

Reactivity of Peroxomonophosphoric Acid in the Oxidation of Benzaldehydes and Dimethyl Sulfoxide in Aqueous Ethanol¹⁾

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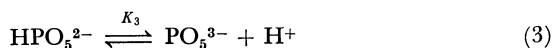
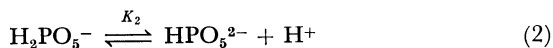
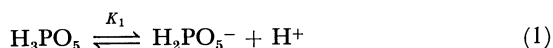
Oxidation of benzaldehydes and dimethyl sulfoxide with peroxomonophosphoric acid (PMPA) has been studied in 40% aqueous EtOH in order to examine the reactivity of undissociated and dissociated PMPA in comparison with that of peroxycarboxylic acid. The reactivity for DMSO was in the order $\text{RCO}_3^- > \text{H}_3\text{PO}_5 > \text{H}_2\text{PO}_5^- > \text{RCO}_3\text{H} > \text{HPO}_5^{2-}$. As in the peroxycarboxylic acid oxidation, PMPA oxidation of substituted benzaldehydes afforded phenols by aryl migration and benzoic acids by hydride migration. The product ratio changed with substituents and pH; salicylaldehyde (*o*-HO) gave only catechol by aryl migration, while *p*-chloro- and unsubstituted benzaldehydes afforded benzoic acids predominantly. The oxidation of aldehydes bearing *p*-MeO and *p*-Me was a borderline case and the migratory ratio of $\text{Ar}\sim/\text{H}\sim$ was higher at lower pH, *i.e.*, the order being $\text{H}_3\text{PO}_5 > \text{H}_2\text{PO}_5^- > \text{HPO}_5^{2-}$. The substituent effect in the apparent k_{obsd} values was very small (*i.e.*, $\rho \approx 0$), but the effect for aryl migration ($k_{\text{Ar}\sim}$) estimated from product selectivity gave $\rho = -2.88$ (σ). The rate for hydride migration ($k_{\text{H}\sim}$) resulted in $\rho = 1.7$ and 2.0 (σ). Reactivity of PMPA in each dissociated form was compared with that of RCO_3H .

Peroxomonophosphoric acid (PMPA) has been known for a long time,²⁾ but its reactivity has not been clarified. Its decomposition³⁾ and reactions with bromide⁴⁾ and iodide ions⁵⁾ were studied kinetically. Reports have been given on PMPA oxidation of organic substances, including the hydroxylation of aromatic rings,⁶⁾ the Baeyer-Villiger (B-V) reaction of acetophenones,⁷⁾ the epoxidation of *trans*-stilbene,⁸⁾ and the oxidation of tertiary amines.⁹⁾

PMPA is a tribasic acid having three dissociated forms.¹⁰⁾ We were interested in the reactivity of each form of PMPA as well as in their possibility as an oxidant with bifunctional catalysis since phosphoric acid is known as such a catalyst.¹¹⁾ The reaction of PMPA is also of interest from a biochemical standpoint, since PMPA might be produced by perhydrolysis of pyrophosphoric acids¹²⁾ with oxygen species such as H_2O_2 or O_2^- .¹³⁾ When we had almost completed our experiment a kinetic study on the PMPA oxidation of benzaldehydes was reported,¹⁴⁾ the conclusion of which differing from ours.

Results and Discussion

Peroxomonophosphoric acid (PMPA) dissociates into three forms, affording $\text{p}K_1 = 1.1$, $\text{p}K_2 = 5.2$, and $\text{p}K_3 = 12.7$ in water.¹⁰⁾ Oxidation of dimethyl sulfoxide



(DMSO) and benzaldehydes with PMPA was carried out in the presence of 0.4 mM EDTA in 40% aqueous ethanol at 25 °C. The decrease of PMPA was monitored by iodometric titration in 5% AcOH; its spontaneous decomposition was very slow in the absence of added substrates. Products were determined by GLC directly or after methylation with dimethyl sulfate for phenols or with diazomethane for carboxylic acids.

