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# OXIDATION KINETICS OF *p*-AMINODIPHENYLAMINE WITH PEROXYDISULPHATE

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**The kinetics of oxidation of *p*-aminodiphenylamine with the peroxydisulphate ion were investigated spectrophotometrically. The oxidation was accompanied by the appearance of a wine-red colour, which changed to become colourless. The reaction rate was measured by the stopped-flow technique with a UV spectrophotometer. The reactions proceeded with second-order kinetics, first-order for each individual reactant. Cationic micelles (cetyltrimethyl ammonium bromide) caused an enhancement in the reaction rate followed by inhibition at higher concentrations. Anionic micelles (sodium dodecyl sulphate), on the other hand, had a slightly retarding effect. The effects of radical scavenger, pH and ionic strength on the fast oxidation rate were examined. A mechanism consistent with the observations is discussed.**

## INTRODUCTION

The peroxydisulphate ion is a strong oxidizing agent with a standard oxidation–reduction potential of 2·01 V.[1] It decomposes in aqueous media with the formation of either one sulphate radical ion or two sulphate radical species. It can oxidize a large number of organic substrates, including aromatic secondary and tertiary amines.[2,3] In the majority of these oxidations, the oxidation rate follows first-order kinetics in amine and also in peroxydisulphate. Moreover, the oxidation process is slow unless a suitable catalyst is present. The standard catalysts are the Ag(I) and Cu(II) ions.

The rates of reactions catalysed by these ions are almost independent of the reducer concentration, but depend upon the peroxydisulphate and catalyst concentrations. Electron-donating substituents of aromatic amines enhance the reaction rate and electron-attracting substituents slow it down.[4,5] In this laboratory, the oxidation kinetics of *p*-nitrodiphenylamine (*p*-$NO_2$-DPA) have recently been investigated.[6] The data obtained showed a quite slow rate. The reaction was accelerated substantially when Ag(I) ions were present. We report here the oxidation kinetics of another substituted diphenylamine derivative, *p*-aminodiphenylamine (*p*-$NH_2$-DPA), with the same oxidant, both in homogeneous medium and in the presence of aggregates of ionic surfactants.

## EXPERIMENTAL

*Materials.* Potassium peroxydisulphate (Merck) was used after recrystallization from distilled water and drying at room temperature under vacuum. Its stock solution was always prepared daily to ensure constant concentration for each kinetic run and was tested iodometrically. Sodium dodecyl sulphate (SDS; BDH) was recrystallized from ethanol. Cetyltrimethyl ammonium bromide (CTAB; BDH), was recrystallized from a methanol–water mixture. *p*-$NH_2$-DPA (Aldrich) was used as received. Its solution was prepared in aqueous ethanol (7% v/v) and was protected from light by a dark cover in order to avoid the possible self-oxidation.

*Kinetic measurements.* The fast reaction rate was measured with a HI-TECH, SF-3L stopped-flow spectrophotometer, interfaced with an Apple IIe computer for data collection as changes in signal voltage or absorbance with time.

The measurements were performed under pseudo-first-order conditions, i.e. the $S_2O_8^{2-}$/substrate concentration ratio was 1400. The slow part of the reaction was followed with a Shimadzu 2100-S UV/vis. recording spectrophotometer operated with a Shimadzu data acquisition system. The reaction temperature was adjusted by a Shimadzu electronic temperature control unit with an accuracy of ±0·1 °C.

## RESULTS

All oxidations were carried out under first-order conditions, with a large excess of the $S_2O_8^{2-}$ ion. The absorbance of *p*-$NH_2$-DPA in the presence of $S_2O_8^{2-}$ changed with time as shown in Figure 1.

