TABLE IV

THE EFFECTS OF SUBSTITUENTS IN α-METHYLSTILBENES

k/k_0 and $\log(k/k_0)$ (in parentheses), in benzene at $10°$; k/k_0 is the relative rate of substituted vs. unsubstituted α-methylstilbenes for the same PBA

p-Substit. in α-methyl-stilbene	p-Substituent in PBA		
	MeO	H	Cl
MeO	4.75 (0.677)	4.84 (0.686)	4.82 (0.683)
Me	1.88 (.276)	2.17 (.336)	1.98 (.297)
Cl	0.615 (−0.212)	0.653 (−0.185)	0.586 (−0.232)

values of k/k_0 increase from small values for p-methoxy-PBA (lowest reactivity) through the maximum for PBA, and then decrease again with p-chloro-PBA (highest reactivity). On the other hand, in the case of p-chloro-α-methylstilbene, k/k_0 decreases from p-methoxy-PBA to PBA and increases again from PBA to p-chloro-PBA.

Facts i and ii cited above may be ascribed to (a) a correlation between selectivity and reactivity, and (b) a change in the resonance contribution, which affects k/k_0 inversely to (a).[22]

With p-methoxy- and p-methyl-α-methylstilbenes, the effect of the selectivity–reactivity relationship slightly exceeds the increase of resonance effect, and thus larger values of k/k_0 were observed for PBA than for p-chloro-PBA. However, the decrease of resonance effect in the transition state may be more important than the selectivity relationship with p-methoxy-PBA, so that k/k_0 decreases from PBA to p-methoxy-PBA. With p-chloro-α-methylstilbene, the decrease of resonance effect is less important and its increase is important; therefore the reverse is true.

Selectivity and the Nature of the Transition State.—The substituent constants in electrophilic

(22) The change of k/k_0 may be interpreted as follows: with p-methyl- and p-methoxy-α-methylstilbenes where the resonance interaction in the transition state seems to be larger than with α-methylstilbene, the effect of p-chloro substituent in PBA seems less important, since the increase of the resonance contribution approaches a limiting value determined by other less variable effects such as the steric effect.

reactions, σ^+, are given by eq. 1. On the other hand, Brown and his co-workers showed the linear correlation 3 between the $para$ partial rate factor and the selectivity factor, S_f, defined by

$$S_f = \log (p_f/m_f); \; \log p_f = \alpha \times S_f \quad (3)$$

Hence, the following equations are derived, where σ_I and σ_R are the inductive and resonance contribution in σ value, respectively.

$$\log p_f = \rho(\sigma_I + \sigma_R + r\Delta_R) \quad (4a)$$

$$\log m_f = \rho\sigma_I \quad (4b)$$

$$S_f = \rho(\sigma_R + r\Delta\sigma_R) \quad (4c)$$

On substitution of 4 into 3, α is given in 5.

$$\alpha = \frac{\sigma_I + \sigma_R + r\Delta\sigma_R}{\sigma_R + r\Delta\sigma_R} \quad (5)$$

The value of α in eq. 5 should vary with r. Hence, with electron-releasing substituents where $r\Delta\sigma_R$ is comparatively important, α decreases with an increase of r, since σ_I, σ_R and $\Delta\sigma_R$ are all negative and r is positive. In other words, in a series of electrophilic reactions, an intermolecular selectivity p_f becomes smaller compared with an intramolecular selectivity S_f with an increase of r, or the resonance contribution in the transition state.

Equation 5 may be transformed into 6. On substituting Brown's value of $\alpha = 1.36$ into eq. 6, the parameter r is calculated to be 0.92 which is

$$r = \frac{\sigma_I + (1 - \alpha)\sigma_R}{\Delta\sigma_R(\alpha - 1)} \quad (6)$$

smaller than r in Deno's[14] σ^+ (evaluated by Yukawa[16] 1.00) and than r in Brown's[15] $\sigma^+ (1.33)$.[16] This change in r agrees with the above discussion.

For the epoxidation of α-methylstilbenes, r was estimated to be $0.5\sim0.6$, and this smaller value may be due to smaller electron demand of the reaction where no carbonium ion is involved.

