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Peroxy Acid Oxidations. II.† A Kinetic and Mechanistic Study of Oxidation of α-Diketones

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The kinetics of Baeyer-Villiger oxidation of biacetyl and benzil by peroxomonophosphoric acid and peroxomonosulfuric acid have been studied in different pH ranges at 308 K. The reactions are second order; first order each in peroxy acid and in diketone concentrations at constant pH. The oxidation rate is strongly pH-dependent; the rate increases with increase in pH. From the pH-rate data the reactivity of different peroxo species, in the oxidation, has been determined. A mechanism consistent with rate-determining nucleophilic attack of peroxo species on carbonyl carbon of the diketone molecule has been proposed. Acetic acid and benzoic acid are respectively found to be the products of oxidation of biacetyl and benzil.

Oxidation of α-diketones by peroxidic reagents[1)] have been reported to yield carboxylic acids. These reactions are known to involve the intermediary formation of anhydrides which on hydrolysis yield corresponding carboxylic acids. In the reaction[2)] of benzil with H_2O_2, in benzene, Leffler isolated benzoic anhydride, which gave benzoic acid on hydrolysis. The first kinetic study on the oxidation of benzils by peracetic acid in the presence of H_2SO_4 was reported by Furuya et al.[3)] They described this reaction as a sort of Baeyer-Villiger reaction; both the acid-catalyzed and uncatalyzed oxidations have been discussed. Foote and Sawaki,[4)] in the oxidation of benzil by alkaline H_2O_2, have ruled out the dioxetane and epoxide mechanisms basing on high energy requirements, product and isotopic studies; the acyclic Baeyer-Villiger type mechanism was supported.

Although peroxomonophosphoric acid and peroxomonosulfuric acid are known to be potential Baeyer-Villiger reagents, there have been only a few reports on the oxidation of carbonyl compounds using these peroxy acids. Recently we reported our studies[5)] on the oxidation of acetylacetone by peroxomonophosphoric acid in alkaline pH.

As part of an effort to study the oxidation of dicarbonyl compounds by peroxy acids, we wish to report here the kinetic studies on the Baeyer-Villiger oxidation of α-diketones by peroxomonophosphoric acid (PMPA) and peroxomonosulfuric acid (PMSA) in aqueous and in aqueous-acetonitrile solution of different pH. The study has enabled us to estimate the relative reactivities of different peroxo species.

It is of interest that the pH dependence of the oxidation rate is quite contrary to that observed in the acetylacetone oxidation[6)] in acid pH.

Experimental

PMPA solutions were prepared by acid hydrolysis[7,8)] of $K_4P_2O_8$. The potassium salt of Caro's acid, oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), was obtained from Dupont Chemical Co., U. S. A., and was used to prepare PMSA solutions. All other chemicals used were of AnalaR grade. Biacetyl (Riedel) was distilled just before use (bp 89—91 °C). Benzil was prepared by means[9)] of benzoin obtained from benzaldehyde, and was recrystallized from ethanol, mp 94 °C (lit, mp 94—96 °C). Acetonitrile was distilled over P_2O_5 (bp 80—82 °C). Sodium perchlorate, prepared in situ by neutralizing perchloric acid with carbonate-free sodium hydroxide, was used for adjusting ionic strength of the medium. All the solutions were prepared in doubly distilled water, the second distillation being from $KMnO_4$. Acidity of the solution was maintained by adding calculated amounts of $HClO_4$ or standard buffers. Measurements of pH were made on a Systronics Digital pH Meter 335.

The kinetics was followed by measuring the rate of disappearance of peroxy acid, the estimation of which was made iodometrically using standard thiosulfate; PMPA estimation was done in an acetate buffer of pH 4—5 with a drop of ammonium molybdate solution.[10)] The observed second-order rate constant (k_2' obs) was calculated by dividing pseudo-first-order rate constant with respect to peroxy acid disappearance by the substrate concentration. The rate constants were reproducible to ±5%. The self-decomposition of PMPA or PMSA was found to be either nil or negligibly small under our experimental conditions. The temperature was constant to within ±0.1 °C. Computations were done with a DCM Micro System 1121.

