On the Mechanism of the Perborate Oxidation of Organic Sulfides in Glacial Acetic Acid

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Perborate solution in glacial acetic acid generates peracetic acid on aging, and the peracetic acid oxidation of organic sulfides is fast. The oxidation with fresh solutions of perborate in acetic acid is smooth and is second order, uncatalyzed by acid; hydrogen peroxide is the oxidizing species. The oxidation conforms to the Exner and Hammett relations.

Introduction

Sodium perborate is a cheap, nontoxic, stable, easily handled, large-scale industrial chemical, primarily used in detergents as a bleaching agent. It is a peroxo salt with anionic formula[1] $B_2(O_2)_2(OH)_4{}^{2-}$. In glacial acetic acid it is a highly effective reagent, the oxidant of choice, for the oxidation of organic sulfides.[2,3] The present study, the first report on the kinetics of perborate oxidation under anhydrous conditions, reveals the active oxidizing species in glacial acetic acid. In aqueous solution perborate generates hydrogen peroxide, and kinetic studies on perborate oxidation in aqueous and partly aqueous media are many.[4–8] Oxidation of organic sulfides is of interest; one application involves oxidation of bis(2-chloroethyl) sulfide for decontamination and stock-pile destruction.[9] Reports on the kinetics of oxidation of organic sulfides by heavy metals are numerous;[10–14] but use of heavy metals causes environmental constraints. The kinetic study on perborate oxidation in aqueous *tert*-butyl alcohol shows that the oxidation of dialkyl, alkyl aryl, and diaryl sulfides is acid-catalyzed and occurs through different mechanisms.[15]

Results and Discussion

The kinetics of the reaction, studied in glacial acetic acid under the condition [sulfide] > [perborate], was followed by estimating the unchanged oxidizing agent iodometrically. On mixing the aged solution of perborate in acetic acid with the sulfide of desired concentration in acetic acid, there is a rapid drop of titre, followed by a smooth slow oxidation. With aging, the fraction of the oxidation that occurs rapidly on mixing increases, but the specific rate of the remaining part of the oxidation is constant – an observation not so far reported. Under second order conditions, a plot of log ([oxidant]$_0$ [sulfide]/[sulfide]$_0$ [oxidant]) versus time is linear, and with aging the *y* intercept increases (Figure 1); the least-squares slope of the linear plot affords the second order rate constant k_2, and the rate constants are reproducible to ±4%. Each kinetic run was made with a fresh solution of perborate. Constancy of the second order rate constants at different initial concentrations of the reactants confirms the order of the oxidation (Table 1).

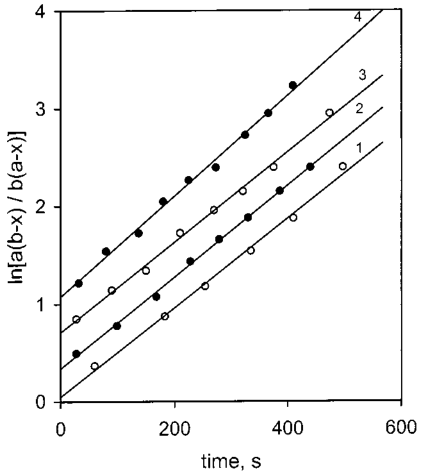

Figure 1. Aging effect of perborate in acetic acid; oxidation of diethyl sulfide; aging: 1. 0.25 h; 2. 2.0 h; 3. 4.25 h; 4. 6.5 h; *a* = [oxidant]$_0$, *b* = [sulfide]$_0$, (*a* − *x*) = [oxidant], (*b* − *x*) = [sulfide]

Table 1. Perborate oxidation of sulfides in acetic acid

10^3[perborate]$_0$ mol dm^{-3}	10^2[sulfide]$_0$ mol dm^{-3}	10^3k_2 dm^3 mol^{-1} s^{-1}		
		EtSEt[a]	PhSPh[b]	$PhSCH_2COOH$[b]
5.0	2.0	210 (210)[c]	5.0 (5.0)	6.8 (6.9)
8.0	2.0	–	5.3	7.0
10.0	2.0	210	–	–
12.0	2.0	210	5.0	7.0
5.0	1.0	210	–	6.8
5.0	3.0	210	4.9	–
5.0	4.0	210	–	7.0
5.0	5.0	–	5.3	–

[a] 30 °C. – [b] 50 °C. – [c] Values in parentheses are those of hydrogen peroxide.

The oxidation is independent of acidity of the medium; the specific oxidation rate remains constant at different acidities. The acidity of the medium, at fixed composition of acetic acid, was increased by the addition of trichlo-

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roacetic acid (Table 2). Boric acid and borate do not influence the oxidation. The specific oxidation rate in the presence of a large excess of orthoboric acid or metaborate is the same as that in the absence of these (Table 3). The oxidation rate decreases with decreasing composition of acetic acid (Table 4). The concentration of acetic acid was decreased by the addition of methanol.

