BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1604—1608 (1969)

Epoxidation of Eight- and Twelve-Membered Cyclic Olefins with Hydrogen Peroxide in the Presence of Metal Oxide Catalysts*[1]

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(Received April 25, 1968)

The oxidation of eight- and twelve-membered cyclic olefins by H_2O_2 was carried out in various alcohols using some metal oxides as catalysts. In contrast to the case of cyclohexene and norbornene, which can be hydroxylated, the oxidation of 1,5,9-cyclododecatriene, cyclododecene, 1,3- and 1,5-cyclooctadiene and cyclooctene with H_2O_2 in the presence of selenium dioxide resulted in selective formation of the corresponding monoepoxides. The following rate equation was obtained with cyclooctene (COE) in isopropanol:

$$-\mathrm{d}[H_2O_2]/\mathrm{d}t = k_3'[SeO_2][H_2O_2] + k_3''[SeO_2][H_2O_2][COE].$$

It is well known that the oxygen compounds of some heavy metals, such as tungsten, selenium, vanadium, osmium, molybdenum and chromium, catalyze the H_2O_2 oxidation in characteristic fashion. The oxidation of olefins yields α-diols as the main product.[1-4] Epoxide formation as intermediate was suggested for WO_3 and SeO_2 catalyzed reactions.[3,4] The present paper describes some results obtained on the H_2O_2 oxidation of eight- and twelve- membered cyclic olefins in the presence of metal oxides, especially selenium dioxide.

Experimental

Materials. Commercial cycloolefins were distilled to remove antioxidants before use. *trans, cis*-1,5-Cyclodecadiene was prepared by the cooligomerization of butadiene with ethylene using a catalyst composed of nickel acetylacetonate, triphenyl phosphite and triethylaluminum. Hydrogen peroxide and selenium dioxide (G. R. grade) were used without further purification. Alcohols of G. R. grade were distilled and used as solvents in the preparation, but for the kinetic purposes, they were dried by refluxing over magnesium or calcium metal.

Preparative Experiments. SeO_2 was dissolved in alcohol, olefin was then added, and the alcoholic solution of H_2O_2 was added dropwise with agitation and cooling within 2 hr. After agitation for further several hours, the reaction mixture was washed with aqueous solutions of sodium bisulfite and sodium carbonate. The ether extract of aqueous washings and other organic layers were brought together and dried over sodium sulfate. The product was distilled under reduced pressure. The determination of the amount of epoxide formed was carried out with the hydrogen chloride-dioxane-method,[5] in which the optimal reaction time of epoxide with H_2O_2 was pre-determined for each epoxide.

Kinetic Procedure. The reaction was carried out in alcoholic media at 25—50°C with the following initial concentration ranges of reagents: $[SeO_2]_0=3.33-26.67$ mmol/*l*, $[\text{Olefin}]_0=0.300-1.333$ mol/*l*, $[H_2O_2]_0=0.147-0.294$ mol/*l*, $[H_2O]_0=29.8$ mmol/*l*. Aliquots were taken out at intervals, the reaction was stopped by addition of an alcoholic potassium hydroxide solution, and the peroxide content was determined iodometrically.

Results and Discussion

Oxidation of Several Cylcoolefins. The results of oxidation of *trans,trans,cis*-1,5,9-cyclododecatriene (*t,t,c*-CDT) under various reaction conditions are shown in Table 1.

In contrast to the oxidation of cyclohexene,[4] epoxide was produced selectively regardless of solvents. The content of water exhibited little effect on the selectivity of epoxide. 9,10-Epoxy-1,5-cyclododecadiene was obtained by distillation of the product: bp 102°C/2.5 mmHg, n_D^{20} 1.5017. Found: C, 80.72; H, 10.03%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%. The infrared spectrum, which was identical with that reported,[6] showed strong absorption bands of *trans* and *cis* double bonds at 972cm^{-1} and 700 cm^{-1}, respectively. Meanwhile, gas chromatography indicated the presence of two isomers in a molar ratio of 97 to 3,

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*1 A part of this paper was presented at the 6th Meeting of the Oil Chemical Society of Japan, Nagoya, Oct. 1967.

