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Peroxy Acid Oxidations. I. A Kinetic and Mechanistic Study of Oxidation of Acetylacetone by Peroxomonophosphoric Acid and Hydrogen Peroxide in Alkaline Medium

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The kinetics of oxidation of acetylacetone by peroxomonophosphoric acid and hydrogen peroxide have been investigated in the pH range 8—13.7. The oxidations by peroxomonophosphoric acid at 308 K and I= 0.6 mol dm^{-3} follow the rate expressions,

$$\text{(i)}\quad -\frac{\mathrm{d[PMPA]}_T}{\mathrm{d}t} = \{k_1[\mathrm{A}]+k_2[\mathrm{A}^-]\}[\mathrm{HPO_5}^{2-}]$$

in the pH range 8—10.63, where k_1=1.96 dm^3 mol^{-1} s^{-1} and k_2=0.177 dm^3 mol^{-1} s^{-1}, and

$$\text{(ii)}\quad -\frac{\mathrm{d[PMPA]}_T}{\mathrm{d}t} = \{k_3[\mathrm{A}]+k_4[\mathrm{A}^-]\}[\mathrm{HPO_5}^{2-}]+\{k_5[\mathrm{A}]+k_6[\mathrm{A}^-]\}[\mathrm{PO_5}^{3-}]$$

in the pH range 11.5—13.7, where k_3=30.4 dm^3 mol^{-1} s^{-1} and $k_6 \approx 0$. The rate law for hydrogen peroxide oxidations in the pH range 9.2—13 at 308 K and I=0.1 mol dm^{-3} is given by,

$$-\frac{\mathrm{d[Hydrogen\ peroxide]}_T}{\mathrm{d}t} = \{k_7[\mathrm{A}]+k_8[\mathrm{A}^-]\}[\mathrm{H_2O_2}]+\{k_9[\mathrm{A}]+k_{10}[\mathrm{A}^-]\}[\mathrm{HO_2}^-]$$

the k_7 and k_{10} values being 0.393 dm^3 mol^{-1} s^{-1} and 0.143×10^{-2} dm^3 mol^{-1} s^{-1} respectively. A and A$^-$ represent the diketo and enol form of acetylacetone respectively. The kinetic data and activation parameters are consistent with nucleophilic attack by peroxo species on both diketo and enol form of acetylacetone followed by oxygen–oxygen bond fission.

Studies[1–4] on oxidation of β-diketones by various peroxy compounds, e.g. peroxy acetic acid, peroxy benzoic acid and diperoxy phthalic acid have shown that enolizable β-dicarbonyl compound first reacted with the peroxy acid forming α-hydroxy diketone which on further reaction with peroxy acid or on hydrolytic cleavage afforded the observed products. Epoxidation of the enol form of the diketone was considered to be the reasonable path for the formation of hydroxy ketone.

Payne examined[5] oxidation of a series of β-diketones with hydrogen peroxide in *t*-butyl alcohol in presence of a mineral acid catalyst and reported that the reaction involved the formation of an intermediate cyclic peroxide which underwent acid-catalyzed decomposition to yield products.

The oxidation of β-diketones ($\mathrm{R^1CO\cdot CR^2R^3COR^4}$) with alkaline hydrogen peroxide[6] afforded two types of carboxylic acids depending upon the nature of R^2 and R^3. The unsubstituted β-diketone (in which both R^2 and R^3 are H) suffered an oxidative cleavage producing formic acid (from the central carbon atom) and the acid corresponding to the acyl group involved. The 2-monosubstituted 1,3-diketones underwent two types of reactions (i) an oxidative rearrangement involving migration of R^1 or R^4 from C$_1$ or C$_3$ to C$_2$, yielding the corresponding carboxylic acids, and (ii) an oxidative cleavage similar to that suffered by the unsubstituted β-diketones. The 2,2-disubstituted 1,3-diketones underwent only oxidative rearrangement. The oxidation mechanisms have been discussed on the basis of product studies.

