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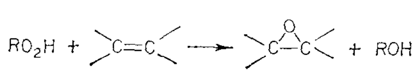
Selective Olefin Epoxidation at High Hydroperoxide-to-Olefin Ratios

Metal catalyzed epoxidation of olefins with organic hydroperoxides has received considerable attention in recent years. Numerous different homogeneous and heterogeneous catalysts have been reported to catalyze the following reaction,



with the best results obtained with homogeneous molybdenum calalysts (*1*). It has been proposed that complex formation between the transition metal catalyst and the hydroperoxide renders the hydroperoxide oxygen more electrophilic and thus more liable to attack the olefin double bond (*2*). The transition metal catalyst can also catalyze the homolytic decomposition of the hydroperoxide (*3*), thus resulting in low epoxide yields. This is especially true at high hydroperoxide-to-olefin ratios (*4*). This is the likely reason why the patent disclosing this technology specifically suggests that the epoxidation of olefins with organic hydroperoxides be carried out in an excess of olefin by adding the hydroperoxide to the olefin, preferably in increments (*4*).

We have found that selective epoxidation of olefins with cumene hydroperoxide (CHP) can be accomplished at high CHP-to-olefin ratios. This can only be done if barium oxide is present in the reaction mixture. The following experiments report how this was accomplished.

To prepare cumene hydroperoxide, a mixture of 50 ml cumene and 0.2 g BaO was heated to 110°C in a reactor. To this mixture was added 1 ml of cumene hydroperoxide as an initiator. Oxygen was bubbled through the reaction mixture at a rate of 100 ml/min. After 1 hr a 13 wt% cumene hydroperoxide in cumene solution was obtained. Most of the oxygen was then removed by flushing with nitrogen and a nitrogen blanket was maintained in the reactor during subsequent addition and reaction with 1-octene. A 20 ml sample of 1-octene at about 20°C containing 0.5 g molybdenum naphthenate (4.6 wt% Mo) was then introduced in 25 min in a continuous stream while the reactor temperature was maintained at 120°C. The reaction mixture was cooled to room temperature and a small sample was titrated iodometrically to determine the final CHP concentration. A 90.5% conversion of CHP was obtained. The amount of 1-octene oxide in the product was determined by gas chromatography. The percentage selectivity to 1-octene oxide based on the CHP converted was 95%.

The same experiment was run with the exception that a 50 ml solution containing 13 wt% CHP was prepared by adding commercially available CHP. The CHP solution was charged to a glass reactor, 0.2 g BaO were added to the CHP solution, and the reaction was conducted as cited above. An 89% conversion of CHP was obtained with a selectivity of 93.5% to 1-octene oxide.

To demonstrate the importance of having BaO present, the reaction was conducted without BaO. There was 100% conversion of CHP, however, no 1-octene oxide was formed.

A series of experiments was then made to compare the stabilizing effect of barium oxide with a number of other materials as

TABLE 1

Evaluation of Metal Oxides for Obtaining Selective Epoxidation

Co-catalyst	Wt%	Mol/100 g	Reaction time (hr)	% CHP converted	Selectivity[a]
None	—		1.0	100	9
NiO	0.30	0.040	1.0	100	5
MgO	0.08	0.020	1.0	100	11
CaO	0.30	0.052	0.75	100	8
SrO	0.30	0.030	1.25	98	41
BaO	0.30	0.020	1.0	91	95
NaOH	0.30	0.075	1.25	75	3.7
KOH	0.30	0.055	1.5	76	3.9
ZnO	0.30	0.037	0.1	100	10.5

[a] Selectivity = (moles 1-octene oxide formed/moles CHP reacted) × 100.

potential stabilizing agents. These runs were carried out by adding (over 20–30 min) 20 ml of 1-octene containing 1 wt% molybdenum naphthenate to a 50 ml solution of 13 wt% CHP at 120°C in a nitrogen atmosphere. The results of these runs are given in Table 1 which gives the conversion of CHP and corresponding selectivity values to 1-octene oxide. From these data it is obvious that barium oxide is a unique material in permitting selective epoxidation to occur.

The ability of BaO to inhibit the catalytic decomposition of hydroperoxide was further studied by conducting two experiments involving a 14% *t*-butyl hydroperoxide-xylene solution. Figure 1 shows data for the decomposition of *t*-butyl hydroperoxide at 110°C in the presence of (a) 0.02 wt% molybdenum naphthenate and (b) 0.02 wt% molybdenum naphthenate plus 0.4 wt% barium oxide. After 1 hr, only 5% of the *t*-butyl hydroperoxide was decomposed using BaO, whereas, without BaO 55% was decomposed.

