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Kinetics and Mechanism of Perborate Oxidation of Organic Sulphides

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Abstract: *The perborate oxidation of organic sulphides to sulphoxides is first order in perborate. It is first order with respect to diethyl and diphenyl sulphides, and the rate increases linearly with [MeSPh]. In highly acidic medium the oxidation exhibits first order dependence on [acid]. The oxidation is inhibited by NaCl and enhanced by increase in solvent polarity. Metaborate has no influence on the oxidation rates. The rates of oxidation by hydrogen peroxide, and hydrogen peroxide with metaborate are about two-third of the perborate oxidation rates. Electron-releasing groups accelerate and electron-withdrawing groups retard the oxidation. In the oxidation of diethyl sulphide attack of protonated perboric acid on sulphide and in methyl phenyl sulphide (i) attack of protonated perboric acid on sulphide, and (ii) breakdown of protonated perboric acid to yield* $H_2BO_3^+$ *which reacts with the substrate in a fast step are suggested as rate-determining. In diphenyl sulphide* $H_2BO_3^+$ *is proposed as the oxidising species.*

Sodium perborate ($NaBO_3.4H_2O$) is a non-toxic cheap large scale industrial chemical primarily used as a source of 'active oxygen' in detergents and as a mild antiseptic. This active oxygen has the oxidising properties of hydrogen peroxide. Pmr spectral analysis[1] and X-ray diffraction studies[2] conclude perborate as a true peroxysalt with water of crystallisation. Perborate is a heterocycle and is in 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 acquires stronger electrophilicity by the coordination with borate.[3] The byproduct is completely innocuous and this stable and easily handled crystalline substance oxidises organic sulphides to either sulphoxides or sulphones, and anilines to azo compounds.[4] The mechanism of perborate oxidation has not been studied in detail and we report here the kinetics and mechanism of perborate oxidation of organic sulphides. Recently we have investigated perborate oxidation of quinol.[5]

EXPERIMENTAL

Materials. Sodium perborate, $NaBO_3.4H_2O$, (Riedel) was used without further purification. Sulphides were prepared using standard methods and were distilled before use. All other chemicals were of analytical grade.

Kinetics. Rate studies were made under pseudo-unimolecular conditions with a large excess of sulphide over perborate at constant temperature in aqueous *t*-butanol in presence of perchloric acid. The progress of the oxidation was followed by estimation of unconsumed perborate at different time intervals. Standardisation of perborate solution and estimation of unreacted perborate in the reaction mixture were done by draining 5 ml aliquot into a fresh hot (*ca.* 65°C) mixture of 10 ml of 5 mol dm^{-3} sulphuric acid and 10 ml of 2% potassium iodide solution,. and the liberated iodine was titrated against standardised thio to the starch end point. The course of the oxidation was followed for about two-half lives. The pseudo-first-order rate constant (k) was calculated from the slope of the linear plot of log titre versus time by the method of least squares and was reproducible within ±5%.

Stoichiometry. At 30°C perborate in slight excess was allowed to react with (i) diethyl sulphide in 0.5 mol dm^{-3} perchloric acid in 30% aqueous *t*-butanol, (ii) methyl phenyl sulphide in 1 mol dm^{-3} perchloric acid in 30% aqueous *t*-butanol and (iii) diphenyl sulphide in 1 mol dm^{-3} perchloric acid in 50% aqueous *t*-butanol, and estimation of unreacted perborate after 2,3,6 and 21 hours in (i), 6 and 7 hours in (ii) and 6 and 8 hours in (iii) showed that 1 mole equivalent of perborate has reacted with 1 mole equivalent of sulphides.

