Kinetics of the Baeyer–Villiger Reaction of Aromatic Ketones with Perbenzoic Acid[1]

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The Baeyer–Villiger reaction of acetophenones with perbenzoic acid has been studied kinetically in 40% aqueous ethanol and in organic solvents at 25.0°. The rate–pH profiles are similar to those for the reaction of benzaldehydes with aryl migration.[2] Acid catalysis by perchloric acid in 40% ethanol is not correlated with acidity function but is proportional to $[HClO_4]$ at its higher concentration. The Baeyer–Villiger reaction with pure perbenzoic acid is very slow in organic solvents and acetic acid catalyzes only the carbonyl addition, while trifluoroacetic acid effectively establishes the addition equilibrium and catalyzes also the migration. Carbonyl addition is rate-determining under some conditions for the Baeyer–Villiger reaction of the ketones especially with strongly electron-releasing groups, and the addition rate of perbenzoate ion to *o*- and *p*-HOC_6H_4COR satisfies the Taft equation to give $\rho^* = 1.3–1.6$ (σ^*) and $\delta = 0.6–0.8$. The rate of the Baeyer–Villiger reaction in the presence of a suitable catalyst is governed by that of migration step, and the apparent rate for ring-substituted acetophenones affords ρ values of 1.5–2.4 (σ^+). The kinetic suggests that the acid catalyst is not proton but general acid.

Most features of the Baeyer–Villiger (B–V) reaction are well understood.[3–6] The rate for peracid oxidation of ketones is, for most cases, first order both in peracid and ketone and is acid catalyzed by strong acid.[5,7] A rate-determining, concerted migration in the peracid–carbonyl adduct (I) was demonstrated[7] and recently confirmed by ^{14}C-isotope effect,[8] where no observation of the isotope effect for the exceptional case of *p*-methoxyacetophenone was explained on the basis of strong electron-releasing power of *p*-methoxy group,[8] but an alternative explanation seems also to be possible, of a rate-controlling carbonyl addition of peracid, as demonstrated in our hands for the B–V reaction of benzaldehydes having a strong electron-releasing group.[2a]

Another obscure point in the B–V reaction is about the nature of acid catalysis, *i.e.*, general or specific, and which step is subject to the catalysis, carbonyl addition, and/or migration step. The present report summarizes our kinetic results for the B–V reaction of aromatic ketones with perbenzoic acid (PBA), and states that carbonyl addition is rate determining in some cases and that general acid catalysis is operative both for carbonyl addition and migration.

Results

The reaction of acetophenones in 40 vol. % ethanol was undertaken in the presence of 10^{-4} *M* ethylenediaminetetraacetate (EDTA) to minimize the catalytic decomposition of PBA, although the effect of EDTA is usually very small. The B–V reaction satisfied the second-order kinetics shown in eq 1. The rate was

$$v = k_{obsd}[ArCOR][PBA] \qquad (1)$$

mostly followed by iodometry of PBA with reproducibility of ±5%, the rates of which were identical with these obtained from the decrease of carbonyl absorbance of the ketone. The migrating group in the present reaction is practically the aryl alone as reported with trifluoroperacetic acid.[7,9]

Effect of Acids and Bases in 40% Aqueous Ethanol.— The rates varies with the substituent and pH (Figure 1). For example, *o*-hydroxyacetophenone is highly reactive at pH >2, but almost inactive at pH <2. Also, the relative reactivity of *p*-hydroxy- *vs.* *p*-methoxyacetophenone is reversed at pH range of 1–5.

The observed rate in 40% ethanol is expressed as

$$k_{obsd} = k_{HA}[HA] + k_0 + k_{PBA^-}[PBA^-] \qquad (2)$$

Here, PBA^- is perbenzoate ion and HA is general acid (perchloric acid in this case). The lines for *o*- and *p*-hydroxyacetophenones in Figure 1 are those calculated from the values of k_{HA}, k_0, and k_{PBA^-} in Table I.

TABLE I

SUMMARY OF RATE DATA FOR PBA OXIDATION OF ACETOPHENONES, XC_6H_4COMe, IN 40% ETHANOL AT 25.0°

X	k_{HA},[a] M^{-2} sec^{-1}	k_0, M^{-1} sec^{-1}	k_{PBA^-}, M^{-1} sec^{-1}
p-HO	1.33×10^{-3}	$<0.05 \times 10^{-3}$	1.10
o-HO	Very small	$\sim 0.13 \times 10^{-3}$	27.0
p-MeO	0.54×10^{-3}	(0.50×10^{-3})[b]	
p-Me	Very small	$\sim 0.15 \times 10^{-3}$	

[a] Here HA = $HClO_4$. [b] Value at pH 6.