The present study concerns with the kinetics and mechanism of oxidation of acetylacetone by peroxomonophosphoric acid (PMPA) and by hydrogen peroxide in aqueous alkaline medium. The oxidations have been studied in the pH range 8—14 and the reactivities of various peroxo species are discussed.

Experimental

All the chemicals used were of reagent grade or of certified purity. Doubly distilled water was used in preparing solutions. Acetylacetone was distilled just before use and the fractions distilling at 139—140 °C were collected rejecting the large head and tail portions. Peroxomonophosphoric acid was prepared[7–10] by the acid hydrolysis of potassium peroxodiphosphate. For each experiment, PMPA was prepared afresh with care so that further hydrolysis of PMPA to hydrogen peroxide was suppressed. Perchloric acid (Baker analyzed, 70%), used for hydrolysis, was neutralized by addition of requisite amount of carbonate-free sodium hydroxide. The ionic strength of the medium was maintained with sodium perchlorate which was prepared in situ in the oxidation flask by neutralizing HClO$_4$ with NaOH. The pH of the solution, adjusted with standard buffers or carbonate-free NaOH, was determined using a Systronics digital pH meter Model 335. Reactions were followed by measuring the rate of disappearance of PMPA which was estimated by iodometry at pH 4—5 with a drop of ammonium molybdate solution. In case of hydrogen peroxide oxidations, the kinetics was followed by measuring the rate of disappearance of H_2O_2 by the usual iodometric procedure.[11] Due allowance was given to the self decomposition of peroxide while computing the oxidation rates. In case of H_2O_2 the reaction could not be followed at pH>13 in view of slowness of the reaction and high decomposition of the oxidant. The agreement between replicate runs was within ±5%.

Results and Discussion

The kinetics of oxidation of acetylacetone (diketone) by peroxomonophosphoric acid and by hydrogen peroxide have been investigated in aqueous alkaline medium at 308 K.

Plots of log titer versus time are linear for well over three half-lives showing the first order nature of the oxidation with respect to the peroxo compound. The first order disappearance of peroxide is further supported by the fact that the pseudo first order rate constant (k_1') does not change with the variation of initial peroxide concentration.

The oxidation (by both PMPA and H_2O_2) also exhibits a first order dependence on [diketone], as shown by the constancy of the second order rate constants $k_2'(=k_1'/[\text{diketone}])$ for varying initial diketone concentrations (Tables 1 and 4).

Ionic strength (I) of the medium was varied with $NaClO_4$. For PMPA oxidations, I was varied in the range 0.2—0.8 mol dm^{-3}, and for H_2O_2 oxidations in the range 0.1—0.4 mol dm^{-3}. The rate increased with increase of ionic strength (Tables 1 and 4).

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

[diketone] × 10^2 mol dm^{-3}	[PMPA] × 10^4 mol dm^{-3}	$k_2'\times10^3$ dm^3 mol^{-1} s^{-1} [b)]
1.02	2.61	76.4
1.01	3.91	70.8
1.04	4.82	68.3
1.01	5.2	75.7
1.06	8.38	84.2
0.31	6.2	85.0
0.51	5.11	82.8
2.14	5.35	80.2
1.03	4.76	55.5[c)]
1.03	5.11	90.0[d)]
1.03	5.45	108[e)]
1.06	5.65	75.8[f)]
1.04	5.56	82.6[g)]
1.01	5.93	38.2[h)]
1.08	5.42	53.0[i)]
1.06	4.98	99.5[j)]

a) [OH$^-$] = 0.1 mol dm^{-3}, I = 0.4 mol dm^{-3}, aqueous medium, 308 K. b) Observed second order rate constant. c) I = 0.2 mol dm^{-3}. d) I = 0.6 mol dm^{-3}. e) I = 0.8 mol dm^{-3}. f) [Acrylamide] = 5 × 10^{-3} mol dm^{-3}. g) [EDTA] = 5 × 10^{-4} mol dm^{-3}. h) At 298 K. i) At 303 K. j) At 313 K.

The oxidation rate is insensitive to the addition of acrylamide indicating absence of radicals in the reaction system. Addition of EDTA also does not affect the oxidation rate (Table 1).

