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Metal-Catalyzed Epoxidation of Olefins with Organic Hydroperoxides

I. A Comparison of Various Metal Catalysts

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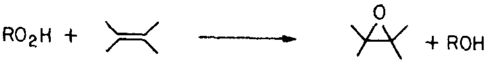
Cyclohexene and 1-octene have been epoxidized in the liquid phase with *tert*-butyl hydroperoxide in the presence of a wide variety of transition-metal catalysts. The reactions occurring in these systems involve competing metal-catalyzed epoxidation and metal-catalyzed homolytic decomposition of the hydroperoxide. Subsequent reactions of the radicals produced in the latter reaction are responsible for the formation of many of the by-products observed.

It is concluded that an active epoxidation catalyst should be both a weak oxidant and a fairly strong Lewis acid. These requirements are best met by compounds of certain metals in high oxidation states [Mo(VI), W(VI), Ti(IV)].

Many of the epoxidations described are subject to autoretardation by the coproduct *tert*-butanol, the extent of which increases in the order W < Mo < Ti < V.

INTRODUCTION

It is known (*1–12*) that compounds of certain transition metals, notably Mo, W, Ti and V catalyze the liquid-phase epoxidation of olefins with alkyl hydroperoxides.



(1)

Both homogeneous (*1–11*) and heterogeneous (*12*) catalysts have been described. Soluble molybdenum complexes, such as $Mo(CO)_6$, were generally found to give the highest rates and selectivities to epoxide. The stereospecificity of the reaction and the high yields of epoxides obtained with a wide variety of olefins are consistent with a heterolytic mechanism (*2, 5*).

We have recently shown (*11*) that the molybdenum-catalyzed reactions involve competing epoxidation and molybdenum-catalyzed homolytic decomposition of the hydroperoxide. The active epoxidation catalyst was found to be Mo(VI).

We have now examined a variety of transition-metal catalysts which have been reported (*3*) to catalyze reaction (1). Our objectives were (a) to establish whether or not our reaction scheme developed for the molybdenum-catalyzed reactions is generally applicable; (b) to compare the various transition-metal catalysts quantitatively; and (c) to determine the factors affecting catalytic activity. Cyclohexene and 1-octene were used as model olefins of different reactivity.

METHODS

Materials. *tert*-Butyl hydroperoxide was vacuum distilled and was 99% pure by iodometric titration. Olefins were purified by passing them through a column of basic alumina prior to use. Authentic samples of epoxides were prepared by standard procedures. 3-*tert*-Butylperoxy-1-cyclohexene, 3-*tert*-butylperoxy-1-octene and 1-*tert*-butylperoxy-3-octene were prepared by the method of Kharasch *et al.* (*13*). Authentic samples of other products were either commercially available or synthesized by standard procedures. $Mo(CO)_6$ and $W(CO)_6$ (Varlacoid), $TiO(acac)_2$,* $Cr(acac)_3$, Th$(acac)_4$ and $Zr(acac)_4$ (Alfa Inorganics) and $VO(acac)_2$ (EGA Chemie) were used as received. $Ti(OBu)_4$, $Nb(OBu)_5$, Ta$(OBu)_5$ and $Zr(OPr\text{-}i)_4$ were prepared by alcoholysis of the corresponding metal chlorides. $UO_2(acac)_2$ was synthesized by the method of Gilman *et al.* (*14a*) and $UO_2Cl_2 \cdot 2HMPA$** by the method of Majumdar, Bhattacharyya and Bera (*14b*). $MoO_2(acac)_2$ was prepared by the method of Gehrke and Veal (*15*). 2% TiO_2-on-silica was obtained by impregnation of silica with $TiCl_4$ (*12a*) and had a surface area of 352 m^2 g^{-1}.

Procedure for kinetic studies. Reactions were carried out under an atmosphere of nitrogen. A quantity of 25 ml of a solution of *tert*-butyl hydroperoxide (5 mmol) and the olefin (50 mmol) in benzene was warmed to 80°C and the catalyst (0.05 mmol) added as a solid or as a solution in a small amount of benzene. Aliquots were removed at time intervals and analyzed for epoxide by glc on a 2-m silicone gum rubber column (methylvinyl, on acid-washed silanized Chromosorb W) using an internal standard (chlorobenzene or *o*-dichlorobenzene). Hydroperoxide conversions were determined by iodometric titration. All other products were determined by glc at the end of the reaction (2-m Carbowax 20M or 2-m silicone gum rubber column). Oxygen was quantitatively determined by gas chromatography of the gas phase on a 2-m activated charcoal column.

Isolation of catalyst from the cyclohexene reaction. A solution of *tert*-butyl hydroperoxide (5 g), cyclohexene (10 g) and $Ti(OBu)_4$ (0.5 g) in benzene (50 ml) was kept at 90°C for 3 hr. The solution was evaporated *in vacuo* and the residue was triturated with pentane to give a cream-colored solid [0.26 g; mp > 300°C (benzene/pentane)]. The product was soluble in benzene and chloroform. Analysis: calcd for $C_6H_{11}TiO_4$: C, 37.0; H, 5.6; Ti, 24.6%; found: C, 37.9; H, 5.7; Ti, 23.9%. When $TiO(acac)_2$ was used in place of $Ti(OBu)_4$ the same product (ir) was isolated. Reaction of epoxycyclohexane (1.0 g), *tert*-butyl hydroperoxide (1.0 g) and $Ti(OBu)_4$ (0.5 g) in benzene (25 ml) at 80°C also afforded the above-described complex (0.20 g). Hydrolysis of the complex with methanolic HCl yielded cyclohexane-1,2-diol.