A possible explanation why barium oxide permits selective epoxidation under these conditions may be related to its basic character which aids in stabilizing a molybdenum–hydroperoxide intermediate. In considering the basicity of oxides, combined oxygen can act as an electron donor. The greater the negative charge on the oxygen atom, the stronger the basic character of the oxide (*5*). Take and co-workers (*6*) found good agreement between observed and expected basic properties for alkaline earth oxides based on H_- indicator experiments. Tanabe and Fukuda reported (*7*) the order of basic strength to be BaO > SrO > CaO > MgO based on the catalyzed decomposition of diacetone alcohol, a reaction which is base-catalyzed. Similarly, Saito and Tanabe (*8*) found a good correlation between the catalytic activity of benzaldehyde esterification catalyzed by alkaline earth oxides and surface basicity of oxides as measured by indicators.

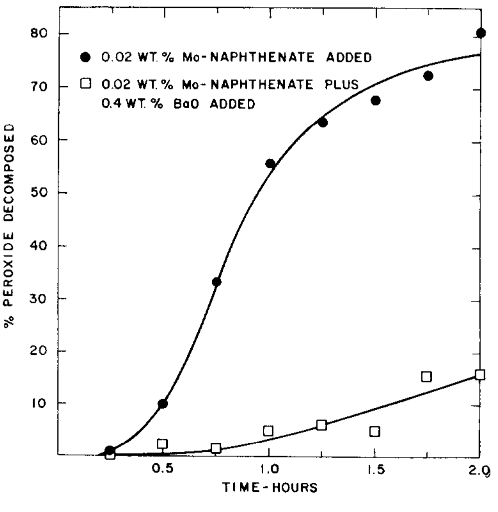
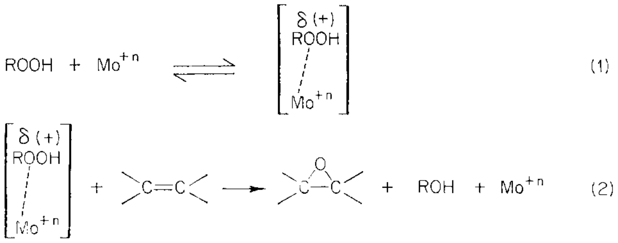
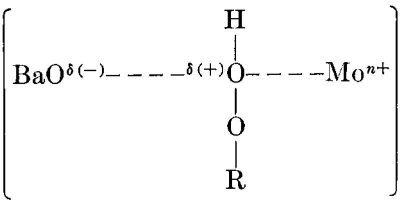


FIG. 1. Decomposition of *t*-butyl hydroperoxide.

Sheng and Zajacek (*1*) proposed a mechanism involving the hydroperoxide transition state:



Assuming that this type of complex is involved, the barium oxide could complex to the hydroperoxide through the oxygen atom due to its negative character (basicity).



$$\left[\mathrm{BaO}^{\delta(-)}----{}^{\delta(+)}\underset{\underset{\mathrm{R}}{|}}{\underset{\mathrm{O}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{O}}}----\mathrm{Mo}^{n+}\right]$$

This could result in stabilizing the hydroperoxide towards radical chain decomposition permitting selective epoxidation to take place via the hydroperoxide–molybdenum–olefin transition state proposed by Sheng and Zajacek (*1*). Without barium oxide CHP is rapidly decomposed, catalyzed by molybdenum compounds according to the following reactions:

$$M^{n+} + \mathrm{ROOH} \rightarrow M^{(n-1)+} + \mathrm{R\text{-}O_2}\cdot + \mathrm{H}^+, \quad (3)$$

$$M^{(n-1)+} + \mathrm{ROOH} \rightarrow M^{n+} + \mathrm{R\text{-}O}\cdot + \mathrm{OH}^-, \quad (4)$$

$$2\,\mathrm{RO_2}\cdot \rightarrow 2\,\mathrm{RO}\cdot + \mathrm{O_2}. \quad (5)$$

Selective epoxidation occurs without BaO only at high olefin-to-hydroperoxide ratios, which is likely due to the ability of the olefin to act as a radical scavenger.

SrO is the next best oxide for improving selectivity which would be expected based on its basicity. After that there is little difference between the results obtained using CaO and MgO. If a ternary Mo–peroxide–BaO complex is involved, it is expected that the epoxidation rate would be retarded compared to when other oxides of lower basicity are used. This was found to be true from experiments conducted in our laboratory and can be seen to a certain extent from data in Table 1, for experiments conducted with BaO, SrO and CaO. The poor results obtained using powdered samples of NaOH, KOH and ZnO would be expected based on the findings of Take *et al.* (*6*) where it was found that these materials have low basicities and would have little tendency to form a ternary complex. This would result in permitting the catalytic decomposition of CHP to occur as was observed. The low selectivity obtained with NiO is in agreement with a report that MoO_3, Fe_2O_3, V_2O_5, and NiO are good catalysts for CHP decomposition (*9*).

Of course, a simpler but related explanation of the results can be offered by postulating that BaO functions as an effective radical scavenger, i.e., terminating reactions 3–5, thus permitting selective epoxidation to proceed. This possibility is a subject of current research.

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