Kinetics of the Peroxybenzoic Acid Epoxidation of Substituted Propenes and 2-Butenes in Benzene

By Yoshiro Ogata and Iwao Tabushi

The rates of the epoxidation of 3-substituted 1-propenes and 1,4-disubstituted 2-butenes with peroxybenzoic acid in benzene have been measured. In general, electron-releasing groups accelerated the reaction, while no appreciable steric effect was observed with the substituents used. The substituent effect in propenes yields two straight lines in plots of $\log k$ vs. the σ^* of Taft, which is explained by a less efficient transmission of polar effect of electron-releasing groups and by an asymmetric attack of peroxyacid on the double-bonded carbon atoms. The substituent effect in 2-butenes is discussed in terms of additive hyperconjugation of hydrogen atoms at the 1- and 4- positions as well as by an inductive effect. The abnormally high reactivity of allyl alcohol is ascribed to activation by hydrogen bonding.

It is well known that the peroxyacid epoxidation of ethylene derivatives involves an electrophilic attack by the peroxyacid.[1] Our paper on the epoxi-

(1) For examples, see (a) D. Swern, $Chem.\ Revs.$, **45**, 1 (1949); (b) D. Swern. "Organic Reactions," Vol. 7, John Wiley and Sons, Inc.,

dation of α-methylstilbenes[2] reported that the effects of substituents showed deviations from

New York, N. Y., 1953, p. 378; (c) Ya. K. Syrkin and I. I. Moiseef, $Prog.\ Chem.\ USSR$, **29**, 425 (1960).

(2) Y. Ogata and I. Tabushi, $J.\ Am.\ Chem.\ Soc.$, **83**, 3440 (1961).

Hammett's equation and the results were explained by resonance interaction[3] and asymmetric attack. The present paper describes substituent effects in the epoxidations of 3-substituted propenes and 1,4-disubstituted 2-butenes by peroxybenzoic acid (PBA). These compounds have methylene insulation of the resonance effect. The observed effects are discussed on the basis of the substituent constants obtained from aliphatic compounds[4] and hyperconjugation effect.

Experimental

Materials.—Allyl cyanide was prepared from allyl bromide and cuprous cyanide,[5] allyl phenyl ether from allyl bromide and sodium phenoxide,[6] allyl isopropyl ether from allyl bromide and alkaline aqueous isopropyl alcohol,[7] allylbenzene and 1-heptene from allyl bromide and phenylmagnesium bromide[8] and butylmagnesium chloride,[9] respectively. These compounds were purified by fractional distillations; their boiling points agreed with those in the literature. Commercial allyl bromide and chloride were sometimes found to be contaminated with small amounts of an impurity which was easily oxidized and caused slightly increased rate constants[10] at early stages; hence the purification by the preliminary oxidation with 3 mole % of crystalline PBA was necessary between the fractional distillations. trans-1,4-Dibromo-2-butene (I) was prepared by the addition of bromine to butadiene (99.9% purity) in chloroform below −30°; m.p. 52.5°.[11] trans-1,4-Diphenoxy-2-butene, m.p. 84°, was prepared from I on treatment with an excess of phenol and concd. aqueous alkali.[12] trans-1-Phenyl-4-bromo-2-butene, b.p. 113–114°, was prepared from I and phenylmagnesium bromide.[13] trans-1,4-Diphenyl-2-butene, m.p. 45.5°, was prepared by the sodium amalgam reduction of 1,4-diphenylbutadiene[14] obtained by the condensation of phenylacetic acid and cinnamaldehyde.[15]

The purifications of PBA and solvent benzene are described previously.[2]

The Kinetic Study.—The procedure for rate measurements is the same as in our previous report.[2]

Products.—As an example of the isolation of the product, the epoxidation of allyl isopropyl ether is described.

Peroxybenzoic acid (7 g.) was added to allyl isopropyl ether (5 g.). The mixture was allowed to stand at 10–15° for 2 days until the peracid was practically consumed; then the produced benzoic acid was removed by filtration. Distillation of the filtrate, after recovering the unreacted material (ca. 1 g.), gave a liquid boiling at 130–137° (3.1 g.) and a small amount of liquid of higher boiling point. The main fraction was the epoxide (lit.[16] b.p. 131–134°).

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.40. Found: C, 61.67; H, 10.20.

Similar treatment of allyl bromide gave the corresponding epoxide, epibromohydrin, b.p. 135–138° (lit. 138°).