As shown in the discussion section, a rate-determining step for *o*- and *p*-hydroxyacetophenones is a carbonyl addition of PBA^-. Hence, the apparent rate at pH 4–11 gives the rate for the carbonyl addition of PBA^- (Table II), which fits the Taft equation[10]

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

giving ρ^* and δ values listed at the bottom of Table II.

As apparent in Figure 1, the acid catalysis is rather small and cannot be correlated by acidity function, H_0, which demonstrates no intervention of any conjugate acid of reactants. The plot of k_{obsd} *vs.* $[HClO_4]$ is a curve up to ~0.5 *M* acid and then a straight line at its higher concentration above 0.5 *M* (Figure 2). The slope of this plot gives a catalytic constant, k_{HA}, of 1.33×10^{-3} and 0.54×10^{-3} M^{-2} sec^{-1}, and the intercept of this line is 0.26×10^{-3} and 0.49×10^{-3} M^{-1}

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[1] Contribution No. 181.

[2] (a) Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, **94**, 4189 (1972); (b) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **34**, 3985 (1969).

[3] C. H. Hassall, *Org. React.*, **9**, 73 (1957).

[4] A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, p 144.

[5] P. A. S. Smith, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 579.

[6] S. B. Lee and B. C. Uff, *Quart. Rev.*, **21**, 429 (1967).

[7] M. F. Hawthorne and W. D. Emmons, *J. Amer. Chem. Soc.*, **80**, 6393, 6398 (1958).

[8] B. W. Palmer and A. Fry, *ibid.*, **92**, 2580 (1970).

[9] E. E. Smissman, J. P. Li, and Z. H. Israili, *J. Org. Chem.*, **33**, 4231 (1968).

[10] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 648.

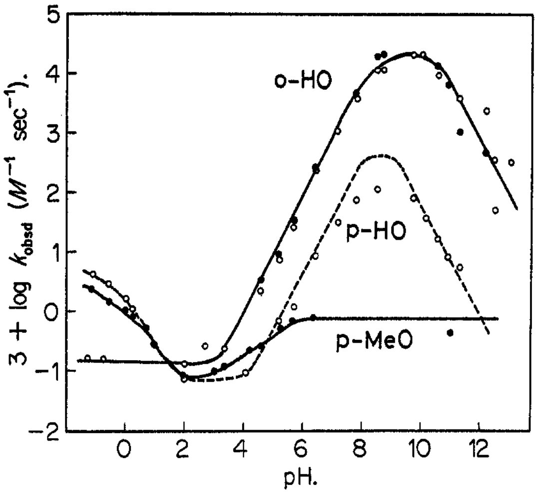


Figure 1.—Rate-pH profiles for the PBA oxidation of substituted acetophenones in 40% ethanol at 25.0°. The lines for *o*-HO and *p*-HOC_6H_4COMe are calculated from the data in Table I.

TABLE II

SUBSTITUENT EFFECT ON THE RATE OF ADDITION OF PERBENZOATE ION TO *o*- AND *p*-HOC_6H_4COR IN 40% ETHANOL AT 25.0°

	pK_a[a]		$k_1^{PBA^-}$, M^{-1} sec^{-1}	
R	*p*-HOC_6H_4-COR[b]	*o*-HOC_6H_4-COR[c]	*p*-HOC_6H_4-COR	*o*-HOC_6H_4-COR
H	8.21	8.45	112[d]	1050[d]
Me	8.72	10.50	1.12	27
Et	8.90	10.73	0.82	22
n-Pr	8.86	10.88	0.56	16
i-Pr	8.92	10.75	0.33	~3
CH_2Cl	8.40		35.4	
Ph	8.63		0.25	
ρ^*[e]			1.63[f]	1.31
δ[e]			0.63[f]	0.81
r[g]			0.991[f]	0.991

[a] Titrated in 40% ethanol at 25 ± 1°. [b] Registry numbers are, respectively, 123-08-0, 99-93-4, 70-70-2, 1009-11-6, 34917-91-4, 6305-04-0, and 1137-42-4. [c] Registry numbers are, respectively, 90-02-8, 118-93-4, 610-99-1, 2887-61-8, and 6640-69-3. [d] Data from ref 2a. [e] Correlated by the Taft equation, $\log (k/k_0) = \rho^*\sigma^* + \delta E_s$, where σ^* was taken from ref 10. [f] These were calculated from the substituents except R = H and Ph. If H's are incorporated in the correlation, the values of $\rho = 1.05$, $\delta = 0.99$, and $r = 0.977$ are obtained. [g] Correlation coefficient.

