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Mechanism and reactivity in perborate oxidation of anilines in acetic acid

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Perborate but not percarbonate in acetic acid generates peracetic acid on standing and the peracetic acid oxidation of anilines is fast. The oxidation with a fresh solution of perborate in acetic acid is smooth and second order but the specific oxidation rate increases with increasing [perborate]$_0$ or [boric acid]. Perborate on dissolution affords hydrogen peroxide and a borate; the latter assists the former in the oxidation. The oxidation rates of anilines under identical conditions do not conform to any of the linear free energy relationships but the reaction rates of molecular anilines do. Perborate oxidation proceeds *via* two reaction paths but the overall oxidation rates of molecular anilines conform to structure–reactivity relationships; the transition states do not differ significantly. Analysis of the oxidation rates of perborate and percarbonate reveals that while perborate oxidation is faster than percarbonate it is at least as selective as the latter.

Introduction

Sodium perborate, a peroxo salt of anionic formula: $B_2(O_2)_2(OH)_4^{2-}$, is a cheap, non-toxic, stable, easily handled, large-scale industrial chemical, extensively used in detergents as a bleaching agent. In glacial acetic acid it is a highly effective reagent, the oxidant of choice,[1–3] and oxidizes anilines to azobenzenes, used in the manufacture of azo dyes, in good yield.[4,5] The literature lacks reports on the mechanism of perborate oxidation in glacial acetic acid and hence this study. Perborate in aqueous solution yields hydrogen peroxide and the kinetic studies in aqueous and partly aqueous acidic media confirm perborate oxidation as hydrogen peroxide oxidation.[6–9] At pH 8.4–10.5 peroxoborate anion also acts as active oxidant.[10] Operation of linear free energy relationships in the oxidation of anilines by a variety of reagents is well known but the perborate oxidation rates of anilines under identical conditions do not conform to any of the structure-reactivity relationships. However, the variation of the reaction rates of molecular anilines is in agreement with the usual Hammett equation. Like sodium perborate, sodium percarbonate is also an inexpensive, innocuous and versatile oxidizing agent being used in functional group oxidations.[1–3] Although these reagents are being employed interchangeably in detergent industry the chemistry of these two peroxygen compounds is distinct in several aspects and so is in organic synthesis.[1–3] Examination of the reactivity and selectivity of these reagents under identical conditions show perborate as more reactive than percarbonate and its selectivity is not less than that of the latter.

Results and discussion

Aging effect of perborate in acetic acid

The kinetics of the oxidation, studied in glacial acetic acid under the condition [aniline] ≫ [perborate], were followed by iodometric estimation of the unconsumed oxidizing agent. The oxidation is sluggish at room temperature but is smooth at 45–65 °C. The decomposition of the oxidant is negligible up to 60 °C and the specific rate of decomposition at 65 °C, measured as $1.2 \times 10^{-5}\ s^{-1}$, is also negligible in comparison with the oxidation rate. Studies on the perborate oxidation of aniline in acetic acid reveal the aging effect of perborate in acetic acid. On mixing the aged solution of perborate in glacial acetic acid with aniline in acetic acid, there is a rapid drop of titre with simultaneous formation of azobenzene followed by a smooth slow oxidation. The UV–visible spectra of the reaction solution confirm the formation of azobenzene on the addition of the aged solution of perborate in acetic acid to solution of aniline in acetic acid, and also during the course of the smooth reaction. With aging of perborate solution in acetic acid, the fraction of the oxidation that occurs rapidly on mixing the reactants increases but the specific rate of the remaining part of the oxidation is constant: a unique observation (Fig. 1). For example, the approximate percentages of the oxidation that occurs rapidly on mixing are 20, 45 and 70 at 0.67, 1.33 and 2.0 h of aging, respectively; the oxidation with perborate solution aged 6 h or more is instantaneous.

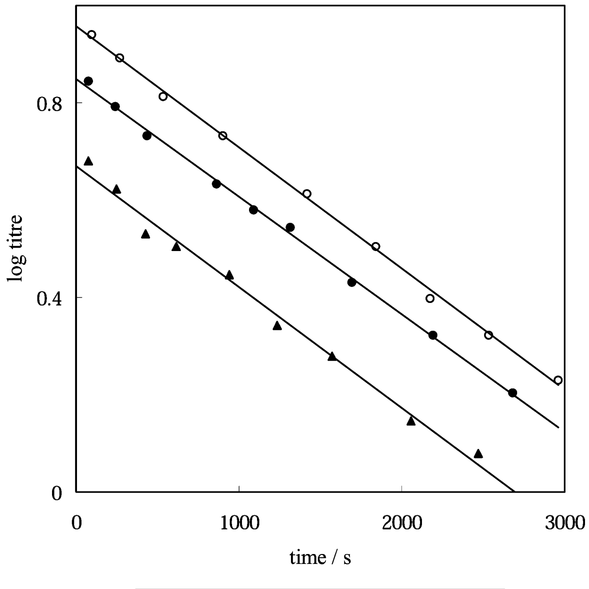

Fig. 1 Aging effect of perborate in acetic acid. Oxidation of aniline (10^2[perborate]$_0$ = 1.0 mol dm^{-3}, [aniline]$_0$ = 0.50 mol dm^{-3}, medium: acetic acid, 60 °C).

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Reaction order

The oxidation, under the condition: [aniline] $\gg$ [perborate] is first order with respect to the oxidant. The kinetics of the reactions, using fresh solution of perborate in acetic acid, was followed from 15 to 80% consumption of the oxidizing agent and the plots of log titre *versus* reaction time are linear. The least squares slopes of the linear plots afford the pseudo-first-order rate constants, k' and the rate constants are reproducible to ±4%. The reaction under the condition: [aniline] $\gg$ [perborate] was also followed spectrophotometrically at 429 nm, the λ_{max} of azobenzene, and the product formation also conforms to pseudo-first-order kinetics (Fig. 2: number of data points, n = 175, correlation coefficient, r = 0.9997, standard error, $s = 3.5 \times 10^{-3}$). The reaction was allowed to go to completion, the absorbance was measured at different time intervals as well as at the completion of the reaction and the concentrations of the unconsumed oxidizing agent at different reaction times obtained. The spectrophotometric study was made at a very low concentration of perborate, a concentration that is too low for iodometric estimation, to ensure that the absorbance of the product formed is within the Beer–Lambert law limit. Hence the reaction rates obtained by the two methods could not be compared.