RESULTS

Product Studies

For our product studies we purposely chose conditions (olefin/*tert*-BuO_2H molar ratio of 1:1) which are not conducive to high epoxide selectivities (based on hydroperoxide consumed). We did this in order to accentuate the differences in selectivity between the various catalysts. In practice the selectivities to epoxide are higher when higher olefin/hydroperoxide ratios are employed.

The results of the epoxidation of cyclohexene by *tert*-butyl hydroperoxide, in benzene at 90°C, in the presence of various transition-metal catalysts are given in Table 1. In general two major products from the olefin were found, epoxycyclohexane and 3-*tert*-butylperoxy-1-cyclohexene (I), together with trace amounts of 2-cyclohexen-1-ol, 2-cyclohexen-1-one, *trans*-cyclohexane-1,2-diol, 2-hydroxycyclohexanone and 2,3-epoxy-cyclohexan-1-ol.

In agreement with the findings of other workers the best catalysts proved to be the homogeneous $Mo(CO)_6$ and $W(CO)_6$ (*2*, *3*) and the heterogeneous TiO_2-on-SiO_2 (*12a*). They all gave roughly the same selectivity (88–94%) to epoxide although the latter two required much longer reaction times than $Mo(CO)_6$. In the presence of these catalysts less than 1% of (I) was formed. Other catalysts afforded increasing amounts of this compound (see Table 1),

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* acac = acetylacetonate.

** HMPA = hexamethylphosphoric triamide.

TABLE 1

Epoxidation of Cyclohexene by *tert*-Butyl Hydroperoxide in Benzene at 90°C[a]

Catalyst[b]	Reaction time (hr)	BuO_2H consumed (%)	Selectivity to Epoxycyclohexane (%)[c]	Selectivity to *tert*-Butylperoxy-cyclohexene (%)[cd]
$Mo(CO)_6$	2	98	94	<1
$MoO_2(acac)_2$	1	98	94	<1
$W(CO)_6$	18	95	89	1
$WO_2(C_4H_9O_2)_2$[e]	22	38	77	13
TiO_2-on-SiO_2[f]	18	75	88	<1
$Ti(OBu)_4$	20	80	66	22
$TiO(acac)_2$	18	40	38	25
$UO(acac)_2$	18	55	35	36
$UO_2Cl_2(HMPA)_2$	18	22	<5	90
$VO(_2acac)_2$	2.5	96	13	25[g]
$Cr(acac)_3$	2	98	2	30[g]
$Nb(OBu)_5$	20	33	30	36
$Ta(OBu)_5$	20	24	29	34
$Zr(acac)_4$	20	16	6	80
$Th(acac)_4$	18	24	4	16
$Zr(OPr)_4$	18	5	<10	60
SeO_2	18	52	6	84[g]
SeO_2[h]	18	84	42	38

[a] 5 mmol cyclohexene + 5 mmol *tert*-BuO_2H + 0.05 mmol catalyst in benzene (25 ml of solution) under N_2.

[b] acac = acetylacetonate; HMPA = hexamethylphosphoric triamide; OBu = *n*-butoxide; OPr = isopropoxide.

[c] Based on *tert*-BuO_2H consumed.

[d] Assuming 2 mol *tert*-BuO_2H → 1 mol *tert*-butylperoxycyclohexene.

[e] W(VI)-butane-2,3-diol complex.

[f] Heterogeneous; 200 mg of 2% TiO_2-on-SiO_2 used.

[g] Significant amounts of cyclohexenol and cyclohexenone also formed.

[h] Cyclohexene used as the solvent.

TABLE 2

Epxoidation of 1-Octene by *tert*-Butyl Hydroperoxide in Benzene at 90°C[a]

Catalyst	Reaction time (hr)	BuO_2H consumed (%)	Selectivity to Epoxyoctane (%)[b]	Selectivity to *tert*-Butylperoxy-octene (%)[bc]
$Mo(CO)_6$	3	88	64	<1
$Mo(CO)_6$	20	99	64	<1
TiO_2-on-SiO_2	24	31	56	<1
$W(CO)_6$	70	71	34	22
$Ti(OBu)_4$	24	34	10	24
$VO(acac)_2$	4	95	2	6

[a] For conditions see footnote *a* in Table 1.

[b] Based on *tert*-BuO_2H consumed.

[c] Assuming 2 mol *tert*-BuO_2H → 1 mol *tert*-butylperoxyoctene; approx 1:1 mixture of 3-*tert*-butylperoxy-1-octene and 1-*tert*-butylperoxy-3-octene.

TABLE 3

METAL-CATALYZED DECOMPOSITION OF *tert*-BUTYL HYDROPEROXIDE IN BENZENE AT 90°C[a]

Catalyst	Approx $t_{1/2}$ (min)	Yield of O$_2$ (%)[b]
Co(II)octoate[c]	<1	93
Cr(acac)$_3$	7	85
VO(acac)$_2$	13	88
Mo(CO)$_6$	20	80
Ti(OBu)$_4$	300	70
WO$_2$(C$_4$H$_9$O$_2$)$_2$	240	10
W(CO)$_6$	240	<5
TiO$_2$-on-SiO$_2$	1000	<5
None	10,000	nd

[a] 5 mmol *tert*-BuO$_2$H + 0.05 mmol catalyst in benzene (25 ml of solution) under N$_2$.