For both the oxidations, the second order rate constants at four different temperatures are recorded in Tables 1 and 4. Activation parameters have been determined from the linear Arrhenius plots of log k_2' vs. T^{-1}, and are recorded in Table 3.

The energy of activation (E_a), for both the oxidations, lie in the range 46—71 kJ mol^{-1}. Homolytic cleavage of the peroxide bond requires[12] an energy of activation of ≈138 kJ mol^{-1}. Further, (a) bimolecular kinetics (b) negative entropy of activation and (c) insensitivity to radical trapping agents, show that both PMPA and H_2O_2 oxidations involve polar mechanisms.[13]

The study of effect of pH on oxidation rate constitutes a significant part of the oxidation studies. The kinetics of the PMPA oxidation were explored over the pH range 8.3—13.7 (Table 2), and that of H_2O_2 oxidation over the pH range 9.25—13.0 (Table 4). Plots of pH versus log k_2' for both the oxidations are shown in Fig. 1. The sigmoid nature of the plot for PMPA oxidation suggests the participation of various species of PMPA, arising out of the following equilibria (Eqs. 1—3), in the oxidation. In case of H_2O_2, the plot of pH versus log k_2' is a straight line

Table 2. Oxidation of Acetylacetone by Peroxomonophosphoric Acid: Effect of pH[a)]

pH	$k_2'\times10^3$ dm^3 mol^{-1} s^{-1}	$k_{2(\text{calcd})}'\times10^3$ dm^3 mol^{-1} s^{-1}
13.69	25.1	26.1
13.32	51.4	53.6
13.0	90.0	89.5
12.51	160	157
11.82	245	245
11.54	291	291
11.49	305	302
10.63	288	214
10.0	354	325
9.34	618	694
9.19	852	830
8.34	1646	1639

a) [PMPA]=(3.2—5.5)×10^{-4} mol dm^{-3}, [diketone]=(2.02—10.3)×10^{-3} mol dm^{-3}, I=0.6 mol dm^{-3}, 308 K, Aqueous medium.

Table 3. Thermodynamic Parameters at 313 K

Peroxy acid	E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
PMPA[a)]	49.8	47.3	−113
H_2O_2[b)]	68.2	65.8	−69

a) I = 0.4 mol dm^{-3}, [OH$^-$] = 1.0 × 10^{-1} mol dm^{-3}. b) I = 0.1 mol dm^{-3}, [OH$^-$] = 4.6 × 10^{-2} mol dm^{-3}.

Table 4. Oxidation of Acetylacetone by Alkaline Hydrogen Peroxide[a)]

$\frac{[\text{diketone}]\times 10^3}{\text{mol dm}^{-3}}$	$\frac{[H_2O_2]\times 10^3}{\text{mol dm}^{-3}}$	pH	$\frac{I}{\text{mol dm}^{-3}}$	$\frac{k_2'\times 10^3}{\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}}$	$\frac{k_{2(\text{calcd})}'\times 10^3}{\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}}$
50.0	2.3	13.0	0.4	11.6	
50.0	17.5	13.0	0.4	14.6	
1.27	2.21	12.65	0.1	11.9	
2.5	2.21	12.65	0.1	11.0	
5.06	2.19	12.65	0.1	10.6	
10.2	2.2	12.65	0.1	12.6	
5.06	2.7	12.69	0.2	12.6	
5.06	2.2	12.69	0.4	15.4	
5.03	2.2	12.65	0.1	17.2[b)]	
5.03	2.4	12.65	0.1	30.2[c)]	
5.03	2.2	12.65	0.1	38.0[d)]	
5.1	2.65	12.94	0.15	6.7	6.7
5.1	2.2	12.66	0.1	10.6	11.1
6.2	2.6	11.52	0.1	28.6	64.6
5.1	2.6	10.83	0.1	48.2	99.5
5.1	3.4	10.16	0.1	106	123
5.1	1.7	9.66	0.1	147	155
5.03	2.1	9.26	0.1	203	203

a) Aqueous medium, 308 K. b) At 313 K. c) At 318 K. d) At 323 K.

