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Kinetic Studies on Perborate Oxidation in Non-aqueous Media. Oxidation of Diphenylamine

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Solution of perborate in glacial acetic acid generates peracetic acid on aging and the peracetic acid oxidation of diphenylamine is fast. Hydrogen peroxide in glacial acetic acid does not yield peracetic acid on standing; also, the hydrogen peroxide oxidation rate is only two-third of perborate. The aging effect was overcome by dissolving perborate in 1,2-diols. The oxidation in 1,2-diols-acetic acid is zero order in the oxidizing agent, whereas the same oxidation with fresh solution of perborate in acetic acid is first order with respect to the oxidizing agent. However, the rate of the former and the specific rate of the latter show first order dependence on [perborate]$_0$. The reactions proceed *via* two paths, one is first order and the other is zero order in diphenylamine. In 1,2-diols-acetic acid, the perborate oxidation is slower than hydrogen peroxide. The reaction mechanism is discussed and the rate laws derived.

Key words: kinetics, mechanism, perborate, oxidation

Sodium perborate ($NaBO_3 \cdot 4H_2O$), a true peroxo salt of anionic formula: $B_2(O_2)_2(OH)_4^{2-}$ is a cheap, environment friendly, easily handled, stable, large-scale industrial chemical, extensively used in detergents as a bleaching agent [1]. In aqueous and partly aqueous solutions it affords hydrogen peroxide, which acts as the oxidizing agent [1–6]. Perborate in glacial acetic acid is a highly effective reagent, the oxidant of choice [7–9]; the mechanism of oxidation in acetic acid is unknown and hence this study. Diphenylamine, a redox indicator, is the model substrate; oxidation of diphenylamine yields different products, depending upon the oxidants and the conditions employed [10–12].

EXPERIMENTAL

Materials: Sodium perborate, $NaBO_3 \cdot 4H_2O$ (SD Fine) and diphenylamine (Merck) were used as received. Acetic acid was refluxed over chromium(VI) oxide for 6 h and distilled through a column. Methanol was purified by standard method. Ethylene glycol and propylene glycol (Merck) were distilled and used. All the chemicals used were of AR or LR grade.

Kinetics: Solutions of perborate in glacial acetic acid were prepared, standardized iodometrically and used afresh for the oxidation in glacial acetic acid. For the reaction in 1,2-diols-acetic acid, perborate was dissolved in ethylene glycol or propylene glycol and estimated iodometrically. The reaction was initiated by the addition of perborate solution to the amine in acetic acid. The progress of the oxidation, with the amine in large excess and at constant temperature, was followed by iodometric estimation of the unconsumed oxidizing agent.

Product analysis: Addition of sodium perborate (0.05 mol) in portions to diphenylamine (0.05 mol) in glacial acetic acid (30 mL) at 65°C followed by digestion (6 h) and dilution with water precipitates the product. The product, insoluble in petroleum ether (40–60°C), was identified as diphenylhydroxylamine by IR and UV-visible spectra, m.p. (62°C, literature 60°C) and chemical tests. Further, thin layer chromatography (using benzene as solvent and petroleum ether (40–60°C) as elutant on a plate coated with silica gel G and developed in an iodine chamber) shows that the product obtained is a single compound, not a mixture. Hence, the reaction is represented as:

$$Ph_2NH + NaBO_3 \rightarrow Ph_2NOH + NaBO_2$$

The reaction proceeds smoothly at 60–65°C, sluggish below 60°C and the oxidant decomposes above 65 °C. Under the condition: [perborate] > [amine] the decomposition of the oxidant is large and the stoichiometry of the reaction was not determined.

RESULTS AND DISCUSSION

Sodium perborate in glacial acetic acid oxidizes diphenylamine to diphenylhydroxylamine, identified by IR and UV-visible spectra, chemical tests and melting point.