(3) (a) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 965, 971 (1951); see also (b) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957), and (c) R. W. Taft, Jr., *ibid.*, **81**, 5343 (1959).

(4) (a) R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952); (b) **74**, 2729 (1952); (c) **75**, 4231 (1953); (d) **75**, 4534 (1953).

(5) J. V. Supniewski and P. L. Salzberg, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 46.

(6) L. Henry, *Ber.*, **5**, 455 (1872).

(7) R. Skrabal, *Z. physik. Chem.*, **185**, 81 (1939).

(8) M. Tiffeneau, *Compt. rend.*, **139**, 482 (1904).

(9) The preparation is analogous to that from butylmagnesium bromide; see G. B. Kistiakowsky, J. R. Ruhoff, E. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 137 (1936).

(10) Since in most of the kinetic runs a large excess of allyl compound to PBA was used.

(11) E. M. Shantz, *J. Am. Chem. Soc.*, **68**, 2553 (1946).

(12) J. Braun and G. Lemke, *Ber.*, **55**, 3548 (1922).

(13) J. Braun and G. Lemke, *ibid.*, **55**, 3536 (1922).

(14) F. Strus, *Ann.*, **342**, 255 (1905).

(15) B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 229.

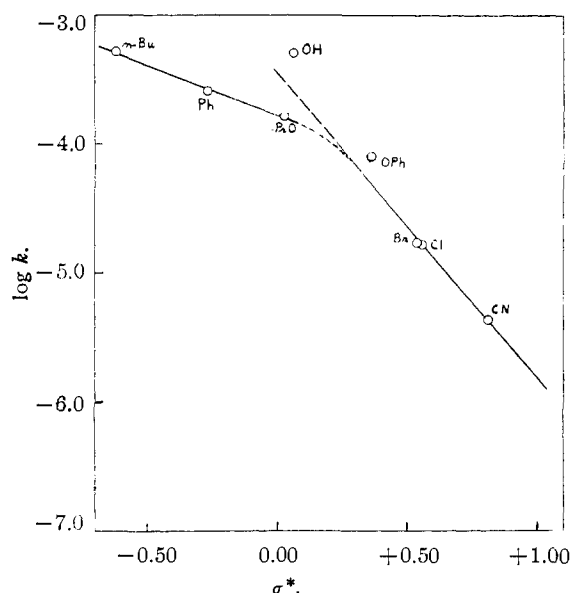(16) F. G. Ponomarev, *Zhur. Obshchĕi Khim.*, **22**, 929 (1952), *C.A.*, **47**, 3794 (1953).

Anal. Calcd. for C_3H_5OBr: C, 26.33; H, 3.68; Br, 58.34. Found: C, 26.75; H, 3.81; Br, 58.32.

Allylbenzene,[17] 1-heptene[18] and allyl alcohol[19] have been reported to give the corresponding epoxides on peroxyacid oxidation.

Results and Discussions

The rate data satisfy the second-order equation, $v = k$[ethylenic compound][PBA], and no appreciable effect of added benzoic acid on the rate was observed. The k-values for ethylenic compounds are listed in Table I.

TABLE I

SECOND-ORDER RATE CONSTANTS OF PBA EPOXIDATIONS OF SUBSTITUTED ETHYLENES IN BENZENE AT 25°

Ethylenic compound	(M)	PBA, M	$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$
Allyl bromide	1.38	0.0375	1.73
	0.468	.0200	5.77[a]
	.935	.0198	5.79[a]
	.932	.0390	5.77[a]
Allyl chloride	1.96	.0371	1.71
Allyl alcohol	0.177	.0358	50.8
	.171	.0353	50.5
	.344	.0353	51.2
	.0895	.0367	48.4
Allyl cyanide	1.65	.0358	0.442
	3.22	.0353	0.433
Allyl phenyl ether	0.367	.0362	7.94
Allyl isopropyl ether	.0505	.0361	16.9
	.104	.0363	16.5
	.202	.0363	15.9
	.202	.0346	16.1[b]
Allylbenzene	.0888	.0358	26.6
	.167	.0352	26.4
1-Heptene	.0520	.0344	49.9
	.103	.0345	51.9
1,2-Dibenzylethylene	.0721	.0183	186
	.0479	.0182	191
	.0483	.0184	189
1,4-Diphenoxy-2-butene	.2080	.0348	12.4
	.3336	.0220	13.0
1-Bromo-4-phenoxy-2-butene	.2378	.0358	7.52
	.4740	.0365	7.46
1,4-Dibromo-2-butene	1.218	.0315	0.701
	0.657	.0357	0.693

[a] At 40.0°.   [b] Benzoic acid (0.082M) was added.