sec^{-1} for acetophenones with *p*-HO and *p*-MeO groups, respectively. Other interesting points are as follows. First, the intercept of 0.49×10^{-3} M^{-1} sec^{-1} for *p*-MeO is very close to the rate constant of 0.50×10^{-3} M^{-1} sec^{-1} at pH ~6. Second, the rate of *p*-HO at $[HClO_4] < 0.5$ *M* is identical or slightly less than that of *p*-MeO, a more electron-attracting group.

Effect of Acid and Base in Organic Solvents.—Acid catalysis in organic solvents revealed the similar features of the B–V reaction. The reaction with pure PBA was very slow. Although catalysis by acetic or *m*-chlorobenzoic acid is not appreciable up to 3 *M* concentration in 40% aqueous ethanol, the reaction in benzene is sensitive to these weak acids. The catalysis by acetic acid shows no linear relation between the rate and the acid concentration (see Figure 3A), but at higher concentration the observed rate in benzene gradually approaches to limiting k_{obsd} values of

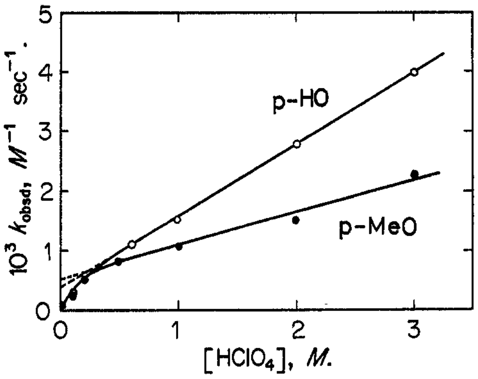


Figure 2.—Dependence of k_{obsd} on perchloric acid concentration for PBA oxidation of substituted acetophenones in 40% ethanol at 25.0°.

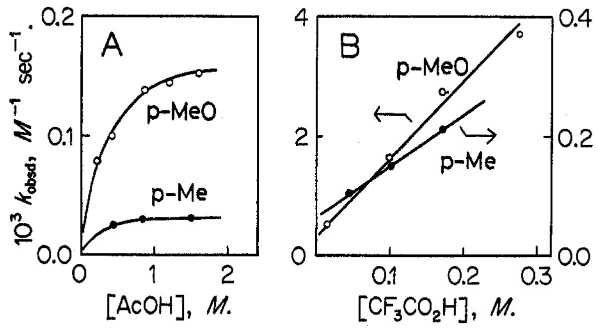


Figure 3.—Dependence of the apparent rate on acid concentration for PBA oxidation of *p*-methoxy- and *p*-methylacetophenones in benzene at 25.0°.

0.18×10^{-3} and 0.04×10^{-3} M^{-1} sec^{-1} for *p*-methoxy- and *p*-methylacetophenones, respectively.

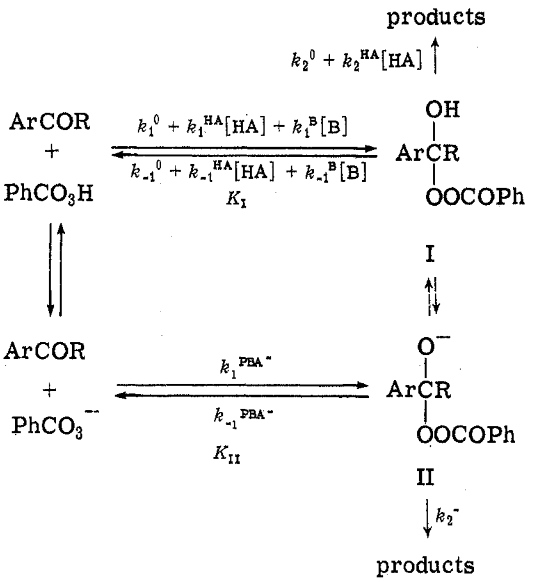
On the other hand, the catalysis by trifluoroacetic acid affords a linear relationship between the rate and the acid concentration. The plot in Figure 3B gives k_{HA} of 2.7×10^{-3} and 0.17×10^{-3} M^{-2} sec^{-1} for *p*-methoxy- and *p*-methylacetophenones, respectively. The intercept gives k_0 of $\sim 0.3 \times 10^{-3}$ for *p*-MeO and 0.07×10^{-3} M^{-1} sec^{-1} for *p*-Me, which agree in order with the above limiting values at higher concentration of acetic acid.