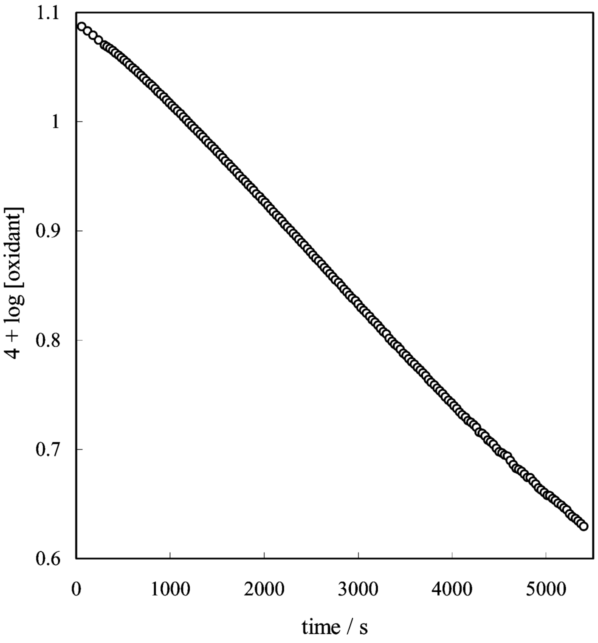

Fig. 2 Spectrophotometric study of oxidation of aniline with fresh solution of perborate in acetic acid (10^3[perborate]$_0$ = 1.25 mol dm^{-3}, [aniline]$_0$ = 0.50 mol dm^{-3}, medium: acetic acid, 50 °C).

The solubility of sodium perborate in a variety of organic solvents was tested; it is insoluble in methanol, ethanol, 2-propanol, *t*-butanol, 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 1,2-diols like ethylene glycol and propylene glycol. Use of ethylene glycol or propylene glycol along with acetic acid is neither convenient nor cost effective; addition of high boiling ethylene glycol or propylene glycol to acetic acid slows down the oxidation, reduces the yield and makes the isolation of the product difficult. Also, experiments show glacial acetic acid as the best solvent for the oxidation. The reaction rate decreases with decreasing content of acetic acid; each kinetic run was made with fresh solution of perborate in acetic acid. For example, on decreasing the content of acetic acid in the reaction medium to 70% v/v, with the addition of methanol, the specific oxidation rate (k') decreases from 6.3×10^{-4} to 0.89×10^{-4} s^{-1} (10^2[perborate]$_0$ = 1.0 mol dm^{-3}, [aniline]$_0$ = 0.5 mol dm^{-3}, 60 °C). The oxidation occurs under anhydrous condition but not in aqueous acetic acid.

It is interesting and also surprising to note that although the reaction is first order in the oxidizing agent, the pseudo-first-order rate constant increases with increasing initial concentration of perborate, [perborate]$_0$; a plot of k' *versus* [perborate]$_0$ is a straight line with a finite y-intercept (Fig. 3). In an attempt to unravel the complexity of the reaction order with respect to perborate, the influence of boric acid on the oxidation rate was examined (10^2[perborate]$_0$ = 1.0 mol dm^{-3}, [aniline]$_0$ = 0.5 mol dm^{-3}, 60 °C). Boric acid enhances the oxidation; initial addition of orthoboric acid increases the oxidation rate and a plot of k' *versus* the sum of the concentrations of perborate and boric acid ([perborate]$_0$ + [boric acid]) is a straight line with a definite y-intercept (Fig. 4). The oxidation is first order with respect to aniline. At fixed [perborate]$_0$, the oxidation rate increases with increasing [aniline]$_0$ and the plot of k' *versus* [aniline]$_0$ is a straight line almost passing through the origin (Fig. 5). The reaction is not by a radical pathway; addition of vinyl monomer, acrylonitrile to the reaction solution (0.10 mol dm^{-3}) does not suppress the reaction. Also, the added vinyl monomer fails to polymerize during the course of the reaction. These results lead to the experimental rate law:

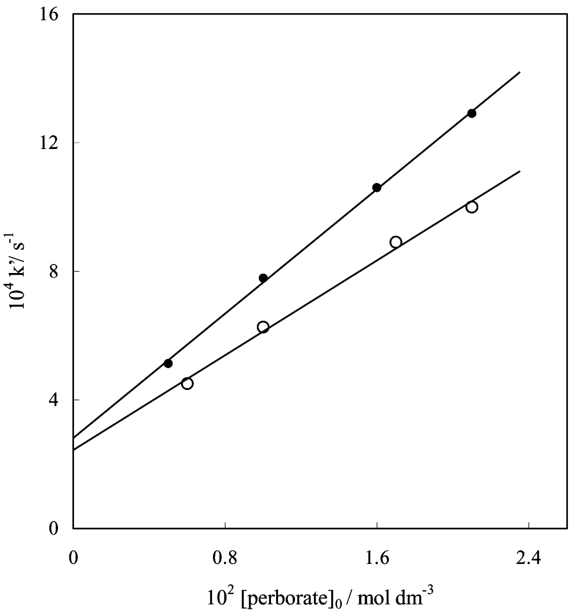

Fig. 3 Variation of k' with [perborate]$_0$ ([Aniline]$_0$ = 0.50 mol dm^{-3}, medium: acetic acid, ○ 60 °C, ● 65 °C).

$$-\mathrm{d[oxidizing\ agent]}/\mathrm{d}t = (A + B[\mathrm{borate}])[\mathrm{aniline}][\mathrm{oxidizing\ agent}]$$

where [borate] = [perborate]$_0$ or [boric acid], and A and B are constants.

