

Autocatalysis in the sodium perborate oxidation of anilines in acetic acid–ethylene glycol

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Received 12 October 2000; accepted 19 February 2001

Abstract

Solutions of sodium perborate (SPB) in glacial acetic acid yield peracetic acid on aging and the peracetic acid oxidation of anilines to azobenzenes is very fast. SPB on dissolution in ethylene glycol affords hydrogen peroxide along with a borate; the oxidation in ethylene glycol–acetic acid is zero order in the oxidizing agent, first order with respect to the borate formed and exhibits Michaelis–Menten dependence on [anilines] except those with highly electron releasing substituent. The borate formed coordinates with anilines and catalyzes the oxidation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Perborate; Substituent; Borate

1. Introduction

Sodium perborate (SPB, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$), a peroxy salt of anionic formula $\text{B}_2(\text{O}_2)_2(\text{OH})_4^{2-}$, is an inexpensive, innocuous, industrial chemical, extensively used in detergents as a bleaching agent [1]. In aqueous solution it yields hydrogen peroxide, and kinetic studies on SPB oxidation in aqueous and partly aqueous media confirm the same [2–6]. In glacial acetic acid it is a highly effective reagent, the oxidant of choice [7–9], and oxidizes anilines to azobenzenes, used in the manufacture of azo dyes, in good yield [10,11]. The literature lacks mechanistic study on SPB oxidation in glacial acetic acid and here we report generation of peracetic acid on aging of SPB solution in acetic acid. Further, SPB dissolved in ethylene glycol yields hydrogen peroxide along with a borate, the latter acts as a catalyst in the oxidation of anilines. Kinetic studies on the oxidation of anilines

are numerous; the reaction rates in basic, neutral and acidic media conform to the Hammett equation or to the dual substituent parameter (DSP) equation [12] but the title oxidation does not.

2. Experimental

2.1. Materials

Sodium perborate, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (SD Fine) was used as received. Anilines were distilled or recrystallized before use. Acetic acid was refluxed over chromium(VI) oxide for 6 h and distilled through a column. Ethylene glycol (S. Merck) was also distilled. All the chemicals used were of AR or LR grade.

2.2. Kinetics

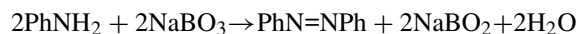
SPB was dissolved in acetic acid or ethylene glycol and standardized iodometrically. The anilines were dissolved in acetic acid. The reaction was initiated by

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adding SPB in acetic acid or ethylene glycol to the anilines in acetic acid. The progress of the oxidation at constant temperature, with the anilines in large excess, was followed by iodometric estimation of the unconsumed oxidizing agent.

2.3. Product analysis

SPB (0.01 mol), dissolved in acetic acid or ethylene glycol, was added to aniline (0.02 mol) in glacial acetic acid at 60°C. After 3 h, the reaction mixture was diluted with water, the solid was separated and identified by its melting point, mixed melting point, IR, UV–VIS and GC-mass spectra (yield: 90%); the GC-mass spectral study shows azobenzene as the only product. The spectra are superimposable with those of the authentic sample. The UV–VIS spectral studies of the reaction solutions, during and after the completion of the oxidation, of all the anilines studied, show the formation of azobenzenes except *p*-methylmercaptoaniline. Hence, the reaction is represented as



3. Results and discussion

The kinetics of the oxidation, studied in glacial acetic acid under the condition $[\text{anilines}] \gg [\text{SPB}]$, was followed by iodometric estimation of the unreacted oxidizing agent. The oxidation is sluggish at room temperature but is smooth at 45–65°C; the decomposition of the oxidant is appreciable above 65°C. Kinetic studies on the SPB oxidation of aniline in acetic acid reveal aging effect of SPB solutions in acetic acid. On mixing the aged solutions of SPB in glacial acetic acid with aniline of required concentration in acetic acid, there is a rapid drop of the initial titre (with the formation of azobenzene) followed by a smooth slow oxidation. The UV–VIS spectra of the reaction solutions confirm the formation of azobenzene. With aging of SPB solutions in acetic acid, 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. For example, the approximate percentages of the oxidation that occurs rapidly on mixing are 20,