For comparison, the B–V reaction of benzaldehydes has been examined, where the acid catalysis similar to the case of acetophenone is observed as shown in Figure 4A. The reaction of anisaldehyde in ethanol is much slower than that in benzene, a more efficient solvent for acid catalysis. The base catalysis by sodium acetate for the establishment of carbonyl addition equilibrium is remarkable; the PBA oxidation of anisaldehyde reaches a constant rate constant of 1.5×10^{-3} M^{-1} sec^{-1} only with 0.002 *M* acetate (Figure 4B). As for the base catalysis of B–V reaction of acetophenones, no reliable data could be obtained because of simultaneous decomposition of PBA.

Discussion

The B–V reaction of acetophenones showed features similar to the case of benzaldehydes.[2a] The reaction is heterolytic, since the oxidation gave high yields of phenols (>90%) and was not affected by addition of oxygen or other radical scavengers, *e.g.*, phenols or EDTA. Probable steps in the present B–V oxidation are shown in Scheme I.

SCHEME I



Rate-Determining Step in 40% Aqueous Ethanol.—Rate-determining, concerted migration was proved by ^{14}C-isotope effect on the *m*-ClPBA oxidation of acetophenones.[8] The absence of isotope effect for the case of *p*-methoxyacetophenone was explained by a strong electron-releasing power of p-methoxy group,[8] but an alternative explanation seems to be more probable as discussed below that carbonyl addition is rate determining.

Evidences for the rate-determining addition to *o*- and *p*-hydroxyacetophenones are as follows. (i) The rate–pH profile at pH >2 is explicable by assuming the rate-controlling carbonyl attack of perbenzoate ion, PBA$^-$ (see Figure 1). That is, the observed rate–pH profiles can be reproduced assuming that the data (k's) for *o*- and *p*-HO in Table I are those of first step (k_1's) in Scheme I (*i.e.*, $k_{obsd} = k_1^0 + k_1^{HA}[HA] + k_1^{PBA^-}\cdot[PBA^-]$). (ii) If the unit slope at pH 4–7 for *o*- and *p*-HO were OH$^-$-catalyzed migration in the carbonyl adduct I, *i.e.*, $k_2 = k_2^{OH}[OH^-]$, catalytic constant k_2^{OH} for the migration step should be $\geq 80 \times 10^{10}$ and $>0.5 \times 10^{10}$ M^{-1} sec^{-1} for *o*- and *p*-HO in 40% ethanol. The rate constants extrapolated to pure water are *ca.* sixfold greater than those in 40% ethanol, *i.e.*, $\sim 500 \times 10^{10}$ and 3×10^{10} M^{-1} sec^{-1}, respectively, which are too fast to be actual.[11] This assumes that a relative ratio of equilibrium constant (K_I) of carbonyl addition of PBA[12] to ArCHO *vs.* that to ArCOMe is ≥ 100, which is not unreasonable in view of other carbonyl addition,[13] and, even if ArCHO/ArCOMe is ~ 1, the assumed constant of 500×10^{10} for *o*-HOC$_6$H$_4$COMe is decreased to 5×10^{10} M^{-1} sec^{-1} which is still too large to be actual.[11] (iii) Relative rates $k_{m\text{-ClPBA}}/k_{PBA}$ ($\Delta pK_a = 0.35$)[14a] are 2.0 ± 0.1 at pH <8 and 1.05 ± 0.20 at pH >10, which may also be explained by a rate-determining carbonyl addition of PBA$^-$. That is, ΔpK_a of 0.35 corresponds to *ca.* twofold concentration of *m*-ClPBA anion compared to PBA anion and then to the observed twofold increase of rate constant in going from PBA to *m*-ClPBA at pH <8, while little increase in the rate observed at pH >10 is explicable in view of no change in the concentration of peracid ion because of 100% dissociation of PBA's at this pH region. (iv) Relative rate of *p*-hydroxy- and *p*-methoxyacetophenones is reversed at pH 2–5 (Figure 1). The reversion suggests a change of rate-controlling steps from C=O addition to migration. Expected order is *p*-HO > *p*-MeO in view of σ value if the overall rate (k_{obsd}) contained the rate of migration step (k_2). These reversion of relative rates are generally understood as a change of rate-determining steps.[14b] (v) The change of dependence of k_{obsd} on [HClO$_4$] at ~0.5 M acid (Figure 2) suggests a change of rate-determining step. These lead to the conclusion of rate-determining carbonyl addition of PBA at least at pH >1. The insensitivity of *o*-hydroxyacetophenone to acid catalysis for the carbonyl addition may be understood by the decrease of basicity of carbonyl oxygen owing to the intramolecular hydrogen bonding. Similar results have also been obtained for the B–V reaction of salicylaldehyde.[2a]

