Hewlett-Packard No. 2801A quartz digital thermometer. Temperatures are believed accurate to +0.04°.

Kinetic measurements for all of the thenils, with the exception of 3,3′-benzo[*b*]thenil, 2,2′-benzo[*b*]thenil, and 5,5′-di(2″-thienyl)-2,2′-thenil, were carried out in the same manner. A sample of the thenil, in the range of 2.5–3.0 mmol, was weighed to 0.1 mg and placed in a 250-ml Teflon screw cap bottle, along with a magnetic stirring bar. The thenil was dissolved in 100.0 ml of equilibrated dioxane with stirring. The solution was continuously stirred during the kinetic run by means of a submersible magnetic stirrer mounted directly beneath the reaction vessel. A 50.00-ml quantity of 0.1 *N* temperature equilibrated potassium hydroxide solution was pipetted into the thenil solution with vigorous stirring. The vessel was sealed with a screw cap arrangement that permitted the insertion and withdrawal of a pipette. A 10.00-ml aliquot of the thenil solution was immediately withdrawn. The aliquot was quenched in a 10-ml sample of ice cold acetone and the clock was started.

The sample was titrated to either a phenolphthalein (pH 8.3) or thymol blue (pH 8.0) end point with 0.01 *N* hydrochloric acid. At various intervals, depending on the rate of potassium hydroxide disappearance, 10-ml aliquots were withdrawn and titrated in the same manner. Simultaneously with the kinetic runs, a blank sample was determined under the same conditions described above, except that the thenil was omitted. In this manner it was possible to correct for any acidic impurity present in the thenil and also for any reaction of the base with the solvent. During the 80° runs and to a lesser extent at 70°, a small correction (by never more than 3%) was found to be necessary. At other temperature, the correction was too small to be measured.

Samples of 3,3′-benzo[*b*]thenil, 2,2′-benzo[*b*]thenil, and 5,5′-di(2″-thienyl)-2,2′-thenil were too insoluble to be determined at the concentrations used above for the other thenils. Accordingly, samples in the range 0.3–0.8 mmol, but never less than 0.1000 g, were used in the kinetic determinations. The amount of dioxane used was 100 ml, but the 50 ml of potassium hydroxide was replaced by 15 ml of potassium hydroxide and 35 ml of water. All other conditions were the same.

Since a mixture of dioxane and water does not constitute an ideal solution in the thermodynamic sense, the following equation was used to calculate the actual volume of the reaction mixture at the start of a given kinetic run

$$V_{\text{mix}} = \frac{v_1(\rho_1) + v_2(\rho_2)}{\rho_{\text{mix}}}$$

where v_1 and v_2 are the volumes of dioxane and water measured out, ρ_1 and ρ_2 are the densities of dioxane and water at a given temperature,[21] and ρ_{mix} is the density of the mixture at the same temperature.[22] In these calculations, the thenils and potassium hydroxide are assumed to behave ideally. All linear plots were refined by least-squares analysis. All calculations were preformed on a Wang 320 electronic calculator.

Acknowledgments.—The authors wish to extend their gratitude to Professor Matt Zabik, Department of Entomology, Michigan State University, for the loan of the Beckman 1019 pH meter.

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[21] F. Horvaka, R. A. Schaefer, and D. Dreisbach, *J. Amer. Chem. Soc.*, **58**, 2264 (1936).

[22] H. Hartmann, *Z. Phys. Chem. (Leipzig)*, **191**, 197 (1942).

Metal-Catalyzed Hydroperoxide Reactions. II.[1] Molybdenum-Catalyzed Epoxidations of Styrene and Some Substituted Styrenes

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A kinetic study has been carried out on the epoxidation of styrene and some substituted styrenes by *tert*-butyl hydroperoxide in the presence of molybdenum naphthenate. In benzene solution the reaction is first order in peroxide (in the range 0.1–0.3 *M*), in alkene (0.2–0.4 *M*), and in catalyst (0.0–4.58 × 10^{-4} g-atom of Mo kg^{-1}). The rates for the substituted styrenes show considerable scatter for attempted correlations with various free-energy relationships; however, a $\rho\sigma$ plot gives $\rho = -1.4 \pm 0.6$ (95% confidence levels). Thus, the rate-determining step presumably involves electrophilic attack upon the alkene. With styrene as solvent the reaction is first order in hydroperoxide but displays no simple dependence on molybdenum concentration. The apparent order in catalyst decreases as its concentration is increased in a manner which, though not fully understood, suggests either some form of special complexing or lack of true solubility in the medium.