Aging effect of perborate solution in acetic acid: The perborate oxidation of diphenylamine, studied in glacial acetic acid, reveals the aging effect of perborate solution in acetic acid. The kinetics of the reaction, studied in glacial acetic acid under the condition: [amine] >> [perborate], was monitored by the iodometric estimation of the unreacted oxidizing agent. On mixing the aged solution of perborate in glacial acetic acid with the amine in acetic acid, there is a rapid drop in [oxidizing agent] 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 – a unique observation. Under pseudo-first order condition of [amine] >> [perborate], plot of log [oxidizing agent] *versus* reaction time is linear and with aging the y-intercept decreases (Fig. 1); the least-squares slope of the linear plot yields the pseudo-first order rate constant (k′) and the rate constant is reproducible to ±5%. The oxidation with perborate solution in acetic acid aged six hours or more is instantaneous.

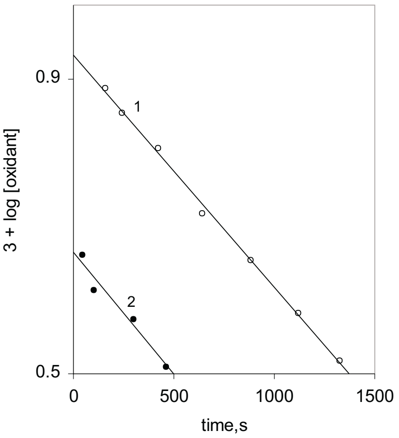

Figure 1. Aging effect of perborate in acetic acid; ([amine] = 0.20 mol dm^{-3}, [perborate]$_0$ = 1.0 × 10^{-2} mol dm^{-3}, temp. = 65°C, 1. Aging: 0 h, 2. Aging: 1 h).

Kinetics of oxidation with perborate in acetic acid: The difficulty due to the aging effect of perborate in glacial acetic acid was overcome by carrying out each kinetic run with a fresh solution of perborate. The oxidation with a fresh solution of perborate in acetic acid, under the condition: [amine] > [perborate], is apparent first order with respect to the oxidizing agent, as evidenced by the linear plot of log [oxidizing agent] *versus* reaction time. It is interesting and also surprising to note that although the reaction is apparent first order in the oxidizing agent, the pseudo-first order rate constant (k′), obtained from the least-squares slope of the pseudo-first order plot, increases with increasing initial concentration of perborate ($[\text{perborate}]_0$) and plot of k′ *versus* $[\text{perborate}]_0$ is a straight line passing through the origin (correlation coefficient, r = 0.997, standard error of estimate, sd = 5.5×10^{-4}; slope = 0.13 dm^3 mol^{-1} s^{-1}). The representative rate data are given in Table 1. The oxidation proceeds *via* two paths; one is first order and the other is zero order with respect to the amine. The oxidation rate increases, but less rapidly with increasing [amine] and plot of k′ *versus* [amine] is a straight line with a finite y-intercept (r = 0.992, sd = 3.5×10^{-5}, slope = 9.2×10^{-4} dm^3 mol^{-1} s^{-1}, y-intercept = 5.7×10^{-4} s^{-1}). Boric acid fails to influence the oxidation. The oxidation rate in the presence of orthoboric acid is the same as that in its absence. The oxidation is slowed down by the addition of methanol; addition of methanol, even to 10% of the reaction medium, suppresses the reaction rate by about 80% but the variation of the dielectric constant of the medium, ε (calculated) is only marginal (Table 3). The anionic micelles also slow down the oxidation. Table 1 presents the reaction rates in the presence of sodium *bis*-2-ethylhexylsulfosuccinate (aerosol-OT) and sodium lauryl sulfate (SLS). Acrylonitrile, a vinyl monomer, suppresses the reaction. The reaction proceeds only at an elevated temperature range (60–65°C), sluggish below 60°C and the oxidant decomposes above 65°C. As the oxidation rates were measured only in a narrow range of temperature (60–65°C) and the reaction proceeds *via* two kinetic paths, the activation parameters were not determined.

