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Kinetics of Oxidation of Carbonyl Compounds by Peroxomonosulfate. Acetaldehyde, Propionaldehyde, and Butyraldehyde

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(Received April 25, 1985)

A kinetic study of oxidation of acetaldehyde, propionaldehyde, and butyraldehyde by peroxomonosulfate (PMS) in the presence of H^+ ion has been carried out. The reaction shows first order dependence each on [PMS] and [Aldehyde]. The reaction shows inverse first order over a particular concentration range of H^+ ion and beyond that first order dependence is observed with respect to $[H^+]$. The inverse hydrogen ion dependence on k_{obsd} may be due to the higher reactivity of SO_5^{2-} than HSO_5^- with aldehydes. The increase in k_{obsd} with increase in $[H^+]$ beyond certain $[H^+]$ can be explained by the formation of protonated carbonyl compounds. The Taft's plot gives ρ^* value of $\approx$5.0 indicating that the reaction is nucleophilic substitution at the carbonyl carbon which then rearranges to products.

In our previous paper[1] we have reported the results of kinetics of oxidations of formaldehyde, formic acid, and formate ion by peroxomonosulfate (PMS). We have observed, in the oxidation of formaldehyde by PMS, that SO_5^{2-} is more reactive than HSO_5^- and this is considered in favor of a nucleophilic substitution reaction of S_N2 type. Earlier workers[2] observed that the oxidation of aldehydes other than formaldehyde proceed through the enol form formed by the interaction between aldehydes and hydrogen ion. Since higher aldehydes, acetaldehyde, propionaldehyde, and butyraldehyde are enolizable, it would be interesting to study whether enol form of aldehydes will also involve in the kinetics. Aldehydes exist both in the hydrated form (*gem*-diol) as well as carbonyl form in aqueous solution.[3] Study of structure-reactivity relationship may throw some light on the nature of the aldehyde species involved in the oxidation reactions with PMS. With these views the kinetics of oxidations of the title aldehydes were undertaken and the results are discussed in this report.

Experimental

Acetaldehyde (SD's), propionaldehyde, butyraldehyde were purified by fractional distillation. Because of the high volatality of some of these aldehydes, the concentrations of the aqueous solutions were determined analytically; the Ponndorf's method[4] adopted by Seigel and Weiss[5] was used for all the aldehydes.

Potassium peroxomonosulfate (Du Pont) was used as such and all other chemicals were of analytical grade. The experimental details are discussed in Ref. 1.

Stoichiometry. The stoichiometry of the reactions were determined, at pH 4.0 and $[H^+]=0.166$ M (1 M=1 mol dm^{-3}), by taking a known excess of [PMS] over [Aldehydes]. The stoichiometry observed were identical at pH 4.0 and $[H^+]=0.166$ M and it could be represented as

$$\text{RCHO} + \text{PMS} \longrightarrow \text{RCOOH (Product)}$$

Acetic acid was detected in the oxidation of acetaldehyde by spot tests.[6] Presence of carboxyl group in other two aldehydes were also confirmed.

Results and Discussion

Oxidations of the aldehydes were carried out under pseudo first-order conditions, with [Aldehydes] have been higher than, at least five times, that of [Peroxomonosulfate]. Analysis of the results indicates that the kinetics of oxidations of aldehydes by PMS are first order. Plots of log [PMS] versus time were linear even up to 70% conversion of [PMS]. The values of k_{obsd} were independent of $[PMS]_0$ and this shows that the order with respect to the [oxidant] is one.

An increase in the concentrations of the aldehydes causes a proportional increase in the rate constant at constant $[H^+]$ and [PMS]. Plots of k_{obsd} versus [Aldehyde] are linear passing through origin (Fig. 1). This clearly proves the oxidations of aldehydes by PMS can be represented by the Eq. 1 as

$$\frac{-d[\text{PMS}]}{dt} = k'[\text{Aldehyde}][\text{PMS}], \qquad (1)$$

where k' represents the rate constant at constant hydrogen ion concentration. The values of k' obtained are tabulated in Table 1.

