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Formation of Peracetic Acid upon Aging of Perborate in Acetic Acid. Kinetics of the Oxidation of S-Phenylmercaptoacetic Acids

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Summary. Upon aging, perborate in glacial acetic acid generates peracetic acid and thus oxidizes S-phenylmercaptoacetic acid rapidly. Perborate dissolved in ethylene glycol, however, does not show the aging effect, and the corresponding oxidation proceeds smoothly. The oxidation is of second order and not acid catalyzed. Boric acid and borate do not influence the oxidation. In the smooth oxidation, H_2O_2 is the reactive species. The oxidation of some *para*-substituted S-phenylmercaptoacetic acids conforms to the *Exner* relationship, indicating operation of a common mechanism. Also, the oxidation obeys the *Hammett* equation with a negative reaction constant. However, the oxidation of *p*-nitro-S-phenylmercaptoacetic acid follows a different kinetic pathway.

Keywords. Perborate; S-Phenylmercaptoacetic acid; Mechanism.

Introduction

Sodium perborate ($NaBO_3 \cdot 4H_2O$) is a cheap, non-toxic, easily handled, stable, large-scale industrial chemical, primarily used in detergent industry as a bleaching agent. It is a true peroxo salt with the anionic formula $B_2(O_2)_2(OH)_4^{2-}$ [1]. In aqueous solution it yields hydrogen peroxide [1], and kinetic studies in aqueous and partly aqueous media are numerous [2–7]. Perborate is an effective oxidizing agent in organic synthesis and is used in glacial acetic acid [8]. It oxidizes sulfides to sulfoxides [8], and this is the first report on the kinetics of perborate oxidation under anhydrous condition. Organic sulfides are important substrates for oxidations; one application involves oxidation of *bis*-(2-chloroethyl) sulfide for decontamination and stockpile destruction [9]. Mechanistic studies on the oxidation of organic sulfides with heavy metals are numerous [10–14]; use of heavy metals results in environmental constraints.

Results and Discussion

The solubility of sodium perborate in a variety of organic solvents was tested; it is insoluble in methanol, ethanol, 2-propanol, *t*-butyl alcohol, dimethylformamide,

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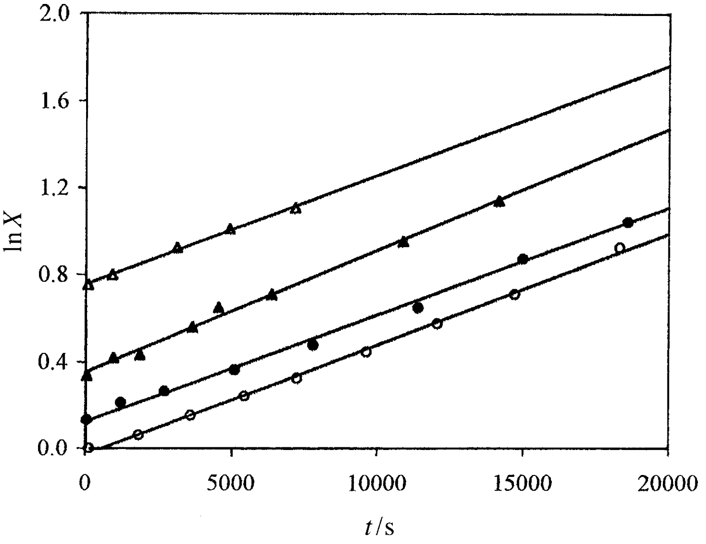

Fig. 1. Aging effect of perborate solution in acetic acid; oxidation of S-phenylmercaptoacetic acid; $X = ([\text{oxidant}]_0 \cdot [\text{substrate}]/[\text{substrate}]_0 \cdot [\text{oxidant}])$; $[\text{oxidant}]_0 = 5.0 \times 10^{-3}\,\text{mol} \cdot \text{dm}^{-3}$; $[\text{substrate}]_0 = 2.0 \times 10^{-2}\,\text{mol} \cdot \text{dm}^{-3}$; acetic acid : ethylene glycol = 75 : 25% (v/v); 50°C; ○ perborate in ethylene glycol; ● perborate in acetic acid (aging: 45 min); ▲ perborate in acetic acid (aging: 225 min); △ perborate in acetic acid (aging: 430 min)