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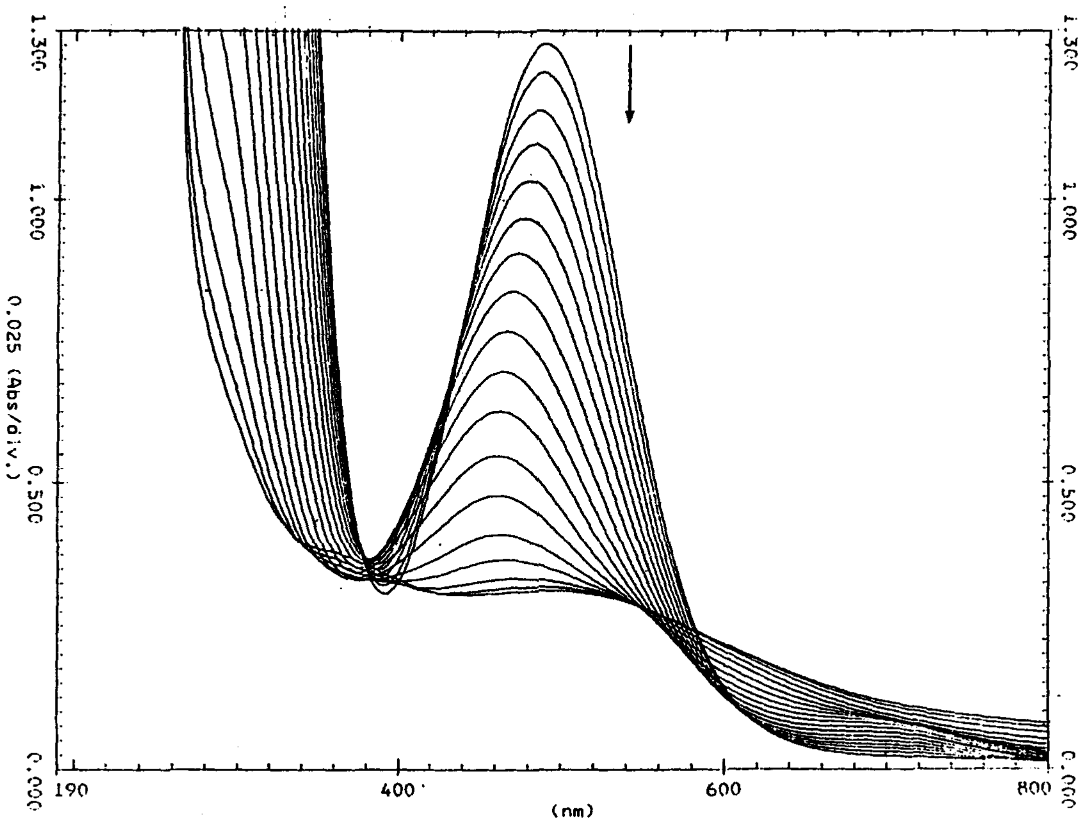


Figure 1. The decrease in absorbance of *p*-aminodiphenylamine in the presence of $S_2O_8^{2-}$ with time. [*p*-$NH_2$-DPA] = $1{\cdot}66\times10^{-4}$ M; [$S_2O_8^{2-}$] = 0·2329 M; $T$ = 30 °C

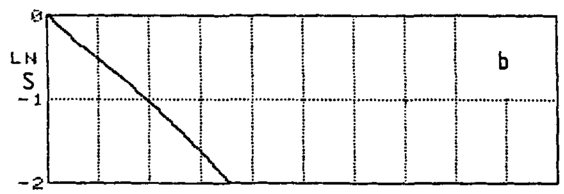


Figure 2. (a) Typical reaction curve observed by using stopped-flow method with spectrophotometer in the oxidation of *p*-aminodiphenylamine with $S_2O_8^{2-}$. [*p*-$NH_2$-DPA] = $1{\cdot}66\times10^{-4}$ M; [$S_2O_8^{2-}$] = 0·2329 M; $T$ = 30 °C. (b) Semilogarithmic plot of the typical curve

Stopped-flow measurements with the spectrophotometer were carried out by mixing equal volumes of the substrate with the oxidant. Typical reaction curves are shown in Figure 2a, where the directions of the signal after mixing both samples indicate an increase of the absorbance. A semilogarithmic plot of the typical reaction curve in exponential function is shown in Figure 2b, calculated directly by computer program connected to the stopped-flow instrument.

### Dependence on [$S_2O_8^{2-}$]

The order of reaction for the oxidant concentration was determined following vant-Hoff's method. At constant substrate concentration the reaction was first order with respect to [$S_2O_8^{2-}$], as revealed by the linear variation of the pseudo-first-order rate constant with [$S_2O_8^{2-}$], and $k_0$/[$S_2O_8^{2-}$] values were constant (Figure 3). The slope of the line is considered as the second-order rate constant, which equals 2·85 $M^{-1}\,s^{-1}$ at 30 °C.