The effect of hydrogen ion concentration on k_{obsd} was studied by varying the $[H^+]$ from $\approx 10^{-4}$ to 0.166 M. In the high pH range, i.e. 4.4 to 3.6, the k_{obsd} decreases on decreasing the pH and the plots of k_{obsd} versus $1/[H^+]$ were linear with intercept (Fig. 2). The values of k_{obsd} are found to decrease with increase in $[H^+]$ (3.5×10^{-3}—0.166 M) till a particular concentration of H^+ and then k_{obsd} increases with increase in $[H^+]$ at constant [Aldehyde] (Table 2). The plots of k_{obsd} versus pH are found to be U-shaped curve (Fig. 3). This shows that different species are involved at different hydrogen ion concentration.

The change in ionic strength of the reaction medium shows a small increase in k_{obsd}. The kinetics

Table 1. Kinetic Parameters for the Oxidation of Aldehydes by PMS at 30 °C and μ=0.25

Substrate	k' a)	k_1	k_2	$\Delta H^{\neq}$
	10^{-1} M^{-1} s^{-1}	10^{-2} M^{-1} s^{-1}	10^4 M^{-1} s^{-1}	kcal mol^{-1}
Acetaldehyde	2.6	10.3	3.3	9.2
Propionaldehyde	2.0	5.1	3.3	10.1
Butyraldehyde	2.0	4.5	3.2	8.1

a) Values are at pH 4.0; 1 M=1 mol dm^{-3}. 1 cal=4.184 J.

Table 2. Dependence of k_{obsd} on [H$^+$] at 30 °C

[H$^+$]	$k_{obsd}/10^{-5}$ s^{-1}		
10^{-3} M	Acetaldehyde a)	Propionaldehyde b)	Butyraldehyde c)
1.75	36.4	25.6	26.1
3.50	30.4	21.0	21.5
5.25	24.0	16.2	17.0
7.00	17.8	12.1	12.3
14.00	10.9	8.0	7.7
21.00	8.2	5.8	6.2
28.00	7.6	5.6	5.8
35.00	7.1	6.0	6.2
50.00	7.5	6.7	7.2
60.00	8.4	7.6	8.3
70.00	9.9	8.8	9.4
105.00	14.7	13.6	14.4
140.00	20.7	21.2	21.0
166.00	26.7	25.3	27.0

a) [Acetaldehyde]=5.6×10^{-3} M; [PMS]=10.5×10^{-4} M; μ=0.25. b) [Propionaldehyde]=7.05×10^{-3} M; [PMS]= 10.5×10^{-4} M; μ=0.25. c) [Butyraldehyde]=6.65×10^{-3} M: μ=0.25.

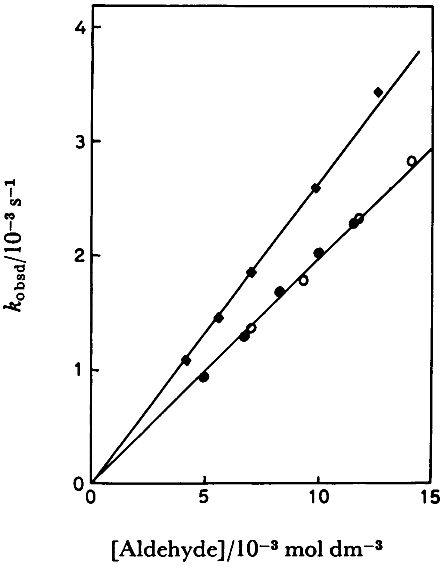


Fig. 1. Plot of k_{obsd} versus [Aldehyde]. [PMS] = 10.5 × 10^{-4} mol dm^{-3}; pH=4.0; μ=0.25; t=30 °C. —■—: Acetaldehyde, —○—: Propionaldehyde, —●—: Butyraldehyde.

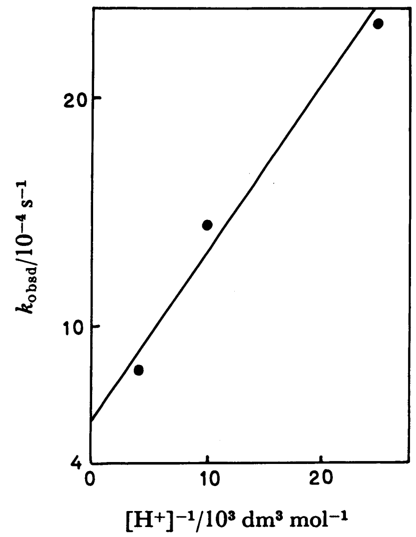


Fig. 2. Plot of k_{obsd} versus 1/[H$^+$] at 30 °C in the pH range 3.6—4.4. [Acetaldehyde] = 5.6 × 10^{-3} mol dm^{-3}; [PMS] = 10.5 × 10^{-4} mol dm^{-3}; μ=0.25.

of the reactions were studied at four different temperatures (30—45 °C) and from the temperature dependence of k_{obsd} the $\Delta H^{\neq}$ values are calculated and tabulated (Table 1).