Oxidation of DMSO. Dimethyl sulfoxide was easily oxidized to sulfone in over 90% yield based

on PMPA consumed. The oxidation follows the second-order rate equation (Eq. 4). The pH-rate profile

$$v = k_{\text{obsd}}[\text{PMPA}][\text{Substrate}] \quad (4)$$

is shown in Fig. 1. The resulting second-order rate constant are 210, 45, and $1.2 \text{ M}^{-1} \text{ s}^{-1}$ for H_3PO_5 , H_2PO_5^- , and HPO_5^{2-} , respectively. The kinetically determined $\text{p}K_1$ and $\text{p}K_2$ values for PMPA in 40% EtOH are 1.6 and 4.6, respectively, close to the reported $\text{p}K_a$ values 1.1 and 5.2, respectively, in water.¹⁰⁾ The difference of *ca.* 0.5 might be partly due to the solvent effect on $\text{p}K_a$ of PMPA.

The Baeyer-Villiger Oxidation of Benzaldehydes. Products. Products from the B-V oxidation of benzaldehydes with PMPA vary with substituents and pH (Table 1). Salicylaldehyde with strong electron-releasing *o*-HO afforded only catechol by aryl migration. The relatively low yields (*i.e.*, 65–75%) of catechol can be ascribed to further oxidation by PMPA. The other aldehydes resulted in the simultaneous formation of phenols by aryl migration and benzoic acids by hydride migration.



We see from Table 1 that the aryl migration is facilitated by an increase in electron-releasing power of ring substituents and by a decrease of pH. Higher pH and electron-attracting groups favor the hydride

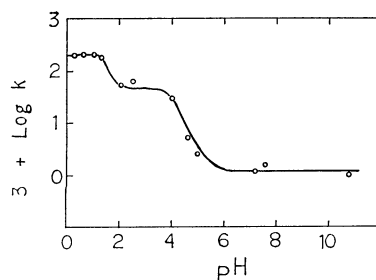


Fig. 1. The pH-rate profile for the PMPA oxidation of DMSO in 40% aqueous EtOH at 25 °C.

TABLE 1. PRODUCTS (%) FROM THE B-V REACTION OF SUBSTITUTED BENZALDEHYDES BY PMPA^{a)}

Substituent	pH 1.3		pH 4.0		pH 7.3		pH 10	
	ArCO ₂ H	ArOH	ArCO ₂ H	ArOH	ArCO ₂ H	ArOH	ArCO ₂ H	ArOH
<i>o</i> -HO	0	65	0	72	0	75	0	73
<i>p</i> -MeO	0	74	2	78	7	45	23	21
<i>p</i> -Me	22	63	42	8	45	4	49	1
H	75	14	83	0	98	0	81	0
<i>p</i> -Cl	61	3	85	0	72	0.4	72	1

a) Reaction with 0.04 M each of H₃PO₅ and ArCHO in 40% EtOH at 25 °C. % Yields are based on the aldehyde consumed and determined by GLC after methylation with dimethyl sulfate for phenols or with diazo-methane for carboxylic acids.

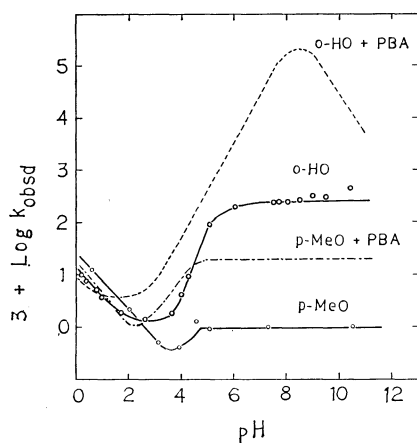
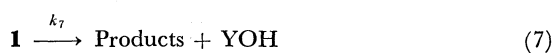
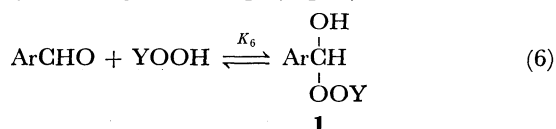