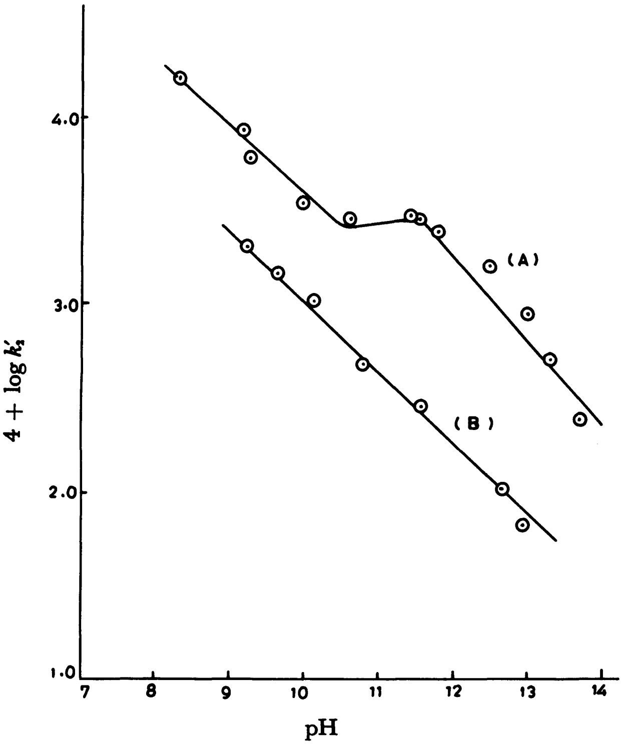

Fig. 1. Plots of log k_2' vs. pH.
A: PMPA-acetylacetone, B: Hydrogen peroxide-acetylacetone.

(r=0.998).

Various equilibria[7)] involving PMPA, in aqueous solution, are

$$H_3PO_5 \overset{K_1}{\rightleftharpoons} H_2PO_5^- + H^+ , \quad (1)$$

$$H_2PO_5^- \overset{K_2}{\rightleftharpoons} HPO_5^{2-} + H^+ , \quad (2)$$

$$HPO_5^{2-} \overset{K_3}{\rightleftharpoons} PO_5^{3-} + H^+ , \quad (3)$$

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

The dissociation equilibrium[14)] for acetylacetone in aqueous solution is

$$CH_3COCH_2COCH_3 \overset{K_a}{\rightleftharpoons} CH_3CO\bar{C}HCOCH_3 + H^+, \quad (4)$$

where $K_a = 1 \times 10^{-9}$.

In the pH region of 8.3—13.7 PMPA exists[7,15)] mainly as HPO_5^{2-} and PO_5^{3-}. As the pK_a of acetylacetone[16)] is 8.95, in this pH region it is present both as a neutral diketone and as an anion.

$$\underset{(A)}{CH_3COCH_2COCH_3} + OH^- \overset{K_4}{\rightleftharpoons}$$

$$\underset{(A^-)}{(CH_3CO\bar{C}HCOCH_3 \leftrightarrow CH_3COCH{=}\overset{O^-}{\overset{|}{C}}CH_3)} + H_2O \quad (5)$$

A and A$^-$ represent the diketo form and the enol form of acetylacetone.

In the alkaline hydrolysis of β-diketones, it was the neutral diketone which cleaved rather than the carbanion or the enol form. The reaction was initiated by the attack of OH$^-$ at the carbonyl carbon; k_{obsd} was reported to be 0.573×10^{-3} min^{-1} at 308 K and [Ba(OH)$_2$]=0.355 mol dm^{-3}.

The reaction of β-diketones with alkaline hydrogen peroxide has been shown[6)] to occur by the attack of hydrogen peroxide ion on carbonyl group. The oxidative cleavage was routed through the formation of an enol epoxide resulting in the formation of acidic products.