In order that the proposed mechanism is realistic in accounting for many of the observed kinetic data, it is necessary to have a knowledge of the possible species of both the oxidant and the substrate and from this the choice of the correct or the most probable species responsible must be made under the existing conditions of the experiment. Peroxomonosulfate, in solution exists as HSO_5^- and SO_5^{2-} due to the equilibrium as in Eq. 2.

$$HSO_5^- \rightleftharpoons SO_5^{2-} + H^+ \qquad (2)$$

The pK_a of the equilibrium[7] is 9.4 and therefore under the experimental conditions namely at pH 4.0 the oxidant exists predominantly as HSO_5^- and to a smaller extent as SO_5^{2-}.

It is well known that aliphatic aldehydes in aqueous solution are partially hydrated.[3] Aldehydes in acidic or neutral medium give various species due to different reactions such as keto-enol tautomerism, hydration, protonation or deprotonation of the *gem*-diol forms.

It was observed that in the oxidations of aliphatic aldehydes by some metal oxidants the rate determining reaction is the enolization of the aldehyde[2] and this enolization reaction is acid catalyzed as

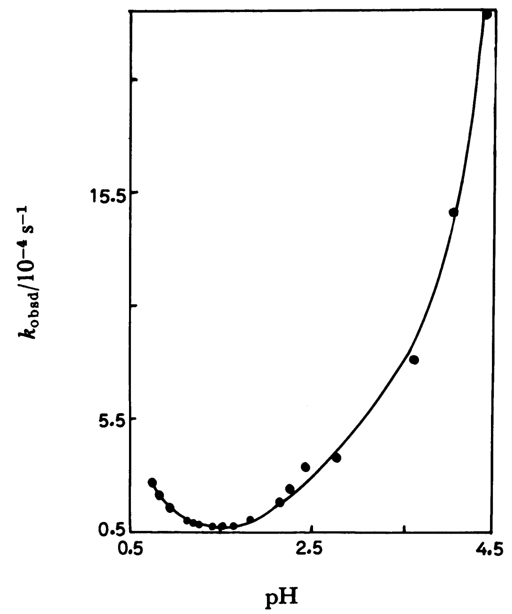


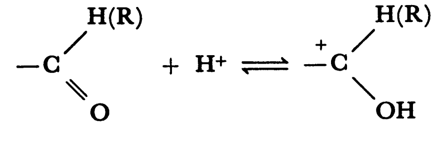
Fig. 3. Plot of k_{obsd} versus pH at 30 °C. [Acetaldehyde]$=5.6\times10^{-3}$ mol dm^{-3}; [PMS]$=10.5\times10^{-4}$ mol dm^{-3}; $\mu=0.25$.

$$RCH_2CHO + H^+ \overset{\text{fast}}{\rightleftharpoons} (RCH_2CHOH)^+, \quad (3)$$

$$(RCH_2CHOH)^+ \xrightarrow[\text{determining}]{\text{rate}} RCH{=}CHOH + H^+. \quad (4)$$

If this enolization were the rate determining reaction in the oxidation by PMS, then the rate of oxidations would be zero order with respect to PMS and the observed stoichiometry for the reaction should be greater than 1:1. The observed experimental facts namely the first order dependence of rate on [PMS] and 1:1 stoichiometry even at [H+]=0.166 M clearly show that enolization reaction can be neglected and it would never be the rate determining reaction under the experimental conditions employed in the oxidations of aldehydes by PMS.

