Hydroperoxide Oxidations Catalyzed by Metals. IV. Molybdenum Hexacarbonyl Catalyzed Epoxidation of 1-Octene[1a]

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Additional kinetic data have been obtained on the epoxidation of 1-octene by cumene and *tert*-butyl hydroperoxide in the presence of molybdenum hexacarbonyl. In the temperature range 71–90°, the new data exhibit apparent first-order dependence on the hydroperoxide. The observed kinetic behavior is compatible with the previously proposed general mechanism for the epoxidation reaction. The kinetics for the molybdenum hexacarbonyl catalyzed epoxidation are consistent with a simple competitive inhibition step involving a coproduct alcohol–catalyst complex in which K_{eq}, the alcohol–catalyst complex equilibrium constant, approximately counterbalances K_p, the hydroperoxide–catalyst complex dissociation constant. In agreement with this interpretation, a plot of $1/k_{obsd}$ *vs.* the initial hydroperoxide concentration was linear. The slope and intercept of these plots were used to determine values of K_{eq} for cumenol of 3.1 and 6.5 M^{-1} at 84.6 and 72.6° and for *tert*-butyl alcohol 5.9 and 6.1 M^{-1} at 84.4 and 71.2°.

Initial kinetic data on the epoxidation of aliphatic olefins by *tert*-butyl hydroperoxide in the presence of molybdenum hexacarbonyl as catalyst indicated that the reaction was first order in olefin, hydroperoxide, and catalyst.[2] The kinetic and chemical data were satisfactorily explained by the mechanism proposed for this new method of epoxidizing olefins. The mechanism consisted of two steps. The initial step was a rapid equilibrium formation of a molybdenum carbonyl–hydroperoxide complex. The second step was the rate-determining reaction of the molybdenum carbonyl–hydroperoxide complex with the olefin to form the epoxide, coproduct alcohol, and the molybdenum catalyst. However, it was observed that the epoxidation reaction was retarded when alcohols were used as solvents. This observation might be expected from the proposed mechanism since an alcohol could compete with the hydroperoxide for the molybdenum catalyst and form a molybdenum–alcohol complex. If a molybdenum–alcohol complex did form, some retardation of the reaction rate and deviation from apparent first-order dependence on hydroperoxide would be expected as an epoxidation reaction proceeded and coproduct alcohol was produced. A kinetic study of the epoxidation of cyclohexene by *tert*-butyl hydroperoxide in the presence of vanadyl acetylacetonate as catalyst showed that the coproduct *tert*-butyl alcohol very strongly inhibits the vanadium-catalyzed reaction and the rate dependence on hydroperoxide is analogous to the Michaelis–Menten equation for enzyme catalysis.[3] This paper suggested that the first-order dependence on hydroperoxide in the molybdenum-catalyzed reaction was a result of only partial activation of the molybdenum hexacarbonyl during the kinetic experiments.

Additional kinetic studies with 1-octene and molybdenum hexacarbonyl were made to determine the range of conditions for which the observation of first-order dependence on hydroperoxide was valid and to reconcile the experimental data with the proposed mechanism for the molybdenum-catalyzed epoxidation.

Results

Kinetic studies with molybdenum hexacarbonyl, as catalyst, were made over a temperature range of 71–91° using a large excess of 1-octene and both *tert*-butyl hydroperoxide and cumene hydroperoxide. The rate data were obtained by measurement of changes in hydroperoxide concentration. In addition, analysis of selected samples by gas chromatography demonstrated that the epoxidation proceeded in high yield. Hence, the 1:1 stoichiometry for epoxide formation was maintained while side reactions such as decomposition of the hydroperoxide were negligible. This has been demonstrated in previous reports on this reaction.[2–5]

In the kinetic experiments, the reaction flask was fitted with a continuously adjustable manostat attached to a vacuum pump which permitted the pressure and, because the solvent was under reflux, the temperature of the system to be controlled within narrow limits. Temperature variation was ±0.1°.

Since the reactions were carried out in a large excess of 1-octene, the data for the epoxidation reaction were plotted in the first-order form shown in Figures 1 and 2. For both *tert*-butyl hydroperoxide and cumene hydroperoxide, short induction periods were observed. These induction periods were related to the conversion of the molybdenum hexacarbonyl into the active catalyst.[2,5] Thus, the plots show a minor displacement of the straight line from the origin.