Alkenes are readily epoxidized by organic hydroperoxides in the presence of catalytic amounts of molybdenum and vanadium compounds.[2–7] The kinetics of the epoxidation have been reported for 1- and 2-octene in the presence of molybdenum hexacarbonyl[4,5] and for cyclohexene with vanadium acetylacetonate.[7] The former reaction is first order in catalyst and alkene,[4] and apparently first order in peroxide, but the first-order rate constants obtained vary with initial peroxide concentration.[5] The vanadium-catalyzed cyclohexene epoxidation is also first order in catalyst and alkene, but the rate dependence on peroxide has been shown to be analogous to the Michaelis–Menten equation for enzyme catalysis.[7] Two noticeable features of this latter reaction are the marked inhibition by small quantities of *tert*-butyl alcohol, a reaction product, and rapid catalyst deactivation, effects apparently absent in the molybdenum-catalyzed octene epoxidation.[4,5] The proposed mechanism[4–7] involves rapid reversible complex formation between peroxide and catalyst preceding a rate-determining heterolysis of the complex O–O bond.

This paper describes a kinetic investigation of the molybdenum catalyzed epoxidation of styrene and some substituted styrenes, in order to clarify the position with regard to the kinetics and mechanism of the molybdenum-catalyzed epoxidation and also as part of a general study of substituent effects in aromatic systems.

Results and Discussion

Epoxidations were carried out using *tert*-butyl hydroperoxide (subsequently referred to simply as "peroxide") and followed by iodometric titrations of re-

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[1] (a) The research described in this paper has been carried out under support by the National Research Council of Canada, Grant No. 34-02-01. (b) Part I: G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, **35**, 4007 (1970).

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[3] N. Indictor and W. F. Brill, *J. Org. Chem.*, **30**, 2074 (1965).

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[5] M. N. Sheng, J. G. Zajacek, and T. N. Baker III, Symposium on New Olefin Chemistry, Houston, Texas, Feb. 1970.

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

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

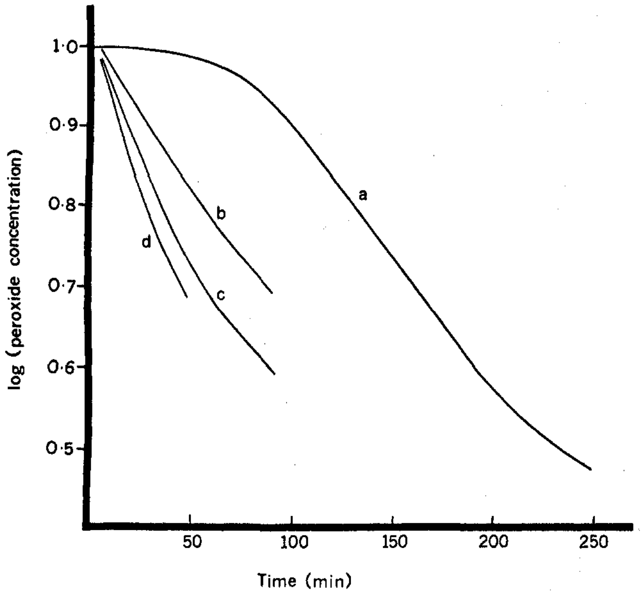
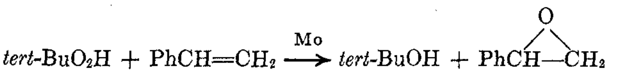


Figure 1.—Semilog plot of peroxide concentration *vs.* time at various catalyst concentrations.