Fig. 2. pH-rate profiles for the PMPA oxidation of substituted benzaldehydes in 40% EtOH at 25.0 °C. The dotted lines are plots for perbenzoic acid (PBA) oxidation from Ref. 15. The solid line for *o*-HO is calculated according to the rate data in Table 3.

migration leading to carboxylic acids. The trend is similar to that of the B-V oxidation with perbenzoic acid (PBA).¹⁵⁾

Mechanism. In case of the PBA oxidation of salicylaldehyde the rate-determining step is the addition of PBA to C=O.¹⁵⁾ Since the pK_a values of the aldehydes and PBA are 8.45 and 8.5, respectively, in 40% EtOH,¹⁵⁾ the pH-rate profile gives a bell-shaped curve (dotted line, Fig. 2). The oxidation with PMPA afforded a similar profile (Fig. 2); the observed slopes of *ca.* -0.5 at pH < 2 suggest an acid-catalysis, while horizontal lines at pH 5–10 indicate no catalysis by H⁺ or HO⁻. If the addition of PMPA to C=O were rate-limiting, the rate should slow down at pH above 9 on the basis of the dissociation of salicylaldehyde, which was not the case. This is in contrast to the PBA case, suggesting that the addition to C=O is not rate-determining. The rate is determined by the migration step (Eq. 7). Here, YOOH



is H₃PO₅, H₂PO₅⁻, or HPO₅²⁻. In the neutral region, the most prevalent species is H₂PO₅⁻, so that the

TABLE 2. SUBSTITUENT EFFECT ON THE B-V REACTION OF BENZALDEHYDES WITH PMPA IN 40% EtOH AT 25.0 °C^{a)}

Substituent	10 ³ <i>k</i> /M ⁻¹ s ⁻¹			
	pH 1.3	pH 4	pH 7.3	pH 10
A) Observed second-order rate constant (<i>k</i> _{obsd}) ^{b)}				
<i>p</i> -MeO	13.9 (2.1) ^{c)}	0.43 (9) ^{c)}	1.08 (13) ^{c)}	0.93 (13) ^{c)}
<i>p</i> -Me	8.6	0.35	0.49	0.98
H	8.0	0.39	0.45	1.17
<i>p</i> -Cl	10.1 (4.4) ^{c)}	0.98 (14) ^{c)}	1.22 (18) ^{c)}	0.97 (220) ^{c)}
B) Rates for aryl migration (<i>k</i> _{Ar~}) ^{d)}				
<i>p</i> -MeO	10.3	0.33	0.49	0.19
<i>p</i> -Me	5.4	0.028	0.020	0.014
H	1.2	0	≈ 0	≈ 0
<i>p</i> -Cl	0.27	0	0.004	0.01
ρ (<i>vs.</i> σ)	-2.88	^{e)}	^{e)}	^{e)}
C) Rates for hydride migration (<i>k</i> _{H~}) ^{d)}				
<i>p</i> -MeO	0	0.010	0.075	0.22
<i>p</i> -Me	1.9	0.15	0.22	0.48
H	5.9	0.33	0.44	0.95
<i>p</i> -Cl	6.2	0.83	0.87	0.70
ρ (<i>vs.</i> σ)	^{e)}	1.74	<i>ca.</i> 2.0	^{e)}

a) Reaction with 0.01–0.05 M each of benzaldehyde and PMPA. b) Observed rate constant determined iodometrically. c) For comparison, the *k*_{obsd} values for PBA (Ref. 17) are shown in parentheses. d) Rate constants for aryl or hydride migration obtained by dividing *k*_{obsd} values by product selectivities in Table 1. e) Numbers of data were too small, the correlation being poor.

departing group YOH from **1** is H₂PO₄⁻ (pK_a = 7.2), which is significantly less potent as a departing group than benzoic acid (pK_a = 4.2) in the PBA oxidation. The rate of rearrangement of **1** (*i.e.*, *k*₇) is then substantially lowered, leading to the establishment of preequilibrium 6 for the PMPA case.