In contrast to stilbenes and/or α-methylstilbenes having conjugation between ethylenic bond and benzene ring, these propenes and butenes have no such resonance because of the separation of the ethylene bond from the functional group by a methylene group. The difference in steric effect among 3-substituted propenes may be negligibly small, since they have a common methylene group. The constancy of steric effect is seen in the approximate constancy of steric substituent constants, E_s, by Taft[4]: n-BuCH$_2$, −0.40; PhCH$_2$, −0.38; Ph(CH$_2$)$_2$ (and probably i-PrOCH$_2$ and PhOCH$_2$), −0.43; n-Pr (and probably CH$_2$CN), −0.36; CH$_2$Cl (and probably CH$_2$Br), −0.19.

(17) J. Böeseken and J. S. P. Blumberger, *Rec. trav. chim.*, **47**, 839 (1928).

(18) J. Levy and R. Pernot, *Bull. soc. chim. France*, [4] **49**, 1838 (1931).

(19) N. Prileschajew, *Ber.*, **42**, 4811 (1909); *J. Russ. Phys. Chem. Soc.*, **43**, 609 (1911).

Fig. 1.—Plots of σ^* vs. log k for the PBA epoxidation of $CH_2{=}CHCH_2X$ by PBA.

Furthermore, rates of peroxyacetic acid epoxidation of ethylenes show a regular increase on the introduction of one or two methyl groups as is obvious from a comparison of ethylene, propylene and isobutene or 2-butene.[20] This means that the steric reaction constant δ is small in Taft's equation[4]

$$\log (k/k_0) = \rho^*\sigma^* + \delta E_s \qquad (1)$$

Therefore, the variation of δE_s is negligible in 3-substituted 1-propenes and, inasmuch as the inductive effect only is operating, the equation should be simplified to

$$\log (k/k_0) = \rho^*\sigma^* \qquad (2)$$

Just as the σ-values in aromatic electrophilic substitution vary according to the supplementary resonance contribution, the σ^*-values in aliphatic electrophilic reactions such as this epoxidation may vary with supplementary hyperconjugation, although Taft paid little attention to this because most of the reactions selected by him were nucleophilic. Hence it is not surprising that the σ^*-values vary in this reaction.

Plots of log k at 25° vs. Taft's σ^{*21} gave two different straight lines with slopes of -0.76 and -2.44 and with a bend in the neighborhood of unsubstituted ethylene ($\sigma^*=0$), as shown in Fig. 1. A similar abnormal substituent effect was observed in the relative rates of halogen addition to double bond.[22] For example, the rate increase with the introduction of a methyl group ($\sigma^* = -0.490$) is comparatively small (Δ log k = $+0.302$), whereas the rate decreases with that of CH_2Cl ($\sigma^* = 0.560$, Δ log k = -1.721), CH_2Br (0.540, -1.886), CH_2CN (0.810, -2.568) or $(CH_2Cl)_2$ ($\Sigma\sigma^* = 1.120$, -3.620) are much larger.

(20) See Swern's list of k-values for the epoxidation; D. Swern, Chem. Revs., 45, 49 (1949).
(21) The Taft's value of σ^* estimated on the basis of methyl substituent was corrected to use the value for hydrogen as the standard.
(22) J. R. Shelton and L. Lee, J. Org. Chem., 25, 428 (1960). See also, S. V. Anantakrishnan and C. K. Ingold, J. Chem. Soc., 1396 (1935); P. W. Robertson, J. K. Heyes and B. E. Swedlund, ibid., 1014 (1952).

A considerable upward deviation from the line was observed with allyl alcohol and also a slight deviation with allyl phenyl ether.