sidual peroxide. To inhibit any concurrent homolytic processes (styrene polymerization, etc.), a small quantity of di-*tert*-butyl-*p*-cresol was added to each run. Thus the reaction could be considered to obey the stoichiometry of the equation



$$tert\text{-BuO}_2\text{H} + \text{PhCH{=}CH}_2 \xrightarrow{\text{Mo}} tert\text{-BuOH} + \text{PhCH{-}CH}_2 \text{ (O bridging)}$$

The quantitative yield of epoxide, based on peroxide reduced, was demonstrated (Experimental Section) as it has been in many previous reports.[2-7]

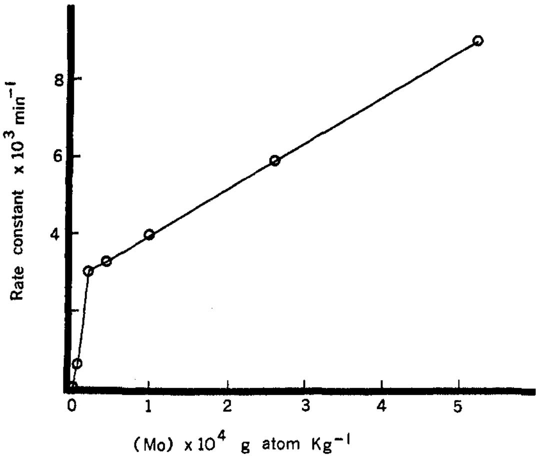


Figure 2.—First-order rate constants *vs.* catalyst concentration.

TABLE I
PSEUDO-FIRST-ORDER RATE CONSTANTS AND 95% CONFIDENCE LEVELS FOR MOLYBDENUM-CATALYZED EPOXIDATION OF STYRENE[a]

	[*tert*-BuOOH]$_0$,[b] *M*	[*tert*-BuOH]$_0$,[c] *M*	Rate constant × 10^3 min^{-1}	Confidence level
a	0.25	0.0	4.0	0.3
b	0.40	0.0	3.9	0.2
c	0.25	0.25	4.1	0.3

[a] Reactions conditions: molybdenum naphthenate (1.01×10^{-4} g-atom kg^{-1}) and peroxide in styrene at 60.0°. [b] Initial peroxide concentration. [c] Initial *tert*-butyl alcohol concentration.

TABLE II
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE EPOXIDATION OF STYRENE[a] AT 60°

Mo[b] concentration × 10^4 g-atom kg^{-1}	Rate constant × 10^3 min^{-1}	95% confidence level
0.000	0.00	
0.070	0.57	0.07
0.213	3.02	0.50
0.441	3.14	0.07
1.011	4.00	0.3
2.627	5.95	0.37
5.535	8.89	0.48

[a] Reaction conditions: *tert*-butyl hydroperoxide (0.25 *M*) in styrene. [b] As molybdenum naphthenate.

Epoxidations in Styrene.—Under the kinetic conditions subsequently described no reaction occurred in the absence of either catalyst or styrene. Molybdenum hexacarbonyl when used as a catalyst had an induction period (when very little reaction took place) of 5–30 min (Figure 1, a); this has been attributed to a need to lose one CO ligand prior to reaction.[4] In view of the necessity of determining initial rates, molybdenum naphthenate was used in all subsequent kinetic runs to avoid this induction period. Kinetic runs in styrene at 60° showed the following features. (1) Catalyst degradation occurred readily, deviations in the rates being measurable when the reaction had proceeded between 10 and 30%. The higher the catalyst concentration, the lower the percentage of reaction at which such deviations become apparent (Figure 1, b–d). (2) The reaction is first order in peroxide in the range 0.1–0.4 *M* as shown by the linearity of the plot of log (peroxide) *vs.* time over the initial part of the reaction (Figure 1, b–d). The pseudo-first-order rate constant so determined was independent both of initial peroxide concentration and of added initial *tert*-butyl alcohol (0.25 *M*) (Table I). (3) Yields of styrene oxide, determined for run a, Table I at 25 and 50% reduction, were quantitative within the limits of the vpc analysis (±4%). This included both linear and nonlinear sections of the plot (Figure 1, b). (4) The rate dependence on catalyst concentration was complex. Table II lists pseudo-first-order rate constants for peroxide disappearance as a function of molybdenum concentration, and Figure 2 shows a plot of this function. The plot is linear in the range 0.2–5.5 × 10^{-4} g-atom of Mo kg^{-1}, with a slope less than unity. Below 0.2 the slope is greater than unity, the line passing through the origin. A log–log plot indicates an apparent order of $^3/_2$ at the lower concentrations and of $^1/_2$ at higher. Either order can be rationalized on the basis of catalyst dimers and/or special complexing, but it is difficult to encompass both in a single mechanism. We are forced to note that odd changing orders are more common than otherwise for metal ion catalyzed hydroperoxide reactions and that there is disagreement over whether the phenomenon is due to complexation or to lack of true solubility of the catalyst in the medium.[8] The medium effect is emphasized by the fact that the reactions using dilute solu-