The PMPA oxidation of *p*-anisaldehyde (*p*-MeO) is substantially slower than that of salicylaldehyde at pH > 3, but slightly faster at pH < 2 (Fig. 2). The rates for the other aldehydes are similar to that of anisaldehyde, the *k*_{obsd} values not varying with substituent, *i.e.*, $\rho \approx 0$ (Table 2-A). It can be assumed that the ρ value for *K*₆ is close to the ρ value of 1.6

TABLE 3. COMPARISON OF THE REACTIVITIES OF PMPA AND PEROXYCARBOXYLIC ACID TOWARD VARIOUS SUBSTRATES

Oxidant YOOH	pK _a of YOH ^{b)}	Second-order rate constant, 10 ³ k/M ⁻¹ s ^{-1a)}					
		I ⁻ c)	Br ⁻ d)	Stilbene ^{e)}	DMSO	<i>o</i> -HOC ₆ H ₄ CHO	PhCOMe ^{f)}
Mechanism ^{g)}		one	one	one	one	two	two
Solvent		H ₂ O	H ₂ O	dioxane	40% EtOH	40% EtOH	MeCN
H ₃ PO ₅	2.1	2 × 10 ⁶	8 × 10 ³	0.11	210	≈ 1 ^{h)}	2.9
H ₂ PO ₅ ⁻	7.2	6 × 10 ⁴	32		45	≈ 1	
HPO ₅ ²⁻	12.7	4 × 10 ²			1.2	230	
PhCO ₃ H	4.2	3 × 10 ⁶	3 × 10 ²	0.20 ⁱ⁾	26	5	0.015 ^{j)}
PhCO ₃ ⁻					(330) ^{j)}	1 × 10 ⁶	

a) Rate constant at 25 °C. b) The pK_a of parent acid in water. c) Ref. 5. d) J. O. Edwards, "Peroxide Reaction Mechanism," Interscience, New York (1962), p. 73. e) Ref. 8. f) Ref. 7. g) One: one-step electrophilic oxidation. Two: two-step reaction involving an addition and a rearrangement step. h) Rate constant for the acid catalysis at pH < 1 is $k_H = 9 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$, obtained from a rate equation: $v = k_H [\text{HClO}_4][\text{aldehyde}] \times [\text{PMPA}]$. i) Peracetic acid. j) Nucleophilic oxidation of sulfoxide *via* two-step reaction.

(σ) for the H₂O₂ addition (Y=H, Eq. 6).¹⁵⁾ The apparent zero value of ρ for k_{obsd} might be due to the cancellation, since $k_{\text{obsd}} = k_7 K_6$, between a positive ρ value for K_6 and a negative ρ value for k_7 . Negative ρ values for aryl and hydride migration are well known.¹⁵⁻¹⁷⁾ Such a cancellation is often observed in reactions involving carbonyl addition.¹⁸⁾

A mechanism was postulated for the PMPA oxidation of benzaldehydes, which involves a rate-determining attack of PMPA on benzaldehyde hydrates, ArCH(OH)₂.¹⁴⁾ However, the scheme is questionable. (i) No reaction is known in which the nucleophilic attack on tetrahedral carbons such as aldehyde hydrate is much faster than that on free aldehyde ArCHO. (ii) Benzaldehydes exist essentially as free aldehydes ArCHO under these conditions of aqueous EtOH; an exception is *p*-nitrobenzaldehyde, where 20% of the aldehyde exists as its hydrated form.¹⁹⁾ Likewise, the addition equilibrium of HO⁻ instead of H₂O shifts to the free ArCHO rather than to the adduct ArCH(OH)O⁻ at pH < 14.²⁰⁾ Thus the C=O addition scheme is favorable, since both concentration and reactivity of the free aldehydes are much higher than those of the hydrates.

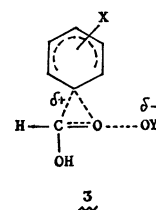
Polybasic acids such as phosphoric acid are sometimes effective as a bifunctional catalyst.¹¹⁾ We intended to examine such a possibility in the addition to C=O, *e.g.*, an intermolecular acid-catalysis (2a) or an intramolecular base-catalysis (2b). However,



the addition to C=O was not rate-determining even in the case of salicylaldehyde with the most facile migratory aptitude; no such catalysis could be examined.

