# Kinetics and Mechanism of the Baeyer–Villiger Reaction of Benzaldehydes with Perbenzoic Acids

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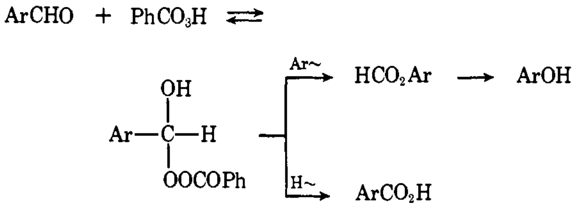
**Abstract**: The Baeyer–Villiger (B–V) reaction of benzaldehydes with perbenzoic acids to give phenols and/or acids has been studied kinetically at various pH's in 40% aqueous ethanol. The pH dependence of the rate differs significantly with each substituent in the aldehydes. The pH–products profile shows a break at pH 8–9 and a slight acid catalysis for aryl migration at pH <1. Kinetic isotope effects for benzaldehyde-*1-d* resulted in $k_H/k_D$ = 1.4–3.0 for hydride migration and 1.0 for aryl migration. The effect of substituents in perbenzoic acids affords $\rho$ values of *ca.* 0.3–0.4 for most benzaldehydes, while $\rho \sim 0$ for *o*- and *p*-hydroxybenzaldehydes at pH >9. Relative migratory aptitude from the product ratios indicates a large negative $\rho$ value of $-4$ to $-5$ ($\sigma^+$) for aryl migration, and that electron-releasing ortho substituents accelerate aryl migration *ca.* ten times as fast as the para isomers, revealing the relative unimportance of steric effect. These results are summarized by a mechanism where a rate-determining step changes from carbonyl addition to a migration step with changing substituents in the aldehydes, anisaldehyde being a borderline case. The nature of hydride and aryl migration is discussed on the basis of these data.

Migration to peroxidic oxygen has been extensively studied and is recognized as an intramolecular nucleophilic substitution on an oxygen atom.[1–4] These are characterized by a large negative $\rho$ value for migrating groups (*e.g.*, $-5.1$,[5] $-4.57$,[6] and $-3.78$[7]) and by a moderately positive value for leaving groups (*e.g.*, 1.34,[8a] 1.21,[8b] and 1.36[8c]). The Baeyer–Villiger (B–V) reaction involves a carbonyl addition step followed by 1,2 rearrangement of the same features. Rate-determining migration has been shown by the negative $\rho$ value (*e.g.*, $-1.1$[9] and $-1.36$[10]) and more conclusively by the $^{14}C$ isotope effect[10] for peracid oxidation of substituted acetophenones.

The B–V reaction in aqueous or aquo-organic media, especially in alkaline solution, is less studied except for the well-known Dakin reaction, although these aqueous systems seem to disclose more clearly the nature of the reaction. The perbenzoic acid (PBA) oxidation of benzaldehydes can have two migrating groups, hydrogen and aryl (eq 1a and 1b). Their selectivity for migration changes sharply with substituent and pH and affords positive $\rho$ values of 1.1–1.8 for the hydrogen shift at pH 1–12.[11] The present report summarizes the kinetics and mechanism of the B–V reaction of benzaldehydes in ethanol-water (40:60 v/v), provides evidences for a rate-determining carbonyl addition in some cases, and discusses the nature of aryl and hydride migration.



(1a)

(1b)

## Results

The Baeyer–Villiger (B–V) reaction of benzaldehydes with perbenzoic acid (PBA) satisfied second-order kinetics (eq 2),[11] and generally there is no significant difference between the rate determined by the titrimetry of PBA and that by carbonyl absorbance of the aldehyde. The reproducibility of the rate data within a probable error of ±5% together with no effect of phenols, EDTA, oxygen, and the initial concentrations suggests a nonradical nature of the present reaction.

$$v = k_{\text{obsd}}[\text{ArCHO}]_s[\text{PhCO}_3\text{H}]_s \qquad (2)$$

**Effect of pH.** The dependence of rate on pH and $H_0$ varies substantially by ring substituent in benzaldehydes as shown in Figures 1 and 2. *o*- and *p*-hydroxybenzaldehydes afford only phenols by aryl migration and their pH–rate profiles give slopes of +1.0 at pH 4–7 and −1 at pH >9, while acid catalysis appears at pH <2. The acidity effect differs by substituents; the slope for *p*-HO is close to unity, but deviates downward at higher acidity (Figure 1).

The rate for anisaldehyde is independent of pH at pH >5, while the product distribution changes at pH ~8.5. Acid catalysis is operative at pH <2, and hence a rate minimum appears at pH ~2. The apparent rate of consumption of PBA is larger than that of anisaldehyde within a factor of 2. The difference increases in the absence of EDTA and PBA may be consumed,

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(1) E. G. E. Hawkins, "Organic Peroxides," E. & F. F. Spon, London, 1961.

(2) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, p 144.

(3) P. A. S. Smith, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 568.

(4) J. B. Lee and B. C. Uff, *Quart. Rev., Chem. Soc.*, **21**, 449 (1967).

(5) K. Nelson, quoted by S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80**, 169 (1958).

(6) A. W. De R. Van Stevenick and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **79**, 413 (1960).

(7) G. H. Anderson and J. G. Smith, *Can. J. Chem.*, **46**, 1553, 1561 (1968).

(8) (a) P. D. Bartlett and J. L. Kice, *J. Amer. Chem. Soc.*, **75**, 5591 (1953); (b) N. N. Yablokova, V. A. Yablokov, and V. A. Shushunov, *Chem. Abstr.*, **64**, 17378*e* (1966); (c) P. D. Bartlett and B. T. Storey, *J. Amer. Chem. Soc.*, **80**, 4954 (1958); P. D. Bartlett and T. G. Traylor, *ibid.*, **83**, 856 (1961).

(9) M. F. Hawthorne and W. D. Emmons, *ibid.*, **80**, 6393, 6398 (1958).

(10) B. W. Palmer and A. Fry, *ibid.*, **92**, 2580 (1970).

(11) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **34**, 3985 (1969).

Table I. Substituent Effects for Apparent Rate of PBA Oxidation of $XC_6H_4CHO$ and for $H_2O_2$ Addition Equilibrium in 40% Ethanol at 25.0°

| | B-V oxidation | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $k_p \times 10^3$ $M^{-1}$ sec$^{-1}$ [a] | | | $k_o/k_p$ [a] | | | $H_2O_2$ addition | |
| X | pH 0.7 | pH 3 | pH 11 | pH 0.7 | pH 3 | pH 11 | $K_p$,[b] $M^{-1}$ | $K_o/K_p$ [b] |
| HO | 4.1[c] | 1.0[c] | ~200[c] | 1.2[c] | 26[c] | ~100[c] | 0.03 | ~2 |
| MeO | 4.1[c] | 3.3[c] | 20 | 2.4[c] | 2.1[c] | | 0.07 | ~5 |
| Me | 2.60 | 2.52 | 29 | 0.95 | 1.00 | | 0.14 | 2.5 |
| Cl | 4.69 | 10.7 | 120 | 0.40 | 0.17 | 0.43 | 0.63 | 2.5 |
| $O_2N$ | 7.23 | 77 | 2010 | 0.55 | 0.13 | 0.21 | | |

[a] Subscripts o and p represent ortho and para substituents and the rate constant for o-X ($k_o$) can be calculated from $k_o = k_p(k_o/k_p)$. [b] The equilibrium constants for $X\text{-}C_6H_4CHO + H_2O_2 \rightleftarrows X\text{-}C_6H_4CH(OH)OOH$, which were estimated by determining C=O absorbance of the aldehydes at 270–280 or 310–340 mμ (for o-HO and o-MeO). Subscript are the same as in footnote a. [c] Main migrating group is aryl.

partially by the radical decomposition, but mostly by the oxidation of produced formate to carbonate.[12]

o-Methoxybenzaldehyde also gives a similar pH–rate profile at pH <4, its rate being ca. 2.2 times as fast as that of para isomer. The rate at pH >5, however, cannot be determined because of the appearance of turbidity probably due to acetal formation. The same turbidity appears in the case of o-methylbenzaldehyde at pH >4.