Carbonyl compounds are partially hydrated by water, the reaction being catalyzed by acids and bases.[3] The vast majority of the reactions with carbonyl compounds involve nucleophilic attack on the carbonyl carbon atom and the electrophilic attack, usually protonation, on the oxygen. The product formed between carbonyl compound and H$^+$ is responsible for acid catalysis.[8] Usually protonation of aliphatic carbonyl compounds are depicted as in Eq. 5.


$$-C(=O)-H(R) + H^+ \rightleftharpoons -\overset{+}{C}(-OH)-H(R) \quad (5)$$

Extensive kinetic and spectral evidence indicates that protonated species is largely responsible for nucleophilic attack at the carbonyl carbon atom. Therefore we can safely assume that in aqueous solution and in the presence of hydrogen ion, aldehydes will exist as free aldehydic form, hydrated form (*gem*-diol) and protonated species.

Based on the experimental observation the most probable pathway will be

$$HSO_5^- \overset{K}{\rightleftharpoons} SO_5^{2-} + H^+, \quad (6)$$

$$\text{Aldehyde} + HSO_5^- \xrightarrow{k_1} \text{Products}, \quad (7)$$

$$\text{Aldehyde} + SO_5^{2-} \xrightarrow{k_2} \text{Products}. \quad (8)$$

As a first approximation, we can assume that at very low hydrogen ion concentration (pH 3.6 to 4.4) Eq. 5 can be neglected. Therefore at high pH the rate equation becomes

$$\frac{-d[\text{PMS}]}{dt} = k_1[\text{Aldehyde}][HSO_5^-] + k_2K\frac{[\text{Aldehyde}][HSO_5^-]}{[H^+]}$$

$$k_{obsd} = k_1[\text{Aldehyde}] + \frac{k_2K[\text{Aldehyde}]}{[H^+]}. \quad (9)$$

This equation explains the observed effect of [Aldehyde] and [H$^+$] (in the rage of pH 3.6 to 4.4) on k_{obsd}. At constant [H$^+$], the plots of k_{obsd} versus [Aldehyde] (Fig. 1) should give ($k_1+k_2K/[H^+]$) as slope which is equal to k' in Eq. 1. Similarly at constant [Aldehyde], plots of k_{obsd} versus 1/[H$^+$] should give k_2K[Aldehyde] as slope and k_1[Aldehyde] as intercept (Fig. 2). From the intercept and slope we can calculate the values of k_1 and k_2 knowing the literature value[7] of K as 3.98×10^{-10}. Perusal of the values in Table 1 shows that k_2 is approximately five order of magnitude greater than k_1. The higher reactivity of SO_5^{2-} than that of HSO_5^- may be considered to be in favor of nucleophilic attack by the peroxide.

Careful examination of the results in Table 2 shows that the protonation of the aldehydes (Eq. 5) is still less significant in the hydrogen ion concentration in the range of 1.75—21.0$\times10^{-3}$ M (in the pH range of 1.68 to 2.76). In the k_{obsd} versus [H$^+$] curves, the effect of [H$^+$] in this range can also be explained by the Eq. 9. The values* for k_1' and k_2' are (at pH 1.68—2.76)

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* For clarity the values of k_1 and k_2 obtained in the hydrogen ion concentrations (1.75—21.0$\times10^{-3}$ M) are denoted as k_1' and k_2'. In the plot of k_{obsd} versus 1/[H$^+$] the data point corresponding to [H$^+$]$=1.75\times10^{-3}$ M deviates from the straight line in all these three aldehydes. All other points fit well nicely in the plot and therefore the point corresponding to [H$^+$]$=1.75\times10^{-3}$ M was omitted in the plot to calculate k_1' and k_2'.

	k_1' M^{-1} s^{-1}	k_2' M^{-1} s^{-1}
Acetaldehyde	7.5×10^{-3}	4.5×10^{5},
Propionaldehyde	4.2×10^{-3}	3.4×10^{5},
Butyraldehyde	4.5×10^{-3}	2.6×10^{5}.