[b] For complete reaction; based on amount of *tert*-BuO$_2$H charged.

[c] Estimated from values determined at 25°C (*16*).

the structure of which was confirmed by comparison (ir, NMR, glc) with an authentic sample.

1-Octene, being less reactive than cyclohexene, gave significantly lower selectivities to the epoxide (Table 2). Furthermore, the spread in selectivities between the various catalysts was much wider than with cyclohexene. The heterogeneous TiO$_2$-on-SiO$_2$ catalyst (*12a*) gave a selectivity to 1,2-epoxyoctane similar to that observed with Mo(CO)$_6$ and significantly higher than that found with the homogeneous Ti(OBu)$_4$ catalyst. In addition to 1,2-epoxyoctane, 3-*tert*-butylperoxy-1-octene (II) and 1-*tert*-butylperoxy-3-octene (III) were formed, together with trace amounts of 1-octen-3-ol, 1-octen-3-one and 3-octen-1-al.

Metal-Catalyzed Decomposition of tert-Butyl Hydroperoxide in the Absence of an Olefin

The results of the reactions of *tert*-butyl hydroperoxide, in the absence of an olefin, in benzene and cyclohexane at 90°C, in the presence of Mo, Ti, W, and Cr catalysts are shown in Tables 3 and 4. In general, they were similar to those obtained with redox catalysts such as cobalt (*16*). Thus, in benzene at 90°C *tert*-butyl hydroperoxide was catalytically decomposed to *tert*-butanol and oxygen (Table 3). In cyclohexane, decomposition of the hydroperoxide was slower (Table 4) and afforded *tert*-butanol together with oxidation products of the solvent (cyclohexanol, cyclohexanone and *tert*-butylperoxycyclohexane). The molybdenum-catalyzed decomposition of *tert*-butyl hydroperoxide in several sol-

TABLE 4

METAL-CATALYZED DECOMPOSITION OF *tert*-BUTYL HYDROPEROXIDE IN CYCLOHEXANE AT 90°C[a]

Catalyst	Reaction time (hr)	BuO$_2$H consumed (%)	Products (%)[b]		
			Cyclohexanol	Cyclohexanone	*tert*-Butylperoxy-cyclohexane
Co(II)octoate[c]	0.05	99	22	14	11[d]
Cr(acac)$_3$	1	99	48	5	28
VO(acac)$_2$	2	81	34	6	12
Mo(CO)$_6$	6	95	47	9	14
W(CO)$_6$	24	49	28	6	3
TiO$_2$-on-SiO$_2$	24	46	4	1	2
TiO(acac)$_2$[e]	24	52	21	7	6
Ti(OBu)$_4$	24	73	24	10	5
None	24	6	nd	nd	nd

[a] For conditions see footnote *a* in Table 3.

[b] Based on *tert*-BuO$_2$H consumed.

[c] 0.0057 *M* catalyst + 0.1–0.3 *M* *tert*-BuO$_2$H at 81.5°C (*16*).

[d] Oxygen (22%) was also found.

[e] Heterogeneous [TiO$_2$(acac)$_2$ is insoluble in cyclohexane].

vents has previously been reported (*11*). The rates of decomposition (qualitative) decreased in the order Cr > V > Mo > W,Ti.

The results obtained with the homogeneous tungsten catalysts and the heterogeneous TiO_2-on-SiO_2 differed from those observed with the other catalysts. Thus, with the former catalysts only small amounts of oxygen were formed in benzene (Table 3), along with water, isobutene and isobutene oxide. The rate of hydroperoxide decomposition in the presence of TiO_2-on-SiO_2 was very low compared to that found with the other catalysts. Also, with this catalyst there was very little formation of oxidation products in cyclohexane (Table 4).

Kinetic Studies

We have studied the kinetics of the epoxidation of cyclohexene and 1-octene by *tert*-butyl hydroperoxide, at 80°C in benzene, in the presence of the more active catalysts (Mo, W, Ti and V compounds). In these studies, except for the molybdenum-catalyzed epoxidation of cyclohexene, an olefin/hydroperoxide molar ratio of 10:1 (2 and 0.2 *M*) was employed. This ratio provided for a reasonable rate of reaction with, in most cases, simple pseudo-first-order kinetics and a high selectivity to epoxide.

Other workers have shown (*4–7*) that these metal-catalyzed epoxidations are first order in both olefin and hydroperoxide.* The molybdenum-catalyzed reactions were found (*5*, *11*) to be first order in catalyst. The full rate expression is given by:

$$\text{rate} = d[\text{epoxide}]/dt = k_3[\text{catalyst}][\text{olefin}][\text{RO}_2\text{H}].$$

As long as the catalyst remains unchanged during the reaction this reduces to:

$$\text{rate} = k_2[\text{olefin}][\text{RO}_2\text{H}],$$

which, for a high olefin/hydroperoxide ratio, reduces further to the pseudo-first-order rate equations

$$\text{rate} = k_1[\text{RO}_2\text{H}],$$

where $k_1 = k_2[\text{olefin}] = k_3[\text{catalyst}][\text{olefin}]$.