Kinetics of oxidation with peracetic acid and hydrogen peroxide in acetic acid: Perborate in glacial acetic acid is likely to generate peracetic acid [7,8], the latter is a potent oxidant. Perborate in aqueous and partly aqueous media yields hydrogen peroxide that acts as the oxidizing agent [1–6]. Hence, it is relevant to compare the rate of perborate oxidation with those of peracetic acid and hydrogen peroxide. Kinetic study with peracetic acid under identical condition reveals that the peracetic acid oxidation is very fast; too fast to follow by titrimetry. Experiments with hydrogen peroxide in glacial acetic acid show that perborate in acetic acid is a better oxidant than hydrogen peroxide; the oxidation rate of hydrogen peroxide is only two-third of perborate. Also, chemical tests show that hydrogen peroxide in glacial acetic acid does not generate peracetic acid on aging.

Table 1. Perborate oxidation in glacial acetic acid at 65°C.

10^2[perborate]$_0$ mol dm^{-3}	[amine]$_0$ mol dm^{-3}	10^4k′ s^{-1}
0.8	0.50	9.2
1.0	0.50	10.8
1.5	0.50	18.1
1.8	0.50	22.2
1.0	0.10	6.5
1.0	0.20	7.4
1.0	0.30	8.5
1.0	0.75	12.3
1.0^a	0.50	10.4
1.0^b	0.50	5.3
1.0^c	0.50	6.2
1.0^d	0.50	4.3

[a] $10^2[H_3BO_3]_0 = 1.0$ mol dm^{-3}.
[b] 10^3[Aerosol-OT]$_0$ = 8.0 mol dm^{-3}.
[c] 10^2[SLS]$_0$ = 5.0 mol dm^{-3}.
[d] CH_2CHCN:AcOH = 5:95 (% v/v).

Table 2. Oxidation with hydrogen peroxide, perborate and peracetic acid in glacial acetic acid.

Oxidant	H_2O_2	perborate	CH_3COOOH
10^4k′/s^{-1}	2.1	3.5	fast

10^2[oxidant]$_0$ = 1.0 mol dm^{-3}, [amine]$_0$ = 0.50 mol dm^{-3}, 60°C.

Table 3. Influence of solvent.

AcOH % (v/v)	MeOH % (v/v)	ε	10^4k′ s^{-1}
100	0	6.2	10.8
90	10	8.9	2.3
80	20	11.5	1.7
70	30	14.2	1.3

10^2[perborate]$_0$ = 1.0 mol dm^{-3}, [amine]$_0$ = 0.50 mol dm^{-3}, 65°C.

Mechanism of oxidation in acetic acid: In glacial acetic acid perborate is unlikely to exist as peroxoborate anion, $(HO)_3B(OOH)^-$; the pK$_a$ of perboric acid is 7.91, whereas that of acetic acid is 4.76 [13]. Perborate in glacial acetic acid generates peracetic acid on standing. Chemical tests confirm the formation of peracetic acid on aging of perborate solution in glacial acetic acid. Peracetic acid in acetic acid even in the absence of mineral acid liberates iodine from potassium iodide quantitatively, whereas hydrogen peroxide requires the presence of mineral acid; hydrogen peroxide is also estimated permanganometrically but not peracetic acid [14]. Further, the presence of hydrogen peroxide in fresh solutions of perborate in acetic acid was confirmed by testing with chromium(VI); with hydrogen peroxide chromium(VI) forms oxodiperoxochromium(VI) that absorbs at 580 nm. Also, chemical tests reveal the absence of peracetic acid in fresh solutions of perborate in glacial acetic acid [14]. Generation of peracetic acid on aging of perborate solution in glacial acetic acid, confirmed by chemical tests, and the instantaneous oxidation of diphenylamine by peracetic acid explain the rapid drop of the [oxidizing agent] on mixing of an aged solution of perborate in acetic acid with the amine. Peracetic acid is formed slowly on aging, and on mixing it oxidizes the amine instantaneously. Experiments confirm that the generation of peracetic acid on aging of perborate solution in glacial acetic acid is much slower that the oxidation of the amine with fresh solution of perborate.