Product Study. A solution of PMSA (1.2×10^{-4} mol) in water (10 ml) was added to a solution of benzil (5×10^{-4} mol) in acetonitrile (10 ml). Before the addition was started the pH was adjusted to 10. The reaction mixture was allowed to stand for 12 h at room temperature. It was then poured into water (100 ml) and acidified with dil HCl. The product extracted with chloroform was identified as benzoic acid (mp 122 °C).

In the oxidation of biacetyl, the product acetic acid was detected by spot tests.[11)]

The stoichiometry of the PMSA-biacetyl reaction with excess PMSA over biacetyl was determined by estimating the left over PMSA when the reaction was complete (PMSA= 27.5×10^{-4} mol dm^{-3}, biacetyl=9.84×10^{-4} mol dm^{-3}, pH= 4.08, 308 K). The biacetyl: PMSA ratio for the reaction was found to be 0.91. The overall reaction can, hence, be represented as,

$$HSO_5^- + CH_3COCOCH_3 + H_2O \rightarrow 2CH_3COOH + HSO_4^-.$$

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†Part I, Ref. 5.

Results and Discussion

The kinetics of oxidation of biacetyl and benzil by peroxomonophosphoric acid and by peroxomonosulfuric acid have been investigated at 308 K. The reactions, at constant pH and ionic strength, I, were shown to exhibit second-order kinetics; first order each in peroxy acid concentration and in diketone concentration (Tables 1 and 2), the rate law being,

$$\text{Rate} = k_2' \,[\text{Peroxy acid}]_t\, [\text{Diketone}],$$

where k_2' is the observed second-order rate constant and 't' denotes total concentration.

The rate was not influenced by ionic strength. Addition of acrylamide also had no effect on the oxidation rate (Tables 1 and 2).

The kinetics of oxidation of biacetyl and benzil by PMPA have been investigated in the pH ranges 0—5.5 and 7.2—11 respectively, and that by PMSA in the pH ranges 0.3—4 and 5—9.7. The influence of pH on the oxidation rate are presented in Tables 3 and 4, and shown in Fig. 1.

It is observed, in both PMPA and PMSA reactions with biacetyl, that variation of pH in the lower range (0—1.3 in PMPA and 0—0.7 in PMSA oxidation) did not significantly change the rate. However, the rate increased linearly with pH in the range 2.1—5.5 in PMPA oxidation, and 1—4 in PMSA oxidation. Such an observation is quite contrary to that made in the oxidation of acetylacetone,[6] a β-diketone, by PMPA in the pH range 0.4—7.75, where the rate first decreased with increase of pH in the range 0.4—3, and then increased (pH range 4—7.75).

In case of benzil, the rate (in both PMPA and PMSA oxidations) increased with increase of pH. The reactions were instantaneous at pH values higher than the

Table 1. Oxidation of Biacetyl by Peroxomonophosphoric Acid[a)]

10^3[diketone] mol dm^{-3}	10^4[PMPA] mol dm^{-3}	$10^3\,k'_2$[b)] dm^3 mol^{-1} s^{-1}
5.01	7.51	14.3
9.82	8.88	16.8
20.0	7.51	16.2
10.9	2.29	18.4
10.9	10.7	15.6
10.3	6.10	14.7[c)]
10.3	5.89	15.7[d)]
11.2	6.03	15.9[e)]

a) [H$^+$]=0.1 mol dm^{-3}, I=0.3 mol dm^{-3}, aqueous, 308 K. b) Observed second-order rate constant. c) I=0.15 mol dm^{-3}. d) I=0.5 mol dm^{-3}. e) [Acrylamide]= 5.0×10^{-3} mol dm^{-3}.

Table 2. Oxidation of Biacetyl by Peroxomonosulfuric Acid[a)]

10^3[diketone] mol dm^{-3}	10^4[PMSA] mol dm^{-3}	$10^3\,k'_2$ dm^3 mol^{-1} s^{-1}
11.0	3.85	27.0
10.5	5.47	26.4
10.2	11.6	27.0
10.6	28.1	32.2
7.07	6.09	26.9
10.5	5.47	26.4
22.1	5.9	28.6
40.9	5.76	31.8
10.5	5.72	27.5[b)]
10.5	5.29	33.3[c)]
10.5	5.24	44.6[d)]

a) [H$^+$]=0.1 mol dm^{-3}, I=0.3 mol dm^{-3}, aqueous, 308K, b) I=0.2 mol dm^{-3}, c) I=0.5 mol dm^{-3}, d) I=0.5 mol dm^{-3}.