The kinetic data obtained for both *tert*-butyl and cumene hydroperoxide over the temperature range 71–91° at a high olefin concentration provided an excellent fit for pseudo-first-order dependence on the hydroperoxide. However, when the initial *tert*-butyl or cumene hydroperoxide concentration was varied at a specific temperature, the slopes of the psuedo-first-order plots, the observed pseudo-first-order rate constant (k_{obsd}), were found to be concentration dependent This is shown in Figure 3 for cumene hydroperoxide. For both hydroperoxides, the observed pseudo-first-order rate constant (k_{obsd}) increased as the initial concentra-

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(2) International Oxidation Symposium, San Francisco, Calif., Aug 1967; M. N. Sheng and J. G. Zajacek, *Advan. Chem. Ser.*, **76**, 418 (1968).

(3) E. S. Gould, R. R. Hiatt, and K. C. Irwin, *J. Amer. Chem. Soc.*, **90**, 4573 (1968).

(4) M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, **35**, 1839 (1970).

(5) G. R. Howe and R. R. Hiatt, *ibid.*, **36**, 2493 (1971).

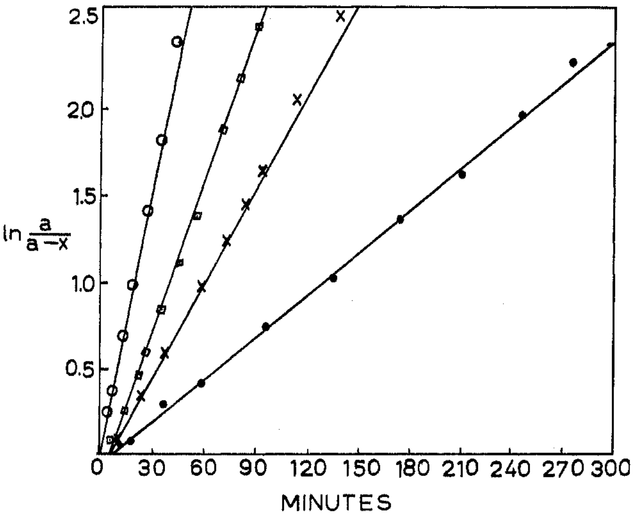


Figure 1.—First-order plot for the epoxidation of 1-octene by *tert*-butyl hydroperoxide with molybdenum hexacarbonyl catalyst. Molar concentration: 1-octene 6.27, *tert*-butyl hydroperoxide 0.212, molybdenum hexacarbonyl 4.48 × 10^{-4}. Reaction temperature (±0.1°): ⊙, 91.5°; ⊡, 84.3°; ×, 79.3°; ●, 71.2°.

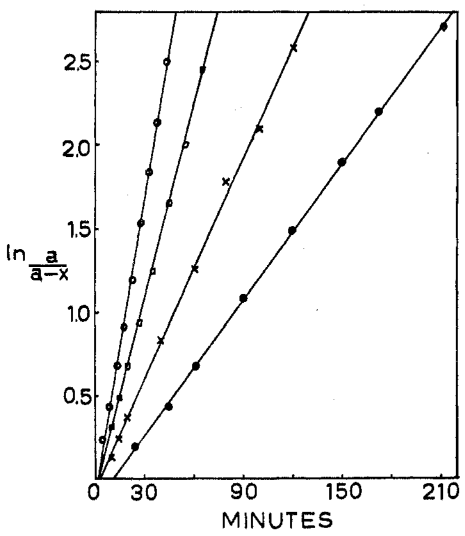


Figure 2.—First-order plot for the epoxidation of 1-octene by cumene hydroperoxide with molybdenum hexacarbonyl catalyst. Molar concentration: 1-octene 6.0, cumene hydroperoxide 0.18, molybdenum hexacarbonyl 4.4 × 10^{-4}. Reaction temperature (±0.1°): ⊙, 89.7°; ⊡, 84.6°; ×, 78.8°; ●, 72.6°.

tion of the hydroperoxide was decreased. These data are summarized in Table I. These experimental results confirm that the rate of epoxidation of 1-octene by either *tert*-butyl or cumene hydroperoxide in the presence of molybdenum hexacarbonyl is not *simple* first order in hydroperoxide as previously reported.[2]

