Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

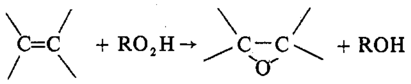
Metal Ion Catalysis of Oxygen-Transfer Reactions. II. Vanadium and Molybdenum Chelates as Catalysts in the Epoxidation of Cycloalkenes[1]

CHAN-CHENG SU, JOHN W. REED, and EDWIN S. GOULD*

Received June 12, 1972

The reactions of *tert*-butyl hydroperoxide with cyclohexene or cyclooctene, as catalyzed by a number of chelated diketonates of VO^{2+}, by $(n\text{-BuO})_3VO$, and by $MoO_2(acac)_2$, are highly selective and yield only *tert*-butyl alcohol and the corresponding epoxycycloalkanes. Rate laws for the vanadium-catalyzed systems are consistent with reaction *via* rate-determining attack of olefin on a vanadium(V)–hydroperoxide complex. Association constants for the complexes and activation parameters associated with the various vanadium catalysts are different, indicating that these catalysts retain, at least in part, their ligand environments when converted to catalytically active species. Competitive inhibition by *t*-BuOH, reflecting the formation of catalyst–alcohol complexes, is observed in all cases; association constants for four of these alcohol complexes have been evaluated. Epoxidations of cyclohexene catalyzed by $MoO_2(acac)_2$ proceed approximately 10^2 as rapidly as those by the vanadium complexes under corresponding conditions. Kinetic behavior in the molybdenum system is consistent with the formation of molybdenum–hydroperoxide and molybdenum–olefin complexes, as well as a molybdenum–hydroperoxide–olefin complex. Arguments are presented supporting the view that the molybdenum-catalyzed epoxidation, like those involving vanadium, proceeds by reaction of olefin with a metal–hydroperoxide complex, rather than through the ternary complex.

The epoxidation of olefins using hydroperoxides or H_2O_2 in the presence of catalysts derived from vanadium, molybdenum, or tungsten[2]



is highly selective and, under favorable conditions, leads to quantitative yields of epoxides. Several workers[2b–d] have suggested that this reaction is heterolytic, rather than free radical, in character, and an earlier study[2c] of the reaction in the presence of vanadyl acetylacetonate, $VO(acac)_2$, provided evidence of the intervention of a hydroperoxide–vanadium(V) complex and of severe competitive inhibition by alcohols, which are products when hydroperoxides are employed as oxidants. However, questions were left unanswered as to how the nature of the catalyzed reaction was affected by variation in the identity or oxidation state of the catalytic metal or by change in its ligand environment. The present report is directed toward partial resolution of these points; in addition, it presents further information concerning the changes occurring when $VO(acac)_2$, a typical catalyst, is transformed to the principal active species during the early stages of reaction.

Experimental Section

Materials. Vanadyl acetylacetonate, $VO(acac)_2$ (J. T. Baker), was recrystallized three times from anhydrous acetone; the purified chelate dissolved in benzene without leaving a residue. Since benzene solutions of this and other vanadyl chelates showed some deterioration on standing in air for several hours,[2c,3] each series of experiments employed a freshly prepared solution of metal chelate. Vanadium(III) acetylacetonate, $V(acac)_3$ (J. T. Baker), was purified by dissolving in anhydrous ether and recrystallized and dried under nitrogen. The pure complex consisted of brown needles and dissolved readily in benzene. Benzene solutions again deteriorated gradually on standing. Vanadyl bis(dipivaloylmethide), $VO(dpm)_2$, was prepared by the method of Selbin and coworkers[4] and sublimed *in vacuo* before use.

Vanadyl hexafluoroacetylacetonate, $VO(hfac)_2$, was prepared[4,5] by dissolving 1.0 g of hydrated vanadyl sulfate in 5 ml of water, adjusting the solution to pH 3 by addition of aqueous Na_2CO_3, allowing it to stand for 10 min, and then slowly adding, with stirring, 1.6 ml of hexafluoroacetylacetone. During this addition, the pH was kept at 3 by adding 5% Na_2CO_3. The mixture of green and white precipitates was filtered, the white material dissolved by leaching with water, and the crude green product recrystallized from benzene and dried under nitrogen.

Vanadyl bis(2-thenoyltrifluoroacetonate), $VO(tfac)_2$,[6] was prepared by heating together, with stirring, a mixture of 2.0 g of V_2O_5, 5 ml of water, 2 ml of concentrated H_2SO_4, and 10 ml of ethanol. After 20 min of reaction time, the preparation was filtered, and to the filtrate was added 1 g of 2-thenoyltrifluoroacetone. The preparation was then neutralized with aqueous Na_2CO_3, and the resulting gray-brown precipitate was filtered. The crude product was recrystallized from absolute ethanol.

Dioxomolybdenum(VI) acetylacetonate, $MoO_2(acac)_2$ (Climax Molybdenum Co.), was purified by dissolving carefully in hot acetylacetone at 135°, decolorizing with activated charcoal, and then cooling, with intermittent agitation, under nitrogen. The recrystallized material, which was dried under N_2, could be kept unchanged over $CaCl_2$ for several months. A correctly purified product dissolved readily in benzene without residue, but the benzene solution decomposed gradually. The activity of this catalyst in benzene solution depended critically on the purity of benzene. In spectroquality benzene, previously dried by passage through neutral activated alumina (W-200 Neutral, Act. Super I, Woelm, Eschwege, Germany), the solution was stable for about 60 min; when other grades of alumina were used to dry the benzene, chelate solutions became cloudy very shortly after preparation. Attempts to recrystallize this catalyst from benzene, acetone, ether, or dioxane were unsuccessful. The pure product in benzene gives λ_{max} at 318 nm (ϵ 8.8×10^3).

