SHORT PAPER

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Generation of peracetic acid on aging of perborate solution in acetic acid: kinetics of oxidation of organic sulfides[†]

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Perborate in acetic acid generates peracetic acid on aging and affords H_2O_2 in ethylene glycol; the oxidations of dialkyl, alkyl aryl and diaryl sulfides in ethylene glycol–acetic acid are second order and uncatalysed by acid, and follow a common mechanism.

Keywords: peracetic acid, perborate, organic sulfides

Introduction

Sodium perborate ($NaBO_3.4H_2O$), a peroxo salt of anionic formula:[1] $B_2(O_2)_2(OH)_4^{2-}$, is an inexpensive, innocuous, easily handled, stable, large-scale industrial chemical, extensively used in detergents. In aqueous and partly aqueous solutions it yields H_2O_2 which acts as the oxidising agent.[2–6] Perborate in glacial acetic acid is an effective oxidising agent in organic synthesis and oxidises sulfides to sulfoxides in good yield.[7,8] Here we report the kinetics of the oxidations under anhydrous conditions. Perborate oxidations of dialkyl, alkyl aryl and diaryl sulfides in aqueous *t*-butyl alcohol are acid catalysed and involve different mechanisms.[9]

Experimental

Sodium perborate was used as received. Sulfides were prepared by following standard procedures and redistilled before use. Acetic acid was refluxed over chromium(VI) oxide for 6 h and distilled through a column. Ethylene glycol was also distilled. All other chemicals were of analytical grade.

Perborate was dissolved in acetic acid or ethylene glycol and standardised iodometrically. The sulfides were dissolved in acetic acid. The reaction was initiated by the addition of perborate solution to sulfide in acetic acid. The progress of the oxidation, under the condition: [sulfide] >> or > [perborate], at constant temperature was followed up to at least two half-lives by iodometric estimation of the unconsumed oxidising agent.

Stoichiometric study on the oxidation of diethyl sulfide, in ethylene glycol–glacial acetic acid at 30 °C with excess of perborate, reveals that 1 mol of the sulfide consumes 1 mol of the oxidant. Further, investigation with dimethyl sulfoxide (DMSO) in ethylene glycol–acetic acid, under the condition: [DMSO] >> [perborate], shows that the oxidation of sulfoxide does not take place under the experimental conditions. Stoichiometric studies with methyl phenyl and diphenyl sulfides could not be made as the oxidations are sluggish at 30°C and proceed only at elevated temperatures; at high temperatures and under the condition [perborate] >> [sulfide], the oxidant decomposes.

Perborate (0.005 mol) was added to the sulfides (0.005 mol) in glacial acetic acid at 50 °C. After 0.5 h (diethyl sulfide) to 3 h (diphenyl sulfide), acetic acid was neutralised; the product was extracted with diethyl ether and identified as the corresponding sulfoxide by infrared spectra.

Results and discussion

Solubility of sodium perborate in a variety of organic solvents was tested; it is insoluble in methanol, ethanol, 2-propanol, *t*-butyl alcohol, dimethylformamide, dioxane, acetonitrile, 2-ethoxyethanol, 2-butoxyethanol, 2-methoxypentan-2,4-diol, glycerol, *etc*., but dissolves readily in acetic acid and less so in ethylene glycol. The kinetics of the oxidations in acetic acid-ethylene glycol, under the condition: [sulfide] >> or > [perborate], were studied by iodometric estimation of the unreacted oxidising agent. On mixing the aged solution of perborate in acetic acid with the sulfide of desired concentration in acetic acid and ethylene glycol, there is a rapid drop of [oxidant] 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, both under second order and pseudo-first order conditions – an observation not so far reported. Plots of log ($[\text{oxidant}]_0$ [sulfide] / $[\text{sulfide}]_0$ [oxidant]) versus time under second order conditions and log titre versus time under pseudo-first order conditions are linear (Figs 1 and 2). Similar results were obtained with perborate dissolved in acetic acid and the kinetics carried out in acetic acid. Kinetic studies in ethylene glycol–acetic acid with perborate dissolved in ethylene glycol do not show the rapid drop of [oxidant] on mixing, due to aging of perborate in ethylene glycol.