Discussion

An understanding of the kinetic results was achieved by adding a third step to the proposed general mechanism for the epoxidation reaction catalyzed by molybdenum compounds. The additional step accounts for the observed retardation of the rate of the reaction by postulating the formation of a reversible complex between the catalyst and coproduct alcohol. There is ample evidence to support this postulate in prior studies.[2,3,5,6] The basic reaction mechanism then

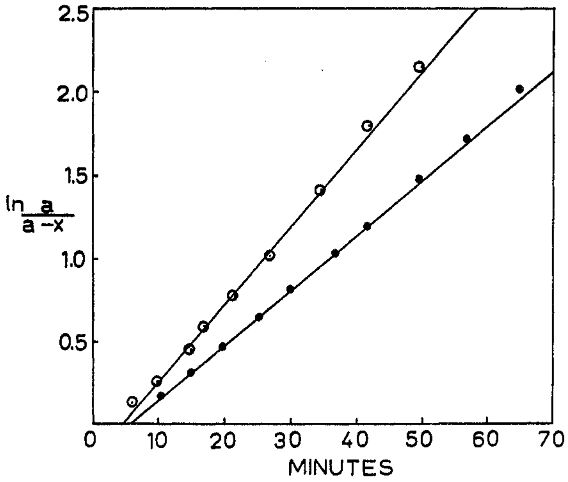


Figure 3.—First-order plot for the epoxidation of 1-octene by different concentrations of cumene hydroperoxide at 84.5°. Molar concentration: 1-octene 6.0, molybdenum hexacarbonyl 4.4 × 10^{-4}, cumene hydroperoxide 0.09 (⊙), 0.27 (●).

TABLE I
OBSERVED RATE CONSTANT FOR THE MOLYBDENUM HEXACARBONYL CATALYZED EPOXIDATION OF 1-OCTENE AT VARIOUS HYDROPEROXIDE CONCENTRATIONS

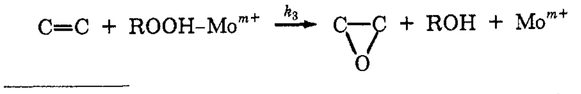
Hydroperoxide, M	$k_{obsd} \times 10^4$, sec^{-1}	$1/k_{obsd} \times 10^{-3}$, sec
t-BuOOH[a] (71.2°)		
0.417	1.05 ± 0.03	9.52
0.208	1.49 ± 0.04	6.71
0.070	2.76 ± 0.15	3.62
t-BuOOH (84.4°)		
0.318	3.36 ± 0.16	2.98
0.212	4.84 ± 0.15	2.07
0.159	4.65 ± 0.15	2.15
0.106	5.80 ± 0.15	1.72
0.053	7.00 ± 0.30	1.27
CuOOH[b] (84.6°)		
0.270	5.69 ± 0.11	1.76
0.180	6.70 ± 0.25	1.49
0.135	7.30 ± 0.25	1.37
0.090	8.25 ± 0.20	1.21
CuOOH (72.6°)		
0.27	1.80 ± 0.09	5.56
0.18	2.32 ± 0.08	4.31
0.09	2.97 ± 0.12	3.37
0.045	4.04 ± 0.14	2.48

[a] 1-Octene, 6.27 *M*; $Mo(CO)_6$, 4.48 × 10^{-4} *M*. [b] 1-Octene, 6.0 *M*; $Mo(CO)_6$ 4.4 × 10^{-4} *M*.

includes (1) a reversible complex formation between the active catalyst (Mo^{m+}) and the hydroperoxide, (2) a reversible inhibition by the coproduct alcohol, and (3) the reaction of the hydroperoxide–molybdenum complex with olefin to form the epoxide and by-product alcohol.

$$\mathrm{ROOH} + \mathrm{Mo}^{m+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ROOH\text{-}Mo}^{m+} \quad (1)$$

$$\mathrm{ROH} + \mathrm{Mo}^{m+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{ROH\text{-}Mo}^{m+} \quad (2)$$


(3)

$$\mathrm{C{=}C} + \mathrm{ROOH\text{-}Mo}^{m+} \xrightarrow{k_3} \underset{\mathrm{O}}{\mathrm{C{-}C}} + \mathrm{ROH} + \mathrm{Mo}^{m+} \quad (3)$$

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[6] M. I. Farberov, G. A. Stozhkova, and A. V. Bondarenko, *Neftekhimiya*, **11**, 578 (1971).