The smooth and slow oxidation with fresh solution of perborate in glacial acetic acid (i) is first order with respect to the oxidizing agent, as evident from the linear plot of log [oxidizing agent] *versus* reaction time, (ii) shows first order dependence on the initial concentration of perborate ($[\text{perborate}]_0$) as seen from the linear variation of k′ with $[\text{perborate}]_0$ and (iii) is through two paths – one is first order in diphenylamine and the other is independent of [amine] as shown by the linear k′ *versus* [amine] plot with a finite y-intercept. Hence, the experimental rate law is:

$$-d[\text{oxidizing agent}]/dt = (A[\text{amine}] + B)\,[\text{perborate}]_0\,[\text{oxidizing agent}]$$

where A and B are constants.

The reaction was carried out in glacial acetic acid and the substrate, diphenylamine, is a base; the pK_a of the amine is 0.9 [13]. Hence in the reaction medium the amine is in equilibrium with its conjugate acid, $Ph_2NH_2^+$. Hydrogen peroxide and the related oxidants are electrophilic in character; transfer a peroxide oxygen atom to the electron rich nitrogen atom of the amine or abstract an electron from the nitrogen. For both the processes, the activation energies are larger for the conjugate acid than the free base, suggesting the free base as the reactive species of the substrate. Hence, it is more appropriate to correlate the reaction rate with the concentration of the free base, Ph_2NH, rather than the total concentration of the amine ($[\text{amine}] = [Ph_2NH] + [Ph_2NH_2^+]$). The correlation of k′ with the concentration of the free base ($[Ph_2NH]$) also yields similar results. Plot of k′ *versus* $[Ph_2NH]$ is a straight line with a finite y-intercept ($r = 0.991$, $sd = 3.6 \times 10^{-5}$, $\text{slope} = 9.6 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, $\text{intercept} = 5.8 \times 10^{-4}$ s^{-1}); the concentration of the free base was calculated using the pK_as of the amine and acetic acid. Perborate on dissolution in glacial acetic acid yields hydrogen peroxide quantitatively; chemical tests and analytical experiments confirm the same. However, attempts to identify the boron species in the reaction solution by gc-mass spectral study and cyclic voltammetry were unsuccessful.

$$B_2(O_2)_2(OH)_4^{2-} + 4HOAc \rightarrow 2(HO)_2BOAc + 2H_2O_2 + 2OAc^-$$

Ogata and Shimizu [15] suggested the oxidizing species of perborate in glacial acetic acid as hydrogen peroxide coordinated with boric acid although so far there is no report of a linear increase of k′ with [perborate]$_0$ and generation of peracetic acid on standing of perborate solution in acetic acid. Hydrogen peroxide associated with the boron species is a better electrophile than molecular hydrogen peroxide. The oxidation shows first order dependence on [perborate]$_0$ suggesting that hydrogen peroxide associated with the boron species is involved in the oxidation. The oxidation is partly inhibited by acrylonitrile, present in large excess (5% of the reaction medium), indicating the involvement of radical in one of the paths of the oxidation. However, the radical could not be identified by ESR spectral study; the oxidation proceeds only at 60–65°C, whereas the ESR spectrometer operates at 20°C. Rate determining oxygen transfer from hydrogen peroxide associated with the boron species to the amine, and rate limiting generation of radical from hydrogen peroxide associated with the boron species account for the experimental results (Scheme 1).

Scheme 1

$$(HO)_2BOAc + H_2O_2 \rightleftarrows (HO)_2B(OAc)\ldots H_2O_2 \quad K_1$$

Path A:

$$(HO)_2B(OAc)\ldots H_2O_2 + Ph_2NH \rightarrow Ph_2NOH + H_2O + (HO)_2BOAc \quad k_2$$

Path B:

$$(HO)_2B(OAc)\ldots H_2O_2 \rightarrow (HO)_2BOAc + 2HO\cdot \quad k_3$$

$$HO\cdot + Ph_2NH \rightarrow Ph_2NH^{+}\cdot + HO^{-} \quad \text{fast}$$

$$Ph_2NH^{+}\cdot + HO\cdot \rightarrow Ph_2NH(OH)^{+} \rightarrow Ph_2NOH + H^{+} \quad \text{fast}$$