The oxidation is second order, first order each with respect to the oxidant and sulfides. Under the condition: [sulfide] > [perborate], and perborate dissolved in ethylene glycol, the oxidation follows second order kinetics; plots of log ($[\text{oxidant}]_0$ [sulfide] / $[\text{sulfide}]_0$ [oxidant]) versus 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 oxidations as second order reactions (data not given). Also, under pseudo-first order conditions with the sulfide in large excess over the oxidant, plot of log titre versus reaction time is linear and the second order rate constant, calculated from the pseudo-first order rate constant, is in agreement with the second order rate constant obtained under second order conditions; the rate constants are reproducible to ± 3%. The oxidations are uncatalysed by acid, insensitive to the addition of trichloroacetic acid (0.1 mol/dm^3) or sodium acetate (0.1 mol/dm^3). Boric acid and borate do not influence the oxidations; the specific oxidation rates in presence of large excess of orthoboric acid or metaborate are the same as those in absence. Kinetic studies suggest acetic acid as the most suitable solvent for perborate oxidation; the reaction rates increase on increasing the composition of acetic acid (at

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

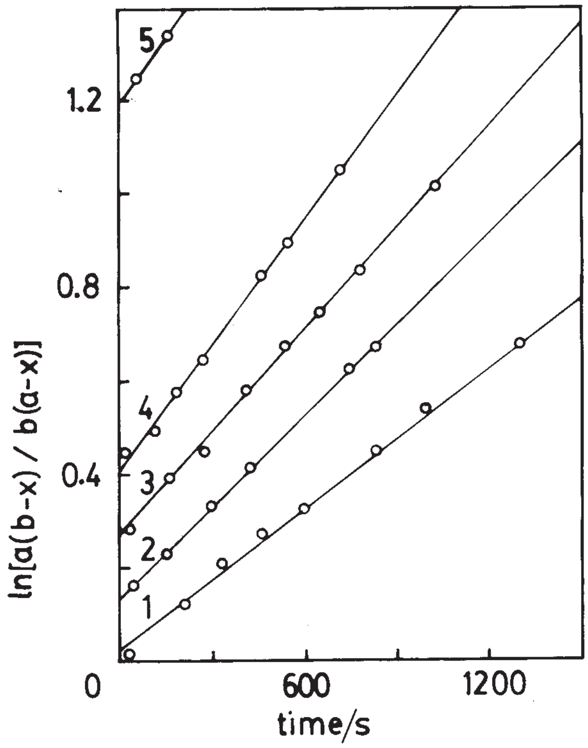

Fig. 1 Aging effect of perborate solution in acetic acid. Oxidation of diethyl sulfide (aging: 1. 1.25 h, 2. 4.75 h, 3. 8.0 h, 4. 12.5 h, 5. 28 h ($[\text{perborate}]_0 = 5.0 \times 10^{-3}$ mol/dm^3, $[\text{sulfide}]_0 = 1.0 \times 10^{-2}$ mol/dm^3, HOAc:EG::3:1 v/v, 30 °C)a: $[\text{oxidant}]_0$, (b – x): [sulfide], b: $[\text{sulfide}]_0$, (a – x): [oxidant]).

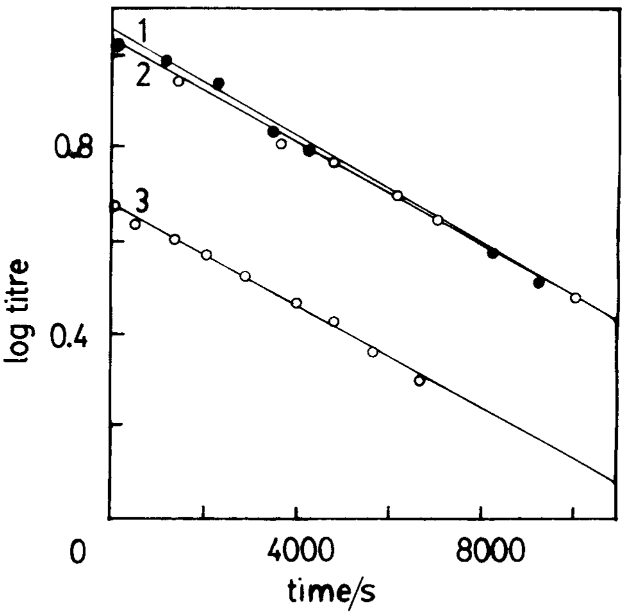

Fig. 2 Aging effect of perborate solution in acetic acid. Oxidation of diphenyl sulfide (1. perborate in ethylene glycol; aging: 2. 1.75 h, 3. 13 h ($[\text{perborate}]_0 = 5.0 \times 10^{-3}$ mol/dm^3, $[\text{sulfide}]_0 = 5.0 \times 10^{-2}$ mol/dm^3, HOAc:EG::3:1 v/v, 50 °C)).