[1] M. Mugdan and D. P. Young, *J. Chem. Soc.*, **1949**, 2988.

[2] N. Sonoda and S. Tsutsumi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 110 (1960).

[3] G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1682 (1957).

[4] N. Sonoda and S. Tsutsumi, This Bulletin, **38**, 958 (1965).

[5] G. Wilke, Japanese Pat. 7822 (1961).

[6] W. Stumpf and K. Rombusch, *Ann. Chem.*, **687**, 136 (1965).

Table 1. Oxidation of *t,t,c*-CDT

Solvent[a]	SeO_2 mol	CDT mol	H_2O_2 %	H_2O_2 mol	H_2O_2/CDT mol/mol	Temp. °C	Time hr	ECDD[b] formed mol	ECDD[b] yield, % *vs.* reacted CDT	ECDD[b] yield, % *vs.* H_2O_2
t-BuOH	0.054	0.36	90	0.44	1.24	25—30	16	0.16	54	37
	0.045	0.71	90	0.44	0.62	25—30	16	0.21	81	49
	0.036	0.75	90	0.30	0.32	25—30	16	0.19	77	63
i-PrOH	0.045	0.60	90	0.30	0.50	25—30	40	0.21	92	70
	0.045	0.60	90	0.60	1.00	25—30	40	0.28	65	46
	0.045	0.60	90	1.60	2.67	25—30	40	0	0	0[c]
	0.045	0.60	90	0.30	0.50	45—50	40	0.15	83	49
	0.090	0.60	60	0.30	0.50	25—30	40	0.22	84	74
	0.045	0.60	30	0.30	0.50	25—30	40	0.12	87	40
n-PrOH	0.045	0.60	90	0.30	0.50	25—30	40	0.10	92	35
EtOH	0.045	0.60	90	0.30	0.50	25—30	40	0.08	83	26

a) 300 m*l* was used.
b) ECDD=9,10-epoxy-1,5-cyclododecadiene.
c) Mono- and diepoxides could not be isolated by distillation.

Table 2. Oxidation of CDE (150 m*l* solvent, 25—30°C, 16 hr)

Solvent	SeO_2 mol	CDE mol	H_2O_2 %	H_2O_2 mol	H_2O_2/CDE mol/mol	ECDA[a] formed mol	ECDA[a] yield, % *vs.* consumed CDE	ECDA[a] yield, % *vs.* H_2O_2	ECDA[a] isomer ratio[b]
t-BuOH	0.023	0.30	90	0.27	0.90	0.167	89	62	75/25
i-PrOH	0.023	0.30	90	0.15	0.50	0.135	96	90	73/27
	0.023	0.30	90	0.30	1.00	0.212	95	71	73/27
	0.023	0.30	90	0.45	1.50	0.283	96	63	74/26
	0.023	0.30	60	0.15	0.50	0.132	95	88	71/29
n-PrOH	0.023	0.30	90	0.15	0.50	0.170	91	82	73/27
EtOH	0.023	0.30	90	0.30	1.00	0.253	—	84	—

a) ECDA=epoxycyclododecane.
b) Determined by gas chromatography.

Table 3. Oxidation of eight-membered cyclic olefins
(35—40°C, 4 hr, in 300 m*l* isopropanol)

Olefin	mol	SeO_2 mol	H_2O_2 %	H_2O_2 mol	H_2O_2/Olef. mol/mol	Epox. formed mol	Unreacted olefin mol	Epox. yield, % *vs.* consumed olefin	Epox. yield, % *vs.* H_2O_2
COE	1.00	0.10	90	0.77	0.77	0.68	0.30	97	68
1,3-COD	1.20	0.12	90	0.60	0.50	0.43	0.68	83	72
1,5-COD	1.20	0.12	90	0.60	0.50	0.45	0.63	79	75

suggesting that *trans* double bond of *t,t,c*-CDT is oxidized more easily than *cis*. This could be attributed to the larger internal strain of the former. Similar results have also been reported recently for the organic peracid oxidation of the same olefin.[7]

Table 2 shows the oxidation results of cyclododecene (CDE).

