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Kinetics and Mechanism of Perborate Oxidation of Aromatic Aldehydes

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The kinetics of oxidation of benzaldehyde by sodium perborate in an acetic acid medium have been studied. The reaction is first order with respect to both oxidant concentration and to the substrate. Hydrogen ion accelerates the rate of reaction. A mechanism involving the formation of an unstable perborate ester, which decomposes to the reaction products, has been suggested. The activation parameters associated with the rate-determining step have been calculated. The effects of various functional groups on the ring at the *meta*, and *para* positions of benzaldehyde have also been examined.

Key words: kinetics, aldehydes, perborate

Sodium perborate ($NaBO_3 \cdot 4H_2O$) is a non-toxic cheap, safe and large scale industrial chemical, primarily used as a source of active oxygen in detergents and as a mild antiseptic. This active oxygen has the oxidizing properties of hydrogen peroxide. NMR spectral analysis [1] and X-ray diffraction studies [2] conclude perborate as a true peroxysalt with crystallization water. Perborate is a heterocyclic and is a dimeric tetrahedral configuration with dihedral angle of 64° and anionic formula: $B_2(O_2)_2(OH)_4^{2-}$. Oxidative study suggests perborate as not peroxoborate but borate peroxyhydrate, hydrogen peroxide acquire stronger electrophilicity by the coordination with borate [3]. The byproduct is completely innocuous and this stable and easily handled crystalline substance oxidizes organic sulphides to sulphoxides or sulphones [4,5], aniline, N-methyl-aniline and N,N-dimethylaniline to azo or nitro compounds [6–10], hydroquinones and phenols into quinones [11], aldehydes to carboxylic acids [12], aliphatic amines to nitro compounds [13]. Although some aromatic as well as aliphatic aldehydes have been oxidized in boiling acetic acid with this reagent [12], the mechanism of oxidation of aromatic aldehyde by this oxidant is not established.

Hence it was of interest to study the mechanism of oxidation of aromatic aldehydes by this oxidant in acetic acid medium. Attempts have been made to study the correlation of structure and reactivity in this reaction.

EXPERIMENTAL

Reagents: All the organic compounds were of AR grade and were further purified by either recrystallization or redistillation just before use. Sodium perborate, $NaBO_3 \cdot 4H_2O$ was of BDH grade. All solutions of benzaldehyde and substituted benzaldehydes were prepared in acetic acid.

Rate measurements: Rate studies were made under pseudo-unimolecular conditions with a large excess of the aldehyde over perborate in 70% (v/v) acetic acid-water mixture. The temperature was kept constant to ± 0.1 K. The progress of the oxidation was followed by estimation of unconsumed perborate at different time intervals. Standardization of perborate solution and estimation of unreacted perborate in the reaction mixture were done by draining 5 ml aliquot into a fresh hot (*ca*. 50°C) mixture of 10 ml of 5 $mol \cdot dm^{-3}$ sulphuric acid and 10 ml of 2% potassium iodide solution, and the liberated iodine was titrated against standardized thiosulphate solution using starch solution as an indicator. The course of the oxidation was followed for up to 70% of the reaction. The pseudo-first-order rate constant (k) was calculated from the slope of the linear plot of log titre *versus* time. Duplicate kinetic runs showed that the rates are reproducible to within ±4%.

Stoichiometry: To determine the stoichiometry, benzaldehyde was treated with an excess of perborate. When the reaction was complete, unreacted perborate was determined iodometrically. Several determinations, using substituted benzaldehydes, indicated a 1:1 stoichiometry.

Product analysis: Sodium perborate tetrahydrate (12 mmole) was added portionwise during 20 min to a stirred solution of the benzaldehyde (10 mmole) in glacial acetic acid (30 ml) held at 45–50°C, and the mixture was stirred for 5 min at this temperature. The reaction mixture was poured onto water and extracted with chloroform. The organic layer was washed successively with water, sodium bicarbonate solution, and water and dried over sodium sulfate. On removal of the solvent, the unreacted benzaldehyde was obtained which was characterized through a 2,4-dinitrophenylhydrazone derivative. The aforementioned sodium bicarbonate extract was cooled in ice and acidified with dilute sulphuric acid, and the precipitated benzoic acid was extracted with pure ether. The ethereal solution was washed with a small amount of water and dried over sodium sulphate. On removal of the solvent, benzoic acid was obtained as colorless flakes (97% yield, m.p. 121°C) and identified by IR spectrum.