The Difference of ρ-Values between Electron-withdrawing and Electron-releasing Groups in Propenes.—The observed difference between values of electron-releasing and electron-withdrawing groups seems to be ascribable partly to the low transmission coefficient of polar effect of electron-releasing groups through the methylene group. Examples of this low transmission are shown in the comparison of Taft's polar substituent constants σ^* for a substituent X itself and that for CH_2X. The ratios $\sigma_X^*/\sigma_{CH_2X}^*$ are with X: methyl, 4.90; ethyl, 5.13; n-propyl, 4.66; acetyl, 1.93; chloromethyl, 1.46. It is apparent that the transmission ratio of the polar effect of electron-releasing groups is ca. $^1/_5$ on the average, while that of electron-withdrawing groups is $^2/_3$–$^1/_2$.[23]

In the transition state of epoxidation, the double bond may have partial single bond character; hence a substituent RCH_2 on C_1 may influence C_2 as a substituent RCH_2CH in part with the above-decreased efficiency. Thus with electron-releasing groups, the effects are smaller because of lower transmission efficiency.

A further probable explanation for the difference in the ρ-values is asymmetric attack. The possibility of an asymmetric transition state (IIb) instead of symmetric state IIa previously has been discussed in terms of the resonance effect.[2] The

$$R{-}\overset{1}{CH_2}{-}\overset{2}{CH}{=\!=\!=}CH_2 \qquad R{-}CH_2{-}CH{=\!=\!=}CH_2$$

IIa   IIb
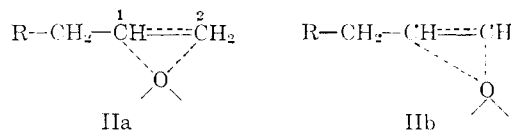
transition states for allylic compounds with electron-releasing groups seem to be more asymmetric than those of electron-withdrawing groups because of the easier stabilization of the partial positive charge in the central carbon atom in propene. Hence, in the transition state II, the inductive effect of CH_2R is less effectively transmitted when R is an electron-releasing group, thus lowering the ρ-value. This assumption of an asymmetric transition state is also supported by the orientations in electrophilic additions of ethylenic compounds. The distribution of charges in the transition state may vary with the change in polar effect of substituent and the activity of reactants. According to Shelton and Lee,[24–26] hyperconjugation is important when the reactants have low activity; e.g., the addition of hydrogen bromide to allyl chloride which obeys the Markownikoff rule,[24] but the inductive effect becomes important when one of the reactants has high activity (e.g., the addition of hypochlorous acid (HO^-Cl^+) to allyl chloride.[25]
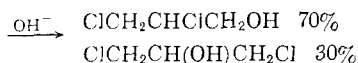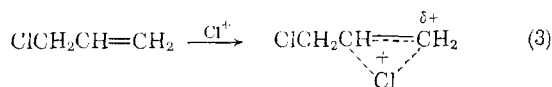
In general, peroxyacids have lower activity; hence the transition state for epoxidation may resemble that of normal (Markownikoff) addition.

(23) On the other hand, phenyl and ω-phenylalkyl groups show abnormal transmission ratios; i.e., $\sigma_{CH_2X}^*$ is larger than σ_X^* in phenyl and $\sigma_{CH_2X}^*$ is positive and σ_X^* is negative in ω-phenylalkyls.
(24) J. R. Shelton and L. Lee, J. Org. Chem., 23, 1876 (1958).
(25) J. R. Shelton and L. Lee, ibid., 24, 1271 (1959).
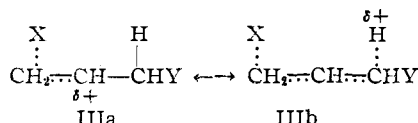(26) J. R. Shelton and L. Lee, ibid., 25, 907 (1960).

$$ClCH_2CH{=}CH_2 \xrightarrow{\;Cl^+\;} ClCH_2CH\overset{\delta+}{=\!=\!=}CH_2 \qquad (3)$$

$$\xrightarrow{\;OH^-\;} \begin{array}{l} ClCH_2CHClCH_2OH \quad 70\% \\ ClCH_2CH(OH)CH_2Cl \quad 30\% \end{array}$$

Furthermore, 1-propenes having electron-withdrawing groups in the 3-position, e.g., allyl chloride, may have rather symmetric transition states in comparison with propene and 1-propenes having electron-releasing groups in the 3-position, since the direction of the inductive and hyperconjugative effects of CH_2X is reversed in the former.