30 °C, 10^2k_2 of Et_2S are 1.8 and 11.9 dm^3/mol/s in 25 and 75% acetic acid; 10^2k_2 of MeSPh at 50 °C are 0.43 and 2.2 dm^3/mol/s in 30 and 75% acetic acid, respectively). Addition of water or methanol or ethanol suppresses the oxidation. In aqueous and partly aqueous media perborate yields H_2O_2.[1–6] The specific rate of oxidation of diphenyl sulfide by H_2O_2 in partly aqueous medium, under identical condition, is the same as that of perborate (1.1×10^{-3} dm^3/mol/s, HOAc:ethylene glycol:H_2O::2:1:1 v/v, 50 °C). Perborate in glacial acetic acid generates peracetic acid. Chemical tests confirm the formation of peracetic acid on aging of perborate solution in acetic acid; quantitative analysis shows that peracetic acid is slowly but quantitatively generated. Also, chemical tests reveal the absence of peracetic acid and the presence of H_2O_2 in fresh solution of perborate in glacial acetic acid. Kinetic experiments, under identical conditions, with peracetic acid as the oxidant in acetic acid–ethylene glycol show that peracetic acid oxidations of diethyl, methyl phenyl and diphenyl sulfides are very much faster than those of perborate; the reactions are too fast to follow by iodometry. These results reveal that peracetic acid is not the oxidising species in the smooth perborate oxidation.

In acetic acid perborate is unlikely to exist as peroxoborate anion, $(HO)_3B(O_2H)^-$; the pK_a of perboric acid[10] is 7.91. The selective solubility of sodium perborate in ethylene glycol suggests break down of the dimeric structure. With 1,2-diols boric acid in aqueous solution forms glycol borates. Similar formation of glycol borate with generation of H_2O_2 on dissolution of perborate in ethylene glycol is possible. Chemical tests confirm formation of H_2O_2 on dissolution of perborate in ethylene glycol; but attempts to identify the boron species in the reaction solution by gas chromatography–mass spectral study were unsuccessful. The oxidising agent of perborate in the smooth oxidation is H_2O_2. On aging of perborate solution in acetic acid, peracetic acid is formed slowly but quantitatively and on mixing, the sulfides are oxidised by the peracetic acid formed instantaneously; generation of peracetic acid on aging of perborate solution in acetic acid is slower than the oxidation of sulfides by H_2O_2.

Perborate oxidations of diethyl, di-*n*-butyl, methyl phenyl, methyl 4-methylphenyl, 3,4-dimethylphenyl methyl, 4-methoxy-3-methylphenyl methyl, 4-aminophenyl methyl, methyl 2-methyl-4-nitrophenyl and diphenyl sulfides follow second order kinetics. The enthalpy and entropy of activation were calculated using Eyring plots (Table 1); the oxidations of alkyl aryl and diphenyl sulfides are sluggish below 40 and 50 °C, respectively and above 65 °C the oxidant decomposes. Analysis of the rate data reveals that electron-releasing substituents enhance the oxidation whereas electron-withdrawing substituent retards the same. The oxidations conform to the Exner relationship. A plot of log $k_{2(60°C)}$ versus log $k_{2(40\,°C)}$ is linear (correlation coefficient, $r = 0.99$; standard error, sd = 0.10; slope = 0.87; number of data sets, $n = 9$); omission of the extrapolated values do not affect the plot significantly ($r = 0.99$, sd = 0.07, $n = 6$, slope = 0.80). The existence of Exner relationship reveals that all the sulfides studied are oxidised through a common mechanism. Correlation analysis of the rates of oxidation of alkyl aryl sulfides shows that excluding 4-aminophenyl methyl sulfide all the substituted phenyl methyl sulfides conform to the Hammett equation at all the temperatures studied (r = 0.995, 0.991, 0.997; sd = 0.09, 0.04, 0.04; reaction constant, ρ = –1.6, –1.4, –1.3 at 40, 50, 60 °C). For the disubstituted compounds the sum of the individual σ-values were used for the correlation. Generally, the *ortho*-substituents exert steric effects and deviate from the usual Hammett plot. Here Taft's σ_0-value[10] (–0.17) was used along with σ_m and σ_p to correlate the rates of *para*-, *meta*- and *ortho*-compounds. Conformity of the oxidation rate of the *ortho*-compound to the Hammett equation (plot not shown) reveals that the steric effect in the title oxidation is as that in the hydrolysis of ethyl 2-methylbenzoate. Although the compounds examined are only a few the *ortho*-substituent does not largely define the plot; even if the *ortho*-compound is dropped