The reactions of enol ethers[18] and enol esters[19] with peroxy acid have been shown to form epoxides as well. Kinetic studies relating to epoxidation using alkaline hydrogen peroxide was reported to involve a nucleophilic attack by hydrogen peroxide ion on the alkene double bond.[20]

It can thus be assumed that in the oxidation of acetylacetone by PMPA and hydrogen peroxide both diketo form and enol form of the diketone are reactive.

In the pH range 8—10.6, PMPA exists[7,13] only as HPO_5^{2-}. The reaction steps in this pH range can, therefore, be presented as

$$HPO_5^{2-} + A \xrightarrow{k_1} \text{Products}, \tag{6}$$

$$HPO_5^{2-} + A^- \xrightarrow{k_2} \text{Products}. \tag{7}$$

The rate law is,

$$\begin{aligned}\text{Rate} &= -\frac{d[\text{PMPA}]_T}{dt} \\ &= k_1[HPO_5^{2-}][A] + k_2[HPO_5^{2-}][A^-]. \end{aligned}\tag{8}$$

$$\text{But}\quad [\text{PMPA}]_T = [HPO_5^{2-}] \tag{9}$$

$$\text{and}\quad [\text{diketone}]_T = [A] + [A^-] \tag{10}$$

$[\text{PMPA}]_T$ and $[\text{diketone}]_T$ represent the total stoichiometric concentration of PMPA and acetylacetone respectively.

From Eqs. 5 and 10,

$$[A] = \frac{K_h[\text{diketone}]_T}{K_h + [OH^-]} \tag{11}$$

$$\text{and}\quad [A^-] = \frac{[\text{diketone}]_T[OH^-]}{K_h + [OH^-]}, \tag{12}$$

$$\text{where}\quad K_h = \frac{[H_2O]}{K_4} \tag{13}$$

Eq. 8, therefore, takes the form,

$$-\frac{d[\text{PMPA}]_T}{dt} = \left\{\frac{k_1K_h + k_2[OH^-]}{K_h + [OH^-]}\right\}[\text{PMPA}]_T[\text{diketone}]_T \tag{14}$$

$$\text{where}\quad k_2' = \frac{k_1K_h + k_2[OH^-]}{K_h + [OH^-]}. \tag{15}$$

Plot of $k_2'(K_h+[OH^-])$ versus $[OH^-]$ (using $K_h=K_w/K_a$), in the pH range 8—10.6, is found to be linear (r=1.00). From the intercept and slope of this plot the values of k_1 and k_2 are calculated to be 1.96 dm^3 mol^{-1} s^{-1} and 0.177 dm^3 mol^{-1} s^{-1} respectively, indicating the diketo form of acetylacetone is more reactive than the enol form. The second order rate constants k_2'(calcd), calculated from Eq. 15 using these kinetically estimated values of k_1 and k_2, are collected in Table 2.

In the pH range 11.5—13.7, the major oxidant species[7] are HPO_5^{2-} and PO_5^{3-}; the concentration of PO_5^{3-} increasing with increase of pH.

The steps of the oxidation in pH region 11.5—13.7 can be written as,

$$HPO_5^{2-} + OH^- \overset{K_5}{\rightleftharpoons} PO_5^{3-} + H_2O, \tag{16}$$

$$HPO_5^{2-} + A \xrightarrow{k_3} \text{Products}, \tag{17}$$

$$HPO_5^{2-} + A^- \xrightarrow{k_4} \text{Products}, \tag{18}$$

$$PO_5^{3-} + A \xrightarrow{k_5} \text{Products}, \tag{19}$$

$$PO_5^{3-} + A^- \xrightarrow{k_6} \text{Products}. \tag{20}$$

The reaction sequence leads to the rate expression,

$$\begin{aligned}-\frac{d[\text{PMPA}]_T}{dt} &= k_3[HPO_5^{2-}][A] + k_4[HPO_5^{2-}][A^-] \\ &\quad + k_5[PO_5^{3-}][A] + k_6[PO_5^{3-}][A^-]\end{aligned} \tag{21}$$