Product Analysis. To sulphides (0.005 mole) in presence of *ca.* 1 mol dm^{-3} perchloric acid (*ca.* 0.5 mol dm^{-3} for diethyl sulphide) in aqueous *t*-butanol perborate (0.005 mole) was added. *t*-Butanol was distilled off under reduced pressure. The products were extracted with ether and identified as sulphoxides by ir spectra. Hence under the conditions studied the oxidation stops at the first stage and is represented as (1).

$$\begin{aligned} \text{EtSEt} + \text{NaBO}_3 &\longrightarrow \text{EtSOEt} + \text{NaBO}_2 \\ \text{MeSPh} + \text{NaBO}_3 &\longrightarrow \text{MeSOPh} + \text{NaBO}_2 \\ \text{PhSPh} + \text{NaBO}_3 &\longrightarrow \text{PhSOPh} + \text{NaBO}_2 \qquad (1) \end{aligned}$$

RESULTS AND DISCUSSION

The oxidation is first order with respect to perborate. Plots of log titre versus time are linear with correlation coefficient (r) of at 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 diethyl and methyl phenyl sulphides, and in the oxidation of diphenyl sulphide correction for decomposition has been effected.

Table 1. Pseudo-First-Order Rate Constants for the Perborate Oxidation of Diethyl, Methyl Phenyl and Diphenyl Sulphides at 40°C.

$10^3[\text{Perborate}]_0$ mol dm^{-3}	$10^2[\text{Sulphide}]_0$ mol dm^{-3}	EtSEt 10^3k [a] s^{-1}	MeSPh 10^4k [b] s^{-1}	PhSPh 10^5k [c] s^{-1}
1.0	2.0	-	6.7	4.3
2.5	2.0	1.8	-	-
3.0	2.0	1.6	6.6	3.8
4.0	2.0	1.6	-	-
2.0	1.0	0.86	6.4	2.1
2.0	1.5	1.2	-	-
2.0	2.0	1.8	7.0	3.9
2.0	2.5	2.3	-	-
2.0	3.0	2.7	9.8	5.7
2.0	3.5	3.3	-	-
2.0	4.0	3.7	11.9	7.9
2.0	5.0	-	12.6	-

[a] $[HClO_4]$ = 0.5 mol dm^{-3}; 30% (v/v) aq. *t*-BuOH
[b] $[HClO_4]$ = 1.0 mol dm^{-3}; 30% (v/v) aq. *t*-BuOH
[c] $[HClO_4]$ = 1.0 mol dm^{-3}; 50% (v/v) aq. *t*-BuOH

Perborate oxidation of diethyl and diphenyl sulphides is first order with respect to the substrate. In the methyl phenyl sulphide oxidation the rate increases with increase in [Sulphide]$_0$. Plots of k versus [Sulphide]$_0$ are linear, passing through the origin in the oxidation of diethyl and diphenyl sulphides (both with r of 0.999) and with a positive intercept in k -axis in methyl phenyl sulphide oxidation (r = 0.978). Alkali fails to catalyse the oxidation and the oxidation is sluggish in low acidic medium. In highly acidic medium the rate increases with increase in acid concentration (Table 2). The oxidation is first order with respect to acid. Plot of k versus [HClO$_4$] is a straight line passing through the origin (r = 0.994).

Table 2. Dependence of the Perborate Oxidation Rates on [HClO$_4$] at 40°C.

[HClO$_4$] mol dm^{-3}	EtSEt 10^3k [a] s^{-1}	MeSPh 10^4k [b] s^{-1}	PhSPh 10^5k [c] s^{-1}
0.3	0.92	-	-
0.5	1.8	-	-
0.7	2.4	4.3	-
1.0	-	6.4	3.9
1.5	-	-	5.4

10^3 [Perborate]$_0$ = 2.0 mol dm^{-3}
[a] 10^2 [EtSEt]$_0$ = 2.0 mol dm^{-3}; 30% (v/v) aq. *t*-BuOH
[b] 10^2 [MeSPh]$_0$ = 1.0 mol dm^{-3}; 30% (v/v) aq. *t*-BuOH
[c] 10^2 [PhSPh]$_0$ = 2.0 mol dm^{-3}; 50% (v/v) aq. *t*-BuOH

Sodium chloride suppresses the oxidation rates. The rates of oxidation decrease moderately with decrease of dielectric constant of the medium (Table 3). 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 4). The pseudo-first-order rate constants for the perborate oxidation of sulphides at different temperatures are listed in Table 5. The electron-releasing groups enhance and electron-withdrawing groups retard the oxidation rate. The activation parameters were calculated by the least square analysis of Eyrings plot.