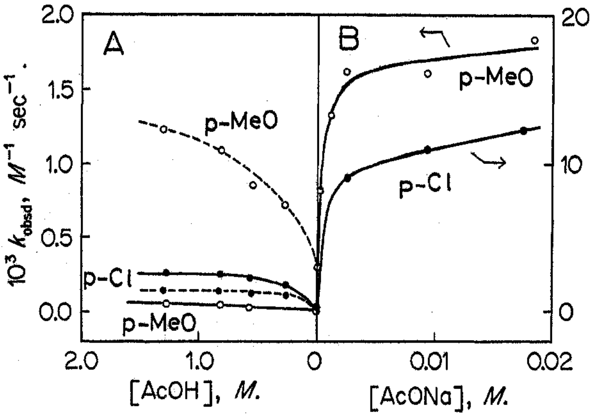


Figure 4.—Acid and base catalyses for the PBA oxidation of substituted benzaldehydes in ethanol (solid line) and in benzene (dotted line) at 25.0°.

PBA oxidation of *p*-methoxyacetophenone showed a rate–pH profile similar to that of anisaldehyde[2a] and seems likewise to be of an intermediary case. At pH >5.5 the rate constant holds a constancy, suggesting a rate-determining migration.[15] The reaction at pH 0.7–5.5 is probably controlled both by addition (k_1) and migration (k_2), but the data were not so reliable as to deduce k_1 value because of the spontaneous decomposition of PBA. The acid-catalyzed migration becomes rate determining at higher acidity, since the intercept at zero acid concentration (Figure 2) is close to the rate at pH ~6.

Rate-Determining Step in Organic Solvents.—The PBA oxidation of acetophenones in benzene and in pure ethanol was very slow without added acid and two types of acid catalyses are shown in Figure 3. The limiting rate constant at very high concentration of acetic acid is of the same magnitude as that at very low

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[11] M. Eigen, *Angew. Chem.*, **75**, 489 (1963).

[12] The equilibrium constants for carbonyl addition of PBA to *o*- and *p*-hydroxybenzaldehydes were assumed to be $\sim 10^{-2}$ M^{-1} which is slightly smaller than those of hydrogen peroxide.[2a]

[13] For example, relative equilibrium constants for ArCHO *vs.* ArCOMe are ~470 for cyanohydrin formation [A. Lapworth, R. H. F. Manske, and E. B. Robinson, *J. Chem. Soc.*, 1976 (1930)] and ~570 for acetal formation [J. M. Bell, D. G. Kubler, P. Sartwell, and R. G. Zepp, *J. Org. Chem.*, **30**, 4284 (1965)].

[14] (a) J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962); P. Robson, *J. Chem. Soc.*, 5170 (1964). (b) W. P. Jencks, "Progress in Physical Organic Chemistry," Vol. 2, Interscience Publishers, New York, N. Y., 1964, p 63.

[15] Carbonyl addition of hydrogen peroxide is catalyzed by H$^+$ and OH$^-$: E. G. Sander and W. P. Jencks, *J. Amer. Chem. Soc.*, **90**, 4377 (1968).

concentration of trifluoroacetic acid. These results are explicable by a shift of a rate-determining step from addition to migration.

This is supported by the following treatment of the acetic acid catalyzed data for the reaction of *p*-methoxyacetophenone in benzene. Assuming (i) a steady-state concentration of I, (ii) that $k_1 = k_1^0 + k_1^{\text{HA}}[\text{HA}] + k_1^{\text{B}}[\text{B}] \simeq k_1^{\text{HA}}[\text{HA}]$, and $k_2 = k_2^0 + k_2^{\text{HA}}[\text{HA}] \simeq k_2^0$, the observed rate may be written as eq 3 (see

$$\frac{1}{k_{\text{obsd}}} = \frac{k_{-1}^{\text{HA}}}{k_1^{\text{HA}} \times k_2^0} + \frac{1}{k_1^{\text{HA}}} \times \frac{1}{[\text{AcOH}]} \qquad (3)$$

Scheme I for notation). The plot of $1/k_{\text{obsd}}$ *vs.* $1/[\text{AcOH}]$ is linear for 0.1–1.59 *M* acetic acid (*cf.* Figure 3A).[16] This affords k_1^{HA} of $0.595 \times 10^{-3}\ M^{-2}\ \text{sec}^{-1}$ and $K_1k_2^0 = 5.3 \times 10^{-3}\ M^{-2}\ \text{sec}^{-1}$.