Scheme 1 leads to the rate law:

$$-d[\text{oxidizing agent}]/dt = K_1(k_2[Ph_2NH] + k_3)[\text{perborate}]_0[\text{oxidizing agent}]$$

with a pseudo-first order rate constant of $k' = K_1(k_2[Ph_2NH] + k_3)[\text{perborate}]_0$. The kinetic constants at 65°C are found as: $K_1k_2 = 9.6 \times 10^{-2}$ dm^6 mol^{-2} s^{-1}; $K_1k_3 = 5.8 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. The specific rate of the oxidation that occurs *via* non-radical mechanism (Path A, $k' = 4.6 \times 10^{-4}$ s^{-1}) is in reasonable agreement with the specific rate of the reaction in presence of a large excess of acrylonitrile, thus supporting the suggested mechanism.

Kinetics of oxidation with perborate in 1,2-diols-acetic acid: The perborate oxidation in glacial acetic acid exhibits an aging effect of perborate in acetic acid. To overcome this difficulty, the solubility of perborate in a variety of organic solvents was tested. Perborate is insoluble in methanol, ethanol, 2-propanol, *t*-butyl alcohol, dimethylformamide, dioxane, acetonitrile, 2-ethoxyethanol, 2-butoxyethanol, 2-methoxypentan-2, 4-diol and glycerol, but dissolves readily in glacial acetic acid and less so in ethylene glycol and propane-1, 2-diol. If perborate were dissolved in ethylene glycol or propylene glycol and the kinetics of the reaction studied in acetic acid-ethylene glycol or acetic acid-propylene glycol no aging effect was observed.

The oxidation studied in acetic acid-ethylene glycol or acetic acid-propylene glycol, using perborate dissolved in ethylene glycol or propylene glycol and under the condition: [amine] >> [perborate], follows an apparent pseudo-zero order kinetics in the time scale of measurement. In a kinetic run, the concentration of the unreacted oxidizing agent decreases linearly with the reaction time as evidenced by the linear plots of [oxidizing agent] *versus* time (Fig. 2). It is interesting and also surprising to note that although the reaction is apparently zero order in the oxidizing agent, the oxidation rates increase with increasing $[\text{perborate}]_0$ and plots of rates *versus* $[\text{perborate}]_0$ afford straight lines passing through the origin ($r = 0.999, 0.9996$; $sd = 4.1 \times 10^{-8}, 3.6 \times 10^{-8}$; slope $= 1.4 \times 10^{-4}, 1.5 \times 10^{-4}\ s^{-1}$ for ethylene glycol and propylene glycol, respectively). Table 4 presents the representative rate data. The zero order kinetics of the oxidation was further confirmed by studying the reaction spectrophotometrically. The reaction solutions, due to product formation, show the maximum absorbance at 377 nm, the wavelength at which the kinetics was followed. The absorbance of the reaction solutions (aliquots were withdrawn at required time intervals and diluted ten times), measured using UVIDEC-340, Jasco spectrophotometer, increases linearly with the reaction time ($10^2[\text{perborate}]_0 = 1.0$ mol dm^{-3}, $[\text{amine}]_0 = 0.50$ mol dm^{-3}, 75 % (v/v) HOAc, 65°C, slope $= 1.85 \times 10^{-4}\ s^{-1}$ (EG-HOAc), $1.6 \times 10^{-4}\ s^{-1}$ (PG-HOAc)). The oxidation occurs *via* two paths; one is first order and the other is zero order with respect to the amine. The oxidation rates increase but less rapidly with increasing [amine]; plots of rates *versus* [amine] are straight lines with finite y-intercepts ($r = 0.999, 0.991$, $sd = 2.4 \times 10^{-8}, 7.1 \times 10^{-8}$, slope $= 1.1 \times 10^{-6}, 1.2 \times 10^{-6}\ s^{-1}$, y-intercept $= 5.6 \times 10^{-7}, 6.7 \times 10^{-7}$ mol dm^{-3} s^{-1} for ethylene glycol and propylene glycol, respectively). Boric acid and borate fail to influence the oxidation. The oxidation rate in the presence of orthoboric acid or metaborate, dissolved in acetic acid, is