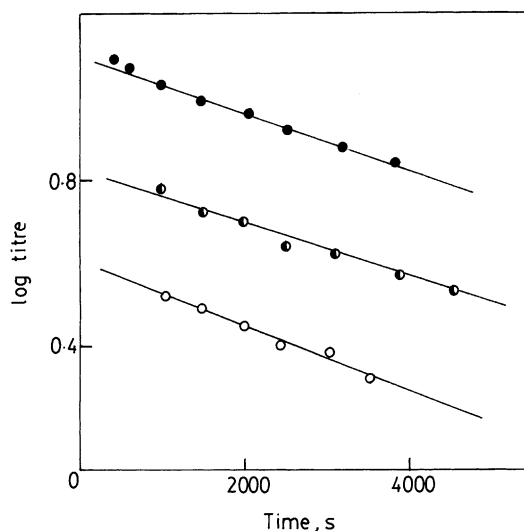


Fig. 1. Perborate oxidation of aniline. $[\text{SPB}]_0 = 1.53 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{aniline}]_0 = 0.50 \text{ mol dm}^{-3}$; medium: glacial acetic acid; temperature 50°C; aging of SPB solution in acetic acid: (●) 0.5 h ($k' = 1.69 \times 10^{-4} \text{ s}^{-1}$, $r = 0.997$, S.D. = 7.49×10^{-3}); (◐) 3.0 h ($k' = 1.53 \times 10^{-4} \text{ s}^{-1}$, $r = 0.995$, S.D. = 8.99×10^{-3}); (○) 6.0 h ($k' = 1.79 \times 10^{-3} \text{ s}^{-1}$, $r = 0.989$, S.D. = 1.19×10^{-2}).

60, 75 and 90 at 0.5, 3.0, 6.0 and 10.0 h of aging, respectively. The smooth slow oxidation is first order with respect to the oxidizing agent. Under pseudo-first order conditions ($[\text{aniline}] \gg [\text{SPB}]$), plot of $\log(\text{titre})$ versus reaction time is linear, and with aging the *y*-intercept decreases (Fig. 1); the least squares slopes of the linear plots afford the pseudo-first order rate constants and the rate constants are reproducible to $\pm 4\%$.

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, 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. If SPB is dissolved in ethylene glycol and the reaction is conducted in acetic acid–ethylene glycol the aging effect is not observed. The oxidation is zero order in the oxidizing agent. In a kinetic run, under the condition that $[\text{aniline}] \gg [\text{SPB}]$, the concentration of the unreacted oxidizing agent decreases linearly, at least up to 80% of the oxidation, with the reaction time (Fig. 2; correlation coefficient, $r = 0.997$, standard error of estimate, S.D. = 0.189).

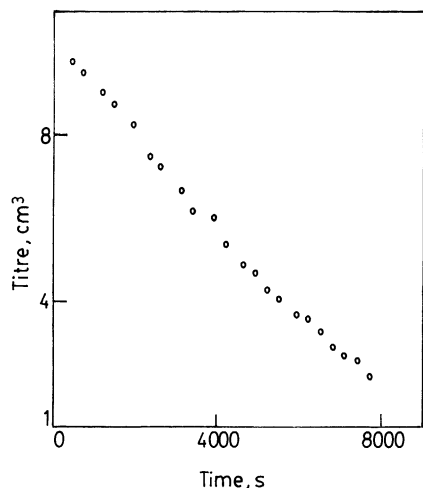


Fig. 2. SPB oxidation in acetic acid–ethylene glycol:pseudo-zero order plot. $[\text{SPB}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{aniline}]_0 = 0.50 \text{ mol dm}^{-3}$; medium: acetic acid:ethylene glycol 3:1; temperature 50°C ; rate $= 1.05 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$; $r = 0.997$, S.D. = 0.189.

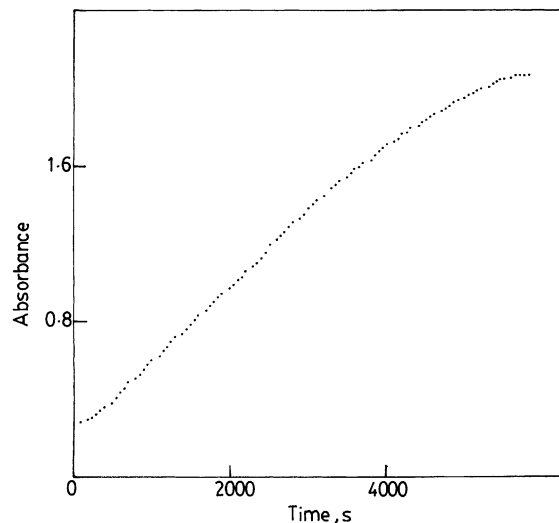


Fig. 3. SPB oxidation in acetic acid–ethylene glycol:pseudo-zero order plot. $[\text{SPB}]_0 = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{aniline}]_0 = 0.50 \text{ mol dm}^{-3}$; medium: acetic acid:ethylene glycol 3:1; temperature 50°C ; $r = 0.999$, S.D. = 0.023.