dioxane, acetonitrile, 2-ethoxyethanol, 2-butoxyethanol, 2-methoxypentan-2,4-diol, and glycerol, but readily dissolves in glacial acetic acid and less so in ethylene glycol. The kinetics of the oxidation in acetic acid-ethylene glycol under the condition [S-phenylmercaptoacetic acid] > [perborate] was followed by iodometric estimation of the unreacted oxidizing agent. Upon mixing the aged solution of perborate in acetic acid with a substrate of desired concentration in acetic acid and ethylene glycol, 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 reported so far. The smooth oxidation follows a second order rate law (Eq. (1)). Plots of $\ln([\text{oxidant}]_0 \cdot [\text{substrate}]/[\text{substrate}]_0 \cdot [\text{oxidant}])$ *vs.* time are linear, but the intercept increases with aging (Fig. 1). If the oxidant is dissolved in ethylene glycol and the kinetics is studied in ethylene glycol – acetic acid, no effect of aging is observed. However, the oxidation remains a second order process, first order each with respect to the oxidant and the substrate. Under the condition [S-phenylmercaptoacetic acid] > [perborate] and perborate dissolved in ethylene glycol, the oxidation follows second order kinetics; plots of $\ln([\text{oxidant}]_0 \cdot [\text{substrate}]/[\text{substrate}]_0 \cdot [\text{oxidant}])$ *vs.* time are linear. Constancy of the second order rate constants (k_2), obtained from the least squares slopes of the second order plots at different initial concentrations of the reactants, confirms the second order law ($[\text{perborate}]_0 = 5 - 15 \times 10^{-3}\,\text{mol} \cdot \text{dm}^{-3}$, $[\text{S-phenylmercaptoacetic acid}]_0 = 1 - 6 \times 10^{-2}\,\text{mol} \cdot \text{dm}^{-3}$, acetic acid : ethylene glycol = 75 : 25 (v/v), 50°C, $k_2 = 3.4 \pm 0.2 \times 10^{-3}\,\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$). Also, under *pseudo*-first order condition ([substrate]≫[oxidant]), plots of log(titre) *vs.* reaction time are linear; the second order rate constant, calculated from the *pseudo*-first order rate constant ($k'/[\text{substrate}] = k_2$), is in agreement with the second order rate constant obtained under second order condition. The oxidation is independent of the 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 trichloroacetic acid ($0.1\,\mathrm{mol}\cdot\mathrm{dm}^{-3}$) and decreased with sodium acetate ($0.1\,\mathrm{mol}\cdot\mathrm{dm}^{-3}$). Boric acid and borate do not influence the oxidation. The specific oxidation rate in presence of a large excess of orthoboric acid ($0.01\,\mathrm{mol}\cdot\mathrm{dm}^{-3}$) or metaborate ($0.01\,\mathrm{mol}\cdot\mathrm{dm}^{-3}$) is the same as in their absence. Kinetic studies suggest acetic acid as the most suitable solvent for perborate oxidation. The oxidation rate increases with increasing content of acetic acid; upon increasing the content of acetic acid from 25% to 75%, the rate constant at 50°C increases from 0.5×10^{-3} to $3.4 \times 10^{-3}\,\mathrm{dm}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{s}^{-1}$.

$$k_2 t = \frac{1}{[\text{substrate}]_0 - [\text{oxidant}]_0} \cdot \ln \frac{[\text{oxidant}]_0 \cdot [\text{substrate}]}{[\text{substrate}]_0 \cdot [\text{oxidant}]} \tag{1}$$

In aqueous and partly aqueous media, perborate yields hydrogen peroxide [1–7]. The specific rate of oxidation of S-phenylmercaptoacetic acid by hydrogen peroxide in aqueous acetic acid, under identical condition, is almost the same as that of perborate. Also, the rate of perborate oxidation under anhydrous condition is comparable with that in partly aqueous media. Perborate in glacial acetic acid generates peracetic acid [8]. A chemical test confirms the formation of peracetic acid upon aging of perborate solution in glacial acetic acid. Also, chemical tests reveal the absence of peracetic acid and the presence of hydrogen peroxide in fresh solutions of perborate in glacial acetic acid. Kinetic studies with peracetic acid under identical condition show that the oxidation of S-phenylmercaptoacetic acid by peracetic acid is very fast.

Perborate in acetic acid is unlikely to exist as peroxoborate anion, $(\mathrm{HO})_3\mathrm{B}(\mathrm{O_2H})^-$; the pK_a value of perboric acid is 7.91, whereas that of acetic acid is 4.76 [15]. The selective solubility of sodium perborate in ethylene glycol suggests a breakdown of the dimeric structure. With 1,2-diols in aqueous solutions boric acid forms glycol borate. A similar formation of glycol borate with generation of hydrogen peroxide on dissolution of perborate in ethylene glycol is possible. A chemical test confirms the formation of hydrogen peroxide on dissolution of perborate in ethylene glycol: $(\mathrm{HO})_4\mathrm{B}_2(\mathrm{O}_2)_2^{2-} + 2(\mathrm{CH_2OH})_2 \rightarrow 2\mathrm{H_2O_2} + 2(\mathrm{CH_2O})_2\mathrm{B}(\mathrm{OH})_2^-$. This set of results reveals hydrogen peroxide as the oxidizing agent of perborate dissolved in ethylene glycol. Also, the observation that the peracetic acid oxidation is very much faster than the perborate oxidation rules out peracetic acid as the oxidizing species in the smooth perborate oxidation. Further, a chemical test confirms the absence of peracetic acid in the solution of perborate in ethylene glycol. Efforts to identify the boron species in the reaction solution by a GC-MS study were unsuccessful. The aging effect is a slow formation of peracetic acid upon aging of the perborate solution in glacial acetic acid; upon mixing, the fast oxidation of S-phenylmercaptoacetic acid by peracetic acid occurs. Generation of peracetic acid upon aging of the perborate solution in acetic acid is slower than the oxidation of S-phenylmercaptoacetic acid by hydrogen peroxide.