Table 3. Oxidation of Biacetyl by Peroxy Acids: Effect of pH[a)]

Peroxy acid	pH	$10^2\,k'_2$ dm^3 mol^{-1} s^{-1}	$10^2\,k'_2$(calcd) dm^3 mol^{-1} s^{-1}
PMPA	0.7	1.78	2.49
	1.0	1.68	3.88
	1.3	1.66	5.40
	2.11	2.20	8.42
	2.78	5.19	11.0
	3.53	20.1	22.5
	3.64	24.7	26.5
	4.38	137	99.3
	4.85	212	235
	5.47	300	557
PMSA	0.3	2.05	2.01
	0.7	2.02	2.29
	1.0	2.64	2.77
	1.3	4.47	3.72
	1.6	8.17	5.62
	1.83	8.87	11.3
	3.08	124	116
	4.08	765	1145

a) Aqueous, I=0.3 mol dm^{-3}, 308 K.

Table 4. Oxidation of Benzil by Peroxy Acids: Effect of pH[a)]

Peroxy acid	pH	$10^2\,k'_2$ dm^3 mol^{-1} s^{-1}	$10^2\,k'_2$(calcd) dm^3 mol^{-1} s^{-1}
PMPA	7.19	0.419	0.716
	7.94	0.864	0.90
	8.25	2.15	1.12
	10.02	27.5	27.5
	10.96	89.5	232
PMSA	5.03	0.50	1.47
	6.07	2.71	2.79
	6.8	9.94	9.12
	7.05	14.1	15.1
	7.1	20.7	16.8
	9.5	1101	1757
	9.7	1660	2063

a) CH_3CN: water=40 : 60 (v/v), I=0.2 mol dm^{-3}, 308 K.

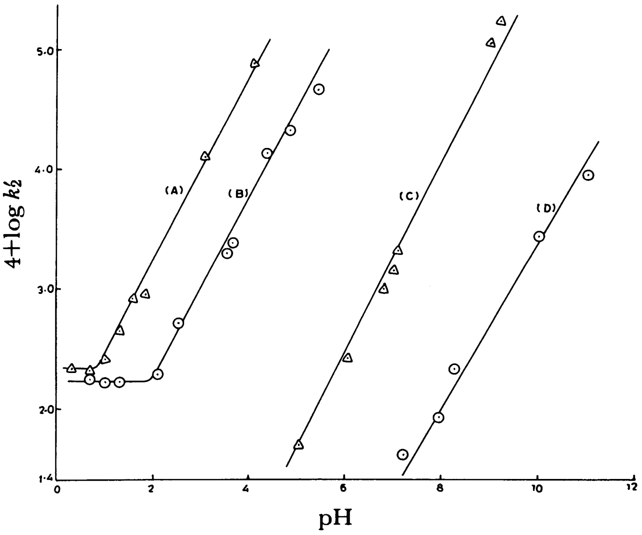


Fig. 1. Plots of $\log k_2'$ vs. pH.
A; PMSA-biacetyl, B; PMPA-biacetyl, C; PMSA-benzil, D; PMPA-benzil.

reported range.

Our attempt to collect a few kinetic runs with H_2O_2 in the presence of H^+, for comparison purpose, was frustrated owing to no definite kinetic order with respect to H_2O_2 disappearance.

PMPA is a tribasic acid having the following dissociation equilibria in solution.[7)]

$$H_3PO_5 \xrightleftharpoons{K_1} H_2PO_5^- + H^+, \tag{1}$$

$$H_2PO_5^- \xrightleftharpoons{K_2} HPO_5^{2-} + H^+, \tag{2}$$

$$HPO_5^{2-} \xrightleftharpoons{K_3} PO_5^{3-} + H^+. \tag{3}$$

The dissociation constants K_1, K_2, and K_3 are 8.0×10^{-2}, 4.2×10^{-6}, and 1.6×10^{-13} mol dm^{-3} respectively at 298 K and I=0.2 mol dm^{-3}.