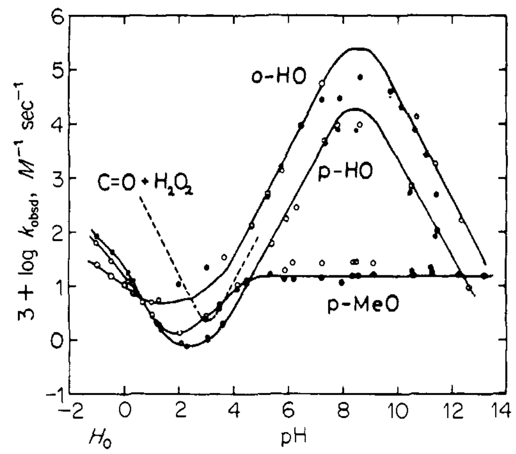

Figure 1. pH–rate profile for the B–V reaction of substituted benzaldehydes with PBA in 40% ethanol at 25.0°. The lines are calculated from rate constants in Table VI. Open circle (○) and filled circle (●) show $k_{obsd}$ estimated by titrimetry of peracid and by uv spectrophotometry of aldehydes, respectively. Dotted line exhibits the rate for C=O addition of $H_2O_2$ to anisaldehyde in water from ref 14.

The PBA oxidation of tolualdehydes revealed another interesting aspect of the B–V reaction. The apparent rate with tolualdehydes remains constant at high acidity, while the per cent aryl migration increases with increasing acidity. The oxidation rate at this pH region, on the other hand, increases slightly with increasing pH up to pH 8 with a maximum slope of 0.17; a similar pH dependence on hydride shift is observed for other aldehydes.[11]

The rate of aryl migration at high acidity (pH <1) is not related to the acidity function but is proportional to the concentration of added perchloric acid.

**Substituent Effect in Benzaldehydes.** As is apparent in Figures 1 and 2, the substituent effect in benzaldehydes varies with pH and Table I lists the apparent rate constants at selected pH's and the resulting ortho/para ratios. Although the data for para substituents do not fit the Hammett relationship, it is apparent that the polar effect is smallest at pH 1–3.

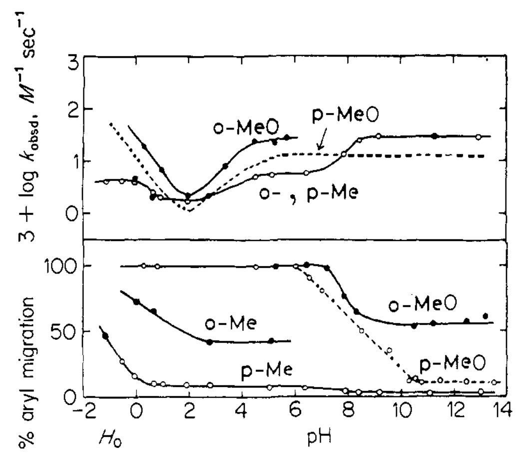

Figure 2. Effect of pH on the rate and products of PBA oxidation of substituted benzaldehydes in 40% ethanol at 25.0°. Per cent aryl migration shows the per cent selectivity for the formation of phenols and 0% means 100% hydride shift. Initial concentration of [PBA] = [ArCHO] = 0.020 $M$; reaction time is 1–20 hr in nitrogen stream. Conversions of the aldehydes were in the range of 70–80% and the total recoveries were 90–100%.

Table I also contains, for comparison, the equilibrium constants for carbonyl addition of hydrogen peroxide. The $K_p$ values for the para isomer afford a $\rho$ value of ca. 1.6 ($\sigma$) and ortho/para ratios of 2–5.[13] Since reported $K_p$'s for p-MeO and p-Cl are 0.18 and 0.88 $M^{-1}$ in water,[14] respectively, the differences are probably due to the solvent effect.[15a]

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[12] Ionic decomposition of PBA is much slower than the present consumption, the maximum rate, $k_{obsd}$, being $5 \times 10^{-3}$ $M^{-1}$ sec$^{-1}$ at pH ~8.5 in 40% ethanol at 25°.

[13] Similar $\rho$ values (1.81) and ortho/para ratios have been reported for the equilibrium constants of C=O addition of semicarbazide: R. Wolfenden and W. P. Jencks, *J. Amer. Chem. Soc.*, **83**, 2763 (1961).

[14] E. G. Sander and W. P. Jencks, *ibid.*, **90**, 4377, 6154 (1968).

[15] (a) For example, $K_p$'s for p-Cl in 40 and 20% ethanol are 0.63 and 0.75, respectively, approaching the reported value of 0.88[14] in water. (b) Alternative determination of the relative migratory aptitude is to correct the product ratio by a rate factor. However, the present reaction gives no accurate value of the rate factor (*i.e.*, $k_2$ value)

**Table II.** Relative Migratory Aptitude for the B–V Reaction of Substituted Benzaldehydes with PBA in 40% Ethanol at 25°[a]

| Migrating group | Acidic (1 $M$ $HClO_4$) | Neutral (pH 3-7) | Alkaline (pH >10) |
|---|---|---|---|
| $o$-$HOC_6H_4$ | >100 | >100 | >100 |
| $p$-$HOC_6H_4$ | >100 | >100 | >100 |
| $o$-$MeOC_6H_4$ | >100 | >100 | ~1.5 |
| $p$-$MeOC_6H_4$ | >100 | 19 | ~0.18 |
| $o$-$MeC_6H_4$ | 2.64 | 0.72 | ~0.04 |
| $p$-$MeC_6H_4$ | 0.17 | 0.07 | ~0.03 |
| $C_6H_5$ | ~0.008 | $<10^{-3}$ | $<10^{-3}$ |
| $p$-$ClC_6H_4$ | ~0.001 | $<10^{-3}$ | $<10^{-3}$ |
| H | (1.00) | (1.00) | (1.00) |
| $\rho(\sigma^+)$[b] | −5.7 | (−3.8) | (−1.6) |

[a] Migratory aptitude relative to hydrogen, Ar/H, calculated from the product ratios, $ArOH/ArCO_2H$. Initial concentrations: [PBA] = [ArCHO] = 0.020 $M$. Reaction time 1–20 hr. Conversions of the aldehydes were in the range of 70–80% and total recoveries were 90–100%. [b] Approximate reaction constant estimated from the para-substituted phenyl migration. The values in parentheses are rough estimates.

Interestingly, the para substituent effects on the rate of the B–V reaction with hydride shift ($\rho$ = 1.1–1.7)[11] are comparable to the effect on $H_2O_2$ addition equilibrium ($K_p$) ($\rho$ = 1.6). The ortho/para ratio ($k_o/k_p$ in Table I) for aldehydes with hydride shift are less than 0.5, while those for aryl migration are much larger than unity. Since the apparent rate of B–V reaction may depend on the rate of C═O addition and/or rearrangement step, one cannot reach the conclusion from these apparent data alone.