Additional transition metal compounds examined for catalytic activity included $Ti(acac)_4$, $(n\text{-BuO})_4Ti$, $(n\text{-BuO})_3VO$, WBr_5, $WOCl_4$, $W(CO)_6$, and vanadyl phthalocyanine. These materials (Research Inorganic Chemical Corp. products) were used as received, as were several molybdenum derivatives.[7] Triphenylphosphine (Matheson) was purified by vacuum sublimation (110°) and was stored at −10°

Cyclohexene (Matheson Chromatoquality), cyclohexane, and benzene (both Matheson Spectroquality) were freshly purified by

---

(1) From the Ph.D. thesis of C.-C. Su, Kent State University, 1972. This work was sponsored jointly by the Petroleum Research Fund of the American Chemical Society (Grant 2868-A3) and the National Science Foundation (Grant GP-23136). Both sources of support are gratefully acknowledged.

(2) (a) J. Kollar, Belgian Patent 641,452 (June 18, 1964); (b) N. Indictor and W. F. Brill, *J. Org. Chem.*, 30, 2074 (1965); (c) E. S. Gould, R. R. Hiatt, and K. C. Irwin, *J. Amer. Chem. Soc.*, 90, 4573 (1968); (d) N. M. Sheng and J. G. Zajacek, *Advan. Chem. Ser.*, 76, 418 (1968); (e) H. Mimoun, I. Seree de Roche, and L. Sajus, *Tetrahedron*, 26, 37 (1970).

(3) T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, 41, 262 (1964).

(4) J. Selbin, G. Maus, and D. L. Johnson, *J. Inorg. Nucl. Chem.*, 29, 1735 (1967). We thank Dr. Nelson Johnson for this material.

(5) R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, 87, 2128 (1965).

(6) (a) M. M. Jones, *J. Amer. Chem. Soc.*, 76, 5995 (1954); (b) R. A. Rowe and M. M. Jones, *Inorg. Syn.*, 5, 114 (1957).

(7) We are indebted to the Climax Molybdenum Co. for gift samples of $MoCl_4$, $(C_6H_5COO)_2MoCl_3$, $MoCl_3$, $MoCl_5$, $Mo(CO)_6$, and $Mo(acac)_3$.

passage through neutral activated alumina (W-200, Woelm) before kinetic runs. Cyclooctene (Matheson, practical) was purified by fractional distillation (bp 140–142°). *tert*-Butyl hydroperoxide (Lucidol 90%) was purified by vacuum distillation, bp 32° (15 mm); samples were stored at −10°.

Analyses. Determination of hydroperoxide (iodometric) and epoxide (*via* glc) have been described.[2c] Chlorobenzene was used as an internal standard in the glc analyses for cyclohexene oxide, whereas *p*-dichlorobenzene was used in the analyses for cyclooctene oxide. The column was 4 ft long and $^1/_4$ in. in diameter and was packed with 12 g of 10% Carbowax (20 M on Chromosorb P, AW, DMCS, 80–100 mesh, Hewlett-Packard). New columns were conditioned at 180° for 2 days and then heated at 200° for 1 hr before passage of carrier gas. Columns deteriorated gradually in separating mixtures containing traces of heavy-metal complexes; such deterioration was more serious with molybdenum than with vanadium complexes. The flow rate of helium, the carrier gas, was 1 cm^3/sec. The sizes of injected samples were 7–12 μl. Cyclohexene oxide analyses were carried out with the oven temperature at 110°; cyclooctene analyses, at 140°. Retention times for the two oxides under respective analysis conditions were 330 and 510 sec. Peak ratios of epoxide to internal standard were adjusted to a value greater than 0.1 for optimum analyses.

Preliminary Observations. Among transition metal derivatives which exhibited marginal catalytic activity, or none at all, in the reactions studied were $Ti(acac)_4$, $(n\text{-}BuO)_4Ti$, vanadyl phthalocyanine, WBr_5, $WOCl_4$, and $W(CO)_6$. The molybdenum compounds $MoOCl_4$, $MoOCl_3$, $MoCl_5$, and $(C_6H_5COO)_2MoCl_3$ were effective catalysts; however, their activities fell far below that of $MoO_2(acac)_2$, whereas work with them involved even greater difficulty in handling. Although $Mo(CO)_6$ and $V(acac)_3$ showed little activity immediately after addition to hydroperoxide–olefin mixtures, these complexes were converted, under our reaction conditions, to catalytically active species; reactions carried out in the presence of these two materials featured irreproducible induction periods.[8]

The rapid formation of a strongly absorbing red species, when excess hydroperoxide is mixed with $VO(acac)_2$, has been reported;[2c] similar changes occur also with the remaining vanadyl diketonates here used, but not with $V(acac)_3$ or $(n\text{-}BuO)_3VO$. These colors disappear on standing, and such fading is most rapid with chelates of the fluorinated diketones. The appearance and fading of the red pigment (λ_{max} 508 nm, ϵ 1.0×10^3 [9]) derived from $VO(acac)_2$ were examined in several solvents, but kinetic data for these reactions were often poorly reproducible. The maximal absorbance (before fading) increases nearly linearly with (BuO_2H) when hydroperoxide is in moderate (three- to tenfold) excess but is nearly independent of (BuO_2H) at high concentrations of the latter. Half-conversion of small concentrations of $VO(acac)_2$ to the red complex in benzene occurs in 5×10^{-4} *M* hydroperoxide, corresponding to an association constant of 2×10^3 M^{-1} at 25°.

The conversion of $VO(acac)_2$ to the red complex in benzene, which could be followed either at 301 or 508 nm, appeared to be first order both in vanadium(IV) and in hydroperoxide, although rates varied erratically from one set of runs to the next. The fading of the complex in benzene was very nearly zero order in vanadium and approximately half order in hydroperoxide. The formation of the red complex proceeds 4–5 times as rapidly in cyclohexene and in 1-octene as in benzene, and in these nonaromatic solvents, the fading of the red pigment is cleanly first order in vanadium, but again half order in hydroperoxide. Carboxylic acids markedly accelerate the conversion of $VO(acac)_2$ to the red complex, but acceleration of disappearance of the complex is slight. Alcohols have virtually no effect on the formation of the red species but retard its disappearance; the alcohol-retarded reactions retain their first-order character in cyclohexane, cyclohexene, and 1-octene. The base 2,6-lutidine affects neither the formation nor the disappearance of the red complex. Investigation of these reactions is being continued.