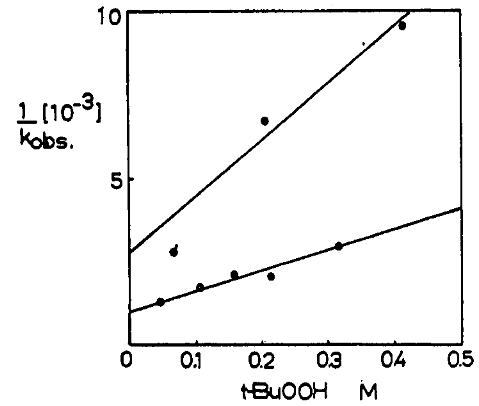

Figure 4.—Plot of the inverse of the observed rate constant for the epoxidation of 1-octene *vs.* the initial *tert*-butyl hydroperoxide concentration with molybdenum hexacarbonyl catalyst: ●, 71.2°, K_{eq} = 6.1 M^{-1}; ⊙, 84.4°, K_{eq} = 5.9 M^{-1}.

When the steady-state assumption is made for the active catalyst species Mo^{m+}, the general rate eq I is

$$\frac{-\mathrm{d(ROOH)}}{\mathrm{d}t} = \frac{\mathrm{d}(\overset{\displaystyle O}{\mathrm{C{-}C}})}{\mathrm{d}t} = \frac{k_3(\mathrm{C{=}C})(\mathrm{ROOH})(\mathrm{Mo})_0}{K_p + K_pK_{eq}(\mathrm{ROH}) + (\mathrm{ROOH})} \quad \text{(I)}$$

derivable, where K_p is the dissociation constant for the catalyst–hydroperoxide complex and K_{eq} is the equilibrium constant for the alcohol–catalyst complex. Since the concentration of alcohol is the difference between the initial and the unreacted hydroperoxide concentration, *i.e.*, (ROH) = $(\mathrm{ROOH})_0$ − (ROOH), eq I can be rewritten as eq Ia

$$\frac{-\mathrm{d(ROOH)}}{\mathrm{d}t} = \frac{k_3(\mathrm{C{=}C})(\mathrm{Mo})_0}{[K_p/(\mathrm{ROOH})] + K_{eq}K_p[(\mathrm{ROOH})_0/(\mathrm{ROOH})] + (1 - K_pK_{eq})} \quad \text{(Ia)}$$

where

$$K_p = [k_{-1} + k_3(\mathrm{C{=}C})]/k_1$$

$$K_{eq} = (\mathrm{ROH\text{-}Mo}^{m+})/(\mathrm{Mo}^{m+})(\mathrm{ROH})$$

This equation is similar to the Michaelis–Menten equation for enzyme catalysis in the presence of a competitive inhibitor.[7] For the molybdenum-catalyzed epoxidation, the coproduct alcohol is the competitive inhibitor *via* a simple alcohol catalyst complex. The experimental observation of apparent first-order dependence of the rate on the hydroperoxide for the molybdenum carbonyl catalyzed epoxidation of 1-octene is shown in Figures 1 and 2. These experimental facts when applied to the rate eq Ia indicate that the term $(1 - K_pK_{eq})$ must be negligible relative to the remaining terms in the denominator. Elimination of this term from eq Ia transforms it into eq II. Equation II

$$\frac{-\mathrm{d(ROOH)}}{\mathrm{d}t} = \frac{k_3(\mathrm{C{=}C})(\mathrm{Mo})_0(\mathrm{ROOH})}{K_p + K_pK_{eq}(\mathrm{ROOH})_0} \quad \text{(II)}$$

explains the apparent first-order dependence on hydroperoxide. Also, eq II may be written in a form where either an observed rate constant (k_{obsd}) or the inverse of the observed rate constant ($1/k_{obsd}$) is obtained (eq III and IV).