In the pH range 0—5.5 PMPA exists[7,8)] as H_3PO_5, $H_2PO_5^-$, and HPO_5^{2-}. The reaction scheme for biacetyl oxidation in this pH range can, therefore, be presented by Eqs. 4—6.

$$H_3PO_5 + \text{biacetyl} \xrightarrow{k_1} \text{products}, \tag{4}$$

$$H_2PO_5^- + \text{biacetyl} \xrightarrow{k_2} \text{products}, \tag{5}$$

$$HPO_5^{2-} + \text{biacetyl} \xrightarrow{k_3} \text{products}, \tag{6}$$

which lead to the rate expression,

$$-\frac{d[\text{PMPA}]_t}{dt} = (k_1[H_3PO_5] + k_2[H_2PO_5^-] + k_3[HPO_5^{2-}])[\text{biacetyl}], \tag{7}$$

where $[\text{PMPA}]_t$ represents the total stoichiometric concentration of PMPA, and can be expressed by Eq. 8.

$$[\text{PMPA}]_t = [H_3PO_5] + [H_2PO_5^-] + [HPO_5^{2-}] \tag{8}$$

From Eqs. 1, 2, and 8 we get,

$$[H_3PO_5] = \frac{[H^+]^2[\text{PMPA}]_t}{K_1K_2 + K_1[H^+] + [H^+]^2}, \tag{9}$$

$$[H_2PO_5^-] = \frac{K_1[H^+][\text{PMPA}]_t}{K_1K_2 + K_1[H^+] + [H^+]^2}, \tag{10}$$

and

$$[HPO_5^{2-}] = \frac{K_1K_2[\text{PMPA}]_t}{K_1K_2 + K_1[H^+] + [H^+]^2}. \tag{11}$$

Substituting Eqs. 9, 10, and 11 in Eq. 7, we get,

$$-\frac{d[\text{PMPA}]_t}{dt} = \left\{\frac{k_1[H^+]^2 + k_2K_1[H^+] + k_3K_1K_2}{K_1K_2 + K_1[H^+] + [H^+]^2}\right\} \times [\text{PMPA}]_t[\text{biacetyl}], \tag{12}$$

or

$$k_2' = \frac{k_1[H^+]^2 + k_2K_1[H^+] + k_3K_1K_2}{K_1K_2 + K_1[H^+] + [H^+]^2}. \tag{13}$$

The values of k_2 and k_3, calculated by a method of least-squares using Eq. 13, are 0.087 and 10.0 dm^3 mol^{-1} s^{-1} respectively. The value of k_1 is small and negative and hence, could be approximated to zero. This allows us to rule out the path involving H_3PO_5 (Eq. 4). These values of k_1, k_2, and k_3 have been used to obtain k_2' calcd, which are presented in Table 3.

The PMPA species contributing to the rate of oxidation of benzil, in the pH range 7—11, are HPO_5^{2-} and PO_5^{3-}. Hence, the steps of the oxidation can be written as,

$$HPO_5^{2-} + OH^- \xrightleftharpoons{K_4} PO_5^{3-} + H_2O, \tag{14}$$

$$HPO_5^{2-} + \text{benzil} \xrightarrow{k_4} \text{products}, \tag{15}$$

$$PO_5^{3-} + \text{benzil} \xrightarrow{k_5} \text{products}. \tag{16}$$

The rate law is,

$$-\frac{d[\text{PMPA}]_t}{dt} = (k_4[HPO_5^{2-}] + k_5[PO_5^{3-}])[\text{benzil}], \tag{17}$$

$$= \left\{\frac{k_4K_h + k_5[OH^-]}{K_h + [OH^-]}\right\}[\text{PMPA}]_t[\text{benzil}], \tag{18}$$

where

$$[\text{PMPA}]_t = [HPO_5^{2-}] + [PO_5^{3-}], \tag{19}$$

and

$$K_h = [H_2O]/K_4. \tag{20}$$

Equation 18 can be rearranged to give Eq. 21

$$k_2' = \frac{k_4K_h + k_5[OH^-]}{K_h + [OH^-]}, \tag{21}$$

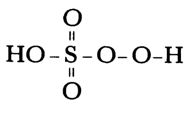
which has been used to calculate the rate constant k_2' (calcd) in Table 4.