All epoxidation reactions studied quantitatively in this series are self-inhibitory. As in earlier work,[2c] inhibition reflects a combination of two effects. The first is a competitive inhibition by *tert*-butyl alcohol, formed along with the epoxide; the second is oxidative destruction of the catalyst, which assumes importance during the later stages of reaction. Rates were measured early in the course of the reaction, under which conditions, the first, but not the second, of these effects had to be taken into account.

Epoxides and *t*-BuOH were the only detectable volatile products from the catalyzed oxidations. The glc analyses of our reaction mixtures showed no traces of unsaturated alcohols or ketones. Epoxidations carried out under reaction conditions similar to ours have been shown [2b,c] to give quantitative yields of epoxide at low hydroperoxide conversions.

Kinetic Studies. Kinetic methods used in these epoxidations were similar to those previously described.[2c] Because the autoinhibitory nature of the reactions precluded obtaining meaningful kinetic points from a single reaction mixture at both early and later stages of reaction, average rates were measured during the first 1–4% of reaction in the presence of known quantities of added *t*-BuOH and then extrapolated to zero alcohol concentration, considering also the alcohol formed during the course of the reaction. Concentrations of catalyst were between 10^{-6} and 10^{-3} *M*, and concentrations of hydroperoxide were between 0.018 and 0.5 *M*. A number of the epoxidations of cyclohexene were carried out with the olefin itself as solvent; the epoxidations of cyclooctene, and those of cyclohexene in which kinetic order in olefin was sought, were carried out in cyclohexane, with the concentration of added olefin between 0.1 and 1.8 *M*. Temperatures were constant to better than 0.1° during a given series of runs.

Before each reaction, both the catalyst solution in benzene (which contained both the catalyst and a measured quantity of internal glc standard) and the olefin–hydroperoxide mixture were allowed 5 min for thermal preequilibration. The solutions were then mixed, and after measured time intervals samples were withdrawn and the reaction was quenched by adding to a solution of Ph_3P (1.2 equiv/equiv of hydroperoxide in the sample) in acetone. The resulting mixtures were kept at Dry Ice temperatures until glc analysis for epoxide. Samples were analyzed as soon as possible after quenching. Detector response was very nearly proportional to epoxide content for 12–15-μl samples containing greater than 0.005 *M* epoxide; between 0.002 and 0.005 *M*, calibration of response with known concentrations of epoxide was necessary. Epoxide concentrations below 0.002 *M* could not be measured satisfactorily.

In runs with extra *t*-BuOH, concentrations of added alcohol were between 0.004 and 0.03 *M*. For the reactions studied, in which conversion to products was less than 5%, rates were, as in earlier work,[2c] linearly related to alcohol concentrations.

Treatment of data for the vanadium-catalyzed reactions was similar to that described.[2c] Epoxidations were first order each in olefin and in catalyst but exhibited a Michaelis-like dependency on hydroperoxide

$$\text{rate} = \frac{k[\text{olefin}][\text{V}_0]}{(1/[\text{P}]K_\text{P}) + 1} \tag{1}$$

where k is a limiting specific rate (at very high ratios of hydroperoxide to catalyst), $[V_0]$ is the total concentration of added vanadium, $[P]$ is the concentration of added hydroperoxide, and K_P is the association constant for the vanadium(V)–hydroperoxide complex, presumed to be the active intermediate. Limiting rates and association constants were evaluated by keeping [olefin] and $[V_0]$ constant, varying $[P]$, and plotting values of rate/$[P]$ *vs.* rate.[10] Such plots were generally nearly linear for reactions catalyzed by the vanadyl chelates, by $(n\text{-}BuO)_3VO$, and by $MoO_2(acac)_2$ (but not for those catalyzed by $V(acac)_3$ or $Mo(CO)_6$) in the temperature range 6–50°; slopes of such plots gave values of K_P, whereas intercepts yielded values of k.

For reactions in olefin inhibited by *t*-BuOH, values of the ratio $\Sigma[VA_n]/[V][A]$ were obtained by the relationship[2c]

$$\frac{\Sigma[\text{VA}_n]}{[\text{V}][\text{A}]} = \frac{[\text{P}]K_\text{P}[([\text{V}_0]k/\text{rate}) - 1] - 1}{[\text{A}]} \tag{2}$$

where $[A]$ is the concentration of alcohol, $\Sigma[VA_n]$ the total of alcohol-bound vanadium, and $[V]$ the concentration of vanadium

---

[8] Sheng and Zajacek[2d] reported no induction periods for the epoxidations of propylene and 1- and 2-butene as catalyzed by $Mo(CO)_6$. We suggest that at the higher reaction temperatures (near 80°) used by these workers, induction periods were short and evaded detection.

[9] This extinction coefficient, which refers to solutions in benzene, was calculated by assuming complete conversion of 9.6×10^{-5} *M* $VO(acac)_2$ to the red complex in the presence of 0.005 *M* hydroperoxide before the onset of fading. Note that the red color is observed only with hydroperoxide in excess. When small portions of hydroperoxide are added to $VO(acac)_2$ in benzene, the charge-transfer band of the chelate at 301 nm disappears, and a new peak develops at 276 nm. This change, during which isosbestic points at 289 and 327 nm are observed, is complete after just 0.5 mol of hydroperoxide has been added per mole of $VO(acac)_2$. Subsequent addition of excess hydroperoxide to the resulting solution yields no detectable quantity of the red complex.