RESULTS AND DISCUSSION

Effect of reactant concentrations: The oxidation is first order with respect to perborate. Plots of log titre *versus* time are linear with correlation coefficient (r) of least 0.995. The pseudo-first-order rate constants (k) remain almost constant at different $[\text{perborate}]_0$ (Table 1). The rate of decomposition of perborate under identical conditions is negligible in comparison with the rates of the oxidation of aldehydes.

The variation in the concentration of the aldehyde shows that the reaction is first order with respect to the aldehyde (Table 1). The plot of $1/k$ against $1/[\text{PhCHO}]_0$ at each temperature gives a straight line, making an intercept on the y-axis. This indicates that the reaction is initiated by the formation of an intermediate compound. Initial addition of metaborate has no influence on the oxidation rates. Under identical conditions the rates of oxidation by hydrogen peroxide, and hydrogen peroxide with metaborate are about two-third of the perborate oxidation rates (Table 2).

Table 1. Rate constants of the oxidation of benzaldehyde by sodium perborate at 323 K in 70% acetic acid-water mixture.

$[PhCHO]_0$, M	10^3[perborate]$_0$, M	10^5 k, s^{-1}
0.1	5.0	5.10
0.2	5.0	11.08
0.3	5.0	13.80
0.5	5.0	25.0
0.75	5.0	37.0
1.00	5.0	49.0
0.5	2.0	25.0
0.5	3.5	24.0
0.5	7.5	24.8
0.5	10.0	26.10
0.5	15.0	25.2

Table 2. The rates of oxidation of benzaldehyde by perborate, hydrogen peroxide with metaborate in 70% (v/v) aqueous acetic acid at 323 K.

10^3[perborate]$_0$, M	$10^3[H_2O_2]_0$, M	10^2[Metaborate]$_0$, M	10^5 k, s^{-1}
5.0	0.0	0.0	25.0
5.0	0.0	1.0	25.0
0.0	2.0	0.0	16.5
0.0	2.0	1.0	16.6

Effect of changing hydrogen ion concentration: In order to find out the effect of hydrogen ion concentration on the rate of the reaction, it has been studied at a constant acetic acid concentration of 70% (v/v), while the acidity is changed by the addition of perchloric acid. When the perchloric acid concentration was changed from 1×10^{-3} to 1×10^{-2} M, the rate was found to increase by 60%.

Effect of changing acetic acid concentration: The kinetics of the reaction has been studied by changing the composition of acetic acid in the reaction mixture, while keeping the oxidant and substrate concentrations unchanged. It has been found that the reaction is slow at lower compositions (<40%) of acetic acid. However, the reaction takes place smoothly at much higher acetic acid concentrations (Table 3), and the pseudo-first-order rate constant changes from 3.8×10^{-5} to 91.9×10^{-5} s^{-1} for a change of acetic acid concentration from 50% to 90%. The increase in rate in acetic acid is high enough to indicate that the dielectric constant [14] of the medium may play an important role. However, for a reaction between ions of similar charge, the rate decreases with the decrease in dielectric constant of the medium. On the other hand, the rate increases with the decrease in dielectric constant when a reaction takes place between ions of opposite charges [15]. The results presented in Table 3 suggest that the slowest reaction may takes place between ions of opposite charge.

Table 3. Effect of acetic acid on the reaction rate of benzaldehyde (0.5 M) and perborate (10×10^{-3} M) at 323 K.

% [ACOH], v/v	10^5 k, s^{-1}
50	3.8
60	10.7
70	25.0
80	55.6
90	91.9

Effect of temperature: The rate constants for the perborate oxidation of aromatic aldehydes at different temperatures are listed in Table 4. The electron-withdrawing groups enhance and electron-releasing groups retard the oxidation rate. The activation parameters have been computed from a plot of log *k* vs. 1/T in the temperature range 323–343 K (Table 4). The activation enthalpies and entropies are linearly related by [16],

$$\Delta H^{\#} = \Delta H_o + \beta\,\Delta S^{\#}$$

where β is the isokinetic temperature and ΔH_0 the enthalpy of activation, when $\Delta S^{\#} = 0$ and usually has no physical significance. The isokinetic temperature obtained from the slope is 474 K (r = 0.997). This linear correlation indicates that a single mechanism is operating throughout the series [17]. This is further confirmed with the Exner plot [18]. When rate measurements at two different temperatures have been made, the experimental data can be treated by

$$\log k\,(T_2) = a + b \log k\,(T_1)$$

where, k (T_2) and k (T_1) are the rate constants at temperatures T_2 and T_1 ($T_2 > T_1$) respectively. Applying this equation, a better correlation is obtained (r = 0.998), when log k (328 K) is plotted against log k (323 K). This serves as an argument that the reactions of all substituted benzaldehydes follow a common mechanism.