From Eq. 16, we have

$$[HPO_5^{2-}] = \frac{[\text{PMPA}]_T K_h'}{K_h' + [OH^-]}, \tag{22}$$

$$\text{and}\quad [PO_5^{3-}] = \frac{[\text{PMPA}]_T[OH^-]}{K_h' + [OH^-]}, \tag{23}$$

$$\text{where}\quad [\text{PMPA}]_T = [HPO_5^{2-}] + [PO_5^{3-}] \tag{24}$$

$$\text{and}\quad K_h' = \frac{[H_2O]}{K_5} \tag{25}$$

Now using Eqs. 11, 12, 22, and 23 in Eq. 21, we get,

$$\begin{aligned}-\frac{d[\text{PMPA}]_T}{dt} &= \left\{\frac{k_3K_h'K_h + (k_5K_h + k_4K_h')[OH^-] + k_6[OH^-]^2}{(K_h' + [OH^-])(K_h + [OH^-])}\right\} \\ &\quad \times [\text{PMPA}]_T[\text{diketone}]_T\end{aligned} \tag{26}$$

$$\text{or}\quad k_2' = \frac{k_3K_h'K_h + (k_5K_h + k_4K_h')[OH^-] + k_6[OH^-]^2}{(K_h' + [OH^-])(K_h + [OH^-])}. \tag{27}$$

A least-squares analysis of Eq. 27 was done (using $K_h'=K_w/K_3$) and the values of k_3, $(k_5K_h/K_h'+k_4)$ and k_6 were obtained as 30.4 dm^3 mol^{-1} s^{-1}, 0.0144 and ≈0 respectively. These values were used to obtain k_2' (calcd) which showed excellent agreement with observed k_2' (Table 2).

Oxidation of acetylacetone by alkaline PMPA resulted in the formation of formic acid and acetic acid. Formic acid could be detected[6] from its reaction with ammoniacal silver nitrate. Acetic acid in presence of formic acid was detected[21] by the color reaction with a solution of sodium nitroprusside containing morpholine. In the reaction of unsubstituted β-diketones with alkaline hydrogen peroxide Cocker and Grayson too have reported[6] the formation of formic acid and acetic acid as oxidation products.

In the present study the formation of formic acid, even under kinetic experimental conditions, suggests that the α-hydroxy-β-diketone produced undergoes hydrolysis and further reaction with the peroxy acid in a fast step forming the products. The formation of hydroxy diketone is presumed to occur by the intermediate formation of epoxy alcohol. The epoxy alcohol supposedly results from the rate-limiting nucleophilic attack of the peroxo species on carbonyl carbon of the diketo form or alkene double bond of the enol form of acetylacetone followed by the oxygen-oxygen bond fission.

The kinetics of oxidation of acetylacetone by hydrogen peroxide have been studied over the pH range 9.2—13.

In dilute aqueous solution hydrogen peroxide is more acidic than water.[22]

$$H_2O_2 \overset{K_6}{\rightleftharpoons} H^+ + HO_2^- \quad (K_6 = 2.24 \times 10^{-12},\ 25\,^\circ C). \tag{28}$$

In the pH region under study since hydrogen peroxide exists as H_2O_2 and HO_2^-, the reaction in this pH range would involve the interaction of these species with both the diketo form and enol form of acetylacetone.

$$H_2O_2 + OH^- \overset{K_7}{\rightleftharpoons} HO_2^- + H_2O, \tag{29}$$

$$H_2O_2 + A \xrightarrow{k_7} \text{Products}, \tag{30}$$

$$H_2O_2 + A^- \xrightarrow{k_8} \text{Products}, \tag{31}$$

$$HO_2^- + A \xrightarrow{k_9} \text{Products}, \tag{32}$$

$$HO_2^- + A^- \xrightarrow{k_{10}} \text{Products}. \tag{33}$$

The above reaction steps would lead to the rate law (Eq. 34)

$$-\frac{d[\text{Hydrogen peroxide}]_T}{dt} = k_7[H_2O_2][A] + k_8[H_2O_2][A^-] + k_9[HO_2^-][A] + k_{10}[HO_2^-][A^-]. \tag{34}$$