In the epoxidation of cyclohexene all of the catalysts, with the exception of $VO(acac)_2$, were found to give, after an initial period, pseudo-first-order kinetics (Fig. 1; the line shown for $Mo(CO)_6$ was calculated from the second-order rate constant, determined at olefin and hydroperoxide concentrations of 0.2 *M* each). The initial change in rate was previously found to be due to a change in the structure of the catalyst (*11*). The calculated second-order rate constants ($k_2 = k_1/[\text{olefin}]$) for epoxidation are given in Table 5; they cor-

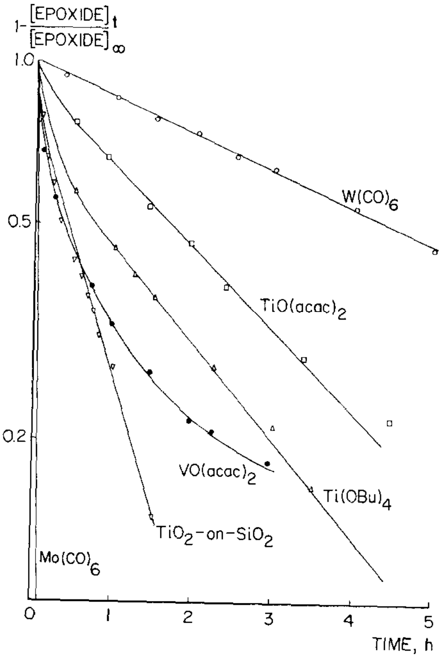

FIG. 1. Metal-catalyzed epoxidations of cyclohexene with *tert*-BuO_2H in benzene at 80°C; (*tert*-BuO_2H, 0.2 *M*; cyclohexene, 2 *M*; catalyst, 0.002 *M*).

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* It has now been shown [T. N. Baker, G. J. Mains, M. N. Sheng and J. G. Zajacek, *J. Org. Chem.* **38**, 1145 (1973)] that although molybdenum-catalyzed epoxidations exhibit an *apparent* first-order dependence in hydroperoxide, the kinetics are in fact more complex due to a slight but significant retardation by the co-product alcohol.

TABLE 5

RATE CONSTANTS AND SELECTIVITIES IN THE EPOXIDATION OF CYCLOHEXENE BY *tert*-BUTYL HYDROPEROXIDE IN BENZENE AT 90°C[a]

Catalyst	k_2[b] × 10^5 (M^{-1} s^{-1})	Selectivity[c] (%)
$Mo(CO)_6$	390	99
$VO(acac)_2$	80[d]	83
TiO_2-on-SiO_2	14	96
$Ti(OBu)_4$	5.0	95
$TiO(acac)_2$	3.6	98
$W(CO)_6$	2.2	96

[a] See "Methods" for conditions.

[b] Second-order rate constant for epoxide formation at the given catalyst concentration (0.002 *M*).

[c] Based on *tert*-BuO_2H charged (100% conversion).

[d] Calculated from the initial rate, which rapidly decreased (see Fig. 1).

respond to the final, constant slopes in Fig. 1. For most catalysts the selectivity to epoxide was >95% but for $VO(acac)_2$ it was not higher than 83%.

In the epoxidation of 1-octene under the same conditions (olefin/hydroperoxide molar ratio: 10:1) high selectivities to epoxide were obtained only with $Mo(CO)_6$ and TiO_2-on-SiO_2 (95 and 90%, respectively); $Ti(OBu)_4$ and $W(CO)_6$ gave moderate selectivities (77 and 72%, respectively) and $VO(acac)_2$ a very poor selectivity (8%) even under these favorable conditions. It was only the $Mo(CO)_6$ (Fig. 2) and $W(CO)_6$-catalyzed reactions which, after an initial period, followed pseudo-first-order kinetics. The rates of titanium- and vanadium-catalyzed reactions decreased continually throughout the reaction and never became constant. Hence, because of the low selectivities and/or the decreasing rates it was impossible to calculate meaningful rate constants for many of these reactions.

The Effect of Added tert-*Butanol*

The continuous decrease in rate of the $VO(acac)_2$-catalyzed epoxidation of cyclohexene has been observed earlier by Gould *et al.* (*6*), who showed that this reaction is autoretarded by the co-product *tert*-butanol, leading to complex kinetics (*6*).

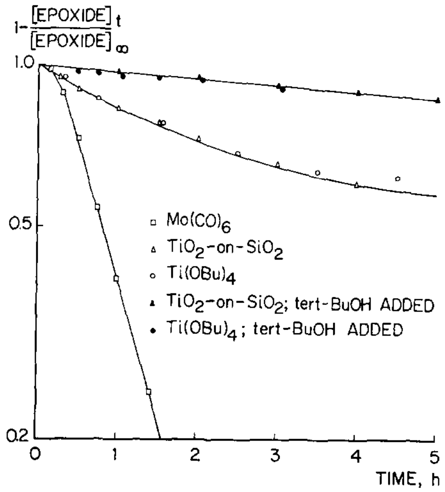


FIG. 2. Epoxidation of 1-octene with *tert*-BuO_2H in benzene at 80°C; (*tert*-BuO_2H, 0.2 *M*; 1-octene, 2 *M*; catalyst, 0.002 *M*).