Table 2. Non-dependence of rate on acidity

$[Cl_3CCOOH]_0$ mol dm^{-3} [a]	0	0.5	1.0
$10^3\ k_2$ dm^3 mol^{-1} s^{-1}	16	15	16

[a] $10^2[EtSEt]_0$ = 2.0 mol dm^{-3}, 10^3[perborate]$_0$ = 5.0 mol dm^{-3}, HOAc:MeOH = 40:60% (v/v), 30 °C.

Table 3. Lack of influence of boric acid and borate

$10^2\ [H_3BO_3]_0$[a] mol dm^{-3}	0	1.0	2.0	0	0
$10^2\ [NaBO_2]_0$ mol dm^{-3}	0	0	0	1.0	1.5
$10\ k_2$ dm^3 mol^{-1} s^{-1}	2.1 (2.1)[b]	2.1	2.1 (2.1)	2.1 (2.1)	2.1

[a] $10^2[EtSEt]_0$ = 2.0 mol dm^{-3},10^3[perborate]$_0$ = 5.0 mol dm^{-3}, medium: glacial acetic acid, 30 °C. − [b] Values in parentheses correspond to hydrogen peroxide oxidation.

Table 4. Solvent effect

HOAc/MeOH % (v/v)	100:0	80:20	60:40	40:60
$10^2\ k_2$[a] dm^3 mol^{-1} s^{-1}	21	10	4.6	1.6

[a] $10^2[EtSEt]_0$ = 2.0 mol dm^{-3}, 10^3[perborate]$_0$ = 5.0 mol dm^{-3}, 30 °C.

Perborate in glacial acetic acid generates peracetic acid. Chemical tests confirm the same.[16] Kinetic studies with peracetic acid under identical condition show that the oxidation of sulfides including *S*-phenylmercaptoacetic acid by peracetic acid is very fast. Also, chemical tests reveal the absence of peracetic acid and the presence of hydrogen peroxide in fresh solutions of perborate in glacial acetic acid. Further, kinetic studies with hydrogen peroxide as the oxidant, using sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) as the source of dry hydrogen peroxide, show that the rates of perborate oxidation of organic sulfides (including *S*-phenylmercaptoacetic acid), under identical conditions, are the same as those of hydrogen peroxide. Also, boric acid and borate do not influence the hydrogen peroxide oxidation. Experiments show that unlike perborate, percarbonate dissolved in glacial acetic acid does not generate peracetic acid on aging; formation of peracetic acid from commercial hydrogen peroxide and glacial acetic acid requires catalytic amounts of mineral acid.[16]

Perborate oxidation of diethyl, di-*n*-butyl, 3,4-dimethylphenyl methyl, 4-methoxy-3-methylphenyl methyl, methyl 2-methyl-4-nitrophenyl, diphenyl sulfides, and 6 *para*-substituted *S*-phenylmercaptoacetic acids follow second order kinetics. The enthalpy of activation and entropy of activation were calculated from the oxidation rates at 45−65 °C using the Eyring plot (for aliphatic sulfides the temperature range is 20−40 °C). The oxidation of aromatic sulfides is sluggish below 45 °C and above 65 °C the oxidant decomposes. Table 5 shows that electron-releasing substituents enhance the oxidation whereas electron-withdrawing substituents retard the same. The oxidation conforms to the Exner relationship; plot of log k_2(65 °C) versus log k_2(45 °C) is linear (correlation coefficient, r = 0.999; standard error of estimate, *sd* = 0.04; slope = 0.971; number of data sets, n = 12). The existence of the Exner relationship reveals that all the sulfides, including *S*-phenylmercaptoacetic acids, are oxidized by a common mechanism.

Analysis of the structure-reactivity relationship reveals that the oxidation of *S*-phenylmercaptoacetic acids conforms to the Hammett equation at all the temperatures studied (r = 0.999, 0.995, 0.998; *sd* = 0.01, 0.03, 0.02; T = 45, 55, 65 °C). The negative ρ values (−0.83, −0.78, −0.77 at 45, 55, and 65 °C, respectively) point to an electron-deficient sulfur atom in the transition state. Further, the reaction constant compares with those of the molybdenum(VI)-[17] and tungsten(VI)-catalyzed[4] perborate (hydrogen per-

Table 5. Perborate oxidation of dialkyl, alkyl aryl, and diaryl sulfides, as well as *S*-phenylmercaptoacetic acids