A mixture of *trans* and *cis* CDE in a molar ratio of 68 to 32 was oxidized to give two isomeric epoxides in an approximately constant ratio. Epoxycyclododecane (a *trans-cis*-mixture with 72 : 28) was isolated by distillation: bp 116—117°C/4.7mmHg, n_D^{20} 1.4763. Found: C, 79.05; H, 12.08%. Calcd for $C_{12}H_{24}O$: C, 79.06; H, 12.17%.

The epoxidation of eight-membered cyclic olefins is summarized in Table 3. An excellent yield was attained with cyclooctene (COE), while lower yields were observed with 1,3- and 1,5-cyclooctadiene (COD).

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7) J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss, "Organic Analysis," Vol. I, ed. by J. Mitchel, Jr., I. M. Kolthoff, E. S. Proskauer and A. Weissberger, Interscience Publishers, New York, N. Y. (1953), p. 135.

TABLE 4. H_2O_2 OXIDATION WITH METAL OXIDE CATALYSTS

Olefin		Catalyst		Solvent *ml*	H_2O_2		Reacn. condn. °C/hr	Epox. formed mol	Epox. yield, %	
	mmol		mol		%	mol			*vs.* consumed olefin	*vs.* H_2O_2
CDT	0.60	WO_3	13	*i*-PrOH 250	90	0.30	35—40/16	0	—	—
	0.60	$H_2WO_4\cdot H_2O$[a]	11	*i*-PrOH 200	90	0.40	30—35/16	0.16	89	40
	0.60	$H_2WO_4\cdot H_2O$	19	*i*-PrOH 205 +H_2O 5	90	0.40	30—35/16	0.21	83	53
	0.60	$H_2WO_4\cdot H_2O$	19	*i*-PrOH 180 +H_2O 30	90	0.40	30—35/16	0.21	76	53
	0.60	$H_2WO_4\cdot H_2O$	11	*t*-BuOH 200	90	0.40	30—35/16	0.23	82	57
	0.60	H_2MoO_4	31	*i*-PrOH 200 +H_2O 30	90	0.40	30—35/16	0.18	91	44
	0.60	V_2O_5	17	*i*-PrOH 200 +H_2O 10	90	0.40	30—35/16	0.19	90	49
CDE	0.60	$H_2WO_4\cdot H_2O$[a]	8	*i*-PrOH 200	90	0.40	30—35/16	0.24	88	61
1,5-COD	0.60	$H_2WO_4\cdot H_2O$[a]	8	*i*-PrOH 200	90	0.40	30—35/4	0.09	23	14
COE	0.60	$H_2WO_4\cdot H_2O$[a]	8	*i*-PrOH 200	90	0.40	30—35/3	0.31		78

a) In these runs the catalyst was added to a hydrogen peroxide solution and agitated for 30 min at room temperature.