Table 4. Rate constants and the activation parameters of the oxidation of substituted benzaldehydes by sodium perborate in 70% acetic acid-water mixture.

Subst	10^5 k, s^{-1}				$\Delta E^{\#}$	$\Delta H^{\#}$	$\Delta G^{\#}$	$-\Delta S^{\#}$
	323 K	328 K	333 K	343 K		Kcal·mol^{-1}		Cal·mol^{-1}·deg^{-1}
H	25.0	30.0	37.0	58.5	9.44	8.80	24.3	47.7
p-CH_3	12.5	15.0	19.5	32.0	11.02	10.38	24.9	44.9
p-OCH_3	4.6	5.1	9.1	14.0	10.52	9.89	24.6	45.7
p-Cl	24.8	32.0	37.2	55.2	8.6	7.96	24.2	50.3
p-NO_2	90.0	105.0	124.4	184.4	7.9	7.26	23.3	49.9
p-CN	72.0	86.1	100.2	150.0	8.1	7.46	23.5	49.7
m-CH_3	15.4	21.2	27.4	40.5	10.5	9.86	24.5	45.3
m-OCH_3	24.6	32.1	41.0	60.1	9.8	9.16	24.2	46.6
m-Cl	29.6	36.8	43.6	63.0	8.2	7.6	24.1	51.2
m-NO_2	57.2	70.0	84.2	124	8.5	7.86	23.7	48.9

Effect of substituents: Effect of substituents on the rate of oxidation has been studied with a number of *para*- and *meta*-substituted benzaldehydes. In general, the rate of reaction is accelerated by electron-withdrawing substituents and retarded by electron-releasing ones (Table 4). A plot of log (k/k_o) *vs.* σ gives a positive slope with ρ values as +1.12 (r = 0.94). Since the reaction rates failed to show a significant correlation with any single-parameter substituents constants, the rates have been analyzed in terms of the dual substituents parameter equation of Taft [19],

$$log\ k = log\ k_o + \sigma_I \rho_I + \sigma_R \rho_R$$

The rates of oxidation of *para*- and *meta*-substituted benzaldehydes were separately correlated with σ_I and one of four σ_R values, viz. σ^o_R, $\sigma^{(AB)}_R$, σ^+_R and σ^-_R. The results are summarized in Table 5.

Table 5. Correlation of rates of oxidation of *para*- and *meta*-substituted benzaldehydes by perborate with substituent parameters at 323 K.

Substituent constants	ρ_I	ρ_R	R	SD	λ	f
			para-substituted			
σ_I, σ^o_R	0.652	1.215	0.972	0.30	1.86	0.08
σ_I, σ^+_R	0.678	0.728	0.9998	0.26	1.07	0.03
σ_I, σ^-_R	0.652	0.995	0.965	0.28	2.29	0.10
$\sigma_I, \sigma^{(AB)}_R$	0.684	1.112	0.982	0.29	1.63	0.05
			meta-substituted			
σ_I, σ^o_R	0.553	0.461	0.9963	0.39	0.835	0.04
σ_I, σ^+_R	0.573	0.271	0.993	0.26	0.473	0.07
σ_I, σ^-_R	0.514	0.401	0.853	0.22	0.780	0.03
$\sigma_I, \sigma^{(AB)}_R$	0.553	0.45	0.959	0.26	0.814	0.06

The results show that the rates of *para*-substituted benzaldehydes show excellent correlation with σ_I and σ^+_R values. The correlation with the other three σ_R values are relatively poor. The coefficient of multiple correlation (R), the standard deviation (SD), and f as the measure of the goodness of fit. f has been defined by Dayal *et al.* [19] as f = SD/RMS, where RMS is the root mean square of the data points (here log k/k_o). The comparison of f values shows that f is smaller for σ^+_R scale than those for other scales. Therefore, it is apparent that the rates of the oxidation of *para*-substituted benzaldehydes by perborate correlate best with σ_I and σ^+_R.