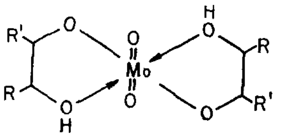
Sheng and Zajacek (*5*) found that the addition of large amounts of *tert*-butanol to molybdenum-catalyzed epoxidations also resulted in a decreased rate of reaction. We have compared the effects of the deliberate addition of *tert*-butanol (*tert*-BuO_2H/*tert*-BuOH molar ratio: 1:1) on the rates of molybdenum-, titanium- and tungsten-catalyzed reactions in order to determine the extent of autoretardation in these reactions.

The addition of *tert*-butanol had little effect on the molybdenum- and tungsten-catalyzed epoxidations. Both homogeneous and heterogeneous titanium-catalyzed reactions showed marked autoretardation with 1-octene (Fig. 2), but not with cyclohexene (Fig. 1). The retarding effect in the case of 1-octene was the same for homogeneous and heterogeneous titanium catalysts (Fig. 2).

Catalyst Isolation

We have previously reported (*11*) that during the early stages of the molybdenum-catalyzed epoxidations the initially added catalyst is converted into a molybdenum (VI)-1,2-diol complex (IV) via reaction with the epoxide in the presence of the hydroperoxide.

It was of interest, therefore, to deter-



(IV)

mine whether other metal catalysts were similarly converted to diol complexes during the reaction. Indeed, we have isolated a Ti(IV)cyclohexane-1,2-diol complex from homogeneous titanium-catalyzed epoxidations of cyclohexene (see "Methods"). Separate experiments showed that the complex is formed via an *in situ* reaction of the catalyst with the epoxide and hydroperoxide. The precise structure of this complex has not been determined but it contains one molecule of diol per titanium atom and its high melting point (>300°C) suggests that it is oligomeric or polymeric [Ti(IV) is known (*17*) to form a wide variety of polymeric complexes with 1,2-diols]. The species present under epoxidation conditions, however, may be monomeric. Whether or not the complex contains a titanyl group (Ti=O) has not been established.

DISCUSSION

The results of our product studies demonstrate that the reaction scheme developed for molybdenum-catalyzed epoxidations (II) can be extended to other metal catalysts. The performance of transition-metal catalysts depends on, among other things, the relative rates of the metal-catalyzed epoxidation and the metal-catalyzed decomposition of the hydroperoxide. These reactions and the factors underlying the differences between the various metals are discussed in the following paragraphs.

Mechanism of the Epoxidation

The high selectivities (Table 5) and the effect of olefin structure on the rate of epoxidation are consistent only with a heterolytic mechanism involving electrophilic attack on the olefin, as suggested earlier by others (*5, 6*).

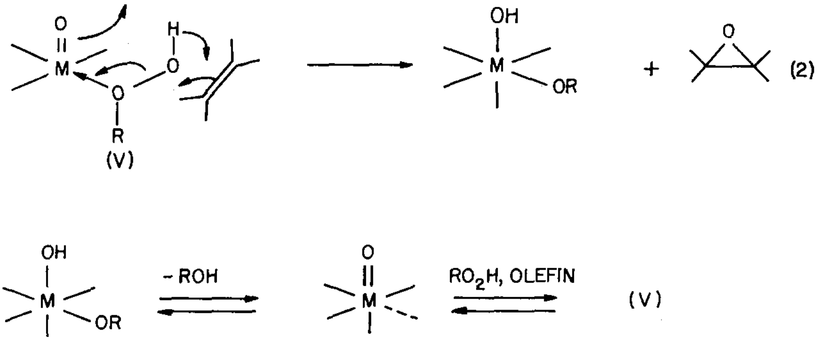
Complexes of metals in low oxidation states (e.g., $Mo(CO)_6$, $W(CO)_6$) are rapidly oxidized by hydroperoxides to their highest oxidation state (*vide infra*). We propose that compounds of the metals in their highest oxidation states [Mo(VI), W(VI), V(V), Ti(IV)] are the actual epoxidation catalysts. Complex formation between the metal catalyst and the hydroperoxide renders the peroxidic oxygens more electrophilic and, hence, more liable to attack by an olefinic double bond. This may be compared to the electron-withdrawing effect of the carbonyl group in organic peroxy acids, which renders the peroxidic oxygens more electrophilic than the corresponding alkyl hydroperoxide.

We envisage two possible mechanisms for the reaction of the catalyst–hydroperoxide complex with the olefin. The first mechanism [Eq. (2)] involves a cyclic transition state where an M=O group in the catalyst functions in a similar manner to the carbonyl group in organic peroxy acids. The M=O group may be part of a soluble metal complex or it may be present on the surface of a heterogeneous catalyst. We prefer this mechanism for those complexes which contain an M=O group (molybdenyl, titanyl, vanadyl, etc.). Apart from the M=O moiety an M—OX group could also act as a proton acceptor. This is visualized in the second mechanism [Eq. (3)]. An analogous mechanism has been proposed (*18*) for the boron-catalyzed epoxidation of olefins.