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[8] R. Hiatt, K. C. Irwin, and C. W. Gould, *J. Org. Chem.*, **33**, 1430 (1968).

tions of styrene in benzene showed good first-order dependence on catalyst concentrations, as shown below.

Styrene Epoxidations in Benzene.—Kinetic studies were carried out using approximately equal concentrations of styrene and peroxide in benzene at 60°. Second-order rate plots (first order in styrene and peroxide) were linear over some 20% of the reaction. Table III lists initial second-order rate constants measured under various conditions. These show that the rate constant is (1) independent of initial peroxide concentration (Table III, runs a and d) and (2) independent of initial, added *tert*-butyl alcohol (a and b), and the rate is first order in molybdenum (a, c–e, Figure 3).

TABLE III

SECOND-ORDER RATE CONSTANTS FOR STYRENE[a] EPOXIDATION IN BENZENE AT 60°

	[*tert*-BuOOH]$_0$,[b] M	[*tert*-BuOH]$_0$,[c] M	[Mo][d]	Rate constant × 10^4 M^{-1} min^{-1}	95% confidence level
a	0.245	0.0	3.10	26.7	2.1
b	0.243	0.25	3.10	26.9	3.0
c	0.237	0.0	2.00	18.4	1.7
d	0.549	0.0	3.22	27.6	2.2
e	0.582	0.0	4.58	42.0	3.1

[a] Initial styrene concentration = 0.4 M. [b] Initial peroxide concentration. [c] Initial *tert*-butyl alcohol concentration. [d] Molybdenum naphthenate concentration (× 10^4 g-atom kg^{-1}).

Epoxidation of Substituted Styrenes in Benzene.—Substituent effects upon rates of metal-catalyzed hydroperoxide epoxidations have been studied only for the case of hydrocarbon substituents in alkyl systems.[4–6] The effect of some heteroatom substituents in aniline upon rates of metal-catalyzed hydroperoxide oxidations have been reported,[1b] and the results obtained have been useful both for interpreting the mechanism of these reactions and for studies upon the nature of substituent effects in general. Consequently, second-order rate constants for the epoxidation in benzene of a series of ring-substituted styrenes were determined using the identical catalyst concentration in every case[9] (3.10 × 10^{-4} g-atom of Mo kg^{-1}). The results (Table IV) show that the meta nitro group decreases the reaction rate and the para methyl increases it, as is to be expected for a reaction including an electron-deficient transition state. The effect of halogen substituents is small and for the para position appears to be in contradiction to the expected order. However, consideration of the 95% confidence levels indicates that the present technique of initial rate determinations is not accurate enough to place too much significance on this apparent reversal of the customary effect.

TABLE IV

SECOND-ORDER RATE CONSTANTS FOR THE EPOXIDATION[a] OF SOME SUBSTITUTED STYRENES IN BENZENE AT 60°

Substituent	Registry no.	Rate constant × 10^4 M^{-1} min^{-1}	95% confidence level
None	100-42-5	26.7	2.1
m-Cl	2039-85-2	21.8	3.0
p-Cl	1073-67-2	30.5	0.25
m-Br	2039-86-3	26.1	2.7
p-Br	2039-82-9	31.0	3.7
m-NO$_2$	586-39-0	3.10	0.5
p-Me	622-97-9	89.6	9.5

[a] Reaction conditions: peroxide (0.25 M), substituted styrene (0.4–0.5 M), and molybdenum naphthenate (3.10 × 10^{-4} g-atom kg^{-1}).