[10] B. H. J. Hofstee, *Nature (London)*, 184, 1296 (1959).

Table I. Kinetic Data for the Epoxidation of Cyclohexene with *tert*-Butyl Hydroperoxide, Catalyzed by $VO(dpm)_2$ (Solvent, Cyclohexene)

Temp, °C	10^5[catalyst], M	$[BuO_2H]$, M	Rate × 10^4 [a]
37.0	5.51	0.0904	5.17
	4.72		4.08
	3.92		3.33
	3.15		2.63
	6.30	0.452	9.15
		0.271	8.24
		0.181	7.16
		0.0904	5.27
		0.0452	3.23
30.0	6.30	0.452	6.19
		0.271	5.56
		0.181	5.05
		0.0904	3.66
		0.0452	2.29
23.0	6.30	0.452	3.86
		0.271	3.47
		0.181	2.96
		0.0904	2.15
		0.0452	1.46
16.0	6.30	0.452	2.61
		0.271	2.26
		0.181	1.99
		0.0904	1.46
		0.452	1.05
9.0	6.30	0.452	1.69
		0.271	1.43
		0.181	1.31
		0.0904	1.09
		0.0452	0.777

[a] Rates in M min^{-1}, extrapolated to zero [*t*-BuOH].

neither tied up in the catalytically active complex nor bound to alcohol. Plots of this ratio *vs.* [A], which showed considerable scatter, sloped upward, indicating inhibitory action by two alcohol-vanadium complexes, VA and VA_2. Slopes of these plots yielded association constants for VA_2, whereas intercepts led to constants for VA.

Results and Discussion

Species absorbing at 508 nm were observed early in the course of the epoxidations catalyzed by each of the vanadium(IV) chelates but not in the reactions of $V(acac)_3$ or $(n\text{-}BuO)_3VO$. These red intermediates may thus be taken as vanadium(IV)-hydroperoxide complexes, analogous to peroxy complexes observed in aqueous systems.[11] The fading of these complexes may be associated with the conversion of vanadium(IV) to vanadium(V). Oxidations of this type have been shown to proceed by radical chains in water,[12] and the erratic kinetic character of these bleachings, in conjunction with the half-order hydroperoxide dependencies observed, suggests a similar picture here. The vanadium(IV)-hydroperoxide complexes play virtually no part in the epoxidation sequence, since they are destroyed before less than 1% conversion to epoxide has occurred. From the high value, 2×10^3 M^{-1}, of the association constant for the vanadyl acetylacetonate-hydroperoxide complex in benzene, we may infer that its oxidation product, which contains the even more electrophilic vanadium(V), is also nearly completely hydroperoxide bound at BuO_2H concentrations near 0.018 M, the lower limit used in the epoxidation experiments.

The kinetic pictures associated with the epoxidations catalyzed by the oxovanadium(IV) chelates and by *n*-butyl vanadate are similar to that for the $VO(acac)_2$-catalyzed reaction.[2c] Data for reactions catalyzed by $VO(dpm)_2$, a representative member of this group, are summarized in Tables I and II. The Michaelis-like dependency on hydroperoxide concentration (eq 1) points to partition of catalyst between two forms, the second having one more hydroperoxide per complex than the first, with the ratio of these forms dependent on [t-BuO_2H]. The first-order dependency on both olefin and catalyst is consistent with a transition state containing a unit of olefin and one unit of the more peroxide-rich form of the catalyst. Hofstee-like plots, from which specific rates and stability constants associated with the active hydroperoxide complex are obtained, are shown in Figure 1. The constants so derived from this and other vanadium-containing catalysts in the group are assembled in Table III.

Table II. Kinetic Data for the Epoxidation of Cyclohexene with *tert*-Butyl Hydroperoxide, Catalyzed by $VO(dpm)_2$ (Solvent, Cyclohexane)[a]

[Olefin], M	Rate × 10^4 [b]	k_2 [c]
1.79	2.67	3.86
1.34	2.08	4.03
0.90	1.44	4.18
0.63	0.99	4.1
0.45	0.73	4.2

[a] Reactions at 37.0°; [P] = 0.181 M. Total concentration of $VO(dpm)_2$, $[V_0]$, is 6.3×10^{-5} M. [b] Rates in M min^{-1}, extrapolated to zero [*t*-BuOH]. [c] Calculated second-order constant (in M^{-1} min^{-1}), $(1/[V_0])(1/K_P[P] + 1)(\text{rate}/[\text{olefin}])$, where K_P is taken as 8.7 M^{-1} (see Table III).

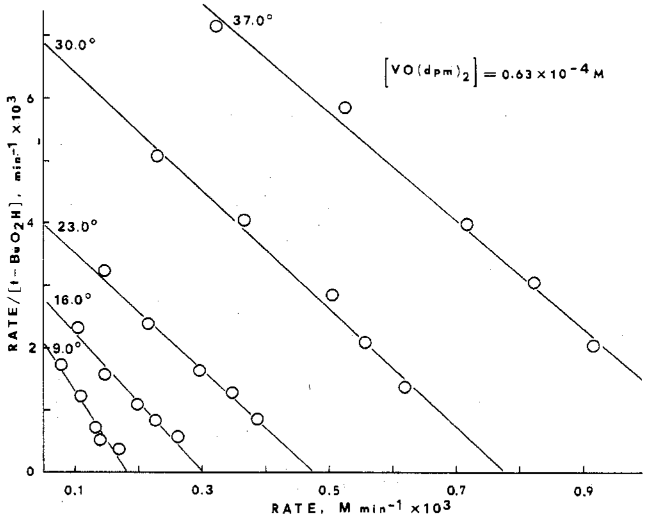


Figure 1. Hofstee-type plot, rate/[hydroperoxide] *vs.* rate, for the epoxidation in cyclohexene using t-BuO_2H. Rates adjusted to zero [*t*-BuOH]. Slopes of the least-squares lines shown yield association constants for the vanadium–hydroperoxide complexes at the temperatures indicated. Intersections with the abscissa yield the specific rates of heterolysis, *k*, summarized in Table III.