Table 3. Effect of Addition of NaCl[a] and Variation of Solvent Composition on the Oxidation Rates at 40°C.

[NaCl] mol dm^{-3}	EtSEt 10^3k [b] s^{-1}	MeSPh 10^4k [c] s^{-1}	*t*-BuOH-H$_2$O % (v/v)	EtSEt 10^3k [b] s^{-1}	MeSPh 10^4k [c] s^{-1}
0	1.8	6.4	30-70	1.8	6.4
0.2	1.1	-	40-60	1.6	-
0.3	-	2.6	50-50	1.4	5.6
0.5	1.0	-	60-40	1.3	-
0.7	1.0	2.7	70-30	1.3	4.1

10^3 [Perborate]$_0$ = 2.0 mol dm^{-3}
[a] Solvent = 30% (v/v) aq. *t*-BuOH
[b] 10^2 [EtSEt]$_0$ = 2.0 mol dm^{-3}; [HClO$_4$] = 0.5 mol dm^{-3}
[c] 10^2 [MeSPh]$_0$ = 1.0 mol dm^{-3}; [HClO$_4$] = 1.0 mol dm^{-3}

Table 4. The Rates of Oxidations by Perborate, Hydrogen Peroxide and Hydrogen Peroxide with Metaborate in 30% (v/v) Aqueous *t*-BuOH at 40°C.

10^3[Perborate]$_0$ mol dm^{-3}	$10^3[H_2O_2]_0$ mol dm^{-3}	10^2[Metaborate]$_0$ mol dm^{-3}	EtSEt 10^3k [a] s^{-1}	MeSPh 10^4k [b] s^{-1}
2.0	0	0	1.8	6.4
2.0	0	1.0	1.9	6.3
0	2.0	0	1.1	3.9
0	2.0	1.0	1.2	4.3

[a] 10^2 [EtSEt]$_0$ = 2.0 mol dm^{-3}; [$HClO_4$] = 0.5 mol dm^{-3}
[b] 10^2 [MeSPh]$_0$ = 1.0 mol dm^{-3}; [$HClO_4$] = 1.0 mol dm^{-3}

Table 5. The Rate Constants and Activation Parameters for the Perborate Oxidation of Sulphides.

Sulphide	10^4k s^{-1} 30	10^4k s^{-1} 40	10^4k s^{-1} 50	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1} 40°C
Diethyl[a]	7.3	18	35	61	102	93
Di-*n*-butyl[a]	7.6	22	38	62	101	93
Methyl phenyl[b]	3.2	6.4	11.6	50	148	96
Methyl *o*-tolyl[b]	1.2	2.2	4.4	50	154	99
Diphenyl[c]	0.13	0.21	0.45	48	181	105

10^3 [Perborate]$_0$ = 2.0 mol dm^{-3}
[a] 10^2 [Sulphide]$_0$ = 2.0 mol dm^{-3}; [$HClO_4$] = 0.5 mol dm^{-3}; solvent: 30% (v/v) aq. *t*-BuOH
[b] 10^2 [Sulphide]$_0$ = 1.0 mol dm^{-3}; [$HClO_4$] = 1.0 mol dm^{-3}; solvent: 30% (v/v) aq. *t*-BuOH
[c] 10^2 [Sulphide]$_0$ = 1.0 mol dm^{-3}; [$HClO_4$] = 1.0 mol dm^{-3}; solvent: 50% (v/v) aq. *t*-BuOH