Oxidation by hydrogen peroxide and peracetic acid

The oxidation of aniline with anhydrous hydrogen peroxide, using sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) as the source of dry hydrogen peroxide,[11–14] under the conditions of perborate oxidation, is slower than the perborate oxidation;[15] the presence of hydrogen peroxide in a solution of percarbonate in glacial acetic acid was also confirmed by chemical tests. The oxidation of aniline by anhydrous hydrogen peroxide in glacial acetic acid, under the condition [aniline]$_0$ $\gg$ [H_2O_2]$_0$ is first order with respect to hydrogen peroxide; plots of log [oxidant] *versus* reaction time are linear. The least squares slope of the linear plot yields the pseudo-first-order rate constant that remains constant (2.3×10^{-4} s^{-1} at [aniline]$_0$ = 0.50 mol dm^{-3} and 60 °C) at

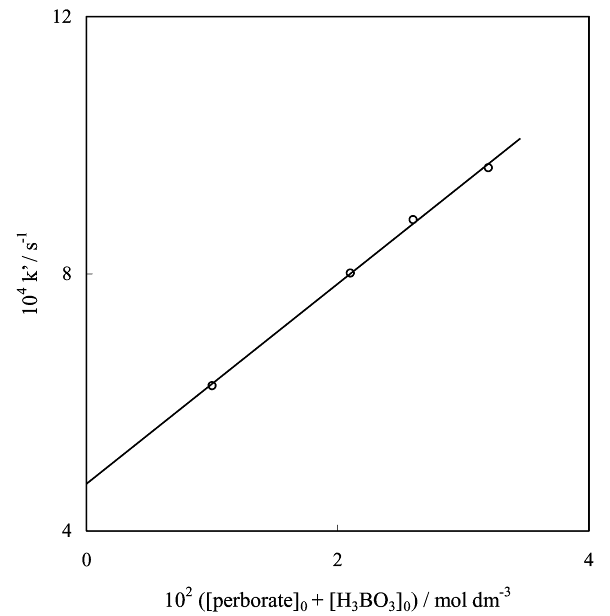

Fig. 4 Influence of boric acid on k' (10^2[perborate]$_0$ = 1.0 mol dm^{-3}, [aniline]$_0$ = 0.50 mol dm^{-3}, medium: acetic acid, 60 °C).

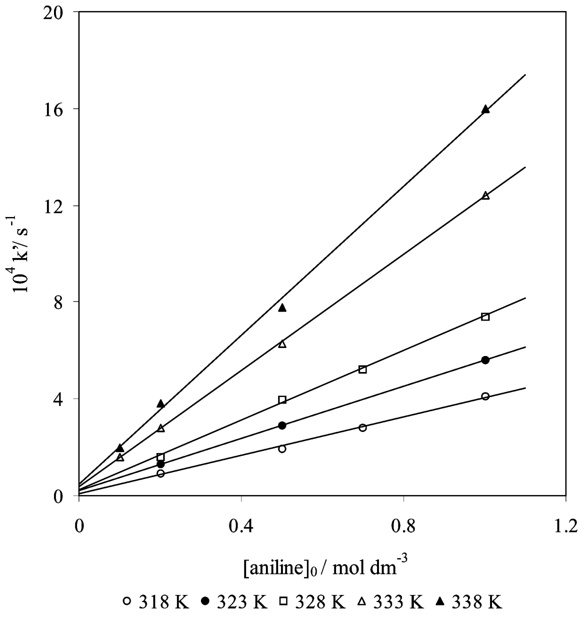

Fig. 5 First order dependence of rate on [aniline] (10^2[perborate]$_0$ = 1.0 mol dm^{-3}, medium: acetic acid).

different initial concentrations of hydrogen peroxide (0.40 × 10^{-2} to 1.8 × 10^{-2} mol dm^{-3}). It is interesting to note that although sodium perborate and sodium percarbonate are used interchangeably in the detergent industry as well as in organic synthesis, unlike the former the latter in glacial acetic acid does not generate peracetic acid on aging. The product of hydrogen peroxide oxidation is also azobenzene, identified by its mp, mixed mp, IR, UV-visible and GC-mass spectra.[15] Experiments with peracetic acid as the oxidant, under the conditions of perborate and hydrogen peroxide oxidations, show that peracetic acid oxidation of aniline is very fast; too fast to follow by titrimetry. The product of the peracetic acid oxidation is also azobenzene, identified by its mp, mixed mp, IR, UV–visible and GC-mass spectra.

Mechanism

Perborate in glacial acetic acid generates peracetic acid. Chemical tests confirm the formation of peracetic acid on aging of perborate solution in acetic acid. Also, chemical tests reveal the absence of peracetic acid in fresh solutions of perborate in acetic acid. Kinetic experiments with fresh solutions of peracetic acid in acetic acid show that peracetic acid oxidation of aniline, under the reported conditions of perborate oxidation, is almost instantaneous. Hence, the aging effect is the slow formation of peracetic acid from perborate in acetic acid; on mixing, aniline is oxidized almost instantaneously by the peracetic acid formed. Experiments show that the generation of peracetic acid on aging of perborate solution in glacial acetic acid is very much slower than the oxidation of aniline with a fresh solution of perborate in acetic acid.