Aryl and Hydride Migration. Although the k_{obsd} values in Table 2-A are little affected by substituents (*i.e.*, $\rho \approx 0$), interesting results for the relative migratory aptitudes were obtained by multiplying the k_{obsd} values by products selectivities in Table 1. The aryl

migration (k_{Ar}) at pH 1.3 affords $\rho = -2.88$ (σ) (Table 2-B). Similar results ($\rho = -2.55$ *vs.* σ) are known for the PMPA oxidation of acetophenones.⁷⁾ These correlations are in contrast to the σ^+ correlation for the B-V reaction with PBA.^{15,16)} The difference might be due to the fact that in the rearrangement of **1** at pH < 2 the departing phosphoric acid (pK_a = 2.1) is a much stronger acid than benzoic acid (pK_a = 4.2). The loosening of O-O bond in the PMPA oxidation is relatively weak, and hence the developing cationic charge (δ^+) in **3** is much lower than in the



PBA case. The interpretation seems to be in line with the observed high rate ratios of *p*-MeO/*p*-Me for the reaction at pH 4 (*i.e.*, H₂PO₅⁻) and pH 7 or 10 (*i.e.*, HPO₅²⁻), suggesting a σ^+ correlation. Since H₂PO₄⁻ (pK_a = 7.2) and HPO₄²⁻ (pK_a = 12.7) are much less potent departing groups as compared with H₃PO₄, the cationic charge in **3** increases leading to the σ^+ correlation at pH > 4. High rate ratios of *p*-MeO/*p*-Me correspond to a σ^+ correlation, small ratios giving rise to σ correlation.

On the other hand, Hammett's equation for the hydride shift gives $\rho = 1.74$ (pH 4) and 2.0 (pH 7.3) with σ correlation (Table 2-C). The same reaction with PMPA in the presence of 0.2 M NaOH gives a ρ value 1.27 (σ) in water.¹⁴⁾ These ρ values are close to 1.6 (σ) for the addition equilibrium of H₂O₂ (Eq. 6).¹⁵⁾ Since $k_{\text{obsd}} = k_7 K_6$, the net ρ value for the hydride shift (*i.e.*, k_7) might be close to zero. Similar ρ values of 1.1–1.8 were obtained at pH 1–12 in the PBA oxidation of benzaldehydes affording hydride shift,¹⁷⁾ which is rather insensitive to acid and base catalysis.¹⁵⁾ The same might be the case for the PMPA oxidation.

Comparison with Peroxycarboxylic Acid. The reac-

tivity of PMPA was compared with that of peroxy-carboxylic acids (Table 3). In one-step electrophilic oxidation, relative reactivities of PMPA and RCO_3H change with substrate. For example, the relative reactivity in the oxidation of bromide ion differs from the corresponding order for iodide ion. The rate order for olefin epoxidation is $\text{RCO}_3\text{H} \geq \text{H}_3\text{PO}_5^{(8)}$ that for the oxidation of DMSO , $\text{H}_3\text{PO}_5 > \text{H}_2\text{PO}_5^- > \text{RCO}_3\text{H} > \text{HPO}_5^{2-}$. The DMSO oxidation with RCO_3^- is of a different mechanism and excluded from the comparison; the alkaline reaction involves two steps, a nucleophilic addition to sulfoxide and its decomposition to sulfone and carboxylate ion,⁽²¹⁾ just as the B-V reaction.

The relative reactivity for the B-V reaction also changes with substrates and pH (Fig. 2, Table 2-A, and Table 3). The rate order for the B-V reaction of benzaldehydes at pH 3–10 is $\text{RCO}_3\text{H} > \text{PMPA}$, but changes to the order $\text{PMPA} > \text{RCO}_3\text{H}$ at the lower pH. This is due to the higher sensitivity of PMPA to acid-catalysis as compared with that of RCO_3H .