A similar plot for the B–V reaction of anisaldehyde is also linear and gives $k_1^{\text{HA}} = 6.85 \times 10^{-3}\ M^{-2}\ \text{sec}^{-1}$ and $K_1k_2^0 = 7.5 \times 10^{-2}\ M^{-2}\ \text{sec}^{-1}$. The ratio of k_1^{HA} (HA = AcOH) for *p*-methoxybenzaldehyde *vs.* *p*-methoxyacetophenone is then 11.5, which is of reasonable magnitude, since a similar ratio of 10–20 has been found for the acid-catalyzed addition of semicarbazide.[17] It is another evidence for the shift of the rate-determining step for the B–V reaction of acetophenone that the similar change is also observed for benzaldehydes with greater facility to carbonyl addition.

In conclusion, acetic acid ($\text{p}K_a = 4.76$)[18] may catalyze only the carbonyl addition of PBA (*i.e.*, $k_1 = k_1^{\text{HA}}$), but not the migration ($k_2 = k_2^0$). On the other hand, trifluoroacetic acid ($\text{p}K_a = 0.23$)[18] establishes rapidly the addition equilibrium (effective even at 0.002 *M*) and catalyzes also the migration ($k_2 = k_2^0 + k_2^{\text{HA}}$).

So far many kinetic results for the B–V reaction of ketones, especially with PBA and peracetic acid, has not been explicable straightforwardly.[3–6,19] This apparently complex kinetics seem to be due to the shift of the rate-determining step and sometimes to the different susceptibilities of the two steps to acid catalysis. Actually, the rate–pH profile in aqueous ethanol (see Figures 1 and 2) and acid–base catalysis (see Figures 3 and 4) seem to demonstrate that the kinetic data might be complex and the resulting Hammett relationship cannot be explained straightforwardly at moderate acidity because of the shift of rate-determining step. Especially, Figure 3 shows that acetic acid can catalyze only C=O addition, but trifluoroacetic acid can catalyze both C=O addition and migration from I. Hence, it is apparent that the observed rate constant in the presence of acetic or benzoic acid with moderate acidity would be consisted of terms of k_1, k_{-1}, and k_2, affording complex results. On the other hand, stronger peracids, *e.g.*, trifluoroperacetic acid[7] and *m*-ClPBA,[8] have resulted in rather clear kinetics probably because of fast establishment of the addition equilibrium in the presence of stronger parent acids.[20]

Carbonyl Addition of PBA.—Rate-determining addition of PBA$^-$ to *o*- and *p*-hydroxyacetophenones is shown above. Similar rate–pH profiles were also obtained for the PBA oxidation with other *o*- and *p*-hydroxyphenyl alkyl ketones and hence gave the addition rate of PBA$^-$ to these ketones at pH range of 5–12. The addition rate satisfied the Taft equation (Table II), showing the operation of both steric and electronic effects.

The ρ^* value of 1.3–1.6 seems to reflect an importance of electronic effect of a similar extent as observed with typical alkaline hydrolysis.[21] Related data is the addition of hydrogen peroxide ion to benzaldehydes;[15] the relative rate constant for *p*-methoxy- *vs.* *p*-chlorobenzaldehydes (1.08:3.74) corresponds to an approximate ρ value of 1.1. The present data of δ 0.6–0.8 seems to reflect a less importance of steric effects in a nucleophilic attack of peroxide. Similar δ of 0.57 was obtained for the acid-catalyzed attack of hydrogen peroxide on aliphatic carboxylic acids while $\rho^* \sim 0$.[22] Although there has been no explicit explanation for the nature of α effects,[23] the present data show at least a trend of peroxidic nucleophiles that a steric requirement is less important and an electric effect is needed to the same extent as with the other nucleophiles.

The acid catalysis for the addition of PBA is more effective in benzene than in pure or aqueous ethanol, because of the preferred hydrogen bonding of the acid catalysts with the more basic solvents.

