where R = *t*-Bu. The same induction period, however, was observed for the Mo-HY_u catalysts, as well as for several Mo-CoHY catalysts with different loadings of Mo. The higher molybdenum-exchanged catalysts contained a significant amount of molybdenum ions in the lower oxidation states and these ions can react with *t*-BuOOH to generate *t*-BuO· in a similar manner as described in reaction (6). Consequently, the enhancement of reaction (6) with low-valent Mo ions could compensate for the adverse effect of reducing the number of acid sites available for reactions (4) and (5) as a result of the exchange reaction.

Propagation. In the proposed mechanism, the chain initiation involves the formation of *t*-BuO· and $t\text{-BuO}_2\cdot$ radicals by the decomposition of *t*-BuOOH over the catalyst surface and their desorption into the cavities of zeolites where the chain propagation and termination proceed (*21*). Both the *t*-BuO· and $t\text{-BuO}_2\cdot$ radicals can abstract the allylic hydrogen of cyclohexene to form cyclohexenyl radicals according to reaction (8). The reaction of cyclohexenyl radicals with the dissolved O_2



(8)

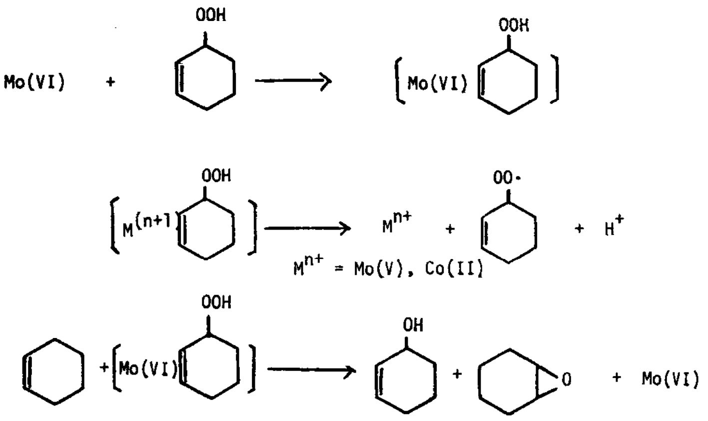
(9)

(10)

(11)

shown in reaction (9) is extremely rapid (*10*). In reaction (10), cyclohexenyl hydroperoxide, the reaction intermediate, is produced by the cyclohexenyl peroxy radical abstracting hydrogen from cyclohexene. In solution the rate constant for chain transfer, reaction (8), is about twice that for reaction (10) (*34, 35*). Addition of $t\text{-BuO}_2\cdot$ radicals to cyclohexene may be responsible for the formation of cyclohexene oxide in the early stages of the cyclohexene oxidation. This reaction together with reaction (11) are the main steps for the formation of the epoxide in the presence of zeolites that contained no molybdenum.

Epoxidation. The homogeneous molybdenum-catalyzed epoxidation of olefins with organic hydroperoxides involves the formation of Mo(VI)–hydroperoxide complexes, reaction (12), the decomposition of the complex, reaction (13), and the oxygen transfer from the complex to the olefin (*9, 10*), reaction (14):



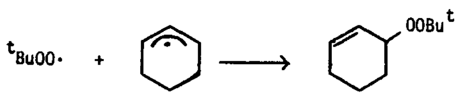
(12)

(13)

(14)

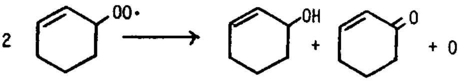
In the present scheme, the cyclohexenyl hydroperoxide presumably coordinates to the molybdenum ion in the zeolite, thereby forming an Mo(VI)–hydroperoxide complex. The formation of comparable amounts of cyclohexene oxide and 2-cyclohexen-1-ol suggests that reaction (14) is the major step for the formation of cyclohexene oxide with Mo-containing zeolite catalysts.

Termination. The stoichiometric reaction of cyclohexene with *t*-BuOOH at 65°C in the presence of Mo(CO)_6 or $\text{Mo}_{1.6}\text{Co}_{3.5}\text{HY}$ catalyst was performed to confirm the formation of 3-*tert*-butyl peroxy-1-cyclohexene (**I**). Two major products, cyclohexene oxide and (**I**), together with minor products 2-cyclohexen-1-ol and 2-cyclohexen-1-one were found, which is in agreement with the previous results of other workers (*7*). The selectivity to (**I**) in the stoichiometric reactions was 61 to 68% after 3 hr of reaction and 37 to 40% after 16 hr. The formation of (**I**) is due to the recombination of $t\text{-BuO}_2\cdot$ with cyclohexenyl radicals as shown in reaction (15). Under catalytic reaction conditions the selectivity for (**I**) was less than 10% for all of the catalysts studied:



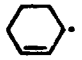
(15)

The formation of comparable amounts of 2-cyclohexen-1-ol and 2-cyclohexen-1-one, particularly with zeolite catalysts without Mo, is consistent with the previously suggested reaction (16):



(16)

In the presence of MoHY the alcohol and ketone products can be produced through reaction sequence (5) and (16), where

R• = 

For the zeolite catalysts without Mo and for Mo supported on γ-Al_2O_3 and SiO_2–Al_2O_3, no decline in the activity was found; however, the reaction rate declined to one-third of the initial value in later stages of the reaction for all of the molybdenum-containing zeolite catalysts. Autoretardation by alcohol coproducts has been reported in the molybdenum-catalyzed epoxidation of cyclohexene with hydroperoxides (*7, 37, 38*). The extent of inhibition is related to the ratio of the equilibrium constants for the formation of molybdenum–hydroperoxide and molybdenum–alcohol complexes. For the molybdenum-exchanged zeolites it seems more likely that the decrease in activity may be due to polymeric peroxides that inhibit the diffusion of the reactant to the Mo ions dispersed throughout the zeolite cavities.

Selectivity and the rate-determining step. The large difference in the selectivity toward cyclohexene oxide between HY_u and $Mo_{3.1}HY_u$ clearly demonstrates that the reaction mechanism changes from autoxidation to a more selective epoxidation. This observation suggests that protons from the Brønsted acid sites of the zeolites and the Mo ions act sequentially in a two-step process (i) to produce the cyclohexenyl hydroperoxide and (ii) to promote the reaction between hydroperoxide and cyclohexene. The ratio of Mo ions to the protons critically determines not only the overall activity, but also the selectivity. By contrast, with the MoCoHY catalysts the ratio of Mo ions to Co ions has a pronounced effect on the rate of epoxidation, but also no influence on the selectivity to the epoxide. As proposed earlier for molybdenum-catalyzed epoxidations in the homogeneous systems (*7, 30*), the selectivity to epoxide is determined by the relative rate of reaction (14) to the rates of reactions (13) and (15). One can conclude from the experimental data that the ratio of Mo to Co has no significant effect on the relative rates of these three reactions.

For the autoxidation of cyclohexene in the presence of a sufficient amount of dissolved oxygen, reaction (10) has been shown to be the rate-determining step (*17*). The Co(II) ions in the zeolites apparently catalyze reactions (9) and (10), and thereby promote the rate of formation of cyclohexenyl hydroperoxide. Moreover, hydroperoxides are decomposed rapidly in the presence of Co(II) ions, but Mo(VI) ions result in considerably more stability. Therefore, it is reasonable to speculate that for MoCoHY catalysts the limiting reagent for reaction (12) is the hydroperoxide. Since the overall reaction is controlled by the rate of formation of the hydroperoxide, the selectivity to the epoxide is independent of the loading of Mo in the MoCoHY catalysts.

Contrary to the MoCoHY catalysts, the selectivity to epoxide increased with increasing Mo loading on the $MoHY_u$ catalysts. This result can be explained by postulating that in the absence of Co(II) reaction (12) is limited by the concentration of Mo, as indicated by the relatively high concentration of free hydroperoxide. For $MoHY_u$ and MoHY catalysts, molybdenum affects only the epoxidation, whereas protons catalyze the decomposition of cyclohexenyl hydroperoxide. Therefore, at lower exchange levels of molybdenum, e.g., for the $Mo_{0.83}HY_u$ catalyst, the nature of cyclohexene oxidation is essentially that of the radical-initiated autoxidation. At higher molybdenum loadings, e.g., the $Mo_{3.1}HY_u$ catalyst, the system is closer to the molybdenum-catalyzed epoxidation of cyclohexene with cyclohexenyl hydroperoxide. For all of the molybdenum-exchanged zeolite catalysts, the formation of cyclohexenyl hydroperoxide, reaction (10), is presumably the rate-determining step.

Effect of Mo loading. The decline in the catalytic activity of molybdenum as the loading increased beyond 1.6 Mo ion per unit cell can be rationalized by the formation of polymeric Mo clusters. Hence, lower catalytic activity can be ascribed to a decrease in the concentration of molybdenum–hydroperoxide complexes. The decrease in activity may also be related to a decrease in crystallinity of the zeolite at the higher loading.