The selective solubility of sodium perborate in acetic acid, ethylene glycol and propylene glycol suggests breakdown of the dimeric structure, $B_2(O_2)_2(OH)_4^{2-}$, on dissolution. In acetic acid perborate is unlikely to exist as the peroxoborate anion, $(HO)_3B(O_2H)^-$. With 1,2-diols, boric acid in aqueous solution forms glycol borates. Similarly, formation of a glycol borate along with the generation of hydrogen peroxide on dissolution of perborate in ethylene glycol and propylene glycol is possible. Chemical tests confirm the formation of hydrogen peroxide on dissolution of perborate in acetic acid, ethylene glycol and propylene glycol; but attempts to identify the boron species in the reaction medium by GC-mass spectrometry and cyclic voltammetry were unsuccessful. Analytical experiments show that on dissolution of perborate in glacial acetic acid, perborate is quantitatively converted into hydrogen peroxide. But the kinetic studies reveal that the perborate oxidation is faster than the oxidation by anhydrous hydrogen peroxide (percarbonate). The experimental rate law points out that the perborate oxidation proceeds *via* two paths; one is independent of the initial concentration of perborate or the concentration of added boric acid and the other exhibits first order dependence on [perborate]$_0$ or added [H_3BO_3]. An examination of the rates of oxidation by perborate and anhydrous hydrogen peroxide (percarbonate) reveals that the perborate oxidation that is independent of the initial concentration of perborate is hydrogen peroxide oxidation. The extrapolated specific rate of the perborate oxidation (k') to zero initial concentration of perborate ([perborate]$_0$ = 0) is the same as the specific rate of the hydrogen peroxide (percarbonate) oxidation. The oxidation that shows first order dependence on [perborate]$_0$ or added [H_3BO_3] is also hydrogen peroxide oxidation but mediated by borate (Scheme 1). Ogata and Shimizu[4] proffered that the oxidizing species of perborate in glacial acetic acid is hydrogen peroxide coordinated with boric acid but failed to observe an increase of k' with increasing [perborate]$_0$ and the generation of peracetic acid on standing of perborate solution in acetic acid. Hydrogen peroxide associated with borate is a better electrophile than molecular hydrogen peroxide. The mechanism of oxidation of anilines by hydrogen peroxide is classical. The electrophilic attack of the peroxide oxygen on the amine nitrogen leading to formation of phenylhydroxylamine is slow and rate determining.[4] Phenylhydroxylamine is further oxidized to nitrosobenzene which in turn couples with aniline, present in a large excess, to yield azobenzene; the latter two reactions are fast. Scheme 1 differs from the mechanism suggested by Ogata and Shimizu[4] as it includes oxidation by molecular hydrogen peroxide; kinetic studies on the perborate oxidation of organic sulfides in glacial acetic acid reveal perborate oxidation as hydrogen peroxide oxidation, the rates of oxidation with perborate and dry hydrogen peroxide

$$H_2O_2 + \text{borate} \Leftrightarrow H_2O_2\cdots\text{borate} \qquad K$$

$$H_2O_2 + PhNH_2 \rightarrow PhNHOH + H_2O \qquad k_1$$

$$H_2O_2\cdots\text{borate} + PhNH_2 \rightarrow PhNHOH + H_2O + \text{borate} \qquad k_2$$

$$H_2O_2 + PhNHOH \rightarrow PhNO + 2H_2O \qquad \text{fast}$$

$$PhNO + PhNH_2 \rightarrow PhN{=}NPh + H_2O \qquad \text{fast}$$

Scheme 1

(percarbonate) under identical conditions are identical.[16] 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. The oxidation is sluggish in aqueous and partly aqueous media and a possible reason is the reduced electrophilicity of hydrogen peroxide due to the association of water molecules. Scheme 1 leads to the rate law:

$$-d[\text{oxidizing agent}]/dt = 2(k_1 + Kk_2[\text{perborate}]_0)[\text{aniline}][\text{oxidizing agent}]$$

with a pseudo-first-order rate constant of $k' = 2(k_1 + Kk_2[\text{perborate}]_0)[\text{aniline}]$.

The rate constants obtained from the slopes and intercepts of the kinetic plots are $10^4k_1 = 2.4$, 2.8 $dm^3\ mol^{-1}\ s^{-1}$; $10^2Kk_2 = 3.7$, 4.8 $dm^6\ mol^{-2}\ s^{-1}$ at 60 and 65 °C, respectively.

Hammett correlation of reactivity

Application of the Hammett correlation to reactions proceeding through two competing mechanisms results in non-linear Hammett plots; one such case is the acetolysis of *threo*-3-aryl-2-butyl brosylates (brosylate = 4-bromobenzene sulfonate) which proceeds *via* two reaction paths, competition between formation of phenonium ions and the solvent assisted process.[17] The perborate oxidation of anilines proceeds *via* two paths but in both cases the oxidizing species is hydrogen peroxide. Hence it is of interest to examine the structure-reactivity relationships in this reaction and 31 anilines were used for this study. The perborate oxidation rates of *para*- and *meta*-substituted anilines in acetic acid do not conform to the usual Hammett equation at any of the temperatures measured (*eg.*, Fig. 6). In anilines, the reaction center is likely to cross-conjugate with the *para*-substituents and correlations of the oxidation rates of *para*- and *meta*-substituted anilines separately using the usual Hammett equation (σ_p or σ_m) or the Brown–Okamoto equation ($\sigma_p{}^+$ or $\sigma_m{}^+$) or the modified Hammett equation ($\sigma_p{}^-$) were also unsuccessful. The oxidation rates measured at 45, 55 and 65 °C were also analyzed in terms of the dual substituent parameter (DSP) equations (*para*: σ_I, σ_R; σ_I, $\sigma_R{}^+$; σ_I, $\sigma_R{}^-$; *F*, *R*; *meta*: σ_I, σ_R; σ_I, $\sigma_R{}^+$; σ_I, $\sigma_R{}^-$; *F*, *R*)[18] but this analysis was unsuccessful. The oxidation rates of *ortho*-substituted anilines also fail to conform to Charton's LDS (localized, delocalized, steric) equations; the carboxy, nitro and methoxycarbonyl substituents individually take either planar or orthogonal orientations requiring appropriate steric substituent constants. The acetyl substituent was excluded due to the non-availability of the steric substituent constant. The values of the substituent constants used are cited elsewhere.[15]

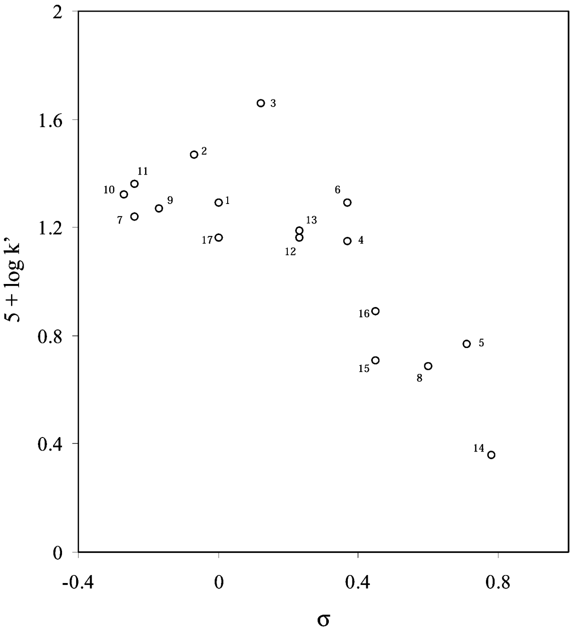

Fig. 6 The Hammett plot with the rate constants obtained under identical conditions at 45 °C.