The least squares slope of the linear plot yields the reaction rate. The order of the reaction was further confirmed by monitoring the formation of the product, azobenzene, spectrophotometrically at 429 nm, the λ_{max} of the reaction solution; the literature value of *cis*-azobenzene in ethanol is 433 nm. The oxidation, under the condition $[\text{aniline}] \gg [\text{SPB}]$, was studied at a very low concentration of SPB to ensure that the absorbance of the product formed is within the Beer–Lambert law limit. The absorbance increases linearly with the reaction time, at least up to 90% completion of the formation of azobenzene (Fig. 3; $r = 0.999$, S.D. = 0.023). The oxidation is photoinsensitive; the reaction rate remains practically the same whether the oxidation is carried out in dark, sunlight, visible (tungsten lamp) or UV (mercury lamp) light. It is interesting and also surprising to note that although the oxidation is zero order with respect to the oxidizing agent, the oxidation rate increases with increasing initial concentration of SPB, $[\text{SPB}]_0$ (Table 1), also an observation not yet reported. Plot of the reaction rate versus $[\text{SPB}]_0$ is a straight line passing through the origin ($r = 0.998$, S.D. = 2.9×10^{-7} , slope = $2.4 \times 10^{-4} \text{ s}^{-1}$). Also, the double logarithmic plot of rate versus $[\text{SPB}]_0$ is linear with a slope of near unity ($r = 0.993$, S.D. = 0.07).

At fixed $[\text{SPB}]_0$, the oxidation rate increases but less rapidly with increasing $[\text{aniline}]$, and attains a limiting value at high $[\text{aniline}]$. The rate– $[\text{aniline}]$ profile (not shown) is a typical Michaelis–Menten dependence. This is further confirmed by the linear double reciprocal plot of rate versus $[\text{aniline}]$ ($r = 0.999$, S.D. = 3.8×10^{-4}) and the statistically balanced Hanes plot of $[\text{aniline}]/\text{rate}$ versus $[\text{aniline}]$ ($r = 0.999$, S.D. = 1.7×10^{-4}), both with positive slopes and intercepts. Kinetic studies at 50, 55 and 65°C yield similar results (data not given).

Addition of trichloroacetic acid (0.15–0.50 mol dm^{-3}) or *p*-toluenesulfonic acid (0.10 mol dm^{-3}) or

Table 1
Variation of the oxidation rate with $[\text{SPB}]_0^a$

| $[\text{SPB}]_0 \times 10^3 \text{ (mol dm}^{-3}\text{)}$ | Rate $\times 10^6 \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ |
|---|--|
| 3.0 | 0.36 |
| 5.0 | 0.46 |
| 6.0 | 0.69 |
| 8.0 | 1.00 |
| 10.0 | 1.10 |
| 20.0 | 3.8 |
| 35.0 | 7.5 |
| 50.0 | 11.3 |

^a Conditions: $[\text{aniline}] = 0.50 \text{ mol dm}^{-3}$; temperature = 50°C ; solvent = acetic acid:ethylene glycol 3:1.

sodium acetate ($0.05\text{--}0.10\text{ mol dm}^{-3}$), at fixed content of acetic acid, fail to influence the oxidation. As the concentration of aniline in the reaction medium is high (0.5 mol dm^{-3}) the addition of the acids fails to enhance the acidity of the medium. The acids were dissolved in ethylene glycol and estimated. Due to the low solubility of *p*-toluenesulfonic acid in ethylene glycol the concentration of the acid could not be increased beyond 0.1 mol dm^{-3} . The oxidation does not occur in methanol–ethylene glycol (3:1 (v/v)) or ethanol–ethylene glycol (3:1 (v/v)) and neither *p*-toluenesulfonic acid (0.10 mol dm^{-3}) nor alkali (0.10 mol dm^{-3}) brings out the oxidation in these solvents. Oxalic acid inhibits the oxidation; the oxidation in acetic acid–ethylene glycol does not occur in the presence of oxalic acid ($0.06\text{--}0.08\text{ mol dm}^{-3}$). Also, the oxidation fails to occur in the presence of methanol (e.g. acetic acid:ethylene glycol:methanol 2:1:1; 5:1:4; 0:1:3 (v/v)). In addition, the oxidation proceeds only in acetic acid or partly acetic acid medium. For example, under the condition: $[\text{SPB}]_0 = 1.0 \times 10^{-2}\text{ mol dm}^{-3}$, $[\text{aniline}]_0 = 0.5\text{ mol dm}^{-3}$, $[\textit{p}\text{-toluenesulfonic acid}]_0 = 5.0 \times 10^{-2}\text{ mol dm}^{-3}$, 50°C , the reaction does not take place in dimethylformamide–ethylene glycol, dioxane–ethylene glycol, 2-propanol–ethylene glycol, ethanol–ethylene glycol and *t*-butyl alcohol–ethylene glycol (1–1 (v/v)). Boric acid and borate do not influence the oxidation; the addition of orthoboric acid (0.01 mol dm^{-3}) or metaborate ($0.01\text{--}0.03\text{ mol dm}^{-3}$) fails to enhance the oxidation rate. The oxidation is conveniently carried out under anhydrous conditions; addition of water slows down the reaction. Also, studies on the oxidation of aniline with sodium perborate, hydrogen peroxide, hydrogen peroxide with boric acid, and hydrogen peroxide with metaborate as oxidants in partly aqueous medium (acetic acid:ethylene glycol:water 65:25:10 (v/v)) reveal that the oxidation is neither zero order nor first order in the oxidizing agent; the rates increase as the reactions proceed (Fig. 4).