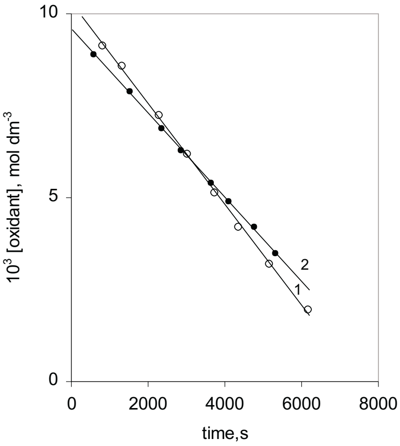

Figure 2. Perborate oxidation of diphenylamine. Pseudo-zero-order plot; ([amine] = 0.50 mol dm^{-3}, temp. = 65°C, 1. ethylene glycol-acetic acid (25–75% (v/v)). 2. propylene glycol-acetic acid (25–75% (v/v)).

the same as that in their absence. Kinetic study reveals acetic acid as the most suitable solvent for perborate oxidation. The reaction rates decrease with decreasing content of acetic acid and the oxidation does not occur in 25% acetic acid. Also, addition of methanol to 50% of the reaction medium arrests the reaction (Table 5). Sodium bis-2-ethylhexylsulfosuccinate (aerosol-OT) has no influence on the reaction rate, whereas sodium lauryl sulfate (SLS) catalyzes the oxidation (Table 4). The oxidation occurs only at 60–65°C, sluggish below 60°C and above 65°C the oxidant decomposes. Since the reaction rates were measured only in a narrow range of temperature and the oxidation proceeds *via* two kinetic routes, the thermodynamic parameters were not determined.

Table 4. Perborate oxidation in 1,2-diols-acetic acid at 65°C.

10^2[perborate]$_0$ mol dm^{-3}	[amine]$_0$ mol dm^{-3}	10^6rate mol dm^{-3} s^{-1}	
		EG-AcOH	PG-AcOH
0.5	0.50	0.50	0.69
1.0	0.50	1.15	1.40
1.5	0.50	1.90	2.23
2.0	0.50		2.96
1.0	0.10	0.65	0.76
1.0	0.20	0.80	0.90
1.0	0.75	1.43	1.61
1.0	1.00	1.68	1.87
1.0[a]	0.50	1.20	1.30
1.0[b]	0.50		1.25
1.0[c]	0.50	1.19	1.30
1.0[d]	0.50	4.05	5.6

1,2-Diol:acetic acid = 1:3 (v/v).
[a] $10^2[NaBO_2]_0 = 1.0$ mol dm^{-3}.
[b] $10^2[H_3BO_3]_0 = 1.0$ mol dm^{-3}.
[c] 10^3[Aerosol-OT]$_0$ = 8.0 mol dm^{-3}.
[d] 10^2[SLS]$_0$ = 5.0 mol dm^{-3}.

Table 5. Oxidation with hydrogen peroxide, perborate and peracetic acid in 1,2-diols-acetic acid at 60°C.

Oxidant	10^6rate mol dm^{-3} s^{-1}	
	EG-AcOH	PG-AcOH
H_2O_2	1.14	0.95
perborate	0.86	0.81
CH_3COOOH	Fast	Fast

10^2[oxidant]$_0$ = 1.0 mol dm^{-3}, [amine]$_0$ = 0.50 mol dm^{-3}, 75% (v/v) AcOH, 60°.

Table 6. Solvent effect on the oxidation with perborate in 1,2-diols.