The K_h value for PMPA species, as determined from Eq. 22 using the literature reported K_3 value, is 6.25×10^{-2} mol dm^{-3}.

$$K_h = K_w/K_3 \tag{22}$$

The statistical analysis of Eq. 21 was repeated by allowing the K_h value to vary until optimal values of k_4 and k_5 were obtained. These values are $K_h=7.35\times10^{-2}$ mol dm^{-3}, $k_4=6.77\times10^{-3}$ dm^3 mol^{-1} s^{-1} and $k_5=188$ dm^3 mol^{-1} s^{-1}.

The structure of peroxomonosulfuric acid has been shown[10] to be



$$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}O{-}H}$$

of which one proton is a sulfuric acid proton and the other is a hydrogen peroxide proton. The pK_a value of the sulfuric acid proton lies in the high acidity region, while the hydrogen peroxide proton has a pK_a value[12] of 9.4.

In aqueous solution PMSA exists as HSO_5^- and SO_5^{2-}

$$HSO_5^- \overset{K_5}{\rightleftharpoons} SO_5^{2-} + H^+,\ K_5 = 4\times10^{-10}\ \mathrm{mol\,dm^{-3}}. \tag{23}$$

For the oxidation of α-diketones by PMSA, in the range of pH studied, the dependence on pH can be explained by a mechanism in which the diketone molecule reacts simultaneously with HSO_5^- and SO_5^{2-} in two parallel reactions.

For biacetyl oxidation, in the pH range 0.3—4, the reaction steps are,

$$HSO_5^- + \text{biacetyl} \xrightarrow{k_6} \text{products}, \tag{24}$$

$$SO_5^{2-} + \text{biacetyl} \xrightarrow{k_7} \text{products}, \tag{25}$$

which follow the rate expression,

$$-\frac{d[\mathrm{PMSA}]_t}{dt} = \left\{k_6[HSO_5^-] + k_7[SO_5^{2-}]\right\}[\text{biacetyl}], \tag{26}$$

from which we get,

$$-\frac{d[\mathrm{PMSA}]_t}{dt} = \frac{k_6[H^+] + k_7K_5}{K_5 + [H^+]}[\mathrm{PMSA}]_t[\text{biacetyl}], \tag{27}$$

where

$$k_2' = \frac{k_6[H^+] + k_7K_5}{K_5 + [H^+]}. \tag{28}$$

In the pH range 0.3—4,

$$K_5 \ll [H^+]. \tag{29}$$

Equation 28 may, therefore, be written as,

$$k_2' = \frac{k_6[H^+] + k_7K_5}{[H^+]}. \tag{30}$$

Equation 30 has been used to determine the reactivity of HSO_5^- and SO_5^{2-} in biacetyl oxidation. The values of k_6 and k_7 are respectively found to be 1.82×10^{-2} dm^3 mol^{-1} s^{-1} and 2.39×10^{6} dm^3 mol^{-1} s^{-1}.

The reaction steps for benzil oxidation, in pH range 5—9.7 are postulated as,

$$HSO_5^- + OH^- \overset{K_6}{\rightleftharpoons} SO_5^{2-} + H_2O, \tag{31}$$

$$HSO_5^- + \text{benzil} \xrightarrow{k_8} \text{products}, \tag{32}$$

$$SO_5^{2-} + \text{benzil} \xrightarrow{k_9} \text{products}. \tag{33}$$

Equations 31—33 lead to the rate equation,

$$k_2' = \frac{k_8K_h' + k_9[OH^-]}{K_h' + [OH^-]}, \tag{34}$$

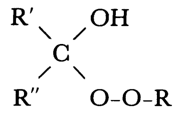
where $K_h' = K_w/K_5$.