The effect of substituents on the oxidation rate in acetic acid–ethylene glycol medium was studied with *p*-acetylamino-, *p*-acetyl-, *p*-bromo-, *m*-carboxy-, *p*-carboxy-, *m*-chloro-, *p*-chloro-, *p*-ethoxy-, *p*-ethoxy-carbonyl-, *m*-methyl-, *p*-methyl-, *m*-methoxy-, *p*-methoxy- and *p*-methylmercapto-anilines along with the parent. In the case of *p*-methylmercaptoaniline it is the oxidation of sulfide to sulfoxide. The reaction

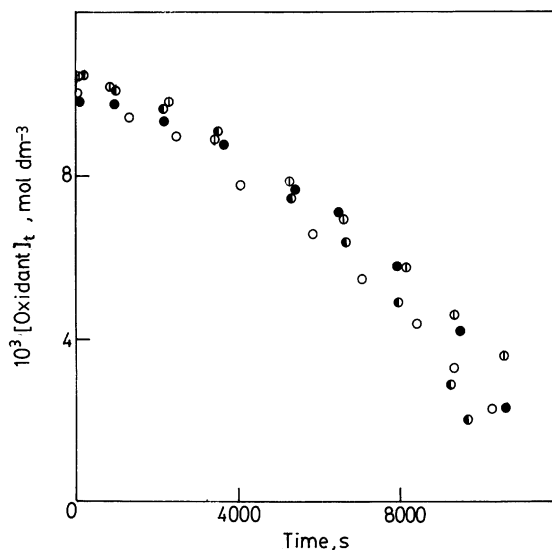


Fig. 4. Oxidation in partly aqueous medium. $[\text{Aniline}]_0 = 0.50\text{ mol dm}^{-3}$; medium: acetic acid:ethylene glycol:water 65:25:10; temperature 50°C ; (○) sodium perborate; (●) hydrogen peroxide; (◐) hydrogen peroxide–metaborate; (◑) hydrogen peroxide–boric acid. $[\text{SPB}]_0 = 1.0 \times 10^{-2}\text{ mol dm}^{-3}$; $[\text{H}_2\text{O}_2]_0 = 1.0 \times 10^{-2}\text{ mol dm}^{-3}$; $[\text{NaBO}_2]_0 = 1.0 \times 10^{-2}\text{ mol dm}^{-3}$; $[\text{H}_3\text{BO}_3]_0 = 1.0 \times 10^{-2}\text{ mol dm}^{-3}$.

fails to yield the corresponding azo compound; the UV–VIS spectral studies of the reaction solutions during and after the completion of the reaction do not show the formation of the corresponding azobenzene. The oxidation of *p*-aminophenyl methyl sulfide (*p*-methylmercaptoaniline) is a clear second order reaction; under second order conditions ($[\text{sulfide}]_0 = (1.0\text{--}2.0) \times 10^{-2}\text{ mol dm}^{-3}$, $[\text{SPB}]_0 = (5.00 \pm 0.05) \times 10^{-3}\text{ mol dm}^{-3}$, acetic acid:ethylene glycol 3:1 (v/v)) plots of $\log([\text{oxidant}]_0[\text{sulfide}]_t/[\text{sulfide}]_0[\text{oxidant}]_t)$ versus reaction time are linear ($r = 0.999$, S.D. = $0.004\text{--}0.019$) and the least squares slopes yield the second order rate constants (1.3×10^{-2} , 3.0×10^{-2} , $6.3 \times 10^{-2}\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ at 40, 50 and 60°C , respectively). Further, the reactions of *m*-methoxy-, *p*-methoxy- and *p*-methyl-anilines, under pseudo-first order conditions with a large excess of aniline, follow neither zero order nor first order kinetics. The oxidation rates increase with the progress of the reactions (Fig. 5); probably, these reactions occur via a branched chain mechanism, the number of chain carriers produced may be larger than those consumed. The oxidation rates of *m*- and *p*-carboxy-anilines

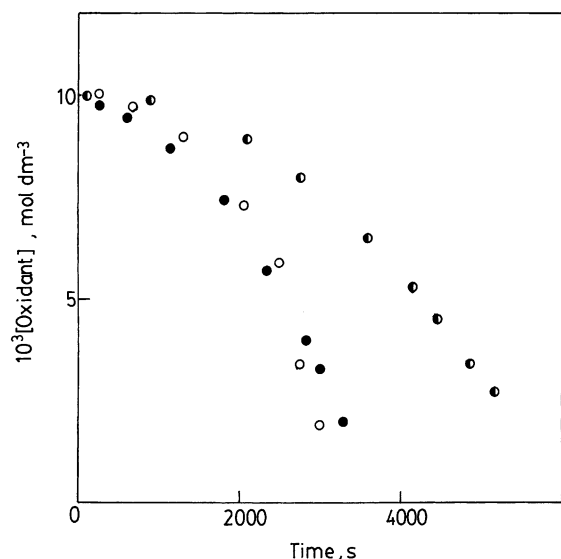


Fig. 5. SPB oxidation of *p*-methoxy-, *m*-methoxy- and *p*-methyl-anilines. (●) *p*-Methoxyaniline; (○) *m*-methoxyaniline; (◐) *p*-methyl-aniline. $[\text{SPB}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{aniline}]_0 = 0.50 \text{ mol dm}^{-3}$; medium: acetic acid:ethylene glycol 3:1; temperature 45°C.