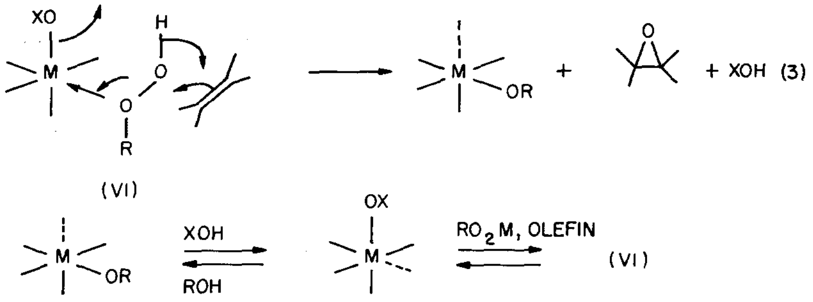
In both mechanisms the main function of the catalyst is to withdraw electrons from the peroxidic oxygens of the hydroperoxide. In doing so the catalyst acts as a Lewis acid. The Lewis acidity of metal complexes increases with increasing oxidation state of the metal and active epoxidation catalysts would, therefore, be expected to be found among compounds of metals in high oxidation states. We have previously shown (*11*) that the active catalysts in molybdenum-catalyzed epoxidations are Mo(VI) complexes.

The Lewis acidity of transition-metal oxides decreases in the order CrO_3 MoO_3 $\gg WO_3 > TiO_2$, V_2O_5, UO_3 (*19*). Thus, it becomes apparent why Mo(VI) is the most

MECHANISM 1



MECHANISM 2



effective epoxidation catalyst. On the basis of its strong Lewis acidity Cr(VI) would also be expected to be a good catalyst. That this is not so must be ascribed to the fact that Cr(VI) is a strong oxidant and readily causes decomposition of the hydroperoxide (*vide infra*).

Lewis acidity will also be influenced by the nature of the ligands surrounding the metal. In practice, however, a ligand effect should be observable only in the initial stages of the reaction in view of the rapid oxidative destruction of the original ligands by reaction with the hydroperoxide (see below). We attribute the high activity of TiO_2-on-SiO_2 to its acidity being higher than that of the homogeneous titanium catalyst [as evidenced by the much higher rate of dehydration of alcohols in the presence of TiO_2-on-SiO_2 (*20*)]. TiO_2 as such is inactive as an epoxidation catalyst (*12a*).

Since the epoxidation step involves no change in oxidation state of the metal there is no reason why the catalytic activity should be restricted to transition-metal complexes. Compounds of nontransition elements which are Lewis acids should also be capable of catalyzing epoxidations. The acidity of nonmetallic oxides decreases in the order $SeO_2 > B_2O_3 > SnO_2$ (*19*). In fact, SeO_2 is roughly as acidic as MoO_3. We have indeed found that SeO_2 catalyzes the epoxidation of olefins by hydroperoxides although it is much less effective than the molybdenum, tungsten and titanium catalysts. This is possibly due to the fact that SeO_2 is a relatively strong oxidant and may readily cause decomposition of the hydroperoxide (see below). Boron (*18*) and tin (*21*) compounds are known to catalyze epoxidations with hydroperoxides but they are much less effective than molybdenum catalysts.

By-product Formation

Low selectivities in metal-catalyzed epoxidations are generally due to a competing metal-catalyzed homolytic decomposition of the hydroperoxide (*11*). Many transition-metal complexes are known (*22*) to initiate the decomposition of hydroperoxides via the redox reactions (4) and (5):

$$\mathrm{M}^{n+} + t\text{-}\mathrm{BuO_2H} \rightarrow \mathrm{M}^{(n-1)+} + t\text{-}\mathrm{BuO_2}\cdot + \mathrm{H}^+, \quad (4)$$

$$\mathrm{M}^{(n-1)+} + t\text{-}\mathrm{BuO_2H} \rightarrow \mathrm{M}^{n+} + t\text{-}\mathrm{BuO}\cdot + \mathrm{HO}^-. \quad (5)$$

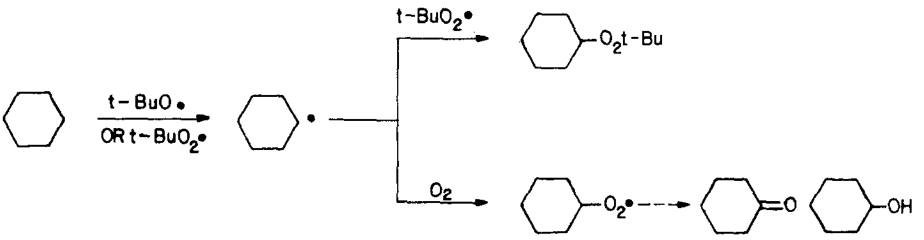
By-products in the epoxidation reactions result from subsequent reactions of the *tert*-butoxy and *tert*-butylperoxy radicals formed in reactions (4) and (5). These reactions, which are dependent on the nature of the solvent and on the molar ratios of the reactants, are outlined below.