More pertinent data for the migrating step are available from the product ratios of phenols *vs.* benzoic acids (Table II).[15b] The relative migratory aptitude was estimated by assuming that the hydride shift is insensitive to nonmigrating ring substituents. This seems to be reasonable if considered with the comparable $\rho$ values for the present B–V oxidation with hydride shift ($\rho$ = 1.1–1.7[11]) and for the $K_p$ of hydrogen peroxide ($\rho$ = 1.6) as shown above.

Table II shows that the aryl migration is sensitive to the polar effect; $\rho$ (*vs.* $\sigma^+$) = −5.7 (1 $M$ acid), −3.8 (neutral), and −1.6 (alkaline), although the last two values are rough estimates. Surprisingly, electron-releasing ortho substituents facilitate aryl migration *ca.* ten times as much as the para isomers.

**Deuterium Isotope Effect.** Kinetic isotope effect, $k_H/k_D$, for the B–V reaction of benzaldehyde-*1-d* holds constancy by changing buffer concentration (Table III); *e.g.*, $k_H/k_D$ = 2.92 and 3.04 with 0.05 and 0.10 $M$ acetate buffer, respectively. Although the isotope effect decreases at lower pH, it is evident that hydride shift is rate determining.

Practically no observation of isotope effect for PBA oxidation of anisaldehyde-*1-d* at pH <5 is convincing since the migrating group is aryl and not hydride. Kinetic isotope effect for anisaldehyde can thus be observed at high pH (11) for the reaction with the hydride shift.

**Substituent Effect in PBA.** In Table IV are summarized the rate data for oxidation of benzaldehydes with substituted PBA's. In most cases, rather small positive $\rho$ values ($\rho$ = 0.2–0.4 ($\sigma$)) are obtained at various pH's with various substituents in the aldehydes.

One remarkable exception in Table IV is a negative $\rho$ value for oxidation of $p$-hydroxybenzaldehyde at pH >9. Similar results were obtained for the case of salicylaldehyde. That is, rate ratios with $m$-chloroperbenzoic acid and PBA ($k_{m\text{-ClPBA}}/k_{PBA}$) are 2.32, 1.97, and 1.47 at pH 5.7, 6.4, and 7.2, respectively, while the ratios are 1.09 and 1.03 at pH 10.1 and 10.6, respectively. These ratios, $k_{m\text{-ClPBA}}/k_{PBA}$, of 0.8–1.1 for $o$- and $p$-hydroxybenzaldehydes show that substituents on the PBA anion have little effect on the rate. About a twofold increase in rate at pH <8 is comparable

**Table III.** Kinetic Isotope Effect for the Oxidation of Benzaldehydes with PBA's in 40% Ethanol at 25.0°

| Substituent in | | $k_D \times 10^3$,[a] $M^{-1}$ sec$^{-1}$ | | | $k_H/k_D$[b] | | |
|---|---|---|---|---|---|---|---|
| $X$-$C_6H_4CDO$ | $Y$-$C_6H_4CO_3H$ | pH 0.7 | pH 4.6 | pH 11 | pH 0.7 | pH 4.6 | pH 11 |
| H | H | 1.96 | 2.45 | 29.1 | 1.70 | 3.03 | 2.31 |
| H | $p$-$O_2N$ | 1.36 | 11.8 | ~50 | 1.36 | 2.42 | ~2.1 |
| $p$-MeO | H | 3.78[c] | 12.4[c] | 12.2 | 1.08[c] | 1.02[c] | 1.72 |
| $p$-MeO | $p$-$O_2N$ | 6.5[c] | | ~44 | 1.07[c] | | ~1.4 |

[a] % D of benzaldehyde-*1-d* and anisaldehyde-*1-d* were 88.9 and 89.8%, respectively, and the tabulated rate constants ($k_D$) are corrected. [b] Deuterium isotope effect with probable error of ±10%. [c] Migrating group is anisyl.

**Table IV.** Substituent Effect on the Apparent Second-Order Rate Constant ($k_{obsd} \times 10^3$ $M^{-1}$ sec$^{-1}$) for the Reaction of Benzaldehydes with Substituted PBA's in 40% Ethanol at 25.0°

| Y in | $C_6H_5CHO$ | | $p$-$MeOC_6H_4CHO$ | | | $p$-$HOC_6H_4CHO$ | | |
|---|---|---|---|---|---|---|---|---|
| $Y$-$C_6H_4CO_3H$ | pH 0.7 | pH 11 | pH 0.7 | pH 5 | pH 11 | pH 0.7 | pH 6.4 | pH 10 |
| H | 3.33 | 68 | 4.07 | 13 | 21.0 | 4.31 | 650 | 470 |
| $p$-Cl | 4.28 | | 4.77 | ~30 | ~34 | 5.12 | | |
| $m$-Cl | 4.95 | | 5.53 | | ~36 | 5.58 | 900 | 390 |
| $p$-$O_2N$ | 7.05 | ~105 | 6.96 | ~60 | ~61 | 6.58 | | |
| | Migrating group[a] | | | | | | | |
| | H | H | Ar | Ar | H | Ar | Ar | Ar |
| $\rho(\sigma)$[b] | 0.44 | (~0.2) | 0.32 | (~1.0) | (~0.61) | 0.25 | (+0.4) | (−0.2) |

[a] Predominant migrating group from product distributions. [b] The values in parentheses show approximate $\rho$ values for comparison.

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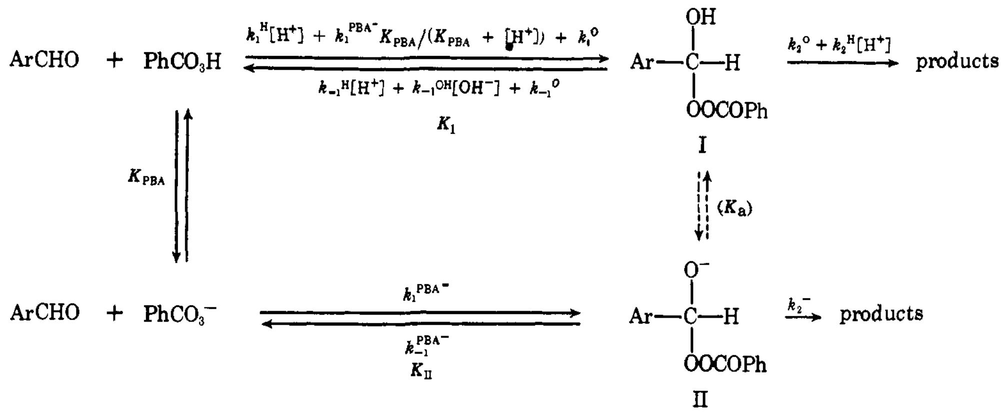
because of a multistep mechanism. Thus, the most reliable migratory aptitude is obtained from the product ratios relative to the hydride shift as an intramolecular reference.