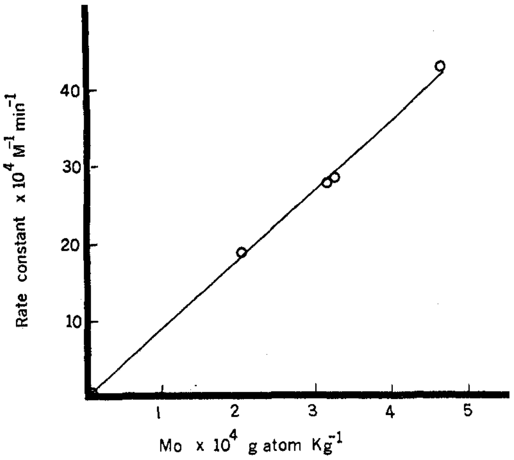

Figure 3.—Second-order rate constants *vs.* catalyst concentration.

Correlation of Substituent Effects by Linear Free-Energy Relationships.—Linear multiple regression analyses were carried out using the relationships discussed in part I,[1b] *viz.*, with Hammett σ constants,[10] with Brown–Okomoto σ^+ constants,[11] with the Yukawa–Tsuno equation,[12] and with the three variable, dual-effect equation discussed in part I.[13] Parameters used in the latter eq 1 are as follows. F and M were

$$\log \frac{k}{k_0} = A + BFX_{\mathrm{SR}} + CMY_{\mathrm{SR}} \qquad (1)$$

from the F and R values of Swain and Lupton.[14] Y_{SR} is the Hückel molecular orbital atom–atom polarizability[15] (π_{RS}) between the carbon atom (S) to which the substituent is attached and the carbon atom (R) which is the reaction center; separate calculations were made using both of the ethylenic carbon atoms (α and β) as reaction centers. All four functional forms of X described in part I[1b] were used, in combination with the appropriate polarizabilities. The normalized standard errors[1b] and variable t statistics for these analyses are given in Table V. In considering these results, the reservation concerning the relative accuracy of the present technique previously discussed should be borne in mind. Nevertheless, the correlations appear to be uniformly poor, especially for the dual effect equations, and there appears to be no linear free-energy relationship between the present reaction and more conven-

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[9] The competitive method of part I[1b] could not be used in the present case due to difficulties in the vpc analysis of these compounds.

[10] L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970.

[11] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[12] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 971 (1959), and preceeding papers.

[13] (a) G. R. Howe, Ph.D. Thesis, University of Leicester, 1969; (b) K. C. C. Bancroft and G. R. Howe, *J. Chem. Soc. B*, in press.

[14] C. G. Swain and E. C. Lupton Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

[15] M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539, 3541, 3546, 3548 (1962), and references therein.

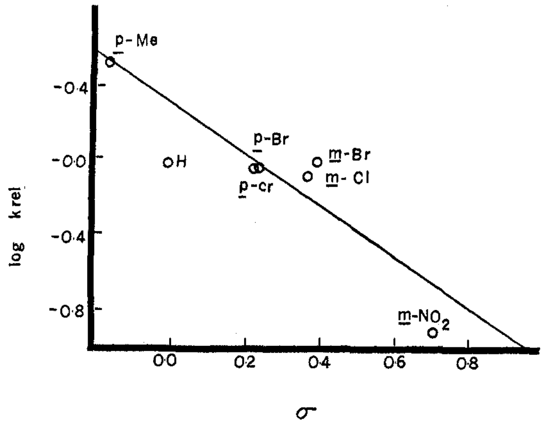


Figure 4.—Log K/K_0 for substituted styrenes *vs.* σ constants.