A least squares solution of Eq. 34, using $K_h' = K_w/K_5$, gave us the values of k_8 and k_9. These values are $k_8=1.34\times10^{-2}$ dm^3 mol^{-1} s^{-1} and $k_9=30.9$ dm^3 mol^{-1} s^{-1}, which have been used to calculate k_2' calcd. in Table 4.

Peroxo species which participate in the reaction with α-diketones are $H_2PO_5^-$, HPO_5^{2-}, and PO_5^{3-} in PMPA oxidation, and HSO_5^- and SO_5^{2-} in PMSA oxidation. From the magnitude of rate constants (Table 5) for these species, it is evident that the reaction is facilitated by the more nucleophilic peroxo species; the reactivity of H_3PO_5 is negligible in the oxidation. The reactivity of SO_5^{2-} is approximately eight orders of magnitude higher than that of HSO_5^- in biacetyl oxidation. The reduced reactivity of benzil might be due to the decrease in electrophilic character of the carbonyl carbon.

Baeyer-Villiger reaction of aldehydes or ketones with hydrogen peroxide or peroxy acids are well-known.[1] Acid catalysis is an important feature of these oxidations.

The fundamental step in the reaction of carbonyl compounds with peroxides is rapid addition[13] of the peroxide molecule to the carbonyl group to give 'Criegee intermediate' of type I,



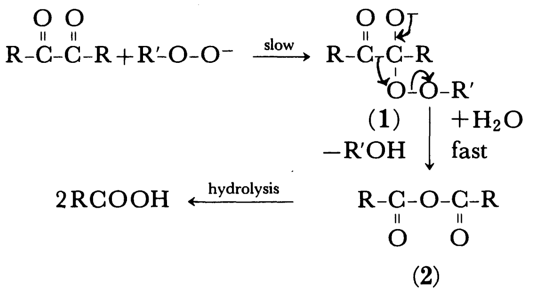
(I)

which then rearranges to give the product. The rate-determining step, in these reactions, may be either addition of peroxy acid to >C=O or migration from adduct depending on the substrate.

In the oxidation[14] of acetophenones by PMPA, cata-

Table 5. Comparison of Second-Order Rate Constants for the Oxidation of α-Diketones by Various Peroxo Species at 308 K

Oxidant	$k'_2/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	
	Biacetyl	Benzil
H_3PO_5	≈ 0	
$H_2PO_5^-$	8.7×10^{-2}	
HPO_5^{2-}	10.0	6.77×10^{-3}
PO_5^{3-}	Very fast	188
HSO_5^-	1.82×10^{-2}	1.34×10^{-2}
SO_5^{2-}	2.39×10^{6}	30.9



($R=CH_3$ or C_6H_5, and $R'OO^-=H_2PO_5^-$, HPO_5^{2-}, PO_5^{3-}, HSO_5^-, or SO_5^{2-}).

Scheme 1.

lyzed by H_2SO_4, the migration step was shown to be rate determining, while in perbenzoic acid oxidation[15] the rate-determining step was the acid-catalyzed addition of peroxy acid to $\rangle C=O$.

α-Diketones have been shown to react readily with Baeyer-Villiger reagents in both acid and alkaline media.[1] The product was either an anhydride or a carboxylic acid depending on the nature of solvent used.

The oxidation of benzil by peracetic acid was reported[3] to be acid-catalyzed. The acid catalysis has been traced to protonation of the carbonyl group, which was then attacked by peroxy acid in a rate-determining step.

In the oxidation of benzil by alkaline H_2O_2, from both product and isotopic studies, it has been established[4] that the reaction involves a Baeyer-Villiger type acyclic mechanism. Even though the migratory aptitude of the acyl group is very low in carbon-to-carbon migrations,[16] the acyl shift to peroxide oxygen has been shown to be facile.[17]

A significant observation, in the present study, is that the reactions are not acid-catalyzed. The increased reactivity in higher pH points to the nucleophilic behavior of peroxo species in the oxidation.

The initial step in the reactions of α-diketones by PMPA or PMSA is now believed to be the rate-determining nucleophilic addition of peroxy acid to the carbonyl carbon to form an adduct **1**. This adduct, can, then rearrange to the anhydride **2**, which is hydrolyzed, under reaction conditions, giving the corresponding carboxylic acid (Scheme 1).

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