could not be determined at high concentration due to their low solubility. The other anilines listed exhibit Michaelis–Menten kinetics; the reaction rates increase but less rapidly with [anilines] and reach limiting values at high concentration. The rates–[anilines] profiles are typical of Michaelis–Menten kinetics. The linear double reciprocal plots of rates versus [anilines] and the statistically sound Hanes plots of [anilines]/rates versus [anilines], both with positive slopes and intercepts, confirm the Michaelis–Menten dependence of

Table 2
Rates of sodium perborate oxidation of anilines^a

| Substituent | Rate $\times 10^7$ (mol dm ⁻³ s ⁻¹) | | | | |
|--|--|-------------------|-------------------|-------------------|-------------------|
| | 0.10 ^b | 0.25 ^b | 0.50 ^b | 0.75 ^b | 1.00 ^b |
| H | 3.3 | 5.1 | 6.6 | 6.9 | 7.3 |
| <i>p</i> -OC ₂ H ₅ | 9.8 | 11.5 | 15.1 | 15.3 | |
| <i>p</i> -Cl | 4.4 | 6.5 | 8.0 | 9.3 | 10.7 |
| <i>p</i> -Br | 4.7 | 7.2 | 8.3 | 9.0 | 9.6 |
| <i>p</i> -NHCOCH ₃ | 1.95 | 3.7 | 6.2 | 8.0 | |
| <i>p</i> -COOC ₂ H ₅ | 3.0 | 4.2 | 5.2 | 5.3 | 5.8 |
| <i>p</i> -COCH ₃ | 7.3 | 16.6 | 27 | 41 | 43 |
| <i>m</i> -CH ₃ | 4.2 | 10.9 | | 18.7 | 19.2 |
| <i>m</i> -Cl | 3.7 | 5.2 | 7.3 | 7.3 | 7.5 |
| <i>p</i> -COOH | | | 8.1 | | |
| <i>m</i> -COOH | | 16.7 | | | |

^a Conditions: $[\text{SPB}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; temperature = 45°C; solvent = acetic acid:ethylene glycol 3:1 (v/v).

^b Concentration of anilines in mol dm⁻³.

the oxidation rate on [anilines]. Table 2 presents the representative rate data. Similar results were obtained at 55 and 65°C (data not presented). The Hanes plots at 45, 55 and 65°C yield the specific rates of decomposition (*k*) of the Michaelis–Menten complexes. The Eyring plots of the decomposition rates at 45, 55 and 65°C afford the activation enthalpies and activation entropies of the decomposition (Table 3).

The decomposition of the Michaelis–Menten complex is neither isoenthalpic nor isentropic but conforms to the compensation law also known as isokinetic relationship [13,14]. The isokinetic temperature is the temperature at which all the substrates of the series react at equal rate; i.e. at the isokinetic temperature the substituent has no influence on the activation free energy. In an isentropic reaction the

Table 3
Specific rates (*k*) and activation parameters of decomposition of the Michaelis–Menten complexes

| Entry | Substituent | $k \times 10^7$ (s ⁻¹) | | | ΔH^\ddagger (kJ mol ⁻¹) | $-\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹) |
|-------|--|------------------------------------|------|------|---|---|
| | | 45°C | 55°C | 65°C | | |
| 1 | H | 8.5 | 14 | 32 | 57 | 185 |
| 2 | <i>p</i> -OC ₂ H ₅ | 17 | 42 | 57 | 53 | 188 |
| 3 | <i>p</i> -Cl | 14 | 38 | 75 | 74 | 126 |
| 4 | <i>p</i> -Br | 10.3 | 39 | 66 | 81 | 105 |
| 5 | <i>p</i> -NHCOCH ₃ | 16 | 57 | 189 | 108 | 18 |
| 6 | <i>p</i> -COOC ₂ H ₅ | 5.7 | 11.4 | 26 | 64 | 164 |
| 7 | <i>p</i> -COCH ₃ | 105 | 239 | 520 | 71 | 117 |
| 8 | <i>m</i> -CH ₃ | 30 | 43 | 70 | 33 | 248 |
| 9 | <i>m</i> -Cl | 8.4 | 20 | 32 | 57 | 184 |