According to Eq. 9, the values of k_1 and k_2 should be independent of H^+ concentration range used. However, comparison of the values of k_1' and k_2' with those of k_1 and k_2 in Table 1 shows that k_1' is ten times smaller than k_1 and $k_2'\approx10k_2$. In this acid range (pH 1.68—2.76) the reactivity of SO_5^{2-} towards aldehyde is approximately eight order of magnitude greater than HSO_5^- which coincides with the results obtained in the oxidation of DMSO by PMS in acid media.[9)] Similar discrepancy in the values of k_1 and k_2 with k_1' and k_2' was also observed in the oxidation of formaldehyde by PMS.[1)] This discrepancy may probably be due to the fact that the equation used to calculate the concentrations of HSO_5^- and SO_5^{2-} may not be correct since the experimental pH was far away from the pK_a value of PMS (9.4).[7)]

At very high hydrogen ion concentrations (35—166$\times10^{-3}$ M, pH 0.78 to 1.46), the observed effect of hydrogen ion on k_{obsd} can be explained by the catalytic effect of hydrogen ion due to the formation of protonated aldehydes as in Eq. 5. In this high hydrogen ion concentration range also the values of k_{obsd} were found to be independent of $[PMS]_0$ at constant $[H^+]$ and [Aldehyde]. This observation helps us to eliminate the possibility of the acid catalyzed hydrolysis of PMS similar to those observed in other peroxides. Further the plots k_{obsd} versus [Aldehyde] at constant $[H^+]$ were found to be linear passing through origin even at this high $[H^+]$. These observations clearly show that acid catalysis, the addition of H^+ on the RCHO to give $RCHOH^+$ which reacts with PMS to give product, is also occurring to a significant extent as

$$\mathrm{RCHO} + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} \mathrm{RCHOH}, \tag{10}$$

$$\mathrm{RCHOH}^+ + \mathrm{PMS} \xrightarrow{k_3} \mathrm{Products}, \tag{11}$$

$$\mathrm{RCHO} + \mathrm{PMS} \xrightarrow{k} \mathrm{Products}. \tag{12}$$

Under these conditions, the rate law becomes

$$k_{obsd} = k_3K_1[\mathrm{RCHO}][\mathrm{H}^+] + k[\mathrm{RCHO}] \tag{13}$$

and this equation explains the observed experimental facts at high $[H^+]$. The magnitude of K_1 may be small so that this catalytic effect have a pronounced effect on k_{obsd} only when $[H^+]>50\times10^{-3}$ M. No such catalytic effect was observed in the oxidation of formaldehyde by PMS even when $[H^+]>100\times10^{-3}$ M. The values of k_3K_1 obtained from the plot of k_{obsd} versus $[H^+]$ are grouped in Table 3.

So far the total analytical concentration of aldehyde is used to evaluate the kinetic parameters tabulated in Table 1. Turning now to the participation of the aldehydes in the keto or in the hydrated form, the relative rate constants can be computed by considering in turn one of the two forms as the only active species as

$$k^{H} = k_{total}(K_d+1)$$
$$k^{CO} = k_{total}(1+K_d^{-1})$$

where k^H, k^{CO}, and k_{total} represent the rate constants for the hydrated form, keto form, and observed rate constant for total analytical concentration of aldehydes, respectively. K_d represents the hydration equilibrium of aldehydes as

$$\mathrm{RCHO} + \mathrm{H_2O} \rightleftharpoons \mathrm{RCH(OH)_2}$$
$$K_d = [\mathrm{RCHO}]/[\mathrm{RCH(OH)_2}]$$

In Table 4, the values of k_1, k_2, k_1^H, k_2^H, k_1^{CO}, and k_2^{CO} are given along with the values[10—13)] of K_d and

Table 3.

Substrate	K_1k_3	$K_1k_3^{CO\,a)}$
	10^{-2} M^{-2} s^{-1}	10^{-2} M^{-2} s^{-1}
Acetaldehyde	31.2	77.8
Propionaldehyde	24.8	42.4
Butyraldehyde	26.3	38.9

a) Values given in this heading correspond to the keto form values of [RCHO].

Table 4.