Aryl Migration.—Rate data for the B–V reaction of ring-substituted acetophenones are summarized in Table III. The reaction conditions are those of rate-determining aryl migration, and the data are correlated with σ^+ to give an apparent ρ value of ~2. In the last column in Table III are listed the data with *m*-ClPBA from the literature;[8] although the data were stated to be well correlated with σ^+, the correlation is rather poor in view of the downward deviation by ~0.5 log unit for *p*-MeO, which seems to us to be due to the change of rate-determining step for *p*-methoxyacetophenone.[24]

TABLE III

APPARENT SECOND-ORDER RATE CONSTANTS ($k_{\text{obsd}} \times 10^3$, M^{-1} SEC^{-1}) FOR THE REACTION OF XC_6H_4COMe WITH PBA AT 25.0°

X[a]	$\sigma^{+\,b}$	2 *M* $HClO_4$ in 40% EtOH	1.2 *M* AcOH in C_6H_6	0.17 *M* CF_3CO_2H in C_6H_6	*m*-ClPBA[c] in $CHCl_3$
p-HO	−0.92	2.78			
p-MeO	−0.778	1.48	0.145	2.75	40.3
p-Me	−0.311	0.13	0.033	0.210	19.1
H	0.00	<0.05	~0.009	~0.035	4.5
p-Cl	0.112	<0.05		~0.022	3.39
ρ	(σ^+)	2.05	~1.5	2.39	~1.8

[a] Registry numbers for the last four entries are, respectively, 100-06-1, 122-00-9, 98-86-2, and 99-91-2. [b] Reference 18, p 204. [c] The B–V reaction with *m*-chloroperbenzoic acid at 32°;[8] the rate was reported to be well correlated with σ^+ to give a ρ value of −1.36, but the correlation is rather poor, *p*-methoxyacetophenone being deviated by ~0.5 log unit.

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[16] The rate constant at 3.50 *M* AcOH (benzene:AcOH, ~2:1) is 0.250 $\times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$, which is ~25% higher than the expected value from the above correlation. This is probably due to solvent effect.

[17] E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.*, **84**, 4319 (1962).

[18] The values in water at 25°: J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 372.

[19] For example, S. L. Fries and A. H. Soloway, *J. Amer. Chem. Soc.*, **73**, 3968 (1951); Y. Yukawa and T. Yokoyama, *J. Chem. Soc. Jap.*, **73**, 371 (1952).

[20] Although Palmer and Fry[8] did not noted the purity of *m*-ClPBA, the purchased peracid is usually not of high purity.

[21] Reference 10, p 605.

[22] Y. Ogata and Y. Sawaki, *Tetrahedron*, **20**, 2065 (1964).

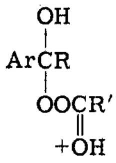
[23] T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, *J. Amer. Chem. Soc.*, **89**, 2106 (1967); R. A. Firestone, *J. Org. Chem.*, **36**, 702 (1971).

[24] Another uncertain point is the reported unreactivity[8] of *p*-nitroacetophenone in spite of the small difference in σ^+ values between *p*-NO_2 and *p*-CN ($\Delta\sigma^+ = 0.131$).

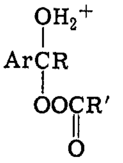
It is also not proper to correlate directly the uncorrected data for a strong electron-attracting group such as NO_2 and CN where methyl group is also a competitive migration one.[7,25]

The ρ value for the migration step cannot be obtained directly from the above data because K_I is unknown. An approximately estimated ρ value for K_I might be near 0.9 if compared with ρ values for other carbonyl addition equilibria in aqueous ethanol (at 20–30°), *e.g.*, ArCHO + H_2O_2 ($\rho = 1.6$),[2a] ArCHO + $H_2NNHCONH_2$ ($\rho = 1.64$),[26] and ArCOMe + $H_2NNHCONH_2$ ($\rho = 0.91$).[27] Thus, the migration in the B–V reaction should possess an approximate ρ value of -3 (σ^+), which is comparable to the ρ value of -4 to -5 for the B–V migration of benzaldehydes[2a] and to other peroxide rearrangements ($\rho = -5.1$,[28] -4.57,[29] and -3.78[30]).