MeOH % (v/v)	AcOH % (v/v)	1,2-diol % (v/v)	ε		10^6rate mol dm^{-3} s^{-1}	
			EG-AcOH	PG-AcOH	EG-AcOH	PG-AcOH
0	75	25	14.1	12.7	1.15	1.40
0	50	50	22.0	19.1	0.54	*
0	25	75	29.8	25.6	sluggish	sluggish
25	50	25	20.7	19.3	*	0.43
50	25	25	27.3	25.9	sluggish	sluggish

10^2[perborate]$_0$ = 1.0 mol dm^{-3}, [amine]$_0$ = 0.50 mol dm^{-3}, 65°C.
*The kinetics is neither pseudo-zero order nor pseudo-first order.

Kinetics of oxidation with peracetic acid and hydrogen peroxide in 1,2-diols-acetic acid: Peracetic acid and hydrogen peroxide are the oxidizing species of perborate, the former in the aged solution of perborate in glacial acetic acid (*vide supra*) and the latter in aqueous and partly aqueous solutions [1–6]. Hence, it is relevant to compare the rate of perborate oxidation with those of peracetic acid and hydrogen peroxide. Kinetic study with peracetic acid in ethylene glycol-acetic acid and propylene glycol-acetic acid, under identical conditions, reveals that the peracetic acid oxidation is fast; too fast to follow by titrimetry. Study with hydrogen peroxide in ethylene glycol-acetic acid and propylene glycol-acetic acid shows hydrogen peroxide as a better oxidant than perborate in 1,2-diols-acetic acid; the perborate oxidation rate is only three-fourth of hydrogen peroxide (Table 5).

Mechanism of perborate oxidation in 1,2-diols-acetic acid: The selective solubility of sodium perborate in ethylene glycol and propylene glycol suggests a breakdown of the dimeric structure: $(HO)_4B_2(O_2)_2^{2-}$. With 1,2-diols in aqueous solution, boric acid forms glycol borates [14]. A similar formation of glycol borate with generation of hydrogen peroxide on dissolution of perborate in ethylene glycol or propylene glycol is possible. Chemical tests confirm the formation of hydrogen peroxide on dissolution of perborate in ethylene glycol or propylene glycol; but attempts to identify the boron species in the reaction solution by GC mass spectrometry were unsuccessful.

$$(HO)_4B_2(O_2)_2^{2-} + 2(CH_2OH)_2 \rightarrow 2H_2O_2 + 2(CH_2O)_2B(OH)_2^-$$

$$(CH_2O)_2B(OH)_2^- + CH_3COOH \rightarrow (CH_2O)_2BOH + CH_3COO^- + H_2O$$

Generation of peracetic acid in the reaction medium followed by the oxidation of the amine by peracetic acid is safely ruled out as the reaction mechanism; the peracetic acid oxidation of the amine in ethylene glycol-acetic acid as well as in propylene glycol-acetic acid is very fast. Also, experiments with perborate in ethylene glycol-acetic acid and propylene glycol-acetic acid show that formation of peracetic acid on aging is very much slower than the oxidation of the amine. The reaction is not a simple hydrogen peroxide oxidation; the perborate oxidation in 1,2-diols-acetic acid is slower than hydrogen peroxide oxidation. The oxidation with perborate in 1,2-diols (i) is zero order in the oxidizing agent as seen from the linear decrease of [oxidizing agent] with reaction time, (ii) reveals first order dependence on $[\text{perborate}]_0$ as is evident from the linear increase of rates with $[\text{perborate}]_0$ and (iii) occurs *via* two kinetic routes – one is first order in diphenylamine and the other is independent of [amine] as shown by the linear rates *versus* [amine] plots with finite y-intercepts. Hence, the experimental rate law is:

$$-d[\text{oxidizing agent}]/dt = (C[\text{amine}] + D)\,[\text{perborate}]_0$$

where C and D are constants.