tional aromatic substitution reactions, in contrast to the vanadium-catalyzed oxidation of substituted anilines.[1b] Presumably interaction between the π MO's of the styrene system and the AO's of the molybdenum ion is sufficient to lead to differences in the differential change of activation enthalpy with respect to substrate structure. With the number of degrees of freedom of the various analyses used, the t values are not statistically significant enough to use the correlational results to interpret mechanism; *e.g.*, one cannot distinguish with any certainty between a greater positive charge on the α carbon atom rather than the β carbon atom in the transition state of the reaction. An illustrative plot of log (k/k_0) *vs* σ constants (which give the best correlation) is shown in Figure 4. The ρ value (−1.37) compares with a value of −1.63 for the hydroperoxide–molybdenum aniline oxidation.[1b]

TABLE V

NORMALIZED STANDARD ERRORS[a] AND VARIABLE t STATISTICS[b] FOR REGRESSION ANALYSES[c]

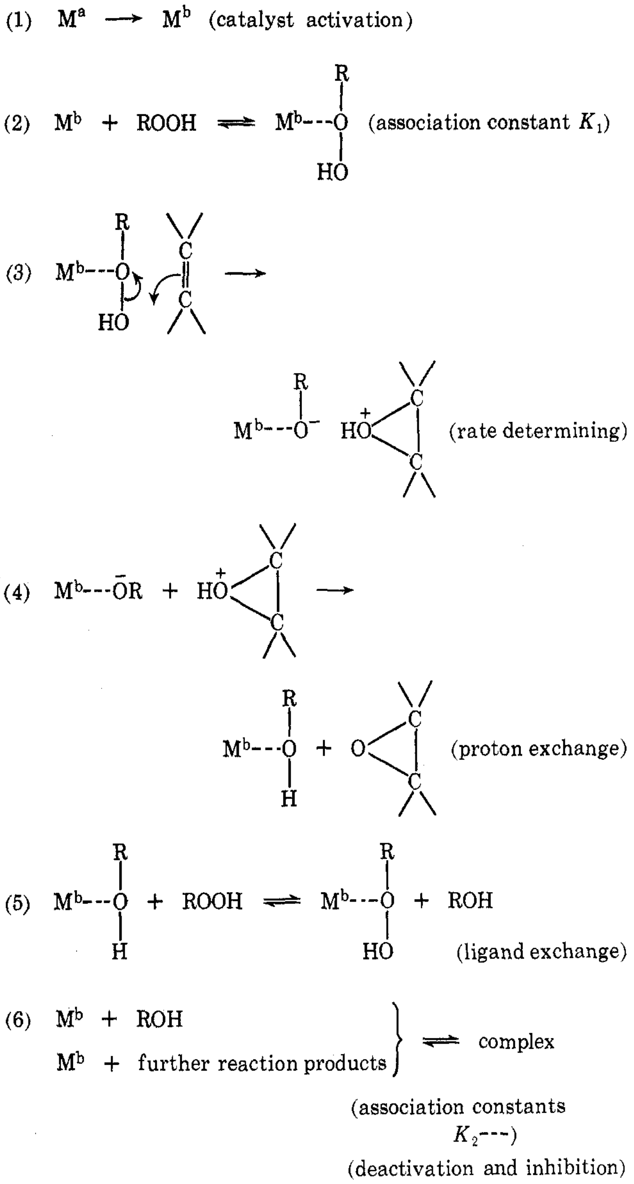
Correlation with		NSE	t_b	t_c
σ		0.53	4.37	
σ^+		0.56	4.09	
Yukawa–Tsuno		0.60	3.43	0.05
Eq 1				
Y	X			
$\pi(\alpha)$	$1/d$	0.69	2.59	1.32
	$1/d^2$	0.69	2.59	1.08
	Cos^-/d	0.72	2.42	2.13
	Cos^-/d^2	0.70	2.50	1.94
$\pi(\beta)$	$1/d$	0.74	2.50	0.96
	$1/d^2$	0.73	2.56	0.75
	Cos^-/d	0.81	2.12	1.61
	Cos^-/d^2	0.79	2.25	1.46

[a] Defined in part I.[1b] [b] t_B = ratio of variable B to standard deviation of B. [c] Using functions log $(k/k_0) = A + BX_1$ or $A + BX_1 + CX_2$ as appropriate.