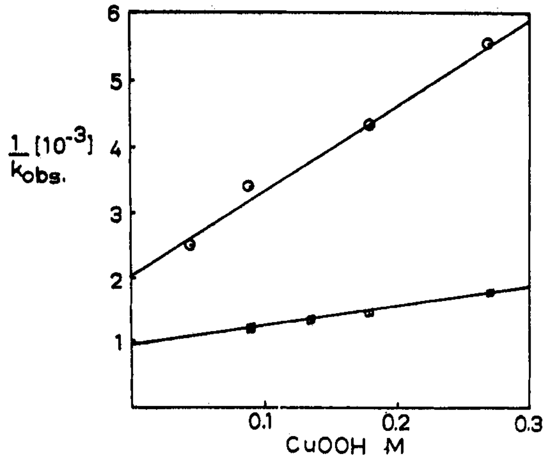

Figure 5.—Plot of the inverse of the observed rate constant for the epoxidation of 1-octene *vs.* the initial cumene hydroperoxide concentration with molybdenum hexacarbonyl catalyst: ⊙, 72.6°, K_{eq} = 6.5 M^{-1}; ⊡, 84.6°, K_{eq} = 3.1 M^{-1}.

$$k_{obsd} = \frac{-\mathrm{d(ROOH)}/\mathrm{d}t}{(\mathrm{ROOH})} = \frac{k_3(\mathrm{C{=}C})(\mathrm{Mo})_0}{K_p + K_pK_{eq}(\mathrm{ROOH})_0} \quad \text{(III)}$$

$$\frac{1}{k_{obsd}} = \frac{K_p}{k_3(\mathrm{C{=}C})(\mathrm{Mo})_0} + \frac{K_pK_{eq}(\mathrm{ROOH})_0}{k_3(\mathrm{C{=}C})(\mathrm{Mo})_0} \quad \text{(IV)}$$

Equation IV provides a way to test the validity of the assumption that term $(1 - K_pK_{eq})$ is small. According to this equation, a plot of the inverse of the observed rate constant *vs.* the initial hydroperoxide concentration must be linear. When the kinetic results listed in Table I for *tert*-butyl and cumene hydroperoxide are plotted in this manner, a good linear fit was obtained at both 71 and 84°. This is shown in Figures 4 and 5.

Equation IV also provides a way to calculate a value for K_{eq}, the equilibrium constant for the alcohol–catalyst complex. The slope of the lines in Figures 4 and 5 divided by the respective intercepts gives values for K_{eq}. The derived values are shown in Table II.

TABLE II
EQUILIBRIUM CONSTANT (K_{eq}) FOR THE MOLYBDENUM CARBONYL–ALCOHOL COMPLEX

	Temp, °C	Slope, sec M^{-1} × 10^{-3}	Intercept, sec × 10^{-3}	K_{eq}, M^{-1}
CuOOH	72.6	12.2 ± 1.0	2.00 ± 0.1	6.5 ± 0.5
	84.6	2.99 ± 0.1	0.95 ± 0.1	3.1 ± 0.3
t-BuOOH	71.2	16.7 ± 5.0	2.75 ± 1.0	6.1 ± 2.0
	84.4	6.01 ± 0.5	1.02 ± 0.1	5.9 ± 0.6

The low values for the equilibrium constant, K_{eq}, and the good fit of the plots support the view that with the molybdenum hexacarbonyl catalyst higher order alcohol–catalyst complexes are not important.

The kinetic data for the molybdenum hexacarbonyl catalyzed epoxidation of 1-octene are self-consistent with the assumption that the term $(1 - K_pK_{eq})$ is negligible compared to the other terms in the denominator of eq II. In terms of the proposed mechanism for the epoxidation reaction, this means the equilibrium constant (K_{eq}) for the formation of the alcohol–catalyst complex must be *approximately* the inverse of the dissociation constant (K_p) for the molybdenum–

[7] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960.

hydroperoxide complex. Thus, the observed first-order dependence of the rate on the hydroperoxide requires during a reaction that the tendency to drift to a higher observed rate constant as a result of the hydroperoxide concentration term in the denominator is balanced by a shift toward a lower observed rate constant as a result of the coproduct alcohol produced.

It is also possible to make the further simplifying assumption that the term $(1 - K_pK_{eq})$ is equal to zero. If this is done, values for k_3 the rate of reaction between the olefin and the hydroperoxide–molybdenum carbonyl complex, and K_p, the dissociation constant for the molybdenum–hydroperoxide complex can be determined. Also, since data are available at two different temperatures, $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$ for the k_3 reaction can be estimated. When this assumption is made for *tert*-butyl hydroperoxide, reasonable values are obtained for these parameters. The numbers are given in Table III. For cumene hydroperoxide, the values calculated for these parameters are unreasonable. This suggests the reaction with cumene hydroperoxide is more complicated then with *tert*-butyl hydroperoxide. The cumene hydroperoxide results are not understood, and calculations of this type are not emphasized because the errors involved in making the underlying assumptions are potentially very large.