Reaction with Hydroperoxide

$$t\text{-}\mathrm{BuO}\cdot + t\text{-}\mathrm{BuO_2H} \rightarrow t\text{-}\mathrm{BuO_2}\cdot + t\text{-}\mathrm{BuOH}, \quad (6)$$

$$2t\text{-}\mathrm{BuO_2}\cdot \rightarrow 2t\text{-}\mathrm{BuO}\cdot + \mathrm{O_2}. \quad (7)$$

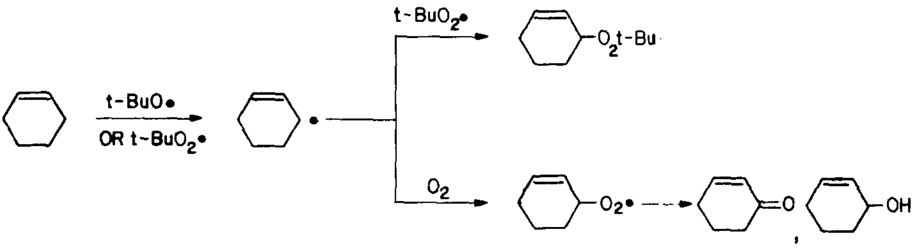
Reaction with Solvent, e.g., Cyclohexane



(8)

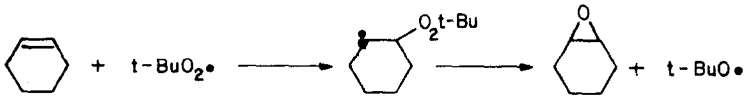
(9)

Reaction with Olefin, e.g., Cyclohexene



(10)

(11)



(12)

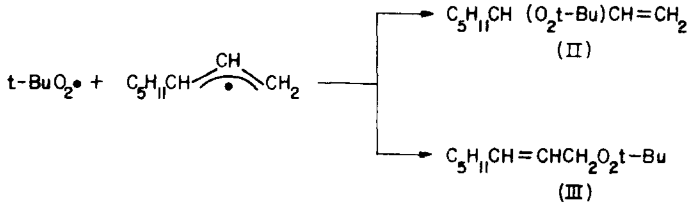
The relative contributions of the various reactions depend on the relative reactivities of the solvent and the olefin to radical attack and on the molar ratios of olefin, hydroperoxide and solvent.

Addition of *tert*-butylperoxy radicals to the double bond [reaction (12)] may be, at least partly, responsible for the formation of epoxides in the reaction of *tert*-butyl hydroperoxide with olefins in the presence of the less active catalysts in Table 1. Epoxide yields of 5–10% and 10–30% have been reported (*23*) for the reaction of *tert*-butyl hydroperoxide with 1-octene and cyclohexene, respectively, in the absence of a catalyst at 100°C.

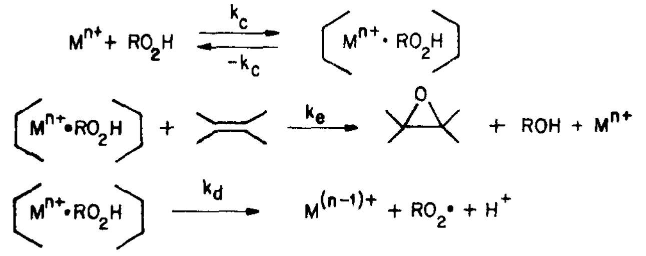
Abstraction of hydrogen from 1-octene affords an unsymmetrical allylic radical, which combines with *tert*-butylperoxy radicals to give (II) and (III) in approximately equal amounts.

Selectivity

In general, our results may be rationalized with a scheme (Eqs. (13)–(15)) involving competing homolytic decomposi-



tion of a catalyst-hydroperoxide complex and its reaction with the olefin, as proposed earlier (*11*) for molybdenum-catalyzed epoxidations.



(13)

(14)

(15)

The selectivity to epoxide is determined by the relative rates of reactions (14) and (15). Assuming that there is no radical-induced chain decomposition of the hydroperoxide (because of the radical scavenging effect of the olefin) and neglecting small amounts of epoxide formed via a radical pathway [Eq. (12)] one obtains the expression:

$$\text{epoxide selectivity} = \{k_e[\text{olefin}]/(k_d + k_e[\text{olefin}])\} \times 100\%,$$

where $k_2 = k_eC$ ($C = k_c/k_{-c}$).

In general, the ease with which transition-metal ions or complexes catalyze the decomposition of hydroperoxides is related to their redox potentials. Hydroperoxides are strong oxidants but weak reducing agents and, hence, reaction (4) is the slower, rate-determining step in hydroperoxide decomposition and is facile only with strong oxidants such as Co(III), Ce(IV) and Pb(IV). The oxidation potentials (E_0(eV) for $M^{n+} + e \rightarrow M^{(n-1)+}$) in aqueous solution are: Co(III), 1.82; Ce(IV), 1.61; Mn(III), 1.51; V(V), 1.0; Mo(VI), 0.2; W(VI), 0.03; Ti(IV), 0.06; and U(VI), 0.05 (*24*). Of course, the oxidation potential is influenced by the ligands surrounding the metal but the above data afford a qualitative picture of the relative oxidizing strengths of complexes of these metals. Examination of the data reveals that all of the epoxidation catalysts, with the exception of vanadium, are weak oxidants in their highest oxidation states. This explains why vanadium catalysts give lower epoxide selectivities than molybdenum, tungsten and titanium catalysts. V(V) is a much stronger oxidant than Mo(VI), W(VI) or Ti(IV) and, hence, more readily causes decomposition of the hydroperoxide. The low activity of other transition-metal catalysts, such as Th(IV) or Zr(IV), which are weak oxidants and do not cause rapid decomposition of the hydroperoxide, is of course due to the fact that they are weak Lewis acids (*vide supra*). However, ZrO_2-on-SiO_2 is a relatively active epoxidation catalyst (*12c*), which is attributable to its Lewis acidity being stronger than that of other Zr(IV) compounds (cf. TiO_2-on-SiO_2).