The rates of *meta*-substituted benzaldehydes show excellent correlation with σ_I and σ^o_R. The comparison of f values shows that f is smaller for σ^o_R scale than those for other scales. This agrees with the observation of Ehrenson *et al.* [20] that the correlation of *meta*-substituted compounds is generally best with σ^o_R scale and *meta*-substituted compounds are less discriminating.

The reaction constants and the statistical data at different temperatures are given in Table 6. The values of λ (*ca.* 1.06) showed that the oxidation of *para*-substituted benzaldehydes is more susceptible to the resonance effect than to the field effect. The selectivity of the reaction is decreased at higher temperature, but this decrease is of similar order for both the field and resonance effects, resulting in the almost constant value of λ at different temperatures.

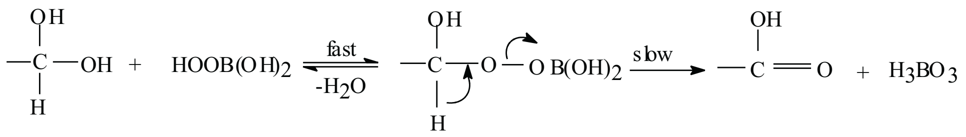
Table 6. Temperature dependence of the reaction constants.

Temp., K	ρ_I	ρ_R	R	SD	λ	f
			para-substituted			
323	0.678	0.728	0.9998	0.26	1.070	0.03
328	0.669	0.707	0.9997	0.24	1.056	0.04
333	0.648	0.660	0.9995	0.23	1.019	0.05
343	0.604	0.653	0.9990	0.22	1.081	0.04
			meta-substituted			
323	0.553	0.461	0.9993	0.39	0.835	0.04
328	0.5648	0.341	0.9983	0.39	0.473	0.04
333	0.548	0.303	0.9853	0.39	0.780	0.04
343	0.536	0.321	0.9599	0.40	0.814	0.042

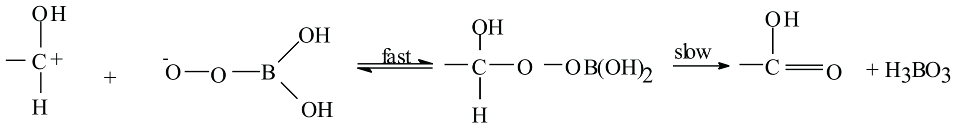
In the oxidation of the *meta*-substituted compounds, λ is *ca.* 0.726 indicating greater importance of the field effect. There is a small increase in the magnitude of the reaction constants with an increase of temperature, but this increase is of similar order for both the effects, reflected in the almost constant value of λ at different temperatures.

The oxidation of benzaldehyde to benzoic acid by potassium permanganate and chromic acid has been studied [21]. The reaction of the former reagent has been established to be acid-catalyzed and is accelerated slightly by the presence of electron-donating groups. It is believed to proceed through the formation and subsequent decomposition of permanganate ester. Under basic conditions, however, the reaction is accelerated by electron-withdrawing groups and is supposed to be a free-radical chain process [22] or to involve a hydride transfer [23]. Likewise, the chromic acid oxidation of benzaldehyde has been shown to proceed through the formation of chromate ester [21,24]. The results indicate that the oxidation of aldehyde by sodium perborate seems to occur through the formation of an intermediate compound followed by its decomposition to give products of reaction. The hydrates of aliphatic aldehydes are well known [25,26], and the oxidation of some aliphatic aldehydes has been shown to occur through intermediate hydrates. Though the hydrate of benzaldehyde has escaped detection in earlier studies [27], later reports indicate that the oxidation of benzaldehyde by some other oxidants also takes place through partially hydrated benzaldehyde [28]. Thus, protonation of the perborate ion and its reaction with the hydrated form of benzaldehyde may take place. It is also possible that the aldehyde molecule remains in the protonated form, which may react with nucleophilic perborate ion to give products. The intermediate ester formation with aromatic aldehydes has been reported in the oxidation by transition metal ions [21,24], but there is no supporting evidence, kinetic or otherwise. Regardless of which scheme is correct, one piece of information is obtained with certainly: the oxidation of benzaldehyde by perborate ion occurs through intermediate perborate ester. Two alternative mechanistic paths (Schemes 1 and 2) are shown.