R in CHO	k_1	k_2	$k_1^{H\,a)}$	$k_2^{H\,a)}$	$k_1^{CO\,b)}$	$k_2^{CO\,b)}$	K_d	$\sigma^{*\,c)}$
	10^{-2} M^{-1} s^{-1}	10^{4} M^{-1} s^{-1}	10^{-2} M^{-1} s^{-1}	10^{4} M^{-1} s^{-1}	10^{-2} M^{-1} s^{-1}	10^{4} M^{-1} s^{-1}		
H	4.0	3.7	4.1	3.7	7204	6666	5.55×10^{-4} d)	0.490
CH_3	10.3	3.3	17.2	5.5	25.6	8.3	0.671e)	0.000
CH_3CH_2	5.1	3.3	12.2	7.9	8.7	5.7	1.408f)	−0.100
$CH_3CH_2CH_2$	4.5	3.2	13.9	9.9	6.7	4.8	2.083g)	−0.115

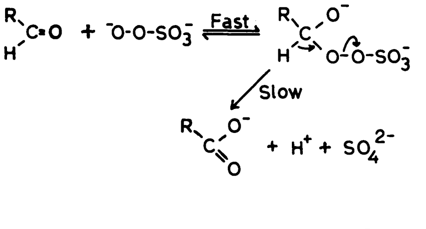
a) Rate corresponding to the hydrated form. b) Rate corresponding to the carbonyl form. c) Ref. 14. d) Ref. 10. e) Ref. 11. f) Ref. 12. g) Ref. 13.

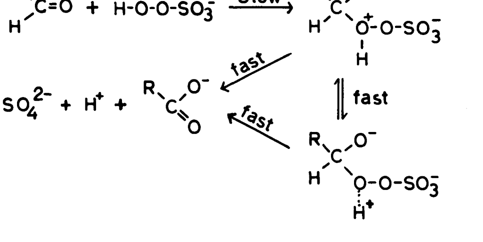
Taft's polar substituent constants[14] σ^*.

If RCHO (keto form) is the active form, the reactivity would be depressed by a factor of ca. $\approx 10^3$ between the extremes in the order HCHO>BuCHO and the values in Table 4 bring out our expectation, whereas no regularity is observed for the hydrated form.

The rates of PMS oxidation of the aldehydes relative to that of acetaldehyde can be obtained by dividing k_1/k_2 of the aldehyde by that of acetaldehyde.** A plot of log $(k_1/k_{1\,\text{acetaldehyde}})^{\text{H}}$ or log $(k_2/k_{2\,\text{acetaldehyde}})^{\text{H}}$ versus σ^* was much less satisfactory whereas log $(k_1/k_{1\,\text{acetaldehyde}})^{\text{CO}}$ or log $(k_2/k_{2\,\text{acetaldehyde}})^{\text{CO}}$ versus σ^* is a good straight line (Fig. 4) with a slope (reaction susceptibility constant ρ^*) of +5.0 and +4.75, respectively.

According to reactivity-selectivity principle,[15–17] the more reactive substrate/oxidant should be less selective than the less reactive one. Since SO_5^{2-} is $\approx 10^6$ times more reactive than HSO_5^-, it should be less selective and hence the observed ρ^* should be less than that for the HSO_5^-. But it would be surprising to note that the reaction susceptibility constants (ρ^*) for the oxidations by HSO_5^- and SO_5^{2-} are almost same and it seems to be an apparent violation of reactivity-selectivity principle. This can be explained if the following reaction schemes are considered for the oxidations by SO_5^{2-} and HSO_5^-.





According to the tetrahedral mechanism of nucleophilic substitution at the carbonyl group,[18] the nucleophile adds on to the trigonal carbonyl carbon to give a tetrahedral intermediate which then decomposes in the rate determining step to give the product. The observed ρ^*_{obsd} for the oxidations of aldehyde by SO_5^{2-} is the combination of the ρ^*s for nucleophilic addition ρ^*_{NA} and the elimination ρ^*_{ES}, i.e. the decomposition into the product as

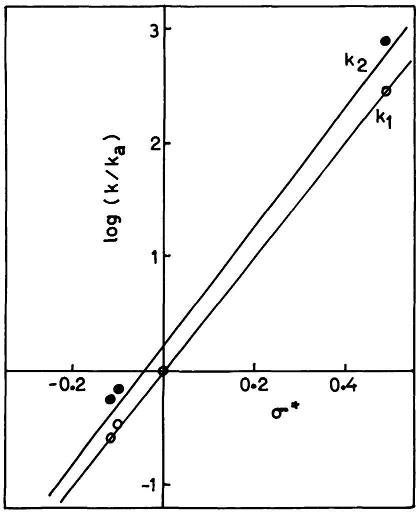


Fig. 4. Taft's plot. k_a represents the rate of acetaldehyde.