Although the rate constants associated with the various vanadium catalysts are not greatly different, the sizable variation both in the stability constants and in the activation parameters (Table IV) indicates that these catalysts retain, at least in part, their ligand environments when converted from their original forms, *via* colored intermediates, to the active vanadium(V) complexes. They are obviously not degraded to a common species. Moreover, the hydroperoxy complexes formed from the fluorinated vanadium chelates are more stable than those formed from $VO(acac)_2$ and $VO(dpm)_2$, in which the metal centers are less electrophilic. Association constants derived from measurements on the $VO(acac)_2$-catalyzed epoxidation of cyclooctene are about 20% less than those obtained from the epoxidation of cyclohexene;[2c] since the two reactions were carried out in

---

(11) See, for example, M. C. R. Symons, *J. Chem. Soc. A*, 1889 (1970).

(12) H. B. Brooks and F. Sicilio, *Inorg. Chem.*, 10, 2530 (1971).

Table III. Limiting Specific Rates (k) and Association Constants (K_P) of Metal-Hydroperoxide Complexes in Epoxidation Mixtures[a]

Catalyst	Temp, °C	k, min^{-1}	K_P, M^{-1}
$(n\text{-BuO})_3VO$	26.0	13.6 ± 0.5	3.2 ± 0.1
	30.0	16.8 ± 0.9	3.2 ± 0.3
	36.0	22.2 ± 0.7	3.6 ± 0.2
	40.0	26.6 ± 2.6	3.5 ± 0.3
$VO(dpm)_2$	9.0	2.88 ± 0.02	16.2 ± 0.1
	16.0	4.8 ± 0.2	11.0 ± 0.2
	23.0	7.9 ± 0.4	9.6 ± 0.2
	30.0	12.3 ± 0.2	9.5 ± 0.5
	37.0	18.4 ± 0.1	8.7 ± 0.2
$VO(hfac)_2$[b]	3.0	8.3	37
	9.5	10	39
	15.5	13	32
	22.0	17	32
$VO(tfac)_2$	30.0	14.7	23
$MoO_2(acac)_2$	30.0	3200[c]	21
$VO(acac)_2$[d]	20.0	2.15 ± 0.04	12.2 ± 0.6
	30.0	3.9 ± 0.1	11.5 ± 0.6
	36.0	5.1 ± 0.2	10.6 ± 0.5
	42.0	7.1 ± 0.4	9.9 ± 0.9

[a] Evaluated from intercepts and slopes of Hofstee-type plots (see Experimental Section and ref 2c); epoxidations of cyclohexene in cyclohexene unless otherwise noted. Catalyst concentrations were 0.0002–0.0007 M for the vanadium complexes and 4 × 10^{-6} M for $MoO_2(acac)_2$. [b] Oxidative deterioration of this catalyst is serious at temperatures above 25°. [c] Specific rate, k, in min^{-1}; see eq 3. [d] Epoxidation of cyclooctene in cyclohexane. Specific rate, k_2, in M^{-1} min^{-1}.

Table IV. Activation Parameters and *t*-BuOH-Inhibition Constants for Metal-Catalyzed Epoxidations of Cyclohexene

Catalyst	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[a] eu	Temp, °C	K_i,[b] M^{-1}	$10^3K_i'$,[b] M^{-2}
$VO(acac)_2$[c]	11.5	−27	41.3	119	21
$VO(dpm)_2$	11.0	−28	37.0	85	9
$(n\text{-BuO})_3VO$	8.4	−38	30.0	44	8
$VO(hfac)_2$	6.2	−43			
$VO(acac)_2$[d]	9.2	−34	36.0	107[e]	11[e]
$MoO_2(acac)_2$	14[f]				

[a] Obtained from variation in k_2, for the rate-determining step, with temperature. Reactions in cyclohexane. Estimated uncertainties are 0.6 kcal/mol in $\Delta H^{\ddagger}$ and 2 eu in $\Delta S^{\ddagger}$. [b] Values obtained from *t*-BuOH-inhibition data (see Experimental Section and ref 2c). Reactions in cyclohexene. [c] Activation parameters differ slightly from those given in ref 2c, which are based on measurements in cyclohexene. [d] Epoxidation of cyclooctene. [e] Inhibition constants for reaction in cyclohexane. [f] Estimated value. See ref 13a.

different hydrocarbons, this may be considered as reasonable agreement.

The K_P values for the reactions involving $VO(acac)_2$ and $VO(dpm)_2$ denote that vanadium is half-converted to the catalytically active species at hydroperoxide concentrations near 0.1 M. If, as we suspect, all vanadium is bound to at least one hydroperoxide at BuO_2H levels well below this value, the reactive species must contain at least two hydroperoxides per vanadium.

Arrhenius plots of log k *vs.* $1/T$ are very nearly linear and yield activation parameters summarized in Table IV. The values of K_P vary much less markedly with temperature than those of k; this circumstance, coupled with the relatively imprecise estimates of K_P, rules out reliable evaluations of the enthalpies of association of the active species.

Table V. Typical Kinetic Data for *tert*-Butyl Alcohol Inhibition of the Epoxidation of Cyclohexene with *tert*-Butyl Hydroperoxide, as Catalyzed by $VO(dpm)_2$[a]

$[t\text{-BuO}_2H]$, M	$10^3[t\text{-BuOH}]$,[b] M	Rate × 10^3, M min^{-1}
0.452	0	9.15[c]
	5.28	8.12
	12.4	6.54
	20.1	5.53
0.271	0	8.24[c]
	5.46	7.04
	11.5	6.55
	18.0	4.52
0.181	0	7.16[c]
	5.63	5.37
	10.7	4.24
	15.2	2.68
0.0904	0	5.27[c]
	5.54	3.83
	8.91	3.16
	13.3	2.04

[a] 37.0°; solvent, cyclohexene; $[VO(dpm)_2]_0 = 6.3 \times 10^{-5}$ M. [b] Average value of [*t*-BuOH]. [c] Extrapolated values.