TABLE 5. RATE DATA OF OXIDATION OF COE

Solvent	$[SeO_2]$ mmol/*l*	$[H_2O_2]_0$ mol/*l*	$[H_2O]_0$ mmol/*l*	$[COE]_0$ mol/*l*	Temp. °C	$(pH)_0$	$(k_1)_0\times10^3$ min^{-1}	$(k_2)_0\times10^1$ *l*·mol^{-1}·min^{-1}
i-PrOH	13.33	0.147	29.8	1.333	25		2.68	2.01
	13.33	0.147	29.8	0.900	25		1.84	1.38
	13.33	0.147	29.8	0.533	25		1.21	0.91
	26.67	0.147	29.8	1.333	30	3.7	7.02	2.63
	20.00	0.147	29.8	1.333	30	4.0	5.24	2.62
	13.33	0.147	29.8	1.333	30	4.1	3.51	2.63
	6.67	0.147	29.8	1.333	30	4.3	1.65	2.46
	3.33	0.147	29.8	1.333	30	4.4	0.68	2.04
	13.33	0.147	29.8	0.900	30	4.2	2.46	1.83
	13.33	0.294	59.6	0.533	30	4.3	1.56	1.17
	26.67	0.147	29.8	0.300	30	4.1	1.84	0.73
	13.33	0.147	740	1.333	30		2.64	1.98
	13.33	0.147	1850	1.333	30		1.93	1.45
	13.33	0.147	3700	1.333	30		1.35	1.02
	13.33	0.147	29.8	1.333	40		5.74	4.30
	13.33	0.147	29.8	0.900	40		3.95	2.96
	13.33	0.147	29.8	0.533	40		2.47	1.85
	13.33	0.147	29.8	0.300	40		1.48	1.11
	13.33	0.147	29.8	0.900	50		6.47	4.85
	13.33	0.147	29.8	0.533	50		4.05	3.04
	13.33	0.147	29.8	0.300	50		2.51	1.88
t-BuOH	13.33	0.147	29.8	1.333	30		9.05	6.78
EtOH	13.33	0.147	29.8	1.333	30		1.61	1.21

Physical properties of the isolated epoxides were as follows: epoxycyclooctane, mp 56—57°C; 3,4-epoxy-1-cyclooctene, bp 74—75°C/13 mmHg, n_D^{20} 1.4832; 5,6-epoxy-1-cyclooctene, bp 80—81°C/18 mmHg, n_D^{20} 1.4890.

The SeO_2 catalyzed H_2O_2 oxidation of *trans, cis*-1,5-cyclodecadiene, however, resulted in the formation of several products including small amounts of epoxides which could not be identified. No examination was made on the possibility of double bond isomerization, though the olefin is known to be a relatively unstable compound, which can easily be isomerized either to *cis,cis*-1,6-cyclodecadiene,[8] or to 1,2-divinylcyclohexane.[9]

The oxidation results with several metal oxides

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[8] P. Heimbach, *Angew. Chem.*, **78**, 604 (1966).

[9] G. Wilke and P. Heimbach, *ibid.*, **75**, 10 (1963).

other than SeO_2 are summarized in Table 4. Epoxides were also obtained in good selectivities with the oxides of tungsten, molybdenum and vanadium as catalysts. All the systems given in Table 4 were heterogeneous because of the poor solubilities of catalysts. With $H_2WO_4 \cdot H_2O$, the amount of distillation residue increased, as did the water content in the reaction medium.

Kinetics on Oxidation of Cyclooctene. The only example of kinetic investigation on H_2O_2 oxidation in the presence of SeO_2 so far seems to be that reported by Ogata and Tabushi,[10] who employed dimethylaniline as substrate. No information has been available on the kinetic behavior of the oxidizing system on olefinic double bond. The fact that the oxidation of cycloolefin was essentially an epoxidation prompted us to the kinetic study. Cyclooctene was chosen as the substrate.

No reaction occurred on treatment of cyclooctene with 90% H_2O_2 alone or SeO_2 alone. The system SeO_2-H_2O_2 in isopropanol shows a very slight decrease in the H_2O_2 concentration only after a long period with agitation.