Substrate[a]	$10^3\ k_2$ dm^3 mol^{-1} s^{-1}			$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J K^{-1} mol^{-1}
	45 °C	55 °C	65 °C		
$(C_2H_5)_2S$	470[b]	740[b]	1150[b]	37	134
$(nC_4H_9)_2S$	830[b]	1480[b]	2630[b]	49	94
m-CH_3,p-$CH_3OC_6H_3SCH_3$	130	260	450	54	93
m,p-$(CH_3)_2C_6H_3SCH_3$	110	200	360	50	106
o-CH_3,p-$NO_2C_6H_3SCH_3$	3.6	6.4	12.4	53	125
$(C_6H_5)_2S$	4.0	7.4	13.7	53	126
p-$CH_3OC_6H_4SCH_2COOH$	8.3	15.3	26	48	133
p-$CH_3C_6H_4SCH_2COOH$	7.0	14.7	24	52	124
$C_6H_5SCH_2COOH$	5.4	10.0	18	51	127
p-$ClC_6H_4SCH_2COOH$	3.3	6.1	11.0	51	134
p-$BrC_6H_4SCH_2COOH$	3.3	6.1	11.0	51	134
p-$NO_2C_6H_4SCH_2COOH$	1.13	2.5	4.3	57	121

[a] 10^2 [sulfide]$_0$ = 2.0 mol dm^{-3}, 10^3[perborate]$_0$ = 5.0 mol dm^{-3}. − [b] Extrapolated using the Arrhenius plot.

oxide) oxidation of *S*-phenylmercaptoacetic acids in aqueous acetic acid [−0.98 (at 45 °C) and −0.55 (at 55 °C), respectively]. Also, the negative entropies of activation indicate a rigid transition state that is likely to be solvated.

In glacial acetic acid perborate is unlikely to exist as the peroxoborate anion; the pK_a of perboric acid[18] is 7.91, but that of acetic acid is 4.76. It is completely converted into hydrogen peroxide; chemical tests confirm the same. Also, the rates of oxidation by perborate are the same as those by hydrogen peroxide (using percarbonate). These results clearly show hydrogen peroxide as the oxidizing agent of perborate in the smooth oxidation. Hence, the mechanism of the smooth oxidation is electrophilic attack of the peroxide oxygen on the sulfur atom. Methanol is a nucleophile, and association of methanol with the electrophilic peroxide oxygen atom may be a reason for the suppression of the oxidation with the addition of methanol.

Generation of peracetic acid on aging of perborate solutions in glacial acetic acid, confirmed by chemical tests, and the fact that oxidation of organic sulfides by peracetic acid is very much faster than that by hydrogen peroxide, explain the rapid drop of titre on mixing of an aged solution of perborate in acetic acid with the sulfides. Peracetic acid is formed slowly on aging, and on mixing it oxidizes the sulfides instantaneously. The oxidation of organic sulfides by perborate in aqueous *tert*-butyl alcohol is acid-catalyzed and occurs only at high acidity ($0.7-1.5$ mol dm^{-3}).[15] A possible explanation is that the nucleophilic solvent molecules associate with hydrogen peroxide and reduce its electrophilicity; only the protonated species is effective in promoting the reaction $RSR' + H_2O_2 \rightarrow RSOR' + H_2O$ (k_2).

Experimental Section

Materials: Sodium perborate, $NaBO_3{\cdot}4H_2O$ (SD. Fine) and sodium percarbonate, $Na_2CO_3{\cdot}1.5H_2O_2$ (Fluka) were used as received. Sulfides, including *S*-phenylmercaptoacetic acids, were prepared using standard methods, and were distilled or recrystallized before use. Acetic acid was heated under reflux for 6 h in the presence of chromium(VI) oxide and distilled through a column. All other chemicals were of analytical grade.

Kinetics: Rate studies were made in glacial acetic acid under second order conditions at constant temperature. For each kinetic run a fresh solution of perborate in glacial acetic acid was prepared, standardized iodometrically, and used without allowing it to stand. The progress of the oxidation, with sulfides in excess over perborate, was followed at least up to 80% by iodometric estimation of the unconsumed oxidizing agent.

Stoichiometry: Stoichiometric study on perborate oxidation of diethyl sulfide in glacial acetic acid at 30 °C, under the condition [perborate] > [sulfide] shows that 1 mol of the sulfide consumes 1 mol of the oxidant. Moreover, investigation with dimethyl sulfoxide (DMSO) in glacial acetic acid, under the condition [DMSO] >> [perborate] reveals that the oxidation of sulfoxide to sulfone does not occur under the experimental conditions. Further, in all cases the kinetic data conform to the second order rate law.

Product Analysis: Perborate (0.005 mol) was added to the sulfide (0.005 mol) in glacial acetic acid at 50°C. After 0.5 h, the acetic acid was neutralized, the product was extracted with diethyl ether and identified as the sulfoxide by its infrared spectrum. Hence the reaction is represented as $RSR' + NaBO_3 \rightarrow RSOR' + NaBO_2$. The yield is 71% (diphenyl sulfide) to 93% (di-*n*-butyl sulfide).[2]

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