Table 1 Perborate oxidation of dialkyl, alkyl aryl and diaryl sulfides in acetic acid–ethylene glycol (3:1, v/v)

Sulfides	10^2 k_2 dm^3/mol/s			ΔH# kJ/mol	-ΔS# J/K/mol
	40	50	60 °C		
$(C_2H_5)_2S$	22	27	42*[a]	32	152
$(n\text{-}C_4H_9)_2S$	18	30	47*[b]	39	134
$C_6H_5SCH_3$	1.1	2.2	3.8	51	121
$p\text{-}CH_3C_6H_4SCH_3$	1.9	3.9	6.1	48	126
$m,p\text{-}(CH_3)_2C_6H_3SCH_3$	3.5	5.5	9.1	39	148
$m\text{-}CH_3,p\text{-}CH_3OC_6H_3SCH_3$	3.8	5.1	10.5	41	143
$o\text{-}CH_3,p\text{-}NO_2C_6H_3SCH_3$	0.10	0.26	0.56	71	76
$p\text{-}NH_2C_6H_4SCH_3$	1.3	3.0	6.3	66	71
$(C_6H_5)_2S$	0.13*[c]	0.26	0.40	47	174

*Extrapolated using Arrhenius plot; [a]12 at 30 °C, [b]11 at 30 °C, [c]0.32 and 0.62 at 55 and 65 °C, respectively.

from the correlation analysis, the reaction constant and also the statistical parameters of the fit remain unaltered (*e.g.* $\rho = -1.6, -1.3$; $r = 0.995, 0.997$; sd = 0.07, 0.04 at 40 and 60 °C, respectively). The negative ρ value indicates development of electron deficient sulfur in the transition state. Hence, the mechanism of oxidation is electrophilic attack of the peroxide oxygen on sulfur. Methanol, ethanol and also ethylene glycol are nucleophiles, and association of the alcohols with the electrophilic peroxide oxygen may be the reason for the suppression of oxidation with the addition of alcohols. Perborate oxidises anilines to azobenzenes.[11] However, UV-visible spectral study reveals that in the presence of sulfide function the amino group is not oxidised; the azo compound is not formed on the oxidation of 4-methylthioaniline. In acid medium the aniline is protonated and the percentage of the free base, calculated from the pK_as of 4-methylthioaniline and acetic acid, is 0.2 only. The rate of 4-aminophenyl methyl sulfide, even on assuming $-NH_3^+$ as the substituent, fails to conform to the Hammett equation. The explanation is as follows. The free base is in equilibrium with the anilinium ion. Due to the electron releasing nature of the amino group ($\sigma = -0.66$), the sulfur is more electron rich in the free base than in its conjugate acid, and the free base is the most probable reactive species; the NH_3^+-group is highly electron withdrawing ($\sigma = 1.70$) resulting in electron deficient sulfur. Existence of 4-aminophenyl methyl sulfide in dual forms complicates the substituent effect. The oxidation of organic sulfides by perborate in aqueous *t*-butyl alcohol is acid catalysed and occurs only at high acidity (0.7–1.5 mol/dm^3).[9] A possible explanation is that the nucleophilic solvent molecules associate with H_2O_2 and reduce its electrophilicity; only the protonated species is effective in bringing out the reaction.

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