Table VI. Typical Kinetic Data for the Epoxidation of Cyclohexene with *tert*-Butyl Hydroperoxide, Catalyzed by $MoO_2(acac)_2$ (Solvent, Cyclohexene–Cyclohexane)

10^6[catalyst], M	$[BuO_2H]$, M	[Olefin], M	$10^3(\text{rate})_{\text{obsd}}$[a]	$10^3(\text{rate})_{\text{calcd}}$[b]
4.18	0.452	9.00	6.40	6.37
	0.271		5.15	5.23
	0.181		4.33	4.28
	0.0904		2.79	2.77
	0.0452		1.60	1.62
4.18	0.452	0.448	0.527	0.535
		0.269	0.367	0.364
		0.179	0.269	0.260
		0.0897	0.138	0.140
		0.0448	0.082	0.073
1.67	0.0904	9.00	1.23	1.11
2.59			1.80	1.71
6.69			4.44	4.43

[a] Rates in M^{-1}; 30.0°; extrapolated to zero [*t*-BuOH]. [b] Rates calculated from eq 3, taking $k = 3.24 \times 10^3$ min^{-1}, $K_{PM} = 21.3$ M^{-1}, $K_{MO} = 6.22$ M^{-1}, and $K_{PMO} = 0.26$ M^{-2} (see text).

A typical set of rate data for epoxidation reactions inhibited by added *t*-BuOH appears in Table V. If the inhibitory action of this alcohol reflects the formation of alcohol-metal complexes which are catalytically inactive, alcohol appears to be competing very effectively for positions at the metal centers, for addition of approximately $^1/_{10}$ mol of alcohol/mol of hydroperoxide reduces the epoxidation rates by half. The degrees of inhibition observed allow calculation of stability constants, K_i and K_i', for mono- and dialcohol complexes, VA and VA_2, to which the catalytically active vanadium species is, in part, diverted.[2c] These constants, pertaining to reactions catalyzed by $VO(dpm)_2$, $VO(acac)_2$, and $(n\text{-BuO})_3VO$, are included in Table IV. As expected, values of K_i fall into the same order as the association constants, K_P, for the corresponding vanadium-hydroperoxide complexes (Table III).

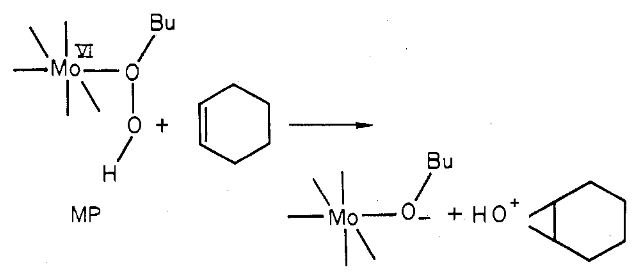
Epoxidations catalyzed by $MoO_2(acac)_2$ proceed approximately 10^2 times as rapidly as those by the active vanadium complexes under corresponding conditions. Moreover, the kinetic picture governing the behavior of this powerful catalyst is rather more complicated. Typical data for molybdenum-catalyzed epoxidations at 30.0° appear in Table VI. Reactions are very nearly first order in catalyst but are of nonintegral order in olefin, with rates more nearly proportional to [olefin] at low concentrations than at high. The olefin dependency is thus similar to that observed with hydroperoxide and indicates partition of olefin into two or more forms of comparable concentrations but differing reactivities. Kinetically significant binary olefin-hydroperoxide complexes may be ruled out, since no evidence arises for these from any of the vanadium experiments. However, the possibility of both a binary olefin-catalyst complex, MO, and a ternary complex, PMO, must be considered, in addition to the hydroperoxide-catalyst complex, PM. In particular, if rate is proportional to the concentration of the ternary complex, the rate law assumes the form

$$\text{rate} = \frac{[\mathrm{M}]_0 k}{\dfrac{1}{K_{\mathrm{PM}}K_{\mathrm{PMO}}[\mathrm{P}][\mathrm{O}]} + \dfrac{1}{K_{\mathrm{PMO}}[\mathrm{O}]} + \dfrac{K_{\mathrm{MO}}}{K_{\mathrm{PM}}K_{\mathrm{PMO}}[\mathrm{P}]} + 1} \tag{3}$$

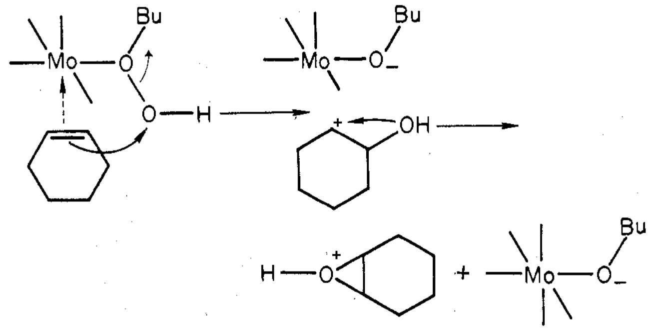
where k is the limiting specific rate (which would be observed if conversion to complex PMO were very nearly complete), $[\mathrm{M}]_0$ is the total concentration of added molybdenum, and the K values are association constants for the various complexes. Simpler expressions apply if one or more of the association constants are vanishingly small.