**Scheme I**



and seems to correspond to the difference of p$K_a$'s of the two peracids (Δp$K_a$ = 0.35).[16]

**Solvent Effect.** The extent of solvent effect on the B-V reaction of anisaldehyde changes with pH and migrating group, although increasing water content accelerates the oxidation. The increment in rate at pH 11 is mainly due to that in aryl migration; *i.e.*, the aryl migration is sensitive to the solvent polarity much more than the hydride shift. The hydride shift is rather insensitive to solvent effect. Thus, the Grunwald–Winstein *m* values in aqueous ethanol and methanol are in a range of 0.1–0.2 for various pH's and substituents.[17] Moreover, net *m* values for the hydride shift step seem to be much smaller on the basis of some positive *m* values for the carbonyl addition equilibria.[15a]

Table V. Solvent Effect on the Rates ($k_{obsd} \times 10^3\ M^{-1}\ sec^{-1}$) of PBA Oxidation of Anisaldehyde in 40% Ethanol at 25.0°

| Vol % EtOH | pH 0.7 | pH 5.2 | pH 11[a] | | | |
|---|---|---|---|---|---|---|
| | $10^3k_{obsd}$ | $10^3k_{obsd}$ | $10^3k_{obsd}$ | (ArOH %) | $k_{Ar\sim}$ | $k_{H\sim}$ |
| 60 | | 6.0 | 10.7 | (12.0) | 1.3 | 9.4 |
| 40 | 4.17 | 17.5 | 19.7 | (14.9) | 3.0 | 18 |
| 30 | 6.86 | 35 | 27.8 | (17.3) | 4.8 | 23 |
| 20 | 9.30 | 67 | 33.3 | (36.7) | 12.2 | 21 |
| | Migrating group | | | | | |
| | Ar | Ar | | | Ar | H |
| *m* value[b] | 0.27 | 0.51 | | | 0.56 | 0.14 |

[a] Observed rate constants ($k_{obsd}$) were divided in two paths, *i.e.*, aryl ($k_{Ar\sim}$) and hydride migration ($k_{H\sim}$). [b] Grunwald–Winstein's *m* value.

## Discussion

**Rate-Determining Step.** Rate-determining and concerted migration have been demonstrated by the $^{14}$C isotope effect on the *m*-ClPBA oxidation of acetophenones.[10] The oxidation of *p*-methoxyacetophenone showed no isotope effect, which was explained in terms of strong electron-donating power.[10] An alternative explanation by a rate-determining carbonyl addition seems, however, to be more probable as shown in Scheme I.

Evidence for rate-determining carbonyl addition of PBA to *o*- and *p*-hydroxybenzaldehydes is summarized below. (i) If the unit slope at pH 2–7 (Figure 1) were due to the OH$^-$-catalyzed aryl migration of I, *i.e.*, $v = k_2^{OH}[OH^-][I]$, the second-order rate constants, $k_2^{OH}$, for migration step would be ~0.4 × 10$^{10}$ $M^{-1}$ sec$^{-1}$ for *p*-HO and ~3.3 × 10$^{10}$ $M^{-1}$ sec$^{-1}$ for *o*-HO in 40% ethanol.[18a] The extrapolated rate constants in water are ~1.8 × 10$^{10}$ $M^{-1}$ sec$^{-1}$ for *p*-HO and ~15 × 10$^{10}$ $M^{-1}$ sec$^{-1}$ for *o*-HO,[19] which are too fast to be real.[20] Here, the equilibrium constants of carbonyl addition are assumed to be near 10$^{-2}$ $M^{-1}$ for those of hydrogen peroxide (see Table I) only after a correction of a statistical factor of 2.[21] (ii) The pH-rate profiles are well explained by assuming dissociation of PBA (p$K_a$ = 8.5 in 40% ethanol) and HO group of the aldehydes.[18b] The lines for *o*- and *p*-HO groups in Figure 1 are calculated from the data in Table VI assuming a slow carbonyl addition (eq 3) and fit the observed rate well. (iii) Rate ratios, $k_{m\text{-ClPBA}}/k_{PBA}$,

Table VI. Summary of Rate Data for B–V Reaction of XC$_6$H$_4$CHO with PBA in 40% Ethanol at 25.0°

| X | $k_1^{H} \times 10^3\ M^{-2}$ sec$^{-1}$ | $k_1^{OH} \times 10^{-8}\ M^{-2}$ sec$^{-1}$[a] | $k_1^{PBA^-}$ $M^{-1}$ sec$^{-1}$[b] | $k_1^{o} \times 10^3\ M^{-1}$ sec$^{-1}$ | Slow step[c] |
|---|---|---|---|---|---|
| *p*-HO | 25 | 0.36 | 112 | 0.6 | C=O |
| *o*-HO | 6 | 3.3 | 1050 | 5 | C=O |
| *p*-MeO[d] | 19 | 2.4 | 760 | 1.0 | C=O + mig |
| *o*-MeO | 39 | 4.8 | 1600 | 2.0 | C=O + mig |

[a] Apparent hydroxide ion catalytic constants are also listed, although an alternate expression, *i.e.*, $k_1^{PBA^-}$, is prefered as noted in the text. [b] Rate constants of carbonyl addition of perbenzoate ion. [c] C=O, carbonyl addition; mig, migration in the carbonyl adduct, I or II. [d] For anisaldehyde, $k_2^{o} = 0.015/K_I$ sec$^{-1}$, $k_2^{H} = 0.030/K_1\ M^{-1}$ sec$^{-1}$, and $k_{-1}^{Y} = k_1^{Y}/K_I$ (Y = H$^+$, OH$^-$, PBA$^-$, and solvent), where $K_I$ is equilibrium constant for carbonyl addition to form I.

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(16) P. Robson, *J. Chem. Soc.*, 5170 (1964).

(17) These *m* values were calculated from the rate data in ref 11.

(18) (a) Since $v = k_2^{OH}[OH^-][I] = k_2^{OH}[OH^-]K_I[ArCHO][PBA] = k_{obsd}[ArCHO][PBA]$, $k_2^{OH}$ is equal to $k_{obsd}/K_1[OH^-]$, which affords the approximate $k_2^{OH}$ values of 0.4 × 10$^{10}$ and 3.3 × 10$^{10}$ $M^{-1}$ sec$^{-1}$ assuming $K_1 \sim 10^{-2}\ M^{-1}$ and using the $k_{obsd}/[OH^-]$ values of 0.36 × 10$^8$ and 3.3 × 10$^8$ sec$^{-1}$ for *p*-HO and *o*-HO, respectively (Figure 1). (b) Titrated p$K_a$'s are 8.45 and 8.21 for *o*- and *p*-hydroxybenzaldehydes, respectively, in 40% ethanol at 25°.

(19) The rate increases with increasing water content by a factor of 4.5 from 40% ethanol to water.

(20) M. Eigen, *Angew. Chem.*, **75**, 489 (1963).

(21) This assumption that the equilibrium constants for carbonyl addition of ROOH are not greatly affected by the p$K_a$ values of ROOH seems to be reasonable, if we consider the case of RSH, a similar strong nucleophile, which showed very small changes in *K*'s with a large variation in the p$K_a$ of RSH.[22] Moreover, there is no reason to assume a greater *K* value for PBA than that of $H_2O_2$.