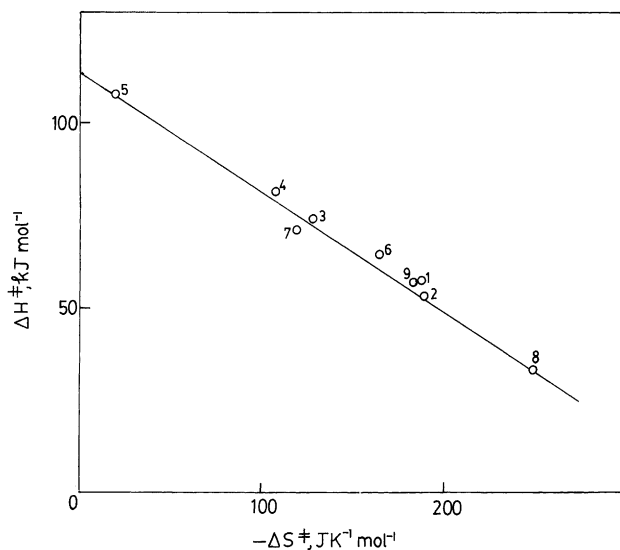


Fig. 6. The isokinetic plot ($r = 0.994$, S.D. = 2.44) (entries as in Table 3).

isokinetic temperature is at infinity and only the enthalpy of activation determines the rate. The isokinetic temperature is zero for an isoenthalpic series and the rate depends on the activation entropy. In the present study, the enthalpy of activation of the decomposition of the Michaelis–Menten complex varies linearly with the activation entropy (Fig. 6; $r = 0.994$, S.D. = 2.44). The validity of the isokinetic relationship is further confirmed by the Exner plot, the linear double logarithmic plot of the decomposition rates at two different temperatures (Fig. 7; $r = 0.962$, S.D. = 0.122). The validity of the isokinetic and Exner relationships suggests that the decomposition of the Michaelis–Menten complexes follow a common mechanism.

The decomposition rates of the Michaelis–Menten complexes of the listed *p*- and *m*-substituted anilines were analyzed in terms of the Hammett equation. The usual Hammett substituent constants fail to explain the variation of the decomposition rate with the substituent. As “cross-conjugation”, conjugation involving the *p*-substituents with the reaction center [15], is likely the σ^+ and σ^- constants were employed in the single parameter correlation but also without success. The failure of all the single parameter equations to explain the variation of the rate leads to the possibility of operation of dual substituent parameter (DSP)

equation. All the DSP equations including the Swain et al. equation fail to account for the variation of the rate with the substituent. The σ_I , σ_R^0 , $\sigma_{R(BA)}$, σ_R^- and σ_R^+ values used are those reported by Dayal et al. [16]. The *F* and *R* values used are those of Swain et al. [17].

Sodium perborate in glacial acetic acid generates peracetic acid. Chemical tests confirm the formation of peracetic acid on aging of SPB in glacial acetic acid [18]. Also, chemical tests reveal the absence of peracetic acid and the presence of hydrogen peroxide in fresh solutions of SPB in acetic acid.¹ Kinetic experiments in glacial acetic acid, as well as in acetic acid–ethylene glycol, show that peracetic acid oxidation of aniline, under the conditions of SPB oxidation, is almost instantaneous. Hence, the aging effect is the slow formation of peracetic acid on aging of SPB solution in acetic acid; on mixing, aniline is oxidized almost instantaneously by peracetic acid formed. Experiments show that the generation of peracetic acid on aging of SPB solution in acetic acid is slower than the oxidation of aniline with fresh solution of SPB in acetic acid.

In acetic acid SPB is unlikely to exist as peroxoborate anion, $(HO)_3B(O_2H)^-$; the pK_a of perboric

¹ Formation of peracetic acid from commercial hydrogen peroxide and glacial acetic acid requires catalytic amount of mineral acid.

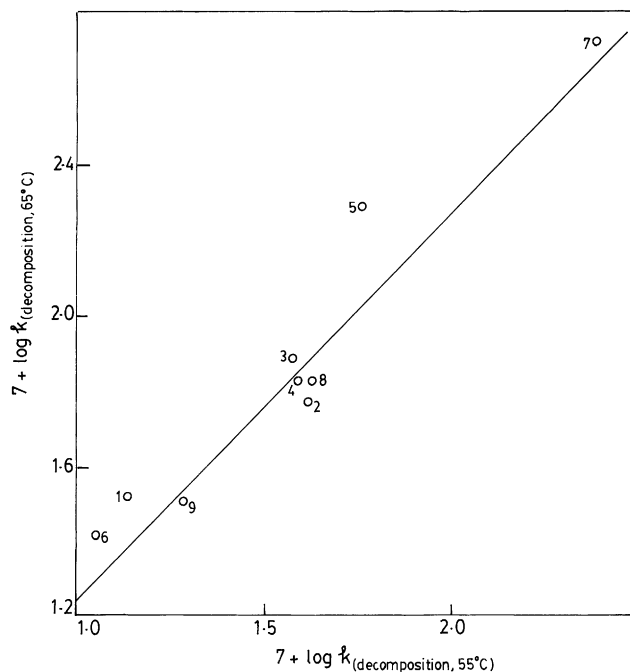
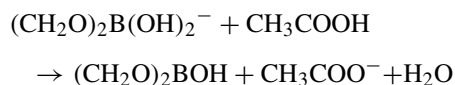
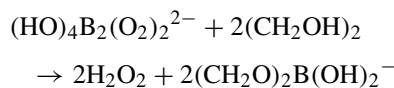