Separate Hofstee-like treatments[10] of measured rates, varying hydroperoxide (while keeping olefin constant), and varying olefin (at constant hydroperoxide) yield plots, the slopes and intercepts of which may, in principle, be used to calculate k and the three K values. However, the association constants so derived are approximate, for they depend mainly on the estimated slopes which, in turn, are determined largely by rates measured at low reagent concentrations, where uncertainty is greatest. These rough values, together with a preliminary value of k, have been subjected to an iterative least-squares refinement, varying all four parameters and minimizing the sum of squares of the type $[(\text{rate})_{\text{obsd}} - (\text{rate})_{\text{calcd}}]^2$, where calculated rates are obtained from eq 3. This refinement converges after six cycles, yielding the parameters $K_{\mathrm{PM}} = 21.3\ M^{-1}$, $K_{\mathrm{MO}} = 6.22\ M^{-1}$, $K_{\mathrm{PMO}} = 0.26\ M^{-2}$, and $k = 3.24 \times 10^3\ \text{sec}^{-1}$. Rates calculated using these parameters are compared to observed rates in Table VI. Similar attempts to fit our rate data to model systems in which each of the three stability constants is, in turn, considered to be negligibly small (but the other parameters are allowed to vary) give poor agreement.[13]

Scheme I



Scheme II



Although the present data point to the existence of a ternary complex, PMO, and to a transition state having the same composition, there is no requirement that the epoxidation pass specifically through PMO, for the kinetic picture is compatible also with sequences in which the rate-determining step is reaction of olefin with complex MP, reaction of hydroperoxide with complex MO, or a combination of these steps. The marked resemblance of the $\mathrm{MoO_2(acac)_2}$-catalyzed epoxidation, not only to epoxidations catalyzed by the vanadium chelates but also to those using $\mathrm{Mo^{VI}}$-peroxy complexes,[2e,14] leads us to favor a sequence featuring attack by olefin on metal-bound hydroperoxide, with the formation of the ternary complex serving only to divert reactants from the oxidation process. The two schemes are indicated schematically. Scheme I is, in essence, that proposed for the vanadium-catalyzed epoxidations,[2c] whereas Scheme II, in which an olefin-metal bond is assumed in the ternary complex, is similar to that suggested by Mimoun for $\mathrm{Mo^{VI}}$-peroxy systems[2e] and that by Collman[15] for a variety of oxygen-transfer reactants catalyzed by d^8 and d^{10} centers where, in many cases, ternary complexes are isolable.

Paths analogous to these, but pertaining to the epoxidation of olefins by $\mathrm{MoO_5{\cdot}PO(NMe_2)_3}$ in methylene chloride, have been considered by Sharpless,[14] who has noted that the activated complex in one of these sequences involves a three-membered ring, the other, a five-membered ring. Several workers[14,16] have suggested, one with slight reservations,[16c] that the rates of dipolar addition reactions to cyclic olefins proceeding through five-membered rings (external to the carbocyclic ring itself) are much more sensitive to the size of the carbocyclic ring than those proceeding through external three-membered rings. The scattered rate data for epoxidations of the type here considered indicate a marked insensitivity toward olefin structure; the rate for the $\mathrm{VO(acac)_2}$-catalyzed epoxidation of cyclooctene is only twice that for cyclohexene,[2c] and a similar ratio of rates applies to the epoxidations of cyclopentene and cyclohexene as catalyzed by vanadium(III) octanoate.[17] Moreover, the $\mathrm{Mo(CO)_6}$-catalyzed epoxidations of cyclohexene and *trans*-2-octene proceed at very nearly the same specific rates at 100°.[2d,18] To the extent, then, that Sharpless' criteria apply to the reac-

---

[13] (a) The complexity of the relationship between rate and the three association constants militates against obtaining accurate values of the enthalpies of association of the complexes PM, MO, and PMO from rate studies at various temperatures. However, if values of (rate)/[P] are plotted against rates (while keeping [olefin] and [catalyst] constant), the intercept, which represents $(\text{rate})_{\text{lim}}$ at very high hydroperoxide concentrations, may be shown to be

$$(\text{rate})_{\text{lim}} = \frac{[\mathrm{M}]_0 k}{(1/K_{\mathrm{PMO}}[\mathrm{O}]) + 1}$$

For measurements at high olefin concentrations and by considering K_{PMO} to be much less sensitive to temperature changes than is k, the variation of $(\text{rate})_{\text{lim}}$ with temperature yields the rough value $\Delta H^{\ddagger} = 14$ kcal/mol. (b) Although the hydroperoxide complexes are represented as PM and PMO, note that each may contain more than one molecule of hydroperoxide. Our measurements indicate merely that both complexes contain *one more* hydroperoxide than is present in that form of Mo(VI) which predominates at the lowest hydroperoxide concentration studied.

[14] K. B. Sharpless, J. M. Townsend, and D. R. Williams, *J. Amer. Chem. Soc.*, **94**, 295 (1972).

[15] J. P. Collman, M. Kubota, and J. W. Hosking, *J. Amer. Chem. Soc.*, **89**, 4809 (1967).

[16] (a) K. D. Bingham, G. D. Meakins, and G. H. Whatham, *Chem. Commun.*, 445 (1966); (b) A. K. Awasthy and J. Rocek, *J. Amer. Chem. Soc.*, **91**, 991 (1969); (c) R. E. Erickson and R. L. Clark, *Tetrahedron Lett.*, 3997 (1969).

[17] E. S. Gould, unpublished experiments, Stanford Research Institute, 1965.

tions at hand, Scheme I, or a minor variant thereof, would appear to be the preferred path.