We conclude that oxidation potential and Lewis acidity play an important role in determining the effectiveness of transition-metal compounds as epoxidation catalysts. Activity may also be affected by other properties, e.g., the size of the metal atom may be important in determining whether or not the geometry of the cyclic transition state for oxygen transfer is favorable.

Autoretardation by tert-*Butanol*

Another factor that influences the rates and selectivities of these epoxidations is autoretardation by the co-product alcohol (*20*). Complex formation between the catalyst and *tert*-butanol will hinder both the formation of a catalyst–hydroperoxide complex and the reaction of the latter with the olefin. The former will lead to a reduced rate and the latter to a reduced selectivity to epoxide.

The extent of autoretardation will be related to the equilibrium constants for the formation of catalyst–hydroperoxide and catalyst–alcohol complexes. This ratio is likely to vary with the metal; our results show that autoretardation by *tert*-butanol increases in the order $W < Mo < Ti < V$, the rates of molybdenum- and tungsten-catalyzed epoxidations being only slightly affected under our conditions. It is not clear at present why autoretardation should play a more important role with 1-octene than with cyclohexene.

REFERENCES

1. For a recent review see HIATT, R., *in* "Oxidation, Techniques and Application in Organic Synthesis" (R. L. Augustine, Ed.), Vol. 2, pp. 113–138. Dekker, New York, 1971.

2. INDICTOR, N., AND BRILL, W. F., *J. Org. Chem.* **30**, 2074 (1965).

3. KOLLAR, J., *U. S. Pat.* 3,350,422 (1967); *U. S. Pat.* 3,351,635 (1967).

4. SHENG, M. N., AND ZAJACEK, J. G., *J. Org. Chem.* **35**, 1839 (1970).

5. SHENG, M. N., AND ZAJACEK, J. G., *Advan. Chem.* **76**, 418 (1968).

6. GOULD, E. S., HIATT, R. R., AND IRWIN, K. C., *J. Amer. Chem. Soc.* **90**, 4573 (1968); SU, C. G., REED, Y. W., AND GOULD, E. S., *Inorg. Chem.* **12**, 337 (1973).

7. HOWE, G. R., AND HIATT, R. R., *J. Org. Chem.* **36**, 2493 (1971).

8. DITMANN, W., *Angew. Makromol. Chem.* **4/5**, 255 (1968).

9. DZHEMILEV, U. M., YUREV, N. P., TOLSTIKOV, G. A., GERSHANOV, F. B., AND RAFIKOV, S. R., *Dokl. Akad. Nauk SSSR* **196**, 588 (1971).

10. KALOUSTIAN, J., LENA, L., AND METZGER, J., *Bull. Soc. Chim. Fr.* 4415 (1971).

11. SHELDON, R. A., *Recl. Trav. Chim.* **92**, 253, 367 (1973).

12. (a) *Brit. Pat.*, 1,249,079 (1971); (b) *Brit. Pat.*, 1,248,185 (1971); (c) *Brit. Pat.* 1,249,082 (1971); (d) *Brit. Pat.*, 1,248,079 (1971).

13. KHARASCH, M. S., PAUSON, P., AND NUDENBERG, W., *J. Org. Chem.* **18**, 322 (1953); KHARASCH, M. S., AND FONO, A., *J. Org. Chem.* **24**, 72 (1959); **23**, 324 (1958).

14. (a) GILMAN, H., JONES, R. G., BINDSCHALLER, E., BLUME, D., KARMES, G., MARTIN, G. A., NOBIS, J. F., THIRTLE, J. R., YALE, H. L., AND YOEMAN, F. A., *J. Amer. Chem. Soc.* **78**, 2790 (1956); (b) MAJUMDAR, A. K., BHATTACHARYYA, R. G., AND BERA, D. C., *Chem. Ind.* (*London*) 730 (1971).

15. GEHRKE, H., AND VEAL, J., *Inorg. Chim. Acta* 623 (1969).

16. HIATT, R., MILL, T., AND MAYO, F. R., *J. Org. Chem.* **33**, 1416 (1968).

17. CLARK, R. J. H., "The Chemistry of Titanium and Vanadium," Elsevier, Amsterdam, 1968; FELD, R., AND COWE, P. L., "The Organic Chemistry of Titanium," Butterworths, London, 1965; SHIHARA, I., SCHWARZ, W. T., AND POST, W. W., *Chem. Rev.* **61**, 1 (1961).

18. WOLF, P. F., AND BARNES, R. K., *J. Org. Chem.* **34**, 3441 (1969).

19. "Table of Periodic Properties of the Elements," copyright Sargent-Welch Scientific Co., Chicago, IL, 1968.

20. SHELDON, R. A., VAN DOORN, J. A., SCHRAM, C. W. A., AND DE JONG, A. J., *J. Catal.* **31**, 438 (1973).

21. Neth. Pat. Applic., 7,110,141 (1971).

22. For a recent review see SOSNOVSKY, G., AND RAWLINSON, D. J., *in* "Organic Peroxides" (D. Swern, Ed.), Vol. 2. Wiley (Interscience), London, 1971.

23. BRILL, W. F., AND INDICTOR, N., *J. Org. Chem.* **29**, 710 (1964).

24. See LATIMER, W. M., "Oxidation Potentials," 2nd ed., Prentice-Hall, New York, 1952.