Effects of the Concentration of Reaction Components. The results of oxidation of COE are summarized in Table 5. In every run, plots of H_2O_2 consumption against reaction time indicated that the rate $-d[H_2O_2]/dt$ was directly proportional to H_2O_2. Water, which was formed by the reaction, did not seem to influence the rate at all, while the apparent value of pH varied slightly (in the range of 0.1 to 0.2) during the course of reaction. Hence the following equation is obtained:

$$-\frac{d[H_2O_2]}{dt} = k_1[H_2O_2] \qquad (1)$$

To determine the effect of SeO_2, rates of H_2O_2 consumption were measured at various initial concentrations of SeO_2, while keeping initial concentration of H_2O_2 and COE constant. The results are given in Fig. 1, which suggests a first order relationship between the rate and $[SeO_2]$. A slight deviation from the direct proportionality as observed for low concentrations of SeO_2 might be ascribed to the decrease in acidity. Combining the result with Eq. (1), we have the following equation:

$$-\frac{d[H_2O_2]}{dt} = k_2[H_2O_2][SeO_2] \qquad (2)$$

In order to determine the effect of cyclooctene concentration, rates were measured varying its initial concentration, and the extrapolated values of $(-d[H_2O_2]/dt)/[H_2O_2]$ at $t=0$, or $(k_1)_0$, were calculated (see Table 5). Although a linear relationship exists between $(k_1)_0/[SeO_2]$ and $[COE]_0$, as shown in Fig. 2, they are not directly proportional to each other. This was proved to be valid for different temperatures applied. Figure 2 gives the equation:

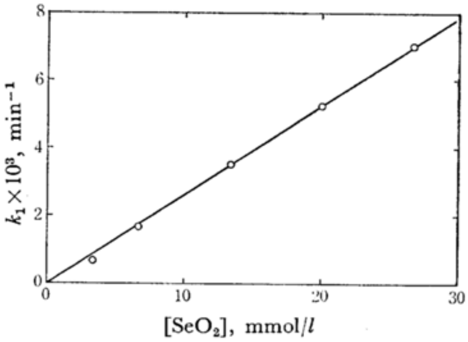

Fig. 1. Effect of concentration of SeO_2 on the rate.
($[COE]_0=1.333$ mol/l, $[H_2O_2]_0=0.147$ mol/l, $[H_2O]_0=29.8$ mmol/l, 30°C, in isopropanol)

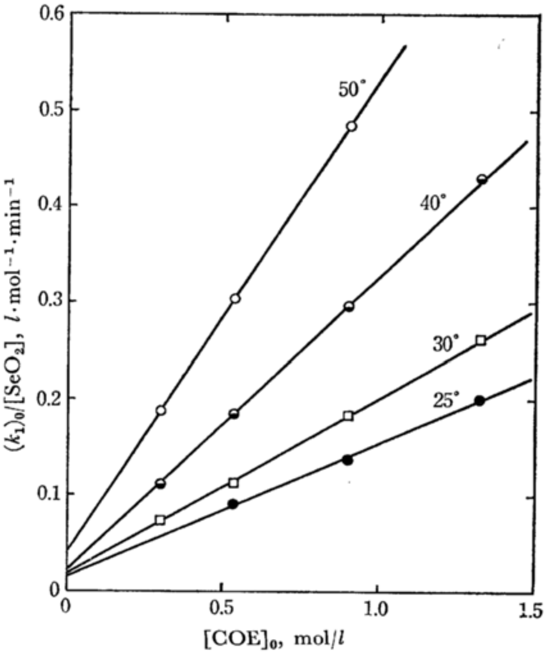

Fig. 2. Effect of initial concentration of COE on the rate.
($[H_2O_2]_0=0.147$ mol/l, $[H_2O]_0=29.8$ mmol/l, in isopropanol)

$$-\frac{d[H_2O_2]}{dt} = k_3'[SeO_2][H_2O_2] + k_3''[SeO_2][H_2O_2][COE] \qquad (3)$$

Table 6 summarizes the values of k_3' and k_3''. For k_3'', the Arrhenius plot gives a straight line, from which apparent activation energy and activation entropy are calculated:

$$\Delta H^{\neq} = 9.67\ \mathrm{kcal\cdot mol^{-1}},$$
$$\Delta S^{\neq} = -38.2\ \mathrm{cal\cdot mol^{-1}\cdot {}^{\circ}C^{-1}}\ (40^{\circ}C).$$

The first term of the right side in Eq. (3) expresses the rate of H_2O_2 consumption, which is of

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[10] Y. Ogata and I. Tabushi, This Bulletin, **32**, 215 (1959).