The exact structural requirements governing catalytic activity of metals in epoxidation remain, in part, elusive. Relevant to the view that a substitution-labile metal center is necessary[2c] are recent reports that dioxomolybdenum(VI) β-diketonates are stereochemically labile, although net exchange with external diketone is slow.[19] Participation by the metal in one-electron redox reactions under epoxidation conditions precludes the selectivity observed and should lead instead to mixtures of products typical of radical oxidations;[20] although the two metals found to be most effective have accessible oxidation states, V(IV) and Mo(V), one unit below maximum, neither state is expected to exist in significant quantity under the strongly oxidizing conditions used. As to the role of positive charge at the metal center, it is apparent that this factor must be kept within bounds. Thus boron(III) and titanium(IV), d^0 systems which are known to form peroxy complexes, are ineffective as epoxidation catalysts, presumably because polarization of the O-O bond is not sufficiently severe to allow heterolysis under the action of nucleophilic olefin. At the other end of the scale are such strongly oxidizing positive centers as Cr(VI), Se(VI), Mn(VII), and Os(VIII). Any catalytic action by these species would, in large part, be overshadowed by the ease with which they are reduced by hydroperoxide, by olefin, or by both. Between these extremes are the active d^0 systems, Mo(VI) and V(V); but why Mo(VI) is the more reactive of the two and why both are superior to W(VI), despite the effectiveness of the latter center in hydroxylic solvents,[21] remain puzzling points.

Registry No. $VO(acac)_2$, 3153-26-2; $VO(dpm)_2$, 16901-82-9; $VO(hfac)_2$, 15819-88-2; $VO(tfac)_2$, 32040-15-6; $MoO_2(acac)_2$, 17524-05-9; $(BuO)_3VO$, 1801-76-9; *t*-BuO_2H, 110-05-4; *t*-BuOH, 75-65-0; cyclohexene, 110-83-8; cyclooctene, 931-88-4.

Acknowledgments. The authors are grateful to Professors Henry Kuska, Thomas Pinnavaia, Harold Kwart, and William Movius for valuable discussions.

(18) These small rate differences in epoxidations may be compared, for example, to rate differences observed in the 1,3 addition of picryl azide: A. S. Bailey and J. E. White, *J. Chem. Soc. B*, 819 (1966). With the latter, which reacts through a five-membered ring transition state, the specific rate for cyclohexene (in $CHCl_3$ at 25°) is $^1/_{50}$th the value for cyclooctene and $^1/_{64}$th that for cyclopentene. The highly strained olefin norbornene reacts 8000 times as rapidly as does cyclohexene with this reagent, whereas the corresponding ratio of epoxidation rates using $MoO_5 \cdot PO(NMe_2)_3$ is only 1.94.[14]

(19) B. M. Craven, K. C. Ramey, and W. B. Wise, *Inorg. Chem.* 10, 2626 (1971); T. J. Pinnavaia and W. R. Clements, *Inorg. Nucl. Chem. Lett.*, 7, 1127 (1971). Both groups of authors note, however, that stereochemical lability in these systems may involve internal twisting rather than Mo-O bond rupture, or perhaps a combination of both processes.

(20) See, for example, E. S. Gould and M. Rado, *J. Catal.*, 13, 238 (1969).

(21) See, for example, K. A. Saegebarth, *J. Org. Chem.*, 24, 1212 (1959).

Contribution from the Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

Structural and Magnetic Properties of Di-μ-hydroxo-tetraglycinatodichromium(III)

JACK T. VEAL,[1a] WILLIAM E. HATFIELD, DAVID Y. JETER,[1b] JUDITH C. HEMPEL, and DEREK J. HODGSON*

Received May 30, 1972

The crystal and molecular structure of di-μ-hydroxo-tetraglycinatodichromium(III), $[Cr(gly)_2OH]_2$, has been determined from three-dimensional single-crystal X-ray data obtained on an automatic four-circle diffractometer using Mo Kα radiation. The complex crystallizes in the space group C_{2h}^5-$P2_1/n$ of the monoclinic system with cell constants $a = 5.691$ (3), $b = 16.920$ (9), $c = 7.900$ (4) Å, and $\beta = 79.90$ (3)°. The observed density is 1.89 (2) g cm^{-3} and that calculated based on two dimeric formula units in the cell is 1.898 g cm^{-3}. A total of 775 independent intensities greater than twice their estimated standard deviations were used in the least-squares refinement and the final value of the conventional R factor (on F) is 0.040. The structure consists of well-separated dimeric pairs of octahedrally coordinated chromium atoms linked by two hydroxo bridges. The Cr-O-Cr-O unit is strictly planar with Cr-Cr and O-O separations of 2.974 (2) and 2.575 (6) Å and a Cr-O-Cr bridging angle of 98.2 (2)°. The two independent bridging Cr-O distances of 1.966 (4) and 1.968 (4) Å are essentially the same. Each glycinate ligand is coordinated through nitrogen and oxygen, the average Cr-O and Cr-N distances being 1.973 (4) and 2.064 (6) Å, respectively. The magnetic susceptibility data show a maximum at 20°K, which suggests that the ground state is a singlet with $2J = -8.4$ cm^{-1} and $g = 1.95$. Inclusion of biquadratic exchange leads to values of $2J = -3.8$ cm^{-1} and $j = 0.37$ cm^{-1}. The room-temperature epr spectrum is also reported. The magnetic properties of the complex are consistent with those found for copper(II) dimers with similar bridging geometry.

Introduction

From recent crystallographic and magnetic studies[2-5] in our laboratory on dihydroxo-bridged copper complexes of the type $[CuL(OH)]_2^{2+}$ we have been able to conclude that the value of $2J$ is systematically related to the Cu-O-Cu bridging angle (ϕ), $2J$ decreasing as ϕ increases and the interaction changing from ferromagnetic to antiferromagnetic at ϕ values between 96 and 99°. It is of great interest to test this hypothesis to see if a similar relationship will hold for bridging systems involving atoms other than copper. Hence, we have undertaken the study of bridged systems involving chromium.

(1) (a) Tennessee Eastman Corp. Fellow, 1971-1972; (b) NSF Trainee, 1968-1971.

(2) J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Commun.*, 1593 (1970).

(3) J. A. Barnes, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 11, 144 (1972).

(4) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 2216 (1972).

(5) D. Y. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 11, 1958 (1972).