Fig. 7. The Exner plot ($r = 0.962$, S.D. = 0.122) (entries as in Table 3).

acid is 7.91 whereas that of acetic acid is 4.76 [19]. The selective solubility of sodium perborate in ethylene glycol suggests breakdown of the dimeric structure, $(\text{HO})_4\text{B}_2(\text{O}_2)_2^{2-}$, on dissolution. With 1,2-diols, boric acid in aqueous solution forms glycol borates [20]. Similarly, formation of glycol borate with generation of hydrogen peroxide on dissolution of SPB in ethylene glycol is possible. Chemical tests confirm formation of hydrogen peroxide on dissolution of SPB in ethylene glycol; but attempts to identify the boron species in the medium by GC-mass spectrometry and cyclic voltammetry were unsuccessful.



Glycol borate is a Lewis acid and anilines are Lewis bases, and they enter into coordination; the electron deficient boron of glycol borate coordinates with the nitrogen of anilines. The Michaelis–Menten

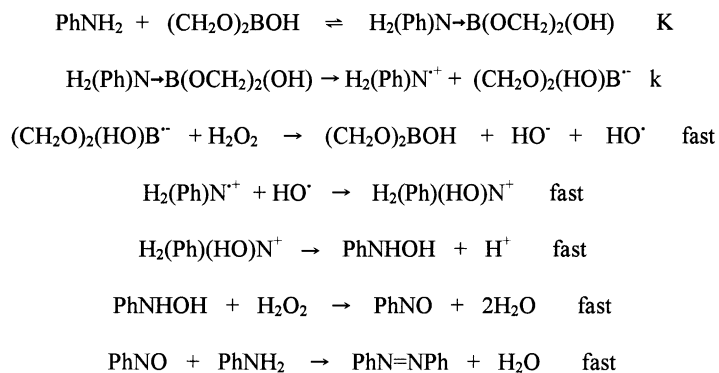
dependence of the oxidation rates on [anilines] confirms formation of complexes in a rapid pre-equilibrium. The non-dependence of the rates on the [oxidizing agent] suggests rate-limiting decomposition of the complex; the oxidant is consumed in a fast step (Scheme 1).

The suggested mechanism leads to the rate law

$$\frac{-d[\text{oxidizing agent}]}{dt} = \frac{Kk[\text{aniline}][\text{SPB}]_0}{(1 + K[\text{aniline}])}$$

where $[\text{SPB}]_0 = [\text{borate}]$.

The above rate law is in agreement with all the experimental findings, viz. the zero order in the oxidizing agent (the rate of consumption of the oxidizing agent as well as the rate of formation of the product are independent of the concentration of the oxidizing agent), the linear increase of the rate with $[\text{SPB}]_0$, the Michaelis–Menten dependence of the rate on [anilines], the generation of peracetic acid on aging of SPB solution in glacial acetic acid, the fast oxidation of anilines by peracetic acid, the identification of hydrogen peroxide in the fresh solutions of SPB in ethylene glycol or acetic acid, etc. A possible



Scheme 1.

explanation for the absence of catalysis by metaborate and orthoboric acid is that these boron species fail to generate aniline radical cation. Oxalate and methanol are nucleophiles and are likely to coordinate with the borate thereby making it inactive. Further support for the mechanism was obtained by dissolving SPB in acetic acid and studying the kinetics of the oxidation in acetic acid–ethylene glycol. The oxidation is first order in the oxidant; plot of $\log[\text{oxidizing agent}]$ versus reaction time is linear (Fig. 8). This shows that SPB dissolved in acetic acid and mixed with ethylene glycol does not yield glycol borate that coordinates with molecular aniline resulting in the generation of aniline

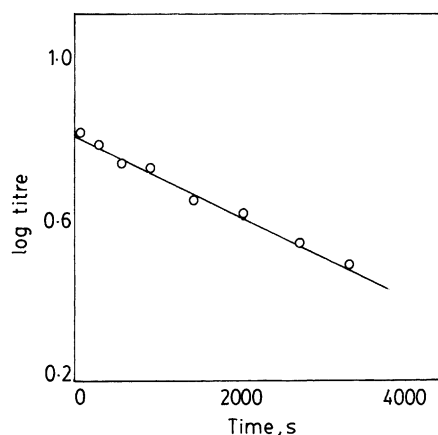


Fig. 8. Oxidation of aniline with SPB in acetic acid: pseudo-first order plot. $[\text{SPB}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{aniline}]_0 = 0.50 \text{ mol dm}^{-3}$; medium: acetic acid:ethylene glycol 3:1; temperature 50°C ; ($r = 0.998$, S.D. = 0.008).

radical cation. However, the nature of the radical ion could not be determined by ESR spectroscopy. The oxidation occurs at $45\text{--}65^\circ\text{C}$ but the ESR spectrum of the reaction solution that shows no signal could be recorded only at room temperature (25°C). The reaction exhibits a rare kinetic behavior that indicates operation of an uncommon mechanism. Although, no literature support for the suggested mechanism is provided the mechanism of copper(II) catalyzed lead tetraacetate oxidation of carboxylic acids is of similar character, homolysis of the lead carboxylate followed by oxidation of the resulting radical by copper(II) [21].