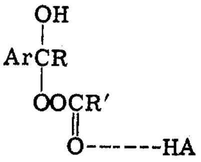
As for the nature of acid catalysis for the migration step, the protonation on the carbonyl (IIIa),[7] acyloxy oxygen,[7] or hydroxyl oxygen (IIIb)[5,6] has been assumed. However, the present study demonstrates no intervention of conjugate acid of I, *i.e.*, IIIa or IIIb of specific proton catalysis, since the rate is not correlated with H_0 function (the slope of log k_{obsd} *vs.* $-H_0$ is less than 0.4) but accelerated slightly by perchloric acid in aqueous ethanol. The catalysis suggests IIIc of general acid catalysis, the position of hydrogen bonding being either on carbonyl (IIIc) or acyloxy oxygen. Finally, the data in the presence of acetic acid clearly reveals that the uncatalyzed migration from I is also operative.


$\mathrm{ArC(OH)(R)OOC(={}^{+}OH)R'}$

IIIa


$\mathrm{ArC({OH_2}^{+})(R)OOC(=O)R'}$

IIIb


$\mathrm{ArC(OH)(R)OOC(=O\cdots HA)R'}$

IIIc

Experimental Section

Materials.—Perbenzoic acids were prepared by the reaction of benzoyl peroxides or chlorides with alkaline hydrogen peroxide[31] and recrystallized from *n*-hexane. *o*- and *p*-hydroxyacetophenones were prepared by the Fries rearrangement of corresponding phenyl esters.[32] Alkyl group and melting or boiling points for *p*-hydroxyphenyl alkyl ketones are as follows: Me, mp 108.8–109.2°; Et, mp 153°; *n*-Pr, mp 90.5–91.5°; *i*-Pr, bp 196–198° (21 mm); CH_2Cl, mp 148–149°; *i*-Bu, bp 175–180° (6 mm); Ph, mp 132–133°. Boiling points for *o*-HOC_6H_4COR are as follows: Me, 109–110° (23 mm); Et, 120–122° (21 mm); *n*-Pr, 91–98° (5 mm); *i*-Pr, bp 121–123° (20 mm). Other ketones were synthesized by Friedel–Crafts acylation and purified by fractional distillation.

Rate and Products.—The B–V reaction of acetophenones in 40 vol. % aqueous ethanol was conducted in the presence of 10^{-4} *M* EDTA to suppress metallic ion catalyzed decomposition of PBA. The rate was determined by iodometry of peracid and/or by uv spectrophotometry of ketone as reported previously.[2]

The produced phenols were determined by uv spectrophotometry or by glc after methylation as reported previously.[2b]

Registry No.—PBA, 93-59-4; *p*-hydroxyphenyl isobutyl ketone, 34887-83-7.

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[25] E. E. Smissman, J. P. Li, and Z. H. Israili, in ref 9 reported an exceptional facile migration of *o*-nitrophenyl group for the B–V reaction of acetophenones, but strangely the anchimeric assistance was not observed for propiophenones.

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Nonbenzenoid Aromatic Systems. VII.[1a] Reactions of Azulenes with Ethylene Oxide or Trimethylene Oxide and Lewis Acids

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A direct β-hydroxyethylation method applied to azulene, 5-methylazulene, and certain 6-substituted (OCH_3, CH_3, Br) azulenes is reported. Reaction of azulene and trimethylene oxide with aluminum chloride yielded 3-(1-azulyl)-1-propanol and 1,1-di(1-azulyl)propane.

Presently, only one literature method is available for the introduction of the 2-hydroxyethyl side chain into the 1 position of azulene (**1a**).[2] Since this procedure is rather lengthy (*N,N*-dimethylamino methylation, quaternization, cyanide displacement, hydrolysis, and reduction), our interest in the solvolytic behavior of 2-(1-azulyl)ethyl tosylate and ring-substituted derivatives[3] prompted us to examine a more direct route for introducing this side chain. We report here such a procedure, which involves reaction of the azulene with ethylene oxide and Lewis acids.

The reaction is a modification of the procedure by Searles[4] for the β-hydroxyethylation of benzene and anisole; the modifications involve the use of methylene chloride as solvent and shorter reaction times. As can be seen from the results listed in Table I, 2-(1-azulyl)ethanol (**2a**) was produced in 41–47% yield (81–85% net yield) with either aluminum chloride or stannic chloride as the Lewis acid. A minor component was identified as the disubstitution product, 1,3-bis(2-hydroxyethyl)azulene (**3**), on the basis of its nmr spectrum. Increasing or decreasing the amounts of Lewis

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[1] (a) For paper VI see R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **37**, 2703 (1972); (b) Phillips Petroleum Co. Fellowship, 1968–1969.

[2] A. G. Anderson, R. G. Anderson, and T. S. Fujita, *J. Org. Chem.*, **27**, 5435 (1962).

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