$$\rho^*_{\text{obsd}} = \rho^*_{\text{NA}} + \rho^*_{\text{ES}}$$

The value of ρ^*_{NA} should be positive and ρ^*_{ES} depends upon the combined opposing influence of the substituent on both the leaving groups/reactions; i.e. C–H which separates as H^+ and also $C\text{–}O\text{–}O\text{–}SO_3^-$ group to give C=O and SO_4^{2-}. The large positive ρ^*_{obsd} shows that the ρ^*_{ES} may also be positive, otherwise ρ^*_{NA} would have a value greater than ρ^*_{obsd}. This means that the highly reactive nucleophile SO_5^{2-} is more selective and this is more unlikely. The observed ρ^*_{obsd} corresponding to k_1, i.e. oxidation by HSO_5^-, is only due to the nucleophilic substitution at the trigonal carbonyl carbon which may be a slow and rate determining step. This clearly explains that though it appears as a violation of reactivity-selectivity principle actually this is not the case since reactivity-selectivity principle can be applied only to the reactions involving same mechanistic pathways.[16,17] The same ρ^* values observed for k_1 and k_2 may be a fortuitous coincidence.

The structure-reactivity analysis can also be made for the acid catalyzed reaction also. The values of k_3K_1 corresponding to the keto form ($k_3K_1^{\text{CO}}$) are also given in Table 3. The electronic effect of the substituents would have opposing effects on K_1 and k_3; the electron-releasing substituents would increase the equilibrium constant K_1 whereas it would decreases the rate k_3. The Taft's plot for the hydrogen ion catalyzed reaction,

$$\log (k'/k'_{\text{acetaldehyde}}) = {}^{\text{H}^+}\rho^*_{\text{obsd}}\sigma^*,$$

where $k'=k_3K_1$, will give the susceptibility parameter (reaction constant) ${}^{\text{H}^+}\rho^*_{\text{obsd}}$ which is the combination of ${}^{\text{H}^+}\rho^*$ due to Eqs. 10 and 11 as

$${}^{\text{H}^+}\rho^*_{\text{obsd}} = {}^{\text{H}^+}\rho^*_{K_1} + {}^{\text{H}^+}\rho^*_{k_3}$$

** Because the values of k_1 and k_2 obtained at high pH range are assumed to be free from other side reactions, these values are used in the correlation analysis.

The value of ${}^{H^+}\rho^*_{k_3}$ would be positive and greater than or at least equal to five since the ρ^* value for the aldehyde reactions with PMS is +5.0 (vide supra). Since the value of ${}^{H^+}\rho^*_{K_1}$ should be negative, the value of ${}^{H^+}\rho^*_{\text{obsd}}$ depends upon the magnitude of ${}^{H^+}\rho^*_{K_1}$. The value obtained for ${}^{H^+}\rho^*_{\text{obsd}}$ is +2.6 and this shows that the magnitude of ${}^{H^+}\rho^*_{K_1}$ is less than ${}^{H^+}\rho^*_{k_3}$. However it should be pointed out at this point that the above discussions are only qualitative since the Taft's plots are made only with the σ^* over a small and close range. The values of ρ^*s will not be accurate and we can not rely upon these numerical values. Therefore the above foregoing discussions should only be considered as an additional evidence which helps us in proposing the reaction scheme. However the value obtained in the analysis of acid catalyzed reaction helps us to explain why formaldehyde does not show the acid catalyzed reaction in our experimental conditions. According to the value of ${}^{H^+}\rho^*_{\text{obsd}}$, the value of k_3K_1 should be 8.3×10^{-3} which is hundred times lesser than the observed values of k_3K_1 for other aldehydes. Therefore we would have observed the acid catalyzed reaction of formaldehyde oxidation by PMS at very high hydrogen ion concentration. This shows although the results are qualitative in nature they are in the correct direction.

The authors acknowledge Prof. N. R. Subbaratnam for his constant encouragements and facilities. M. S. R. acknowledges the U. G. C., New Delhi for the financial assistance (Code No. 277). V. A. expresses his gratitude to the U. G. C. and the authorities of Thiruvalluvar College, Papanasam, for the grant of F. I. P. Fellowship. The authors also acknowledge the referees for their constructive criticisms and suggestions.

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