Mechanism of the Epoxidation.—The metal-catalyzed epoxidation is well established to involve a heterolytic mechanism.[3-7] The difference in kinetic behavior shown by the three kinetic studies so far made, namely the vanadium acetylacetonate catalyzed cyclohexene reaction,[7] the molybdenum hexacarbonyl catalyzed octene epoxidation,[4] and the present study, is however consistent with the previously proposed common mechanism[4,7] shown in generalized format as Scheme I.[16] The first-order dependence in alkene and catalyst shown by all three reactions, the first-order dependence in peroxide shown by the molybdenum catalyzed reactions, and the Michaelis–Menten equation dependence on peroxide shown by the vanadium-catalyzed reaction imply that a single molecule of each reactant is involved in the transition state. This further implies that two of the components have interacted at some prior stage, and a peroxide-catalyst complex seems the logical explanation. The difference in kinetic behavior between vanadium and molybdenum is

SCHEME I

EPOXIDATION MECHANISM



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[16] It should be noted, however, that complete consistency is shown only for dilute reactants in an inert solvent. Kinetic anomalies observed for reactions in neat olefin which are not as yet understood include the variation in pseudo-first-order rate constants with $(RO_2H)_0$ shown by the molybdenum hexacarbonyl–octene reaction[3] and the here reported complexity of rate dependence on molybdenum concentration for the reaction in styrene. Equally inexplicable is the fact that the reaction is not a good route for laboratory synthesis of epoxides if efficient utilization of olefin is required. (R. Hiatt and C. McColeman, unpublished work.) Beyond a certain point no further epoxidation takes place even with hydroperoxide in substantial excess and with fresh catalyst added.

then explained by a much smaller value of K (the complex association constant) in the latter case, when the Michaelis–Menten equation reduces to effective first order in peroxide. The electrophilic nature of the reaction, as indicated by the substituent effects in styrene, implies a strong polarization of the peroxide O–O bond by the catalyst, which suggests that the metal ion is in a comparatively high oxidation state. Correspondingly, one would expect an initial activation of the catalyst from its lower oxidation state, which explains the induction period observed in the case of molybdenum hexacarbonyl. Inhibition by *tert*-butyl alcohol, observed for the vanadium reaction, but not for the molybdenum, has been postulated as being due to competition for the catalyst by the alcohol.[7] In the molybdenum case presumably K_2 (the alcohol–catalyst association constant) is much smaller than K_1. Catalyst deactivation could be caused by catalyst complexing with further reaction products of the epoxidation. This deactivation has been observed in all cases except the molybdenum hexacarbonyl–octene system; in the latter case one suspects the octene further reaction products do not complex; this is borne out by the deactivation shown by molybdenum hexacarbonyl in the present work.

The mechanism shown (Scheme I) fits the experimental facts;[16] inevitably postulates have to be made regarding the relative values of the association constants of the various catalysts with the various reaction components; in the absence of direct experimental evidence concerning such complexes, however, the present scheme does satisfactorily explain the epoxidation observations.

Experimental Section

Materials.—*tert*-Butyl hydroperoxide (*i.e.*, Lucidol) was generally used as received, as a 90% aqueous solution; for some of the kinetic experiments samples were purified to greater than 99.5% peroxide by vacuum distillation, though this made no detectable difference to the kinetics. All other chemicals were purified and dried by standard means. In particular, vpc analysis of styrene and substituted styrenes failed to detect any impurities, using a variety of columns. Molybdenum naphthenate, 3% molybdenum by weight, was used as obtained from K & K Laboratories.

Analyses.—Peroxide concentrations were determined by refluxing an aliquot for 5 min with potassium iodide in 2-propanol–glacial acetic acid (2:1 v/v) followed by thiosulfate titration of the released iodine. Styrene oxide concentrations for the determination of stoichiometry were determined by vpc analysis on a 6 ft × 0.25 in. SE-54 column at 130°, using an F & M Model 700 gas chromatograph equipped with a Disc integrator. For example, in a given instance (Table I, run a), a sample in which 0.055 mmol of peroxide/g had reacted showed the presence of 0.053 mmol/g of styrene oxide.