The Application of Aromatic Substituent Constants to Aliphatic Reactions.—The applications of Hammett's equation for aromatics to the addition of olefins has been attempted by assuming 1- and 2-carbon atoms as m- and p-carbon atoms in the benzene ring, respectively,[27a] using σ or σ^+.[27b]

However, this treatment is valid only in reactions with the most asymmetric transition state and is unsatisfactory for the relatively symmetric epoxidation which should have $\sigma = (\lambda)(\sigma_m^+) + (\mu)\cdot(\sigma_p^+)$, where λ and μ are unknown parameters. We use here Taft's polar substituent constants for the aliphatic series, σ^*,[4,21] the value having the same significance as the inductive substituent constant for aromatics, σ_I,[28] so that it includes no supplementary hyperconjugation effect of III.

$$\underset{\underset{\delta+}{\text{IIIa}}}{\overset{X \qquad H \qquad}{CH_2{\cdots}CH{-}\overset{|}{C}HY}} \longleftrightarrow \underset{\text{IIIb}}{\overset{X \qquad \overset{\delta+}{H}}{CH_2{\cdots}CH{\cdots}\dot{C}HY}}$$

The hyperconjugative effect on orientation, as described in the previous paragraph, suggests that this effect also contributes to the rate. Hence, the relative rate may be developed as

$$\log (k/k_0) = \rho\sigma^* + \rho n\sigma_H + \delta E_s \qquad (4)$$

Here, ρ, σ^*, δ and E_s have the same meanings as those of Taft, σ_H is the hyperconjugation constant and n is the number of α-hydrogen atoms. In a series of 1-propenes, the hyperconjugation term, $\rho n\sigma_H$, and the steric term, δE_s, are both constant, and the equation $\log (k/k_0) = \rho\sigma^*$ is applied.

The Estimation of the Extent of Hyperconjugation.—In 3-substituted 1-propenes, $CH_2{=}CHCH_2{-}X$, the hyperconjugative effect is essentially constant as shown previously. But in 1,4-disubstituted 2-butenes, $XCH_2CH{=}CHCH_2Y$ (IV), the values of k_2 observed in benzene at 25° were considerably larger than those expected from k_2 for the propenes (Tables I, II and Fig. 2). Table II shows the deviations of $\log k_{obs}$ from $\log k_{calc}$ calculated from the data of 3-substituted propenes, assuming additivity of σ'.[29]

(27) (a) For example, see P. B. D. de la Mare, J. Chem. Soc., 3823 (1960); (b) H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958); J. Org. Chem., 22, 485 (1957).

(28) R. W. Taft, Jr., and I. C. Lewis, ibid., 81, 5343 (1959).

(29) σ' was obtained by extrapolation of a log k–σ^* plot of allylic compounds having the electron-withdrawing group X. These values seem to correspond to the total polar substituent effect except for the hyperconjunction. The values of σ' are: n-Bu, −0.055; Ph, 0.065; i-PrO, 0.150; PhO, 0.290.
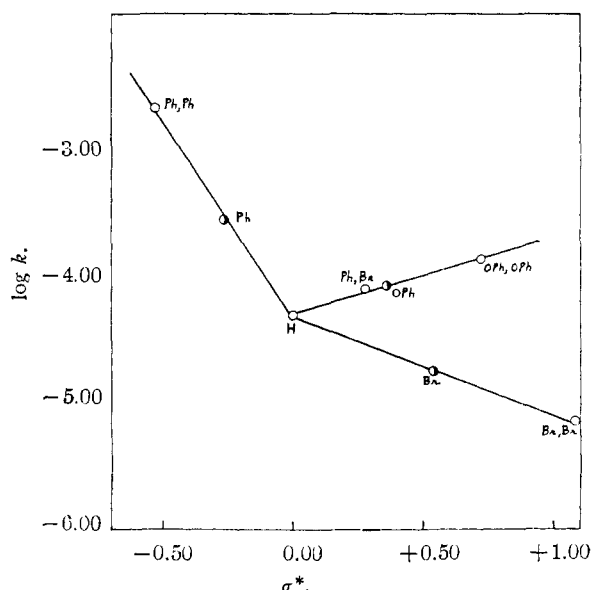

Fig. 2.—Plots of σ^* vs. log k for the PBA epoxidation of $XCH_2CH{=}CH_2$ (●) and $XCH_2CH{=}CHCH_2Y$ (○).