Experimental

GLC analysis was performed with a Yanagimoto 550F gas chromatograph using a column of PEG 20 M on Chromosorb (1 m).

Materials. Peroxomonophosphoric acid (PMPA) was prepared from P_2O_5 and 90% H_2O_2 .⁽⁹⁾ Commercial benzaldehydes were used.

Typical Procedure. The reaction with 0.04 M each of PMPA and benzaldehyde was carried out in 40 vol % EtOH at 25.0 °C. EDTA (0.4 mM) was added to minimize a metallic ion-catalyzed decomposition of PMPA. The pH of solution was maintained with perchloric acid ($\text{pH} < 1$), 0.5 M acetate ($\text{pH} 2.5\text{--}4.4$), 0.5 M phosphate ($\text{pH} 3.7\text{--}6.1$), and 0.5 M carbonate buffers ($\text{pH} 7.5\text{--}10$). The pH values were determined with a glass electrode before and after the reaction. The decrease of PMPA was monitored by iodometric titration in 5% aqueous AcOH. The spontaneous decomposition of PMPA was very slow in the absence of substrate added. Reproducibility of the oxidation kinetics was ascertained to be adequate (*i.e.*, within $\pm 5\%$).

Reaction products were determined by means of GLC directly or after methylation with diazomethane using biphenyl or propiophenone as an internal standard. Catechol was determined after methylation with dimethyl sulfate.

References

- 1) Contribution No. 283.
- 2) a) J. Schmidlin and P. Massini, *Chem. Ber.*, **43**, 1102 (1910); b) G. Toennies, *J. Am. Chem. Soc.*, **59**, 555 (1937).
- 3) E. Koubek, M. L. Hagget, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyrun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963).
- 4) D. H. Fortum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 778 (1960).
- 5) F. Secco and M. Venturini, *J. Chem. Soc., Dalton Trans.*, **1976**, 1410.
- 6) Y. Ogata, I. Urasaki, K. Nagura, and N. Satomi, *Tetrahedron*, **30**, 3021 (1974).
- 7) Y. Ogata, K. Tomizawa, and T. Ikeda, *J. Org. Chem.*, **43**, 2417 (1978).
- 8) Y. Ogata, K. Tomizawa, and T. Ikeda, *J. Org. Chem.*, **44**, 2362 (1979).
- 9) Y. Ogata, K. Tomizawa, and T. Morikawa, *J. Org. Chem.*, **44**, 352 (1979).
- 10) C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, **4**, 552 (1965).
- 11) Y. -N. Lee and G. L. Schmir, *J. Am. Chem. Soc.*, **101**, 6277 (1979), and references cited therein.
- 12) E. E. Conn and P. K. Stumpf, "Outlines of Biochemistry," 4th ed, John Wiley & Sons, Inc., New York, N. Y. (1976), Chaps. 6 and 14.
- 13) The perhydrolysis of acid anhydrides or chlorides with H_2O_2 is very facile to afford peroxy-carboxylic acids; Y. Ogata and Y. Sawaki, *Tetrahedron*, **23**, 3327 (1967).
- 14) G. P. Panigrahi and R. Panda, *Bull. Chem. Soc. Jpn.*, **52**, 3084 (1979).
- 15) Y. Ogata and Y. Sawaki, *J. Am. Chem. Soc.*, **94**, 4189 (1972).
- 16) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **37**, 2953 (1972).
- 17) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **34**, 3985 (1969).
- 18) For example, Y. Ogata and A. Kawasaki, "The Chemistry of the Carbonyl Group," ed by J. Zabicky, Interscience Publishers, London (1970), Vol. 2, p. 42.
- 19) J. M. Sayer, *J. Org. Chem.*, **40**, 2545 (1975).
- 20) a) W. J. Bover and P. Zuman, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 786; b) W. J. Bover and P. Zuman, *J. Am. Chem. Soc.*, **95**, 2531 (1973).
- 21) R. Curci and G. Modena, *Tetrahedron*, **22**, 1227, 1235 (1966).