In acid medium, anilines get protonated and the extent of protonation depends on the substituent. The free bases (molecular anilines) may coordinate with the borate but not the conjugate acids. The concentrations of the free bases in 3:1 (v/v) acetic acid–ethylene glycol at $[\text{anilines}]_{\text{Total}} = 0.50 \text{ mol dm}^{-3}$ ($[\text{anilines}]_{\text{Total}} = [x\text{C}_6\text{H}_4\text{NH}_2] + [x\text{C}_6\text{H}_4\text{NH}_3^+]$), calculated using the reported $\text{p}K_a$ values of the anilinium ions and acetic acid [22], and the concentration of acetic acid, are $4.2 \times 10^{-3} \text{ mol dm}^{-3}$ ($p\text{-OCH}_3$), $5.4 \times 10^{-3} \text{ mol dm}^{-3}$ ($p\text{-OC}_2\text{H}_5$), $7.9 \times 10^{-3} \text{ mol dm}^{-3}$ ($p\text{-CH}_3$), $1.8 \times 10^{-2} \text{ mol dm}^{-3}$ ($m\text{-CH}_3$), $2.3 \times 10^{-2} \text{ mol dm}^{-3}$ (H), $2.6 \times 10^{-2} \text{ mol dm}^{-3}$ ($p\text{-NHCOCH}_3$), $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ($m\text{-OCH}_3$), $7.3 \times 10^{-2} \text{ mol dm}^{-3}$ ($p\text{-Cl}$), $8.8 \times 10^{-2} \text{ mol dm}^{-3}$ ($p\text{-Br}$), 0.15 mol dm^{-3} ($m\text{-Cl}$), 0.18 mol dm^{-3} ($p\text{-COOC}_2\text{H}_5$), 0.24 mol dm^{-3} ($m\text{-COOH}$) and 0.35 mol dm^{-3} ($p\text{-COOH}$). However, the concentrations of the molecular anilines in the reaction medium could not be calculated due to the formation of the Michaelis–Menten (aniline–glycol borate) complex; $[\text{aniline}]_{\text{Total}} = [x\text{C}_6\text{H}_4\text{NH}_2] + [x\text{C}_6\text{H}_4\text{NH}_3^+] +$

[complex]. As the concentrations of the molecular anilines ($[x\text{C}_6\text{H}_4\text{NH}_2]$) are required for the evaluation of the true formation constants of the Michaelis–Menten complexes (K) the latter could not be made.

In kinetic runs, the rates of perborate oxidation of anilines with high electron releasing substituents such as *m*-methoxy, *p*-methoxy and *p*-methyl increase with the reaction time indicating that the chain carriers produced in the course of the reaction are more than those consumed (vide supra). The reaction of *p*-methylmercaptoaniline is the oxidation of sulfide. But, the oxidations of the other anilines listed follow a common mechanism as evidenced by the linear isokinetic and Exner plots. However, it does not conform to the usual and modified Hammett equations and also to the dual substituent parameter (DSP) equations. It is pertinent to note that the oxidation, studied under the condition: $[\text{aniline}] \gg [\text{SPB}]$, with SPB dissolved in ethylene glycol is zero order where as that with SPB in acetic acid is first order in the oxidizing agent. In both cases the presence of hydrogen peroxide in the reaction solution was confirmed by chemical tests. The kinetic results suggest that the oxidation using SPB dissolved in ethylene glycol occurs by the rate-limiting electron transfer where as that using SPB in acetic acid is probably through rate-determining oxygenation of aniline by hydrogen peroxide. The oxidation using SPB in ethylene glycol is clean first order in $[\text{SPB}]_0$ and hence the oxygenation path is insignificant. A possible reason for the insignificant oxygenation in the case of SPB dissolved in ethylene glycol is that the concentration of the free base becomes insignificant due to the addition of SPB dissolved in ethylene glycol; the glycol borate forms an adduct with the free base.

4. Conclusions

Solutions of sodium perborate in glacial acetic acid generate peracetic acid on standing, and the oxidation

of anilines by peracetic acid is instantaneous. Dissolution of sodium perborate in ethylene glycol affords hydrogen peroxide and a borate; the latter catalyzes the oxidation by coordinating with anilines.

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