The deviation, $\Delta \log k$, is nearly constant and corresponds to an increase of hyperconjugation by the introduction of two α-hydrogen atoms. Hence $\log k$ for ethylene ($XCH_2{=}YCH_2{=}H$) should deviate downward by 0.87 because of the lack of α-hydrogen atom, and it is shown in Fig. 2 as H. Figure 2 shows that linear relations exist between $\log k$ and σ^* for a set of H, Ph and Ph_2,

TABLE II

THE CALCULATED AND OBSERVED RATE CONSTANTS FOR 1,4-DISUBSTITUTED 2-BUTENES, $XCH_2CH{=}CHCH_2Y$

Substituent					$\Delta \log$ $k = \log$ $\frac{k_{obs}}{k_{calc}}$
X	Y	$\Sigma\sigma'$	$\log k_{calc}$	$\log k_{obs}$	
Ph	Ph	0.130	−3.73	−2.72	1.01
PhO	PhO	.580	−4.80	−3.91	0.89
Ph	Br	.605	−4.86	−4.12	.74
Br	Br	1.080	−5.99	−5.16	.83
				Av.	0.87

a set of H, Br and Br_2, and a set of H, OPh and $(OPh)_2$, which indicate that the contribution due to steric effect is still negligible in these disubstituted ethylenes and that the hyperconjugative effect is additive.[30] Hence eq. 4 is simplified to

$$\log (k/k_0) = \rho(\sigma^* + n\sigma_H) \qquad (5)$$

Therefore, the hyperconjugative deviation of log k is given by

$$\Delta \log k = \rho\Delta n\sigma_H \qquad (6)$$

where Δ indicates the difference of two values with different numbers of hydrogen atoms. The value of ρ was estimated to be -2.38 from the plots of σ^* vs. log k with propenes and the average value of $\Delta \log k$ in Table II was 0.87 and n was 2; hence the value of σ_H was calculated to be -0.183.

(30) The effect of an asymmetric transition state on $\Delta \log k$ is apparent in Table II. Asymmetric phenylpropene with decreased inductive shift and symmetric diphenylbutene give a larger $\Delta \log k$, while asymmetric phenylpropene and more asymmetric phenylbromobutene with increased inductive shift of bromomethyl give a smaller $\Delta \log k$.
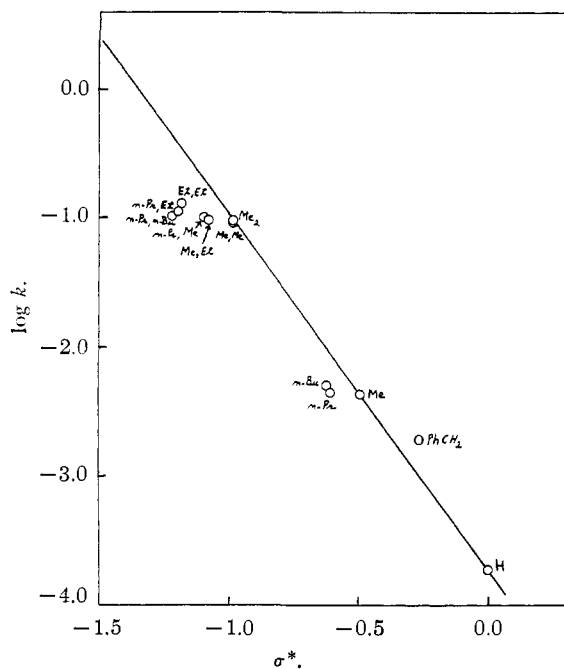
Fig. 3.—Plots of σ^* vs. log k for the peroxyacetic acid epoxidations of ethylene derivatives, XCH=CH$_2$ and XCH=CHY in acetic acid; k in l. mole^{-1} min.$^{-1}$.