The effect of substituents on the oxidation rate was studied with *p*-methoxy-, *p*-methyl-, *p*-chloro-, *p*-bromo-, and *p*-nitro-S-phenylmercaptoacetic acids along with the parent compound. Except *p*-nitro-S-phenylmercaptoacetic acid, the oxidation of all the mercaptoacetic acids studied follows second order kinetics according to

Table 1. Perborate oxidation of S-phenylmercaptoacetic acids (acetic acid : ethylene glycol = 75 : 25% (v/v))

Substituent	$10^3k_2/\mathrm{dm}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{s}^{-1}$		
	50°C	55°C	60°C
p-OCH_3	6.8	8.5	11.5
p-CH_3	4.6	6.7	8.7
H	3.4	4.3	6.2
p-Cl	2.7	3.9	5.3
p-Br	2.4	2.9	4.3

Eq. (2). The oxidation is sluggish below 50°C, and above 60°C the oxidant decomposes. The rate data reveal that electron-releasing substituents enhance the oxidation, whereas electron-withdrawing substituents retard the same (Table 1). The oxidation conforms to the *Exner* relationship; the plot of ln $k_{2(60^\circ\mathrm{C})}$ *vs.* ln $k_{2(50^\circ\mathrm{C})}$ is linear (correlation coefficient: $r = 0.994$; standard error: $s = 0.02$). The validity of the *Exner* relationship reveals that except the nitro-substituted acid all mercaptoacetic acids studied are oxidized by a common mechanism [16]. Correlation analysis of the oxidation rates shows that, excluding *p*-nitro-S-phenylmercaptoacetic acid, all mercaptoacetic acids studied conform to the *Hammett* equation ($r = 0.97$, 0.95, 0.97; $s = 0.05$, 0.06, 0.05; reaction constant $\rho = -0.80$, -0.78, -0.72 at 50, 55, 60°C). The negative ρ value indicates the development of an electron deficient sulfur moiety in the transition state. Hence, the mechanism of the smooth oxidation is an electrophilic attack of the peroxide oxygen on sulfur. Methanol and also ethylene glycol are nucleophiles, and association of methanol or glycol with the electrophilic peroxide oxygen might be the reason for the suppression of oxidation with the addition of methanol or glycol.

$$XC_6H_4SCH_2COOH + H_2O_2 \rightarrow XC_6H_4SOCH_2COOH + H_2O \qquad (2)$$

The oxidation of *p*-nitro-S-phenylmercaptoacetic acid is of zero and first order with respect to the oxidant and the substrate, respectively; under the condition [oxidant]$\ll$ [substrate], a plot of [oxidant] *vs.* time is linear, the expression and rate/[substrate] is constant. Also, under the condition of comparable concentrations of the reactants, a plot of ln[substrate] *vs.* time is linear, showing that the nitro acid with its electron deficient sulfur reacts through a different mechanism, probably *via* formation of a sulfide radical cation. Rate-limiting abstraction of an electron from sulfur by glycol borate, formed according to $(CH_2O)_2B(OH)_2^- + CH_3COOH \rightarrow (CH_2O)_2BOH + CH_3COO^- + H_2O$, and fast reaction of H_2O_2 with the generated radical lead to a rate law of zero order and first order in oxidant and substrate, respectively.

Experimental

Materials

Sodium perborate, $NaBO_3 \cdot 4H_2O$ (SD Fine), was used as received. The S-phenylmercaptoacetic acids were prepared by standard procedures [17] and recrystallized before use. Acetic acid was refluxed over chromium(VI) oxide for 6 h and distilled through a column. Ethylene glycol (Merck) was also distilled. All other chemicals were of analytical grade.

Kinetics

Perborate was dissolved in ethylene glycol and standardized iodometrically. The mercaptoacetic acids were dissolved in acetic acid. The reaction was initiated by the addition of the perborate solution in ethylene glycol to the mercaptoacetic acid in acetic acid. The progress of the oxidation with the substrate in excess over perborate at constant temperature was followed by iodometric measurement of the unconsumed oxidizing agent.

Product analysis

Perborate (0.005 mol) was added to S-phenylmercaptoacetic acid (0.005 mol) in glacial acetic acid at 50°C. After 3 h, the acetic acid was evaporated, the product was extracted with diethyl ether, and identified as phenylsulfinylacetic acid by its infrared spectrum. Hence the reaction can be represented as $X\mathrm{C_6H_4SCH_2COOH} + \mathrm{NaBO_3} \rightarrow X\mathrm{C_6H_4SOCH_2COOH} + \mathrm{NaBO_2}$. Due to the slow decomposition of perborate at the experimental temperature, the stoichiometry of the oxidation could not be determined. However, a separate experiment with the sulfoxide shows that further oxidation of the sulfoxide does not occur at the experimental conditions. Also, upon excluding the nitro acid, the rate data conform to the second order kinetic equation to more than two half-lives and thereby confirm absence of a further oxidation of sulfoxide under the experimental condition.

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