Mechanism and Rate Law

Free perboric acid has demonstrable existence in solution although it has been proved exceedingly difficult to isolate.[6] The possible oxidising species of perborate are perborate itself, perboric acid, protonated perboric acid and hydrogen peroxide.[3,5] If perborate itself can effect the oxidation, contrary to the experimental observation, the reaction should proceed in alkaline medium. The oxidation has been carried out in highly acidic medium and the ionisation constant of perboric acid is reported as (0.6-1.6) x 10^{-8} (approximately).[6] Hence it is concluded that in the reaction medium perborate exists as perboric acid. Ogata and Shimizu[3] have suggested hydrogen peroxide as the oxidising species and it has acquired stronger electrophilicity by the coordination with boric acid which acts as Lewis acid. In the present study, the rates of oxidation by hydrogen peroxide, and hydrogen peroxide with metaborate are only about two-third of perborate oxidation rates. Hence the perborate oxidation is not through hydrogen peroxide. As the oxidation is catalysed by acid perboric acid is unlikely to be the reactive species.

Oxidation of Diethyl Sulphide. The perborate oxidation of diethyl sulphide is first order in perchloric acid and hence protonated perboric acid is suggested as the reactive species. Since the oxidation is also first order in sulphide electrophilic attack of protonated perboric acid on sulphide is proposed as the rate-limiting step (Scheme 1).

$$(HO)_2BOOH + H^+ \rightleftharpoons^{K_1} (HO)_2BO\overset{+}{O}H_2 \qquad (2)$$

$$(HO)_2BO\overset{+}{O}H_2 + EtSEt \xrightarrow{k_2} Et\overset{++}{S}(OH_2)Et + H_2BO_3^- \quad \text{slow} \qquad (3)$$

$$Et\overset{++}{S}(OH_2)Et \longrightarrow Et\overset{+}{S}(OH)Et + H^+ \qquad (4)$$

$$Et\overset{+}{S}(OH)Et \longrightarrow EtSOEt + H^+ \qquad (5)$$

$$H_2BO_3^- + H^+ \longrightarrow H_3BO_3 \qquad (6)$$

Scheme 1.

The rate law for the suggested mechanism is $-d\,[\text{Perborate}]/dt = K_1k_2\,[\text{EtSEt}][H^+][\text{Perborate}]$ (7)
and the pseudo-first-order rate constant, $k = K_1k_2\,[\text{EtSEt}][H^+]$ (8)

Oxidation of Methyl Phenyl Sulphide. The perborate oxidation of methyl phenyl sulphide proceeds via two paths -- one depends on [Sulphide] and the other independent of sulphide concentration -- as evident from the linear plot of k versus [Substrate] with a k -intercept. The oxidation is sluggish at low acidity (even in 0.4 mol dm^{-3} perchloric acid) and is first order in acid at high acidity. Protonated perboric acid is suggested as the reactive species, and rate-limiting electrophilic attack of protonated perboric acid on the substrate and rate-determining breakdown of protonated perboric acid to yield $H_2BO_3^+$ which attacks the substrate in a fast step[5] are proposed as the reaction mechanism (Schemes 2 & 3).

$$(HO)_2BO\overset{+}{O}H_2 + MeSPh \xrightarrow{k_3} Me\overset{++}{S}(OH_2)Ph + H_2BO_3^- \quad \text{slow} \qquad (9)$$

$$Me\overset{++}{S}(OH_2)Ph \longrightarrow Me\overset{+}{S}(OH)Ph + H^+ \qquad (10)$$

$$Me\overset{+}{S}(OH)Ph \longrightarrow MeSOPh + H^+ \qquad (11)$$

Scheme 2.

$$(HO)_2BO\overset{+}{O}H_2 \xrightarrow{k_4} (HO)_2BO^+ + H_2O \quad \text{slow} \qquad (12)$$

$$MeSPh + (HO)_2BO^+ \longrightarrow Me\overset{+}{S}[OB(OH)_2]Ph \qquad (13)$$

$$Me\overset{+}{S}[OB(OH)_2]Ph + H_2O \longrightarrow Me\overset{++}{S}(OH_2)Ph + H_2BO_3^- \qquad (14)$$

Scheme 3.