(22) R. E. Barnett and W. P. Jencks, *J. Amer. Chem. Soc.*, **91**, 6758 (1969).

of 1.4–2.3 at pH <7 and 0.8–1.1 at pH >9 can be explained by the rate-determining addition of perbenzoate ion ($\Delta pK_a = 0.35$). (iv) The rate of *p*-HO at pH 2–5 and pH >12 is lower than that of *p*-MeO, a less electron-releasing group. (v) There appears no large difference between the rates of B–V reaction and that of carbonyl addition of hydrogen peroxide (Figure 1).[14] Hence, the addition of PBA to *o*- and *p*-hydroxybenzaldehydes may be concluded to be rate determining (see Scheme I for notations), *i.e.*,

$$k_{\text{calcd}} = k_1^{\text{H}}[\text{H}^+] + k_1^{\text{PBA}^-}K_{\text{PBA}}/(K_{\text{PBA}} + [\text{H}^+]) + k_1^{\circ} \quad (3)$$

Here, $k_1^{\text{PBA}^-}K_{\text{PBA}}/(K_{\text{PBA}} + [\text{H}^+])$ is preferred to $k_1^{\text{OH}}\cdot[\text{OH}^-]$, since the observed bell-shaped pH–rate profile is only obtainable by assuming $\text{PBA}^-$ as a sole attacking nucleophile; on the other hand, for the expression of the data by means of $k_1^{\text{OH}}[\text{OH}^-]$, two terms, $k_1^{\text{OH}}$ and $k_1^{\text{PBA}^-}$, are necessary for the hydroxide ion catalyzed C=O addition, *i.e.*, $v = k_1^{\text{OH}}[\text{OH}^-][\text{PBA}][\text{ArCHO}] + k_1^{\text{PBA}^-}[\text{PBA}^-][\text{ArCHO}]$. The latter treatment with two terms is unsatisfactory, because the $k_1^{\text{OH}}$ term must vanish since the $k_1^{\text{PBA}^-}$ term obtained from the data at pH >10 is naturally operative at lower pH's than 7 and can adequately reproduce the observed pH–rate profiles (Figure 1). In other words, if both $\text{OH}^-$-catalyzed C=O addition of PBA and the direct addition of $\text{PBA}^-$ were operative, the observed rate at pH 2–7 should be much faster than that expected from the $k_1^{\text{PBA}^-}$ term alone, which was not the case. One important result, left to be explained, that of $k_{m\text{-ClPBA}}/k_{\text{PBA}}$ ratios being 1.1–1.5 at pH <0, may be understood as noted in the next section.

The B–V oxidation of anisaldehyde could be shown to be a borderline case; its rate of reaction at pH >5 is determined by the migration step, while the apparent rate at pH <5 is controlled both by addition and migration. Thus a plot of $1/k_{\text{obsd}}$ *vs.* $1/[\text{OH}^-]$ at pH 2–5 is linear, affording the $k_1^{\text{OH}}$ value of $2.4 \times 10^8$ $M^{-1}$ sec$^{-1}$ in Table VI. Similar treatment gives the $k_1^{\text{H}}$ values. Since the rate at pH <0 is faster than that of pH >5 with rate-determining migration (Figure 1), it is apparent that acid catalysis also operates for the migration step. A steady state assumption for the carbonyl adduct I leads to eq 4. Here, hydroxide ion

$$k_{\text{calcd}} = \frac{\{k_1^{\text{H}}[\text{H}^+] + k_1^{\text{OH}}[\text{OH}^-] + k_1^{\circ}\}\{k_2^{\circ} + k_2^{\text{H}}[\text{H}^+]\}}{k_{-1}^{\text{H}}[\text{H}^+] + k_{-1}^{\text{OH}}[\text{OH}^-] + k_{-1}^{\circ} + k_2^{\circ} + k_2^{\text{H}}[\text{H}^+]} \quad (4)$$

catalyzed C=O addition is expressed as $k_1^{\text{OH}}[\text{OH}^-]$, but a kinetically indistinguishable term, $k_1^{\text{PBA}^-}K_{\text{PBA}}/(K_{\text{PBA}} + [\text{H}^+])$, is more probable as is the case for *o*- and *p*-hydroxybenzaldehydes. The rate constants best fit to the observed rate are summarized in Table VI, but the absolute values of $k_2$'s and $k_{-1}$'s cannot be determined because of the unknown value of $K_{\text{I}}$. The value of $k_{\text{calcd}}$, however, is not affected by that of $K_{\text{I}}$, since $k_2$'s and $k_{-1}$'s are both divided by the same $K_{\text{I}}$ in eq 4, *i.e.*, $k_{-1} = k_1/K_{\text{I}}$ and $k_2^{\circ} + k_2^{\text{H}}[\text{H}^+] \simeq k_2^{\circ} = k_{\text{obsd}}/K_{\text{I}}$ at pH >5, where the migration step is rate determining and no acid catalysis is observed.

The product selectivity changed at pH ~8.5 for PBA oxidation of anisaldehyde in spite of a constant rate at pH >5 (Figure 2). Similar changes in products were also observed at pH ~8 for the benzaldehydes with *o*-MeO and *p*-Me. These breaks in the product–pH profiles may correspond to the ionization of the adduct I to II, and the assumption of the mobile equilibrium between I and II in our previous paper[11] is less tenable as shown below. Thus, the calculated rate constant of $\text{OH}^-$-catalyzed decomposition of I, $k_{-1}^{\text{OH}}$, for anisaldehyde is near the diffusion-controlled rate, *i.e.*, $\sim 0.8 \times 10^{10}$ $M^{-1}$ sec$^{-1}$ in 40% ethanol or $\sim 3.6 \times 10^{10}$ $M^{-1}$ sec$^{-1}$ in water if $K_{\text{I}}$ is less than 0.03 ($k_{-1} = k_1/K_{\text{I}}$).[23] The expected rate for the ionization of hydroxyl proton in I, however, would be much slower than the diffusion-controlled rate because of the lower acidity of hydroxyl group of I in comparison with the rates for carboxylic acid or phenol.[20] These clearly deny the previously assumed fast equilibrium between I and II. Hence, I is formed from ArCHO and PBA, while II is formed from ArCHO and $\text{PBA}^-$. The change of intermediate from I to II at pH 8.5 is explicable on the basis of the dissociation of PBA ($pK_a = 8.5$ in 40% ethanol).

The apparent rate ($k_{\text{obsd}}$) for anisaldehyde holds constancy with varying pH at pH >5 in spite of the change of the intermediate from I to II. The establishment of separate equilibria to form I and II leads to the rate expression $v = k_2^{\circ}[\text{I}] = k_2^{\circ}K_{\text{I}}[\text{ArCHO}]\cdot[\text{PBA}]$ for the reaction *via* I and $v = k_2^-[\text{II}] = k_2^-K_{\text{II}}\cdot[\text{ArCHO}][\text{PBA}^-]$ for the reaction *via* II. Thus, the observed constancy of $k_{\text{obsd}}$ shows $k_2^{\circ}K_{\text{I}} \simeq k_2^-K_{\text{II}}$. While $k_2^-$ should be much larger than $k_2^{\circ}$ owing to the pushing effect of the $\alpha$-oxy anion in II, the same effect should tend to make $K_{\text{I}} \gg K_{\text{II}}$ because of expulsion of $\text{PBA}^-$. Hence, the cancellation of the effect on $k_2$'s ($k_2^- \gg k_2^{\circ}$) with the effect on $K$'s ($K_{\text{I}} \gg K_{\text{II}}$) affords the unexpected constancy of $k_{\text{obsd}}$ at pH >5 for anisaldehyde. Otherwise, there appears a break in the pH–rate profile at pH ~8 for tolualdehydes (Figure 2), and these breaks are rather general for benzaldehydes with electron-attracting groups.[11] The increase of aryl migration at lower pH for tolualdehydes may be explained on the basis of acid catalysis for aryl migration as discussed later.

Rate-determining migration is convincing for the PBA oxidation of other benzaldehydes having Me, H, Cl, and $\text{NO}_2$ groups on the basis of the following evidence. (i) No observation of unit slope in the pH–rate profile is in contrast to the C=O addition of a stronger nucleophile, hydrogen peroxide.[14] (ii) A kinetic deuterium isotope effect is observed (Table III). (iii) The rate for the *p*-HO is much faster than those for the aldehydes in some pH regions. (iv) Formation of hydrogen peroxide is appreciable at high pH by mixing benzaldehydes and PBA's having electron-attracting groups (*p*-Cl, *m*-Cl, and *p*-$\text{NO}_2$). This hydrolysis varies with substituent of PBA in the order of *p*-$\text{NO}_2$ > *m*-Cl > *p*-Cl and proceeds in competition with B–V migration probably by an attack of hydroxide ion on carbonyl carbon of II. This evidence is adequate for concluding a rate-determining migration from I or II.