Reaction rates of molecular anilines

Reports on the kinetics of oxidation of anilines are numerous; the reaction rates in basic, neutral, acidic and non-aqueous media conform to the Hammett equation or to one of its modified forms. Anilines are present as free bases in basic and neutral media but exist in two forms in acidic solutions, as free bases and as conjugate acids. The ratio of the concentrations of the free base to the conjugate acid ($[XC_6H_4NH_2]/[XC_6H_4NH_3{}^+]$) depends on the pK_a of the aniline and the acidity of the medium. The hitherto reported oxidations of anilines were studied under pseudo-first-order conditions of [anilines] ⩾ [oxidant], and [oxidants] at different reaction times were estimated by titrimetry or spectrophotometry. The pseudo-first-order rate constants (k') were obtained from the least squares slopes of log[oxidant] *versus* time plots and the second order rate constant = $k'/[\text{aniline}]_T$ where $[\text{aniline}]_T$ is the total concentration of aniline. Since the pK_a varies from 5.36 (*p*-OCH_3) to −0.28 (*o*-NO_2) and molecular anilines are the easily oxidizable species (nucleophiles) the reported $k'/[\text{aniline}]_T$ values are not the rate constants of the oxidant–molecular aniline reactions. Furthermore, the analysis of structure-reactivity relationships using $k'/[\text{aniline}]_T$ is erroneous. In the reactions of anilines in acid medium the specific reaction rates of anilines are to be obtained using the concentrations of the free bases and not the total concentrations of anilines. The concentrations of the free bases may be deduced from the acid strength of the medium and the pK_a values of the anilines.[15] Although the pK_a values used correspond to those in aqueous solutions, a detailed examination reveals that they may be used to obtain the concentrations of the free bases even in glacial acetic acid. The ratio of the ionization constant of acetic acid to that of anilinium ion results in the equilibrium constant of the reaction $PhNH_2 + HOAc \rightleftharpoons PhNH_3{}^+ + OAc^-$. In the absence of water autoionization of acetic acid is unlikely and hence $[PhNH_3{}^+] = [OAc^-]$; $[PhNH_3{}^+] + [PhNH_2] = [PhNH_2]_T$. Solving the quadratic expression on $[PhNH_2]$ yields $[PhNH_2]$. Since the pK_a values of anilines at the experimental temperatures are unavailable, as an approximation, the pK_a values at 25 °C were used in the calculation; the pK_a values employed are given elsewhere.[15] The specific reaction rates of molecular anilines in glacial acetic acid $\{k = k'/[XC_6H_4NH_2] = 2(k_1 + Kk_2[\text{perborate}]_0)$; $[\text{perborate}]_0 = 1.00 \times 10^{-2}\ mol\ dm^{-3}\}$ thus obtained conform to the usual Hammett equation at all the temperatures studied; Fig. 7 is the Hammett plot at 45 °C ($r = 0.98$, $s = 0.21$, $n = 17$, $\rho = -2.9$ at 45–65 °C). The large deviation of *p*-aminobenzoic acid is likely due to complication of zwitterion formation not allowed for in the calculation of the concentration of the molecular form of the aniline. The *meta*-acid does not deviate significantly and a possible explanation is that zwitterion formation is insignificant. The reaction constant is close to that of the hydrogen peroxide (percarbonate) oxidation of molecular anilines in glacial acetic acid under identical conditions ($\rho = -2.7 \pm 0.1$ at 45–65 °C).[15]

The specific oxidation rates of *ortho*-substituted anilines were analyzed in terms of Charton's LDS equations. The oxidation of *o*-mercaptoaniline is instantaneous. The UV–visible spectra of the reaction solution after the completion of the reaction show absence of formation of azo compound; the reaction is not the oxidation of the amino group but that of the thiol. The reaction of *o*-aminophenol is also too fast to measure; *o*-aminophenol enters into intramolecular hydrogen

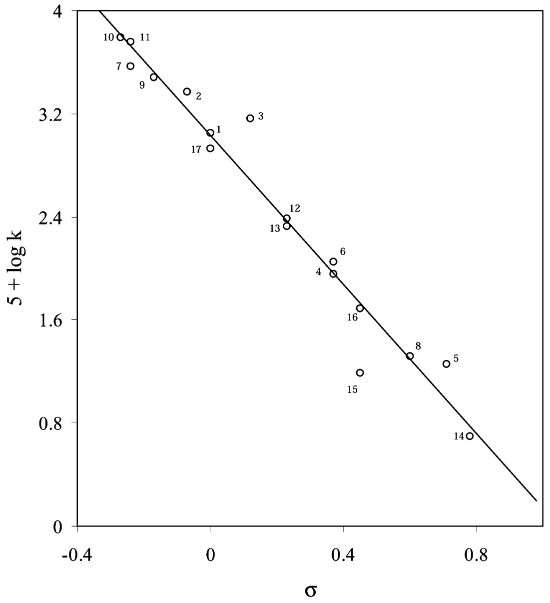

Fig. 7 The Hammett plot using the rate constants of molecular anilines at 45 °C.

bonding. *o*-Phenylenediamine in glacial acetic acid may exist in three forms, *viz.*, $o\text{-}{}^{+}NH_3C_6H_4NH_3^{+}$, $o\text{-}NH_2C_6H_4NH_3^{+}$ and $o\text{-}NH_2C_6H_4NH_2$. Calculation of the individual concentrations, using the pK_a values, shows that *o*-phenylenediamine exists predominantly as $o\text{-}NH_2C_6H_4NH_3^{+}$, the other two forms are present in only trace amounts. The protonated amino group (NH_3^{+}-) is highly electron-demanding, the activation energy for the oxidation of the conjugated acid is likely to be high and hence the free base is the probable reactive species. The k values reported in Table 1 correspond to this species. The oxidation of molecular *o*-phenylenediamine encounters two identical reaction centers; one acts as the substituent and the other as the reaction site. Hence only half of the rate is to be taken into account for the correlation analysis. Because of these complications and also that the reported reaction rates are only the extrapolated values *o*-phenylenediamine was excluded from the regression. Correlation analysis of the specific rates of the *ortho*-substituted molecular anilines in terms of the LDS equations gave results ranging from fairly satisfactory to rather unsatisfactory. The values of the substituent constants used are given elsewhere.[15] Each data set involved 8 points (methyl, methoxy, ethoxy, chloro, nitro, carboxy, methoxycarbonyl and hydrogen), acetyl being omitted due to the unavailability of the steric parameter. Table 2 reveals that σ_R^- is less satisfactory in explaining the variation of the rate with the substituent. This is in accordance with the literature on the oxidation of anilines; most of the satisfactory correlations involve either σ or σ_p^+. The results obtained by using σ_I and σ_R^+ were fairly better and still so when it was assumed that the carboxy and nitro groups were in the orthogonal and methoxycarbonyl substituent in the planar orientations. One of the most satisfactory correlation equations was as follows:

$$\log k = -1.99(\pm 0.18) - 3.14(\pm 0.38)\sigma_I - 0.91(\pm 0.17)\sigma_R^+ - 0.48(\pm 0.20)\upsilon$$

where the temperature was 45 °C; $n = 8$, $100R^2 = 97.1$, $s = 0.222$. The regression coefficients yield the percentages of inductive (σ_I), resonance (σ_R^+) and steric (υ) terms as 69, 20 and 11, respectively at 45 °C. These results are comparable to those of the hydrogen peroxide (percarbonate) oxidation of anilines in glacial acetic acid under identical conditions:

$$\log k = -2.28(\pm 0.15) - 2.90(\pm 0.28)\sigma_I - 1.15(\pm 0.12)\sigma_R^+ - 1.18(\pm 0.35)\upsilon$$

where the temperature was 45 °C; $n = 8$, $100R^2 = 98.6$, $s = 0.156$.[15]

Separation of reaction rates

The satisfactory linear Hammett correlation observed in the perborate oxidation of anilines in glacial acetic acid that occurs through two competing reaction pathways is surprising.[17] A possible explanation is that the transition states of both the competing mechanisms do not differ significantly and so are the reaction constants, ρ. This could be confirmed by analyzing individually the specific rates of hydrogen peroxide (percarbonate) oxidation of molecular anilines[15] and the specific rates of borate assisted hydrogen peroxide oxidation of molecular anilines, the latter may be obtained from the rates of oxidation of molecular anilines by perborate (this work) and by hydrogen peroxide (percarbonate);[15] $k(H_2O_2 \cdots \text{borate}) = k(\text{perborate}) - k(\text{percarbonate})$. The specific rates of borate assisted hydrogen peroxide oxidation of molecular anilines obtained thus conform to the usual Hammett equation at all the temperatures studied; Fig. 8 is the Hammett plot at 55 °C ($r = 0.98$, $s = 0.23$, $n = 17$, $\rho = -3.0$). The reaction constant is close to that of the hydrogen peroxide (percarbonate) oxidation of molecular anilines in glacial acetic acid, obtained under identical conditions ($\rho = -2.7 \pm 0.1$).[15] The correlation of the rates of borate assisted oxidation in terms of Charton's LDS equations is less satisfactory and is explained as follows. The *ortho*-series includes strongly electron-withdrawing substituents like nitro, carboxyl and methoxycarbonyl, and the oxidations of these substrates by percarbonate and perborate are slow. The error in the rates of borate assisted oxidation that is obtained from the difference in the measured rates of perborate and percarbonate oxidations is likely to be significant. This error could be a reason for the less satisfactory correlation.

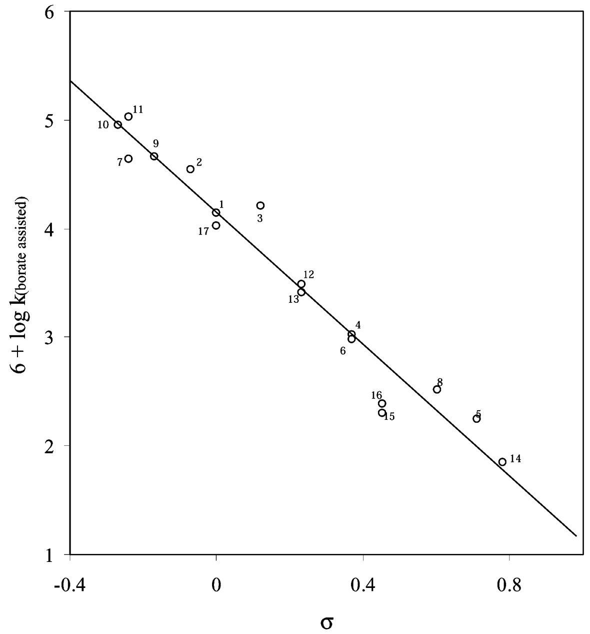

Fig. 8 The Hammett plot for the borate assisted hydrogen peroxide oxidation of molecular anilines at 55 °C.

Reactivity and selectivity of perborate and percarbonate oxidations

Sodium perborate ($NaBO_3\cdot 4H_2O$) and sodium percarbonate ($Na_2CO_3\cdot 1.5H_2O_2$), two cheap, non-toxic, stable, safe, large-scale industrial chemicals primarily employed in the detergent industry, now find extensive usage in organic synthesis.[1–3] The oxidations of anilines by perborate (this work) and percarbonate[15] in glacial acetic acid involve molecular anilines and

Table 1 Pseudo-first-order rate constants (k') and specific oxidation rates of molecular anilines (k) in glacial acetic acid[a]