TABLE III

CALCULATED VALUES BASED ON THE ASSUMPTION $K_p = 1/K_{eq}$

Hydroperoxide	$\Delta H^{\circ\ddagger}$, kcal	$\Delta S^{\circ\ddagger}$, eu	Temp, °C	k_3, l. mol^{-1} sec^{-1}
tert-Butyl	19 ± 1.0	-14 ± 2.0	84.2	0.059 ± 0.002
			71.2	0.021 ± 0.002

Experimental Section

Materials.—The 1-octene (99 mol % purity) and *n*-octane (99 mol % purity) were obtained from Phillips Petroleum Co. Both were percolated through silica gel and distilled in a spinning band column. The olefin, bp 120–121°, was used without further treatment. *tert*-Butyl hydroperoxide (90% purity) was obtained from the Lucidol Division of Pennwalt Co., and cumene hydroperoxide (65% purity) was obtained from Matheson Chemical Co. The hydroperoxides were purified according to Davies[8] and distilled at reduced pressure in all-glass apparatus using a magnetically stirred oil bath and a magnetically stirred distilling flask. The colorless middle fraction, analyzing 100 ± 0.4% purity by iodometric titration,[9] were employed in the kinetic runs. Typical samples of *tert*-butyl hydroperoxide had bp 52° (39 mm); cumene hydroperoxide, bp 53° (0.23 mm). Molybdenum hexacarbonyl was obtained from Matheson Chemical Co.; it was purified by sublimation at reduced pressure and stored in the dark.

Kinetic Procedure.—Kinetic runs were made in a magnetically stirred glass flask fitted with a septum, reflux condenser, catalyst spoon, and calibrated thermometer. A vacuum system with an adjustable manostat controlled the temperature. The reaction was initiated by introduction of the molybdenum hexacarbonyl from the catalyst spoon. When molybdenyl acetylacetonate was the catalyst, a freshly prepared solution of the catalyst in dry benzene was introduced into the mixture with a syringe and needle through the septum. As the reaction proceeded, the temperature was controlled to ±0.1° by adjustment of the manostat. Samples were withdrawn from the system using a syringe. These aliquots were transferred to vials, cooled rapidly in ice, and analyzed for hydroperoxide using an iodometric method. Repeat analyses revealed a reproducibility better than 0.75%. A few samples from kinetic runs at low and high conversion of hydroperoxide were analyzed for epoxide using a Perkin-Elmer Model 226 gas chromatograph equipped with a 150 ft × 0.01 in. Carbowax 1540 capillary column. Sublimed triphenylphosphine was used to remove unreacted hydroperoxide before introducing the sample into the chromatograph. At the high olefin to hydroperoxide ratio used in these runs, the yield of epoxide based on the hydroperoxide converted was nearly quantitative (100 ± 5%) for both cumene and *tert*-butyl hydroperoxide.

In a typical experiment, a mixture of cumene hydroperoxide (0.27 *M*), molybdenum hexacarbonyl (4.4×10^{-4} *M*), 1-octene (6.0 *M*), and *n*-octane, sufficient to make the mixture to the standard volume, was allowed to react at 84.6° through greater than 90% conversion to give samples for which hydroperoxide *vs.* time data were generated. The amount of *n*-octane was varied from run to run to compensate for changes in hydroperoxide concentration. Typical data for this cumene hydroperoxide experiment are given below, where $k_{obsd} = 5.58 \pm 0.12 \times 10^{-4}$ sec^{-1}.

Wt % hydroperoxide	Time, sec
5.712	0
5.479	180
5.156	360
4.531	600
3.923	900
3.179	1260
2.636	1680
1.998	2160
1.414	2700
1.005	3300
0.743	3900
0.512	4500

Registry No.—Molybdenum hexacarbonyl, 13939-06-5; 1-octene, 111-66-0.

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[8] A. G. Davies, "Organic Peroxide," Butterworths, London, 1961, p 114.

[9] D. H. Weeler, *Oil Soap (Chicago)*, **9**, 89 (1932).