The small slope of 0.1–0.2 in the log *k* *vs.* pH plot for various aldehydes with hydride shift still remains

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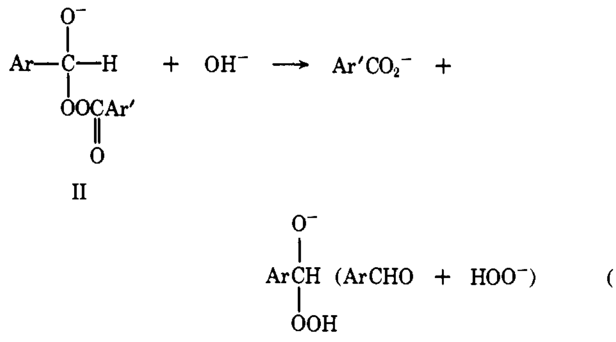
[23] The assumption seems to be reasonable that for anisaldehyde $K_{\text{I}}$ of PBA does not exceed that of $\text{H}_2\text{O}_2$, a stronger nucleophile, *i.e.*, $K_{\text{I}} < 0.035$ for PBA with a statistical correction of 2. The estimate of $k_{-1}^{\text{OH}}$ near the diffusion-controlled rate is not so extraordinary, since the reported value for RSH is actually such a case.[22]



II

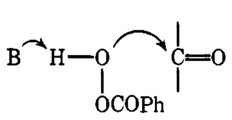
(5)

inexplicable.[24] The observed small slope may result from various factors, *e.g.*, a small sigmoid curve at pH 6–8 on the dissociation of PBA, and a gradual approach of the migration rate to the carbonyl addition at pH <5. These features are visualized to some extent in the case of *p*-tolualdehyde at pH >2 (Figure 2). The latter condition is reflected in the decrease of rate difference between the aldehydes at low pH (Table I), on the smaller $\rho$ values for hydride shift from 1.7 to 1.0,[11] and on the decrease of $k_H/k_D$ at pH 0.7 (Table III).

**Acid and Base Catalysis in Carbonyl Addition.** The addition of hydrogen peroxide to benzaldehydes has been reported to be subject to general acid and base catalysis, the Brønsted's parameters, $\alpha$ and $\beta$, being 1.0 and 0.66, respectively.[14] It is of some interest to compare the reactivity for the carbonyl addition reaction of PBA and hydrogen peroxide.

Apparent hydroxide ion catalytic constants, $k_1^{OH}$, for addition to anisaldehyde are $1.08 \times 10^8$ $M^{-2}$ sec$^{-1}$ for $H_2O_2$[14] and $8.4 \times 10^8$ $M^{-2}$ sec$^{-1}$ for PBA[25] in water; *i.e.*, $k_1^{OH}$ for PBA is, after a statistical correction of 2, *ca.* 15 times that of $H_2O_2$, a stronger nucleophile. This reverse reactivity is well understood by assuming a direct attack of peroxide anion as was the case with hydrogen peroxide.[14] This assumption is shown to be correct in Figure 1, where the rate of C=O addition is expressed as $k_{PBA^-}$[PBA anion][aldehyde], and from the fact that a rate ratio, $k_{m\text{-ClPBA}}/k_{PBA}$, of $\sim$2 is close to the ratio of acidity constants of the two acids (2.2). This leads to a relative reactivity of 300:1 for $HOO^-$ and $PBA^-$, which is of reasonable magnitude in view of the difference of p$K_a$ between HOOH and PBA ($\Delta$p$K_a$ = 3.5). Thiols with p$K_a$ < 8 have been shown to give a $\beta$ value of 1.0 for carbonyl addition and a diffusion-controlled, hydroxide ion catalyzed expulsion of the carbonyl adduct.[22] The latter is very interesting if we remember that the present case of PBA is also close to a diffusion-controlled rate ($k_{-1}^{OH} > 10^{10}$ $M^{-1}$ sec$^{-1}$) as noted in the preceding section.

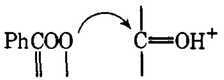
General base catalysis is also observed for the present carbonyl addition of PBA. The catalytic constants for *p*-hydroxybenzaldehyde are $0.36 \times 10^8$, 0.65, 0.020, and $10^{-5}$ $M^{-2}$ sec$^{-1}$ for hydroxide, acetate, monochloroacetate ions, and water, respectively. These values afford a $\beta$ value of 0.73, which is comparable to the case of hydrogen peroxide (0.66)[14] and thiols (0.8).[22] However, a further consideration is meaningless, since



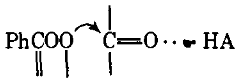
III

it has recently been demonstrated that Brønsted coefficients are not correlated with an extent of proton transfer in a transition state.[26]

As for the acid-catalyzed addition, the rate is not correlated by acidity function, $-H_0$, but proportional to the concentration of perchloric acid added. Since the conjugage acid of aldehydes should be correlated by acidity function, the above result suggests that the addition of PBA is not to a protonated carbonyl (IVa) but to IVb of general acid type. Acid catalysis by



IVa

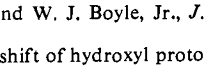


IVb

benzoic acids (p$K_a$ = 3.4–4.2) is not apparent up to the concentration of 3 $M$, but this is ordinary if $\alpha \sim 1$ as reported with hydrogen peroxide.[14] The catalytic constants, $k_1^H$, for proton-catalyzed addition to anisaldehyde are 1.44 $M^{-2}$ sec$^{-1}$ for hydrogen peroxide and 0.075 $M^{-2}$ sec$^{-1}$ for PBA in water,[25] which result in a relative affinity to carbonyl of 11:1 after a statistical correction of 2. This smaller difference in their reactivities than for hydroxide ion catalysis is convincing in view of a lower selectivity in proton catalysis for other carbonyl addition.[14] Indeed, for the addition of hydrogen peroxide, anisaldehyde is reported to be *ca.* 1.7 times more reactive than *p*-chlorobenzaldehyde of weaker basicity.[14]

The data for carbonyl addition in Table VI reveals ortho/para ratios of over unity as are often observed.[13] One exception is the proton-catalyzed addition of PBA to *o*- and *p*-hydroxybenzaldehydes, affording an ortho/para ratio of 0.24, which would be due to the lower basicity of carbonyl oxygen of ortho isomer because of its intramolecular hydrogen bonding.[27]

One question still left to be explained by the above mechanism of rate-determining carbonyl addition is why *m*-ClPBA is more reactive than PBA for acid-catalyzed addition. This may be explainable by assuming a positive $\rho$ value for PBA in V as discussed below. The intermolecular hydrogen bonding of



$$\mathrm{Ph\overset{}{\underset{\underset{\displaystyle O}{\|}}{C}}OO\cdots H\cdots B}$$

V

peracid is well known[28] and general base catalysis for carbonyl addition is also well understood to increase with increasing basicity of B in V, *i.e.*, $\rho < 0$ for B.[29] The above assumption of $\rho > 0$ for PBA seems to us rather reasonable if the extent of proton transfer in-

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(24) A similar low slope has been reported without explanation for PBA oxidation of sulfoxides (R. Curci and G. Modena, *Tetrahedron Lett.*, 1749 (1963); 863 (1965); *Tetrahedron*, 22, 1227, 1235 (1966)) and for peroxide cleavage of benzils [H. Kwart and N. J. Wegemer, *J. Amer. Chem. Soc.*, 83, 2746 (1961)].