Scheme 1



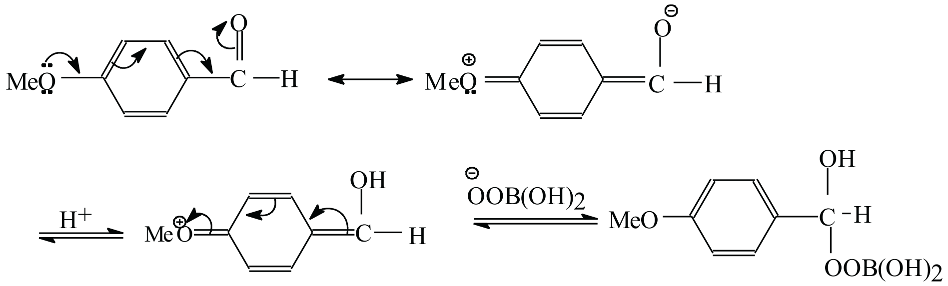
Scheme 2



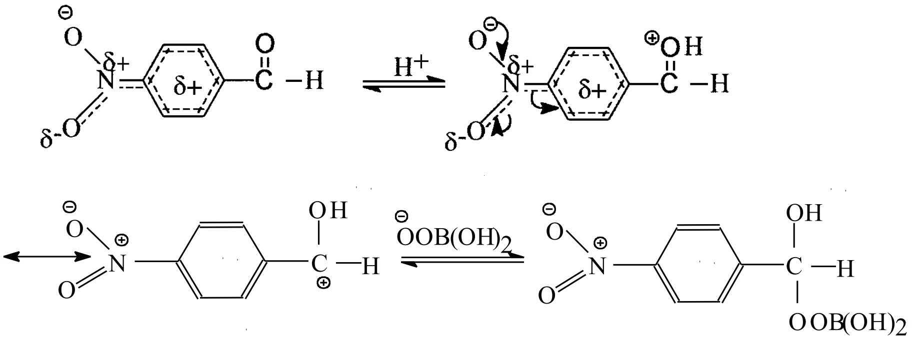
If the foregoing mechanism (Scheme 2) is correct, the attack of the perborate anion on the carbonyl carbon is very crucial, and it will be favored by the generation of a carbonium ion on that carbon. Any structural feature tending to diminish the accumulation of positive charge on this carbon should retard the rate of oxidation. Thus, an electron-releasing group (*e.g.*, a methoxy group, particularly at *ortho* and *para* positions) attached to benzaldehyde should make the rate of oxidation slower (Scheme 3), while an electron-attracting group (*e.g.*, a nitro group) should exhibit the opposite effect, and chlorine will retard the rate slightly when compared to that of unsubstituted benzaldehyde. This is found to be true experimentally. The protonation of carbonyl oxygen precedes the attack of the perborate anion, and it is very likely that the step following the protonation may be rate determining.

Thus, it becomes evident that the rate of oxidation of substituted benzaldehyde is highly influenced by the nature of the substituents. In connection with the oxidation of inorganic compounds by perborate ion, it has been shown [29–31] that the oxidation also takes place with protonated perborate. However, participation of protonated perborate ion seems unlikely in the present study, since the reactions have been carried out in acetic acid medium, unlike those done by previous workers with a high concentration of perchloric acid. On the other hand, the species $(HO)_2BOO^+H_2$ is so reactive with respect to reduction that its reactions are essentially diffusion-controlled [31] outer-sphere processes. In connection with the oxidation of benzaldehyde by chromic acid, Wiberg and Mill [21] have shown that the oxidation takes place between H_2CrO_4 and the hydrated form of benzaldehyde. On the other hand, in the permanganate oxidation of some aromatic aldehydes [22] in neutral and fairly acidic solutions, it has been shown that MnO_4^- reacts with protonated aldehyde to give permanganate ester prior to electron transfer. The observed decrease in the pseudo-first-order rate constant with an increasing dielectric constant of the medium further indicates, that the reaction may take place between two oppositely charged species, and hence the alternative mechanism (Scheme 2) which has been suggested cannot be totally ruled out.

Scheme 3



slower than benzaldehyde



faster than benzaldehyde

The rate of the chromic acid oxidation of benzaldehyde increases with the first power of the concentration of acid chromate ion as well as of benzaldehyde. The permanganate oxidation of benzaldehyde also proceeds at a rate, which is proportional to the concentrations of the aldehyde and permanganate ion. The perborate oxidation of aromatic aldehydes, which has been studied in acetic acid medium, is kinetically dissimilar, and hence the present rate constant values cannot be compared with those obtained earlier with chromic acid or permanganate. However, from the results it appears that even in acetic acid medium, perborate oxidation of the aldehydes proceed at appreciable rates, and hence perborate ion is in no way inferior to other oxidizing agents.

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