		$10^4k'/s^{-1}$			$10^3k/dm^3\ mol^{-1}\ s^{-1}$		
Entry	Substituent	45 °C	55 °C	65 °C	45 °C	55 °C	65 °C
1	H	1.95	3.98	7.78	11.3	23.0	45.0
2	*m*-CH_3	2.97	7.42	13.7	21.8	54.5	101
3	*m*-OH	4.54	9.30	17.0	14.3	29.3	53.6
4	*m*-Cl	1.40	2.58	5.99	1.12	2.06	4.78
5	*m*-NO_2	0.592	1.17	2.16	0.184	0.363	0.670
6	*m*-COOH	1.97	4.38	9.26	0.936	2.08	4.40
7	*m,p*-$(CH_3)_2$	1.73	3.80	8.08	35.4	77.6	165
8	*m,p*-Cl_2	0.486	1.56	3.04	0.209	0.672	1.31
9	*p*-CH_3	1.85	4.40	9.30	30.9	73.4	155
10	*p*-OCH_3	2.10	5.00	11.8	66.0	157	371
11	*p*-OC_2H_5	2.30	6.29	16.5	56.3	154	404
12	*p*-Cl	1.46	3.41	6.15	2.48	5.80	10.5
13	*p*-Br	1.55	3.59	6.49	2.17	5.02	9.08
14	*p*-NO_2	0.229[b]	0.732	2.25	0.0498	0.159	0.489
15	*p*-COOH	0.507	1.22	2.19	0.153	0.369	0.663
16	*p*-$COOC_2H_5$	0.774	1.08	2.99	0.484	0.676	1.87
17	*p*-$NHCOCH_3$	1.45	3.57	10.4	8.39	20.7	60.2
18	*o,m*-Cl_2	0.412	0.903	1.81	0.100	0.220	0.441
19	*o*-CH_3	2.26	4.28	7.90	9.51	18.0	33.2
20	*o*-OCH_3	2.65	5.37	10.7	13.2	26.8	53.3
21	*o*-OC_2H_5	1.90	5.09	10.2	8.34	22.3	44.8
22	*o*-Cl	0.580	1.48	3.02	0.199	0.507	1.03
23	*o*-NO_2	0.260	0.548	1.59	0.0530	0.112	0.324
24	*o*-COOH	2.14	5.44	10.2	0.571	1.45	2.72
25	*o*-$COOCH_3$	0.666	1.26	2.42	0.197	0.373	0.716
26	*o*-$COCH_3$	0.332	0.686	1.26	0.0927	0.192	0.352
27	*o*-NH_2	84.5[c]	373[c]	1510[c]	545	2400	9730
28	-$NHCH_3$	8.87	21.1	55.7	88.6	211	556
29	-$N(CH_3)_2$	2.35	4.95	9.37	45.9	96.7	183
30	*o*-OH	Fast					
31	*o*-SH	Very fast					

[a] $[\text{perborate}]_0 = 0.010\ \text{mol dm}^{-3}$; $[\text{aniline}]_0 = 0.50\ \text{mol dm}^{-3}$. [b] Extrapolated using Arrhenius plot: 1.46 at 60 °C. [c] Extrapolated using Arrhenius plot: 1.32, 7.62, and 38.7 at 20, 30, and 40 °C, respectively.

the oxidizing species in the slow and rate-determining steps. Also, the reactions conform to the Hammett equations. Examination of the oxidation rates of perborate (Table 1) and percarbonate[15] reveals that perborate oxidation is faster than percarbonate. Association of the electron-deficient borate species with hydrogen peroxide leads to increased electrophilicity. Highly reactive systems are often less selective and, if amenable to correlation, show lower susceptibility than similar less reactive systems. The oxidations of anilines by perborate and percarbonate do not conform to the original reactivity–selectivity relationship; although the reactivity of perborate is higher than that of percarbonate the former does not show lower selectivity, the reaction constants are −3.0 and −2.7, respectively. Exner[19] redefined and reexamined the reactivity–selectivity principle (RSP) on an experimental basis, showing that the original narrow definition of RSP is invalid, and formulated the principle in terms of simple mathematical expressions, involving only rate constants and avoiding any σ constants. The rates of oxidation of molecular anilines by perborate and percarbonate at all the temperatures studied were analyzed by the Exner method; the double logarithmic plots of k(perborate) *versus* k(percarbonate) are straight lines (n = 28; r = 0.992, 0.993, 0.992; s = 0.138, 0.130, 0.142; slope, b = 1.04, 1.01, 0.994; intercept, a = 0.438, 0.345, 0.311; mean difference, Δ = 0.322, 0.328, 0.324, at 45, 55 and 65 °C, respectively). Fig. 9 is the RSP plot at 55 °C. Since the slope b is not significantly different from unity, the RSP correlation shows indifferent behavior, *i.e.*, no change in selectivity. While perborate oxidation is faster than percarbonate oxidation it is not less selective than the latter. Also, perborate is of longer shelf life and cheaper than percarbonate; its decomposition is less than that of percarbonate. The experimentally measured reaction rates (k') of perborate and percarbonate oxidations under identical conditions were also analyzed by the Exner method but the results are less satisfactory (logk'(perborate)–logk'(percarbonate) correlations: n = 28; r = 0.933, 0.944, 0.934; s = 0.141, 0.130, 0.140; slope, b = 1.08, 1.00, 0.934; intercept, a = 0.669, 0.326, 0.093; Δ = 0.322, 0.328, 0.324, at 45, 55 and 65 °C, respectively). This is likely to be a consequence of the lack of Hammett correlation using k'.

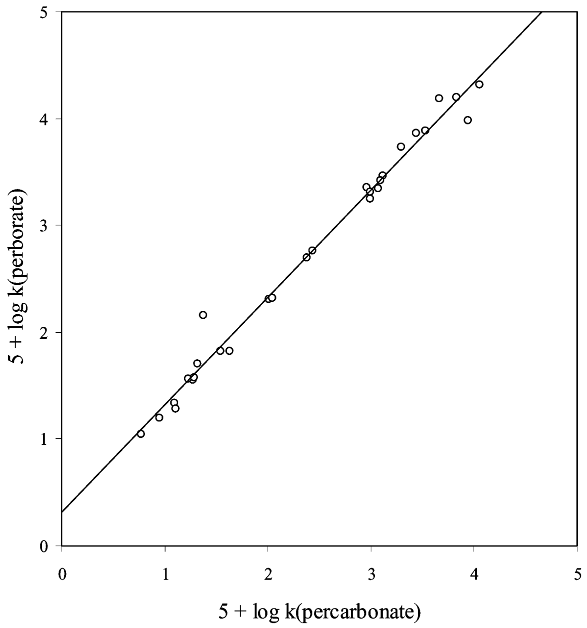

Fig. 9 RSP plot of perborate and percarbonate oxidations of molecular anilines at 55 °C.