The Application of the Hyperconjugative Constant for Ethylene Derivatives in the Peroxyacetic Acid Epoxidations.—As shown in Fig. 3, a straight line was obtained from plots of Taft's σ^{*21} vs. log k_2 for the peroxyacetic acid epoxidation of ethylene derivatives, ethylene, propylene, isobutene and 2-butene. Most of the other 3-substituted 1-propenes except allylbenzene show downward deviations from the line. Since the line involves both inductive and hyperconjugative effects,[31] the slope of the line, ρ_{app}, is given by

$$\rho_{app} = \frac{\log (k/k_0)}{\sigma^*} = \frac{\rho(\sigma^* + n\sigma_H)}{\sigma^*} \qquad (7)$$

Hence

$$\rho = \rho_{app} \Big/ \left(1 + \frac{n\sigma_H}{\sigma^*} \right) \qquad (8)$$

The extent of the deviation of log k from the line depends mainly on the number of α-hydrogen atoms (Table III and Fig. 3). From this deviation, the hyperconjugative constant σ_H is calculated as follows:

The deviation, Δ log k, is given by eq. 6 with given σ^*, ρ being estimated from ρ_{app} by means of eq. 8. Here, Δn is the difference between the number of α-hydrogen atoms corresponding to the line and the number of actual α-hydrogen atoms. For example, the points on the line are H $(\sigma^* = 0, n = 0)$, Me $(\sigma^* = -0.490, n = 3)$

(31) A slight deviation of log k for trimethylethylene may be due to steric effect, since the rate increase by the introduction of methyl group to cyclopentene (Δ log k = 1.068) is smaller than that to ethylene and propylene (Δ log k = 1.345).

and Me$_2$ ($\Sigma\sigma^* = 2 \times (-0.490)$, $n = 2 \times 3$); more negative σ^* will correspond to larger n. The values of Δ log k for monoalkylethylenes, 0.28 (n-Pr, $\sigma^* = -0.605$) and 0.26 (n-Bu, $\sigma^* = -0.620$), give an average value of 0.27 ($\sigma^* = -0.61$). The n-value corresponding to $\sigma^* = -0.61$ is $3 \times (0.61/0.49)$ and the actual n is 2, giving $\Delta n = 1.74$. Substituting these values of Δ log k, Δn and $n/\sigma^* = 3/(-0.490)$ into eq. 6 and 8 give a σ_H of -0.086 by means of eq. 9

$$\sigma_H = \Delta \log k \Big/ \left[\rho_{app} \, \Delta n \left(1 - \frac{n\Delta \log k}{\sigma^* \rho_{app} \, \Delta n} \right) \right] \qquad 9)$$

The values of σ_H calculated similarly for other ethylenes are listed in Table III. These σ_H values

TABLE III

THE VALUES OF σ_H CALCULATED FROM THE EPOXIDATION OF ETHYLENIC COMPOUNDS BY PEROXYACETIC ACID

| Substituent on C$_1$	C$_2$	n	Δ log k	σ_H
n-Pr	H	2		
n-Bu	H	2	-0.27	-0.086
Me	Et	5	$- .265$	$- .090$
Me	n-Pr	5	$- .28$	$- .092$
Et	n-Pr	4	$- .47$	$- .082$
n-Pr	n-Bu	4	$- .60$	$- .097$
			Av.	$\overline{-0.089}$

are nearly constant, but smaller than σ_H obtained from PBA epoxidation of 1-propenes and 2-butenes, suggesting σ_H may depend on the solvent and/or the attacking agent. Hence eq. 4 is extended as

$$\log (k/k_0) = \rho\sigma^* + r\rho n\sigma_H + \delta E_s \qquad (10)$$

where r is a parameter corresponding to the contribution of hyperconjugation.

The Deviation Observed in Allyl Alcohol and Ethers.—Allyl alcohol shows a large deviation upward as shown in Fig. 1. It is probable that this deviation is the activation of PBA due to hydrogen bonding as in IV, as suggested by the activation of PBA itself by the intramolecular hydrogen bonding.[32]

The possibility of a change in reactivities of allyl ethers by the formation of complexes with benzoic acid was eliminated by the observation that the rate showed no appreciable change on the preliminary addition of benzoic acid to the reaction mixture.

IV
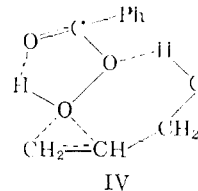
(32) (a) A. Robertson and W. A. Waters, J. Chem. Soc., 1574 (1948); (b) B. M. Lynch and K. H. Pausacker, ibid., 1525 (1955), (c) for the evidences from infrared studies, see H. T. Davison, ibid., 2456 (1951) and G. J. Minkoff, Proc. Roy. Soc. (London), A224, 176 (1954).