TABLE 6. VALUES OF k_3' AND k_3''

Temp. °C	k_3' $l\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$	k_3'' $l^2\cdot\text{mol}^{-2}\cdot\text{min}^{-1}$
25	0.0155	0.138
30	0.017	0.184
40	0.021	0.306
50	0.038	0.495

zeroth order with respect to COE concentration. On the other hand, the rate of H_2O_2 consumption in the system SeO_2–H_2O_2–iPrOH (in the absence of COE) was shown to be much smaller than the corresponding value of the term $k_3'[SeO_2][H_2O_2]$. This fact means that the term expresses mainly reactions of H_2O_2 in which both SeO_2 and COE actually participate. The k_3' values do not satisfy the Arrhenius equation, so that the activation energy is not obtainable. The term may therefore include several reactions, in which COE does and does not participate. Ogata and Tabushi[10] have previously obtained comparable results on the oxidation of dimethylaniline with SeO_2-H_2O_2, and proposed two independent routes for amine oxide formation. Considering our results, this concept is now extended for oxidation of olefinic double bonds as follows:

$$H_2O_2 + SeO_2 \rightleftharpoons \text{Peracid } A_1 \xrightarrow{+\text{Olefin}} H_2SeO_3 + \text{Epoxide} \qquad (4)$$

$$H_2O_2 + SeO_2 \rightleftharpoons \text{Peracid } A_2 \xrightarrow{+\text{Olefin}} H_2SeO_3 + \text{Epoxide} \qquad (5)$$

A highly active peracid A_1 in Eq. (4) would be formed by a slow reaction of H_2O_2 with SeO_2, which then reacts with COE rapidly, whereas a more stable peracid A_2, formed through a fast reaction, would oxidize the olefin slowly. No attempts, however, were made by us to obtain information on the structures of these active peracids.

Effect of Solvents. As Table 5 indicates, less-polar alcohols favor the oxidation.

The effect of water content in the reaction medium is also given in Table 5. It is apparent that an increase in water concentration causes a marked reduction of the rate. As already discussed in the previous report on oxidation of dimethylaniline in methanol-water medium,[10] this effect could be attributed mainly to a hindering action of water in regenerating SeO_2 dehydration of H_2SeO_3, that is formed through the oxidation reaction (see Eqs. 4 and 5). If SeO_2 is not smoothly regenerated, the effective concentration of the oxide is lowered, and then, according to Eqs. (4) and (5), the formation of active peracids may also be hindered.

Hydroxylation and Epoxidation. On studying the hydroxylation of cyclohexene with H_2WO_4-H_2O_2, Payne and Smith[3] proposed a reaction scheme including formation of epoxide as the intermediate. A similar conclusion was also obtained by Sonoda and Tsutsumi for SeO_2-catalyzed hydroxylation of the cycloolefin on the basis of the product analysis.[4] Our results have now provided examples, in which the epoxides can actually be isolated by treating cycloolefins with SeO_2- of H_2WO_4-H_2O_2. It is evident, that the reaction of H_2O_2 with the olefinic double bond in the presence of oxides of W, Se, Mo and V is essentially an epoxidation, and it is also hardly doubtable that the hydroxylation occurs with many olefins as the successive hydrolysis of the epoxide formed. In fact, there seem to exist certain differences between epoxides of cyclohexene and higher-membered cyclic olefins in the ease of ring opening in acidic media.[11] Such differences can not simply be explained through the electronic effect, as is known for epoxides of substituted aliphatic olefins, since we have here no branched chains. Some steric effects such as steric hindrance or internal strain should be considered to play a part.

The authors wish to thank Toa Gosei Chemical Industry Co. for permission to publish these results.

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[11] J. Itakura and H. Tanaka, unpublished results.