(25) The data are extrapolated to 100% water. On the average, a 3.5-fold increase in rate was observed in going from 40% ethanol (Table VI) to 100% water.

(26) F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 511, 512 (1971).

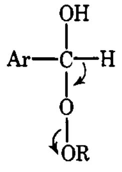
(27) A large chemical shift of hydroxyl proton comparable to that of $CF_3$ or CN groups has been reported for *o*-carbonyl phenols owing to intramolecular hydrogen bonding: M. T. Tribble and J. G. Traynham, *ibid.*, **91**, 379 (1969).

(28) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, **35**, 740 (1970).

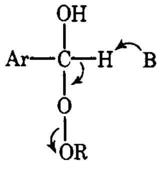
(29) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).

creases the nucleophilicity of peroxidic oxygen in V.[30] Thus, the extent of proton transfer should increase with increasing acidity of PBA's ($\rho > 0$) together with the increase in basicity in B ($\rho < 0$). Such a case has been actually reported for an amine-catalyzed addition of thiols to maleic anhydride.[31]

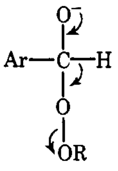
**Hydride and Aryl Migration.** Kinetic behavior for hydride migration are summarized below: (i) deuterium isotope effect of $k_H/k_D = 1.4$–$3.0$; (ii) insensitivity to proton or hydroxide ion catalysis (that is, there was observed neither acid catalysis up to 3 *M* perchloric acid nor hydroxide ion catalysis in a plot of log $k_{obsd}$ *vs.* pH; this shows uncatalyzed hydride migration); (iii) small effect of solvent polarity ($m \sim 0.1$). These clearly demonstrate the nature of hydride shift. That is, the value of $k_H/k_D$ is in the range of that of typical hydride shift,[32] and the relative independence on hydroxide ion also leads to the same conclusion (VIa). These are in sharp contrast with an amine-catalyzed decomposition of benzyl *tert*-butyl peroxide, where an E2-type reaction (VIb) was suggested on the basis of a large isotope effect ($k_H/k_D = 6$).[33] Two factors are responsible for the descrepancy between these decompositions: a large anchimeric assistance of $\alpha$ oxygen[34] in VIa and a large difference in acidities of the departing groups, benzoate and *tert*-butoxide ($\Delta pK_a \sim 15$). The latter seems to be a predominant factor since the carbonyl adducts of hydrogen peroxide or *tert*-butyl hydroperoxide are stable under these conditions.



VIa



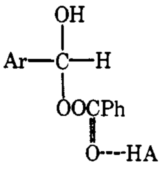
VIb



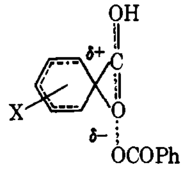
VIc

As discussed above, the pH-rate profiles of the product suggest that the hydride shift occurs more preferably *via* anion VIc at pH >8 than *via* the neutral adduct VIa. It is well known that $\alpha$-oxy anion accelerates hydride shift as a typical case of the Cannizzaro reaction,[35] and hence it is convincing that the apparent rate through VIc is faster than the rate *via* VIa in spite of probable order of $K_{II} < K_I$.[36]

Characteristic points of aryl migration in the B–V reaction are as follows: (i) an insensitivity to hydroxide ion catalysis; (ii) acid catalysis operative only at high acidity (the migration rate is not correlated with acidity function but proportional to [$HClO_4$], suggesting a general acid catalysis *via* the hydrogen-bonded complex (VIIa)); (iii) the considerable effect of solvent polarity ($m \sim 0.5$) as reported for aryl migration in peresters ($m = 0.4$–$0.5$),[37] which reflects a greater separation of charge in the transition state (VIIb). No observation of hydroxide ion catalysis in aryl migration (except hydroxyphenyl) is in contrast to the case of hydride shift. One explanation for this difference is that the transition state VIIb is stabilized almost solely by delocalization of the positive charge and not subject to the pushing effect of $\alpha$-oxy anion because of the instability of the three-membered ring, similar to the case of cyclopropyl anion. A similar argument has been noted for the 1,2 shift.[38]



VIIa



VIIb

**Migratory Aptitude and Ortho Effect.** The migration ratio (Ar/H) changes at pH ~8.5 owing to the change of the intermediate from II to I and then increases at higher acidity because of the acid catalysis in aryl migration. The same result has been reported for the reaction of *p*-methylbenzyl hydroperoxide; the ratio, *p*-tolyl/H, changes from *ca.* 1 for acid-catalyzed migration[39] to a very small value in the $OH^-$-catalyzed migration.[40] A similar increase in the ratio Ph/H with increasing acidity has been reported for pinacol rearrangement (from 0.04 to 7.33)[41] and also for the acid-catalyzed heterolysis of benzhydryl hydroperoxide (from 2.15 to 60).[7] These scattered results may all be summarized by the same feature that aryl migration is acid catalyzed more effectively than hydride shift.

The data in Table II afford the following migratory order for the B–V reaction at neutral and alkaline conditions: *o*- and *p*-$HOC_6H_4 \gg$ *o*-$MeOC_6H_4 >$ *p*-$MeOC_6H_4 > H >$ *o*-$MeC_6H_4 >$ *p*-$MeC_6H_4 \gg C_6H_5$. The order of $^-OC_6H_4 >> HOC_6H_4$ is sure,[42a] but the present observation does not give its magnitude. The order in an acidic solution is the same except for the reverse reactivity between *o*-$MeC_6H_4$ and H. These results show some salient features in the B–V reaction as discussed below.

First, the migratory aptitude in aryl migration affords a large substituent effect with a $\rho$ value of $-4$ to $-5$ ($\sigma^+$). In contrast, the reported $\rho$ values for B–V reactions are small, *e.g.*, $-1.1$ ($\sigma$)[9] and $-1.36$ ($\sigma^+$),[10] but these are based on the apparent rate constant and do not reflect directly the migration aptitude. The present large $\rho$ value for migration is comparable to the reported values for the rearrangements of other peroxides, *e.g.*, $-5.1$ ($\sigma$) for perester,[5] $-4.57$[6] and $-3.78$ ($\sigma^+$)[7] for hydroperoxides. It is rather convincing on

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[30] Of course, negative $\rho$ values should be more general for substituent effects in nucleophiles, but our opinion is that these are of less importance in measuring extent of proton transfer.

[31] B. Dmuchovsky, F. B. Zienty, and W. A. Vredenburgh, *J. Org. Chem.*, **31**, 865 (1966). Although these authors explained their data by ion pairing of thiols, an alternative explanation seems to be possible in terms of the extent of proton transfer as noted above.

[32] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1963, p 362.

[33] Reference 2, p 183; R. P. Bell and A. O. McDougall, *J. Chem. Soc.*, 1697 (1958).

[34] E. Hedaya and S. Winstein, *Tetrahedron Lett.*, 563 (1962); *J. Amer. Chem. Soc.*, **89**, 1661 (1967).

[35] E. S. Gould, "Structure and Mechanism in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 547.

[36] For example, a decrease in $K_{app}$ has been observed at pH > p*K* of RSH for the carbonyl addition equilibrium of RSH.[22]

[37] P. D. Bartlett and B. T. Storey, *J. Amer. Chem. Soc.*, **80**, 4954 (1958); P. D. Bartlett and T. G. Traylor, *ibid.*, **83**, 856 (1961); N. Y. Yablokova, V. A. Yablolov, and A. V. Badyanova, *Kinet. Katal.*, **8**, 49 (1967); *Chem. Abstr.*, **67**, 32147*c* (1967).