But $$[\text{Hydrogen peroxide}]_T = [H_2O_2] + [HO_2^-] \tag{35}$$

From Eqs. 29 and 35,

$$[H_2O_2] = \frac{[\text{Peroxide}]_T K_h''}{K_h'' + [OH^-]} \tag{36}$$

and $$[HO_2^-] = \frac{[\text{Peroxide}]_T [OH^-]}{K_h'' + [OH^-]}, \tag{37}$$

where $$K_h'' = \frac{[H_2O]}{K_7} \tag{38}$$

Using Eqs. 11, 12, 36, and 37 in Eq. 34, we get,

$$-\frac{d[\text{Peroxide}]_T}{dt} = \left\{ \frac{k_7 K_h'' K_h + (k_9 K_h + k_8 K_h'')[OH^-] + k_{10}[OH^-]^2}{(K_h'' + [OH^-])(K_h + [OH^-])} \right\} \times [\text{Peroxide}]_T [\text{Diketone}]_T, \tag{39}$$

where $$k_2' = \frac{k_7 K_h'' K_h + (k_9 K_h + k_8 K_h'')[OH^-] + k_{10}[OH^-]^2}{(K_h'' + [OH^-])(K_h + [OH^-])}. \tag{40}$$

The values of k_7, k_{10}, and $(k_9 K_h / K_h'' + k_8)$ were obtained by least-squares analysis of Eq. 40, and were found to be 0.393 $dm^3\,mol^{-1}\,s^{-1}$, 0.143×10^{-2} $dm^3\,mol^{-1}\,s^{-1}$ and 0.494×10^{-3} respectively. Using these values second order rate constants calculated (k_2' calcd) from Eq. 40 are collected in Table 4.

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References

1) J. Boeseken and J. Jacob, *Recl. Trav. Chim. Pays-Bas*, **55**, 804 (1936).

2) P. Karrer, J. Kebrle, and R. M. Thakkar, *Helv. Chim. Acta*, **33**, 1711 (1950).

3) P. Karrer, J. Kebrle, and U. Albers-Schonberg, *Helv. Chim. Acta*, **34**, 1014 (1951); **35**, 1498 (1952).

4) H. O. House and W. F. Gannon, *J. Org. Chem.*, **23**, 879 (1958).

5) G. B. Payne, *J. Org. Chem.*, **26**, 4793 (1961).

6) W. Cocker and D. H. Grayson, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1347.

7) C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, **4**, 552 (1965).

8) G. P. Panigrahi and R. S. Panda, *Bull. Chem. Soc. Jpn.*, **52**, 3084 (1979).

9) G. P. Panigrahi and R. S. Panda, *Int. J. Chem. Kinet.*, **12**, 491 (1980).

10) G. P. Panigrahi and R. S. Panda, *Bull. Chem. Soc. Jpn.*, **53**, 2366 (1980).

11) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," London (1961), p. 363.

12) L. Pauling, "The Nature of Chemical Bond and the Structure of Molecules and Crystals," Cornell University Press, Ithaca, New York (1960), p. 85.

13) E. J. Behrman and J. O. Edwards, "Progress in Physical Organic Chemistry," ed by A. Streitwieser and R. W. Taft, Interscience, New York (1967), Vol. 4, p. 95.

14) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York (1959), p. 367.

15) R. S. Panda, Ph. D. Thesis, Berhampur University, 1980.

16) "Lange's Handbook of Chemistry," 11th ed, ed by J. A. Dean, McGraw-Hill, New York (1973), pp. 5—16.

17) R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).

18) C. L. Stevens and J. Tazuma, *J. Am. Chem. Soc.*, **76**, 715 (1954).

19) P. D. Gardner, *J. Am. Chem. Soc.*, **78**, 3421 (1956).

20) C. H. Bunton and G. J. Minkoff, *J. Chem. Soc.*, **1949**, 665.

21) F. Feigl, "Spot Tests in Organic Analysis," Elsevier, New York (1960), p. 515.

22) Ref. 14, pp. 5—14.