Kinetic Experiments.—Typically, a solution of styrene (0.4 *M*), *tert*-butyl hydroperoxide (0.25 *M*), and di-*tert*-butyl-*p*-cresol (0.0002 g) (to inhibit homolytic reaction) in benzene (10.00 ml) was allowed to equilibrate at reaction temperature. The reaction was initiated by adding a solution of molybdenum naphthenate in benzene (freshly made up for each run), prewarmed to reaction temperature. Periodically, samples of about 1 g were withdrawn, weighed, and analyzed for peroxide as above.

Registry No.—*tert*-Butyl hydroperoxide, 75-91-2.

Transition Metal Complexes as Selective Isomerization Catalysts. Preparation of Compounds Having an Exocyclic Double Bond

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The selective isomerization of vinylcycloalkenes and vinylcycloalkanes to compounds having an exocyclic double bond has been studied using three metal complexes: $RuCl_2(Ph_3P)_3$ in the presence of air or hydroperoxides, $PtCl_2(Ph_3P)_2$ and $SnCl_2$ under hydrogen pressure, and $IrCl(CO)(Ph_3P)_2$. The reactions are highly selective for retaining the double bond in the exocyclic position in contrast to conventional acid- or base-catalyzed isomerizations and consequently have synthetic utility as a catalytic method for formation of the exocyclic double bond. The ruthenium(II) complex exhibits catalytic activity in the presence of small amounts of air or hydroperoxides but is quite inactive in their absence. A carbonyl complex having high catalytic activity is formed when air or hydroperoxides react with olefin solutions of $RuCl_2(Ph_3P)_3$. The cis/trans ratio of isomers formed varies with the catalyst used showing that in certain instances cis/trans isomerization is not rapid in comparison with double bond migration. A steric argument is offered to explain observed selectivity.

Advances in homogeneous transition metal catalysis during the past decade have provided many useful examples of the selective hydrogenation of unsaturated organic compounds.[1] It is also known that many of the same complexes used in olefin hydrogenation are effective catalysts for olefin isomerization.[2] This paper describes the selective migration of a double bond on a vinyl side chain of a cyclic hydrocarbon into a position exocyclic to the ring by three group VIII metal complexes well known for their ability to catalyze olefin hydrogenation: $RuCl_2(Ph_3P)_3$, shown by Wilkinson[3] and his coworkers to be a selective hydrogenation catalyst; the $PtCl_2(Ph_3P)_2$–$SnCl_2$–H_2 system studied extensively by Bailar;[4] and Vaska's complex,[5] $IrCl(CO)(Ph_3P)_2$. It appears that, as in the case of homogeneous hydrogenation, steric factors govern the course of the reaction and are the cause of the observed selectivity in retaining the exocyclic double bond.

The interconversions between semicyclic, exocyclic, and endocyclic olefins have been extensively studied

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(1) For a recent review of selective hydrogenation, see J. E. Lyons, L. E. Rennick, and J. L. Burmesiter, *Ind. Eng. Chem., Prod. Res. Develop.*, **9**, 2 (1970).

(2) For reviews of olefin isomerization catalyzed by metal complexes, see C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967, Chapter 3; M. Orchin, *Advan. Catal.*, **16**, 1 (1966).

(3) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968), and references cited therein.

(4) (a) R. W. Adams, G. E. Batley, and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **90**, 6051 (1968). (b) J. C. Bailar, Jr., and H. Itatani, *ibid.*, **89**, 1592 (1967); H. A. Tayim and J. C. Bailar, Jr., *ibid.*, **89**, 4300 (1967).

(5) (a) L. Vaska and J. DiLuzio, *ibid.*, **84**, 679 (1962); L. Vaska and R. E. Rhodes, *ibid.*, **87**, 4970 (1965), and references cited therein.