[38] G. A. Russell, ref 3, p 427.

[39] A. Rieche and F. Hitz, *Chem. Ber.*, **62**, 2458 (1929).

[40] E. J. Lorand and E. I. Edwards, *J. Amer. Chem. Soc.*, **77**, 4035 (1955).

[41] C. J. Collins, *ibid.*, **77**, 5517 (1955); C. J. Collins, W. J. Rainey, W. B. Smith, and I. A. Kaye, *ibid.*, **81**, 460 (1959).

[42] (a) For example, R. Baird and S. Winstein, *ibid.*, **85**, 567 (1963); (b) T. Yonezawa, H. Kato, and K. Fukui, *Nippon Kagaku Zasshi*, **87**, 26 (1966).

the basis of assuming a transition state such as VIIb that all these migrations in peroxides show a large $\rho$ value comparable to that of electrophilic aromatic substitution and can be correlated with $\sigma^+$.

The $\rho$ values for the substituent effect in PBA's (the leaving groups) are small, which are in contrast to the large negative $\rho$ values for benzaldehydes, the migrating groups. This difference is rather general in the peroxides rearrangements. For example, the substituent effect in the migrating group of cumyl benzoyl peroxides showed a large negative $\rho$ value of $-5.1$,[5] while that in the leaving group resulted in a moderate $\rho$ value of $+1.22$.[8b] An explanation is that the main driving force for the O–O heterolysis in peroxides is a weakening of the O–O bond induced by an attack of nucelophile on the lowest vacant orbital of the O–O bond,[42b] but not a lowering of the energy level of the antibonding orbital of the O–O bond by introducing electron-attracting substituents.

Second, electron-releasing ortho substituents facilitate aryl migration *ca.* 10 times as fast as the para isomer (Table II). This difference in reactivity results in $\sigma_o^+$ values greater than that of $\sigma_p^+$ by about 0.2 on the basis of an assumed $\rho$ value of $-5$; *i.e.*, $\sigma_o^+ \sim -1.0$ for *o*-MeO and $\sim -0.5$ for *o*-Me group. Similar treatment of *o*-Me has been reported to give $\sigma_o^+$ values of $-0.12$ and $-0.21$ for cumene and benzhydryl hydroperoxides.[7] Other $\sigma_o^+$ values reported are $-0.411$ for *p*-MeO and $-0.233$ for *o*-Me in a gas-phase pyrolysis,[43] where the proximity effect is not appreciable. As for the effect of ortho substituents, especially in reactions in solution, various theories have been discussed,[43,44] but no clear-cut explanation has yet been developed in our opinion. Hence, we note here only a presumption that the approximate value of $\sigma_o^+$, larger than $\sigma_p^+$ from the present B–V reaction, would not always be extraordinary, but rather reflect an intrinsic preponderance of ortho over para positions for the transmission of electronic effect. This explanation seems to be acceptable if we remember the high ortho/para ratios for aromatic hydroxylation with peracid (2.8 for anisole and 4.0 for toluene),[44] and that many other electrophilic substitutions for alkylbenzenes show considerable increase in the ortho/para ratios when going from the *tert*-Bu to the Me group.[44]

Third, the present study shows no steric retardation by ortho substituents in contrast to the reported retardation for B–V reaction of benzophenones[45] or pinacol rearrangements.[46] A larger migratory aptitude of *o*-$MeC_6H_4$ over Ph in hydroperoxide rearrangements was explained in terms of a small steric requirement both in the migration terminus and the origin.[7] However, the present B–V reaction of benzaldehydes resulted in the larger *o*-$MeC_6H_4$/Ph ratio of $\sim$10 than in the case of the hydroperoxide ($\sim$7) in spite of a larger leaving group, benzoate, than the latter, water. This clearly suggests that the steric requirement is rather small in these migrations to oxygen. The predominant steric factor for aryl migration seems to be on the migrating origin. That is, nonmigrating groups in the present B–V reaction are less bulky hydrogen and hydroxyl on the migrating origin, while the more bulky groups are attached to the origin in other reactions, *i.e.*, phenyl and hydroxyl in the B–V reaction of benzophenone,[45] hydrogen, phenyl,[7] and two methyl groups[6] in the hydroperoxide rearrangement. Another typical example for steric retardation of nonmigrating groups is the very low migratory aptitude of *o*-$MeOC_6H_4$, less by a factor of $10^{-3}$ that of *p*-$MeOC_6H_4$, in the pinacol rearrangement.[47]

## Experimental Section

**Materials.** Perbenzoic acids were prepared by the reaction of benzoyl peroxides or chlorides with $H_2O_2$ and recrystallized from *n*-hexane.[48] Tolualdehydes were synthesized from the corresponding benzyl bromides by nitric acid ($\sim$1.5 *M*) and oxidized in $\sim$50% dioxane at 90° for 2 hr.[49] Benzaldehydes were purified by distillation or by recrystallization. Substituent and boiling point are as follows: *o*-MeO,[50] 130.5–131.0° (25 mm); *p*-Me, 109–110° (38 mm); *o*-Me, 108° (42 mm); *o*-Cl, 112.5–113.0° (37 mm); *o*-$NO_2$,[51] 107–110° (3 mm); and other aldehydes are described previously.[11] Benzaldehyde-*1-d* and anisaldehyde-*1-d* were obtained by the method of Schaefer. *et al.*,[52] and their per cent deuterium was determined by nmr[53] to be 88.7 ± 0.4 and 89.8 ± 0.2%, respectively.

**Rates and Products.** The B–V reaction of benzaldehydes with PBA was carried out in 40 vol % ethanol containing $1 \times 10^{-4}$ *M* of EDTA to minimize catalytic decomposition of PBA.[54] The rate was followed by iodometry of the peracid and/or by uv spectroscopy of the aldehyde. Both methods gave the similar rate data except for the reaction near pH 8 where the simultaneous decomposition of peracid is apparent.

The produced acids and phenols were determined by uv spectrophotometry or by glc as described previously.[11]

**Carbonyl Addition of Hydrogen Peroxide.** Equilibrium constants for the $H_2O_2$ addition to benzaldehydes were determined in 40% ethanol at 25° by the uv method.[14] The constants varied slightly with the wavelength used and approximate values are listed in the last column of Table I.

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(43) G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *J. Org. Chem.*, **34**, 2070 (1969).

(44) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965, p 113.

(45) W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, 77, 4679 (1955).

(46) Y. Pocker, ref 3, p 22.

(47) D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 266; T. Matsumoto, R. Goto, T. Asano, and T. Asano, *Nippon Kagaku Zasshi*, **87**, 1076 (1966).

(48) Y. Ogata and Y. Sawaki, *Tetrahedron*, **23**, 3327 (1967).

(49) Y. Ogata, Y. Sawaki, H. Tezuka, and F. Matsunaga, *Kogyo Kagaku Zasshi*, **69**, 901 (1966).

(50) R. N. Icke, C. E. Redemann, B. B. Wisegarver, and G. A. Alles, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 564.

(51) T. Nishimura, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 713.

(52) J. P. Schaefer, B. Horvath, and H. P. Klein, *J. Org. Chem.*, **33**, 2647 (1968).

(53) Similar data of per cent deuterium were also obtained by mass spectroscopy. We are grateful to Mr. M. Sugiura for measuring the mass spectra.

(54) E. Koubeck, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Amer. Chem. Soc.*, **85**, 2263 (1963).