The decline in activity per molybdenum atom (Table 4) suggests the possibility of diffusional limitations; however, using the criterion of Weisz (*39*) that true reaction rates are observed when

$$\frac{dN}{dt}\frac{1}{C_0}\frac{R^2}{D} < 1, \qquad (17)$$

one may show that the reaction rates probably were not limited by diffusion. Here, dN/dt is the reaction rate per unit volume of porous catalyst, C_0 is the reactant concentration external to the catalyst particle, R is the effective radius of the particle, and D is the diffusion coefficient. Data on counterdiffusion in Y-type zeolite are sparse, but if one takes the value of $D = 1.5 \times 10^{-12}$ cm^2 sec^{-1} as reported for the diffusion of cumene into benzene at 65°C in an NaY zeolite (*40*), then the left-hand side of Eq. (17) equals 0.6. Perhaps a more comparable system would be the diffusion of toluene into cyclohexane for which D = 3×10^{-10} cm^2 sec^{-1} at 25°C (*41*). Although diffusion coefficients for cyclic molecules in zeolites are small, it is important to note that the zeolite crystallites are also small. The zeolite crystallites used in this study were in the form of cubes, typically 10^{-4} cm on a side.

Effect of the initial concentration of t-BuOOH. To account for the zero-order dependence of the overall reaction rate in the initial concentration of *t*-BuOOH, the reaction of metal catalysts with alkylperoxy radicals must be considered. Fukuzumi *et al.* (*42*) reported that no *t*-BuO$_2\cdot$ radicals and no oxygen adsorption were observed during the autoxidation of cumene when the ratio of the initial concentration of hydroperoxide to that of Mn(acac)$_2$ catalyst was smaller than a critical value. The peroxy radical produced was postulated to be completely consumed by the termination reaction of RO$_2\cdot$ with Mn(II). Likewise, when hydroperoxide concentrations are low and chain initiation is inefficient, Co(II) can act as an inhibitor by scavenging RO$_2\cdot$ radicals as described in reaction (18):

$$RO_2\cdot + M^{n+} \rightarrow RO_2^- + M^{(n+1)+}. \qquad (18)$$

In fact, inhibition of autoxidation by Co(II) at high concentrations has often been observed in liquid-phase autoxidation (*17, 43, 44*).

The decline in the overall reaction rate as the initial concentration of *t*-BuOOH increased beyond 0.67 *M* may be understood by assuming the formation of an Mo–(*t*-BuOOH)$_2$ complex, which does not lead to epoxidation. The effect of the initial concentration of *t*-BuOOH on the overall reaction rate found in the present study is consistent with that reported for the epoxidation of cyclohexene by ethylbenzene hydroperoxide over molybdenum catalysts (*44, 45*).

Temperature effect. For an exothermic reversible reaction, a negative temperature effect on the reaction rate may be due to the approach to equilibrium. As determined by Sapunov *et al.* (*45*) the equilibrium constant for the complexation of ethylbenzene hydroperoxide with molybdenum was 42 M^{-1} at 60°C and 3 M^{-1} at 70°C. The rate constant for reaction (10), however, increased only 1.5-fold from 60 to 70°C. Therefore, the maximum activity achieved at 65°C could be ascribed to a maximum in the concentration of molybdenum–hydroperoxide complexes.

As an alternative the decline in the activity at higher temperature may be attributed to a change in the concentration of dissolved O$_2$. Assuming that the solubility of O$_2$ in cyclohexane follows Henry's law, the concentration of O$_2$ in the liquid would decrease with the increasing partial pressure of cyclohexene. Hence, the diminishing rate may result from the unfavorable effect of temperature on the concentration of dissolved O$_2$.

CONCLUSIONS

Whereas hydrogen- and cobalt-exchanged Y zeolites are active catalysts for the autoxidation of cyclohexene in the liquid phase, the presence of molybdenum is essential for significant epoxidation activity. Both molybdenum-exchanged hydrogen Y zeolites and molybdenum, cobalt-exchanged HY zeolites exhibit ca. 50% selectivity toward cyclohexene oxide after 50% conversion. Based on a reaction mechanism that involves a hydroperoxide intermediate, this is the maximum selectivity that could be achieved in the metal-catalyzed oxidation of cyclohexene with O_2. The Mo and Co ions act in a synergistic manner to increase the conversion to cyclohexene oxide. As catalysts for the epoxidation of cyclohexene, the molybdenum, cobalt-exchanged HY zeolites are comparable in activity and selectivity to the more active homogeneous catalysts $Co(acac)_2/MoO_2(acac)_2$.

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