For the proposed mechanism the rate equation is derived as (15).

$$-d[\text{Perborate}]/dt = K_1(k_3[\text{MeSPh}] + k_4)[H^+][\text{Perborate}] \qquad (15)$$

The pseudo-first-order rate constant, $k = K_1(k_3[\text{MeSPh}] + k_4)\,[H^+]$ (16)

The percentage of the oxidation by protonated perboric acid (Scheme 2) in 1.0 mol dm^{-3} perchloric acid at 40°C increases from 32 to 65 when $[\text{MeSPh}]_0$ is varied from 0.01 to 0.05 mol dm^{-3}.

Oxidation of Diphenyl Sulphide. The perborate oxidation of diphenyl sulphide is first order each in sulphide and acid. The reactive species may either be protonated perboric acid or $H_2BO_3^+$. $H_2BO_3^+$ is a more potent oxidising species than protonated perboric acid. The rate of formation of $H_2BO_3^+$ under the same acid strength (from MeSPh oxidation study) is larger than the rate of diphenyl sulphide oxidation. Hence in diphenyl sulphide oxidation $H_2BO_3^+$ is suggested as the oxidising species. If protonated perboric acid were to be the reactive species, contrary to the experimental findings, the enthalpy of activation for diphenyl sulphide oxidation should be higher than that for diethyl sulphide as the assistance by way of S-O bond formation will be lesser in diphenyl sulphide than diethyl sulphide. Since the attack of $H_2BO_3^+$ on the substrate lacks bond breaking it is unlikely to be rate limiting. Hence hydrolysis of sulphonium ion (presumed to be formed in steady-state concentration) is proposed as the rate-determining step (Scheme 4).

$$\overset{+}{(HO)_2BOOH_2} \overset{K_5}{\rightleftharpoons} H_2BO_3^+ + H_2O \tag{17}$$

$$H_2BO_3^+ + PhSPh \overset{K_6}{\rightleftharpoons} \overset{+}{Ph_2SOB(OH)_2} \tag{18}$$

$$\overset{+}{Ph_2SOB(OH)_2} + H_2O \xrightarrow{k_7} \overset{++}{Ph_2SOH_2} + H_2BO_3^- \quad \text{slow} \tag{19}$$

$$\overset{++}{Ph_2SOH_2} \longrightarrow \overset{+}{Ph_2SOH} + H^+ \tag{20}$$

$$\overset{+}{Ph_2SOH} \longrightarrow Ph_2SO + H^+ \tag{21}$$

Scheme 4.

The rate law for Scheme 4 is $-d\,[\text{Perborate}]/dt = K_1K_5K_6k_7[\text{PhSPh}][H^+][\text{Perborate}]$ (22)
and the pseudo-first-order rate constant, $k = K_1K_5K_6k_7[\text{PhSPh}][H^+]$ (23)

The kinetic constants at 40°C, calculated from the slopes and intercept of the linear plots, are $K_1k_2 = 0.19$ $dm^6\ mol^{-2}\ s^{-1}$; $K_1k_3 = 1.7 \times 10^{-2}$ $dm^6\ mol^{-2}\ s^{-1}$; $K_1k_4 = 4.4 \times 10^{-4}$ $dm^3\ mol^{-1}\ s^{-1}$ and $K_1K_5K_6k_7 = 1.9 \times 10^{-3}$ $dm^6\ mol^{-2}\ s^{-1}$. The rate laws (7), (15) and (22) accord well with the observed kinetic orders in perborate, sulphides and acid. The proposed mechanism explains the absence of retardation or enhancement by metaborate, moderate positive dielectric effect and the slower oxidation by hydrogen peroxide and hydrogen peroxide with metaborate. A possible explanation for the inhibition by NaCl is that the chloride ion may associate with protonated perboric acid as an ion pair or a loose complex thereby decrease its electrophilicity and also the feasibility of peroxide bond cleavage. The acceleration of the oxidation by electron-releasing and retardation by electron-withdrawing groups also support the mechanism suggested. The decrease in reactivity of methyl *o*-tolyl sulphide, compared with methyl phenyl sulphide, may be due to the steric effect.

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