Table 2 Charton's LDS correlation of the rate constants of perborate oxidation of molecular *ortho*-substituted anilines.[a]

Explanatory variables	45 °C		55 °C		65 °C	
	$100R^2$	s	$100R^2$	s	$100R^2$	s
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}$[b]	88.9	0.382	88.4	0.391	86.0	0.420
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[c]	92.5	0.353	91.9	0.365	90.3	0.387
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[d]	93.8	0.323	94.0	0.315	92.2	0.345
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[e]	93.4	0.333	92.6	0.351	91.6	0.360
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[f]	96.0	0.260	95.9	0.261	95.4	0.265
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[g]	93.8	0.323	93.6	0.325	91.7	0.357
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[h]	92.6	0.353	91.8	0.367	90.1	0.389
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[i]	92.4	0.355	91.9	0.365	89.9	0.393
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}, \upsilon$[j]	95.4	0.277	94.5	0.302	93.8	0.310
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}$[b]	85.6	0.436	85.3	0.440	83.1	0.460
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[c]	87.1	0.464	86.5	0.472	84.7	0.484
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[d]	89.3	0.424	89.7	0.412	87.8	0.432
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[e]	87.7	0.453	86.9	0.465	85.7	0.469
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[f]	91.0	0.387	91.0	0.385	90.5	0.382
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[g]	89.3	0.423	89.6	0.415	87.6	0.436
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[h]	87.0	0.466	86.4	0.473	84.5	0.488
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[i]	87.2	0.463	87.0	0.463	84.6	0.486
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{-}, \upsilon$[j]	89.6	0.416	88.8	0.430	87.9	0.431
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}$[b]	88.6	0.389	88.3	0.392	85.9	0.421
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[c]	93.3	0.333	93.1	0.338	91.7	0.357
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[d]	94.8	0.294	95.5	0.272	93.9	0.307
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[e]	94.3	0.309	93.8	0.320	93.1	0.326
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[f]	97.1	0.222	97.4	0.208	97.1	0.210
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[g]	93.4	0.331	93.5	0.329	91.7	0.358
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[h]	92.9	0.345	92.6	0.350	90.8	0.376
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[i]	92.9	0.345	92.6	0.350	90.8	0.376
$\sigma_{\mathrm{I}}, \sigma_{\mathrm{R}}^{+}, \upsilon$[j]	96.8	0.232	96.2	0.250	95.8	0.253
F, R[b]	92.7	0.311	92.5	0.314	90.3	0.348
F, R, υ[c]	93.3	0.334	93.2	0.335	91.5	0.362
F, R, υ[d]	94.0	0.318	94.5	0.300	92.7	0.334
F, R, υ[e]	94.4	0.305	94.1	0.313	93.0	0.327
F, R, υ[f]	96.2	0.252	96.6	0.237	96.0	0.247
F, R, υ[g]	94.0	0.316	94.3	0.307	92.3	0.344
F, R, υ[h]	93.6	0.328	93.2	0.334	91.5	0.361
F, R, υ[i]	93.3	0.334	93.1	0.338	91.2	0.367
F, R, υ[j]	96.4	0.245	96.0	0.258	95.2	0.270

[a] $n = 8$ (*o*-NH_2 and *o*-$COCH_3$ excluded); $100R^2$: the percentage of variation. [b] $n = 9$, *o*-$COCH_3$ included. [c] COOH: planar, NO_2: planar, $COOCH_3$: planar; [d] COOH: orthogonal, NO_2: planar, $COOCH_3$: planar; [e] COOH: planar, NO_2: orthogonal, $COOCH_3$: planar; [f] COOH: orthogonal, NO_2: orthogonal, $COOCH_3$: planar; [g] COOH: planar, NO_2: planar, $COOCH_3$: orthogonal; [h] COOH: orthogonal, NO_2: planar, $COOCH_3$: orthogonal; [i] COOH: planar, NO_2: orthogonal, $COOCH_3$: orthogonal; [j] COOH: orthogonal, NO_2: orthogonal, $COOCH_3$: orthogonal.

Conclusions

Perborate but not percarbonate in glacial acetic acid generates peracetic acid on standing. The oxidation of anilines with a fresh solution of perborate is faster than with percarbonate. The Hammett correlation of the perborate oxidation rates of anilines in acetic acid under identical conditions is unsatisfactory but the specific reaction rates of molecular anilines conform to the linear free energy relationships. The perborate oxidation occurs *via* two reaction paths but the over all reaction rates of molecular anilines conform to the structure–reactivity relationships, and this is because the transition states do not differ significantly. While the perborate oxidation is faster than the percarbonate oxidation the selectivity of the former is not less than that of the latter.

Experimental

General procedure

Sodium perborate, $NaBO_3.4H_2O$ and sodium percarbonate, $Na_2CO_3.\ 1.5H_2O_2$ (Fluka) were used as such. Anilines (AR or LR) were redistilled or recrystallized prior to use and the identity of the anilines used was confirmed by their physical constants as reported earlier.[15] Acetic acid, AR was refluxed over chromium(VI) oxide for 6 h and distilled through a column. Other chemicals used were also of AR or LR grade. Perborate and percarbonate were dissolved in glacial acetic acid, standardized iodometrically and used immediately. For the experiments with peracetic acid, a solution of peracetic acid in glacial acetic acid was prepared by the standard method, estimated iodometrically and also used immediately. The kinetics of the oxidation at fixed temperature were followed by mixing required volumes of the oxidant and aniline in glacial acetic acid and estimating the unreacted oxidizing agent at different reaction times iodometrically. Perborate (0.01 mol) was added to aniline (0.01 mol) in acetic acid at 65 °C, diluted with water after 4 h; the separated solid was filtered, recrystallized from petroleum ether (40–60) and identified as azobenzene by its mp, mixed mp, IR, UV–visible and GC-mass spectra. The spectra were identical with those of an authentic sample and the GC-mass spectral study showed azobenzene as the only product; the yield was not less than 90%.[5] The UV-visible spectra of the reaction solutions, during and after the completion of the reaction, of all the anilines studied except *p*-mercaptoaniline, *N*-methylaniline and *N*,*N*-dimethylaniline revealed the formation of azobenzenes. Hence the reaction is represented as:

$$2PhNH_2 + 2NaBO_3 \longrightarrow PhN = NPh + 2NaBO_2 + 2H_2O$$

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