The reaction was studied in acetic acid-1,2-diols and in the reaction medium the amine is in equilibrium with its conjugate acid. The oxidation of the conjugate acid requires a higher energy of activation than the free base and the amine reacts through its molecular form. Correlation of the oxidation rates with the concentration of the free base is more appropriate rather than the total concentration of the amine, and the former also yields similar results. Plots of rates *versus* $[Ph_2NH]$ are straight lines with finite y-intercepts ($r = 0.999, 0.991$, $sd = 2.6 \times 10^{-8}, 7.3 \times 10^{-8}$, $slope = 1.2 \times 10^{-6}, 1.3 \times 10^{-6}\ s^{-1}$, $intercept = 5.8 \times 10^{-7}, 6.9 \times 10^{-7}\ mol\ dm^{-3}\ s^{-1}$ in ethylene glycol-acetic acid and propylene glycol-acetic acid, respectively).

Glycol borates are Lewis acids and the amine is a Lewis base, and they are likely to enter into coordination; the electron deficient boron atom of glycol borates coordinates with the nitrogen atom of the amine. The non-dependence of the rates on the [oxidizing agent] indicates that the oxidant is consumed in a fast step; the decomposition of the amine-glycol borate complexes is rate limiting (Path C. Scheme 2). Rate determining generation of free radicals from the glycol borates accounts for the non-dependence of the reaction rates on [oxidizing agent] and [amine] (Path D. Scheme 2). However, the free radicals could not be detected by ESR spectral study; the reaction proceeds only at 60–65°C, whereas the ESR spectrometer works at 20°C.

Scheme 2

Path C:

$$(CH_2O)_2BOH + Ph_2NH \rightleftarrows Ph_2(H)N{\rightarrow}B(OCH_2)_2OH \quad K_4$$

$$Ph_2(H)N{\rightarrow}B(OCH_2)_2OH \rightarrow Ph_2(H)N^{+\cdot} + (CH_2O)_2(HO)B^{-\cdot} \quad k_5$$

Path D:

$$(CH_2O)_2BOH + AcO^- \rightleftarrows [(CH_2O)_2BOH(OAc)]^- \quad K_6$$

$$[(CH_2O)_2BOH(OAc)]^- \rightarrow [(CH_2O)_2BOH]^{-\cdot} + AcO\cdot \quad k_7$$

$$Ph_2NH + AcO\cdot \rightarrow Ph_2(H)N^{+\cdot} + AcO^- \quad \text{fast}$$

$$Ph_2(H)N^{+\cdot} + H_2O_2 \rightarrow Ph_2N^+H(OH) + HO\cdot \quad \text{fast}$$

$$Ph_2N^+H(OH) \rightarrow Ph_2NOH + H^+ \quad \text{fast}$$

$$[(CH_2O)_2BOH]^{-\cdot} + HO\cdot \rightarrow (CH_2O)_2BOH + HO^- \quad \text{fast}$$

Scheme 2 leads to the rate law:

$$-d[\text{oxidizing agent}]/dt = (K_4k_5[\text{amine}] + K_6k_7\,[\text{AcO}^-])[\text{perborate}]_0$$

The reaction rate is the pseudo-zero order rate constant. The rate law is also in agreement with the result that the reaction turns sluggish when acetic acid content in the reaction medium is low; the concentration of acetate ion in the reaction medium is directly proportional to the composition of acetic acid in the medium. A possible reason for the reaction to follow neither pseudo-zero order nor pseudo-first order kinetics at some solvent compositions with 50% acetic acid is that reaction mechanism becomes complicated.

CONCLUSIONS

Sodium perborate on dissolution in acetic acid or 1,2-diols yields H_2O_2 and a boron compound. In a kinetic run the oxidizing agent is consumed and the order determined based on [oxidizing agent] or log [oxidizing agent] *versus* time plots is the order with respect to the oxidizing agent. The concentration of the boron compound formed on dissolution of perborate is equal to the initial concentration of perborate ($[\text{perborate}]_0$) and in a kinetic run, like a catalyst, is of fixed value. The order with respect to $[\text{perborate}]_0$ is the order with respect to the boron compound formed. The dissociation of perborate into an oxidizing agent and a catalyst explains the order with respect to time (determined in a kinetic run) and order with respect to the initial concentration (catalyst).

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