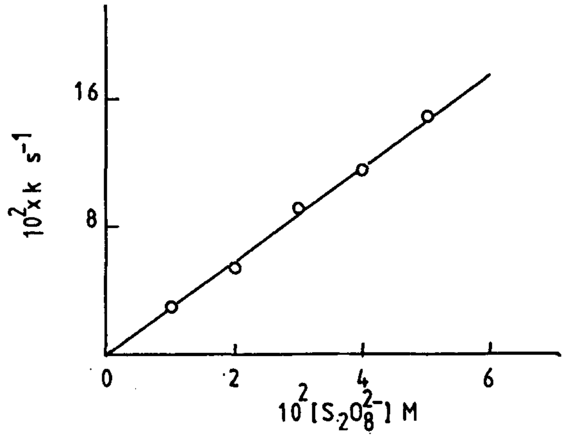


Figure 3. Variation of the rate constant as a function of $S_2O_8^{2-}$ concentration. [$p$-$NH_2$-DPA] = $5 \times 10^{-4}$ M; $T = 30$ °C

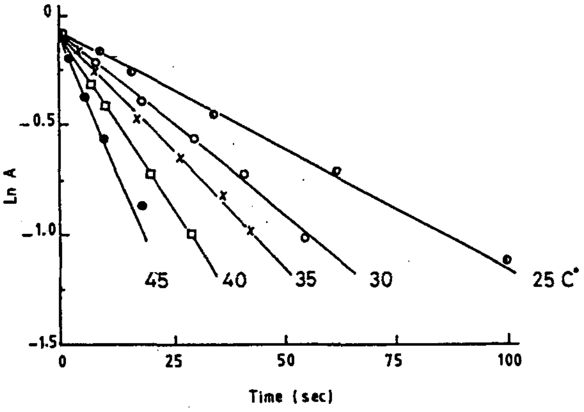


Figure 4. First-order plot at various temperatures for the oxidation process. [$p$-$NH_2$-DPA] = $1{\cdot}66 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = 0·2329 M

### Rate law

Taking into account that the reaction rate follows first-order kinetics for both the substrate and oxidant concentrations, the rate law is therefore:

$$-d[p\text{-}NH_2\text{-DPA}]/dt = k[p\text{-}NH_2\text{-DPA}][S_2O_8^{2-}] \quad (1)$$

### Effect of temperature

The effect of temperature on the reaction rate has been investigated under comparable conditions. The measurements were carried out in the range 25–45 °C, and it is safe to infer that the spontaneous decomposition of the peroxydisulphate within this range was undetectable. Figure 4 exhibits the first order plot at different temperatures for the oxidation reaction. The activation parameters determined from employing an Arrhenius plot and Eyring's equation are summarized in Table 1.

### Effect of micelles

The critical micelle concentration (C.M.C.) of SDS and CTAB was determined in pure water as well as in a medium containing alcohol and peroxydisulphate ion in the same proportions as the reacting medium. The C.M.C. was found to be almost the same in both pure water and in the reaction medium, i.e. $8 \times 10^{-3}$ M for SDS and $9 \times 10^{-4}$ M for CTAB.[7]

The role of SDS, as anionic micelles, in varying the fast oxidation rate is shown in Table 2. Inspection of the data shows a slight decrease in the observed rate constant with an increase in SDS concentration. With

Table 1. Activation parameters for the oxidation of $p$-$NH_2$-DPA with $S_2O_8^{2-}$. [Substrate] = $1{\cdot}66 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = 0·2329 M

| Temp. (°C) | $10^2 \times k_0$ ($s^{-1}$) | $10^2k$ ($M^{-1} s^{-1}$) | $E$ (kJ $mol^{-1}$) | $\Delta H\#$ (kJ $mol^{-1}$) | $\Delta G\#$ (kJ $mol^{-1}$) | $\Delta S\#$ (J $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|---|---|
| 25 | 10·9<br>(0·9) | 46·8<br>(3·9) | | | | |
| 30 | 14·9<br>(1·3) | 63·9<br>(5·6) | | | | |
| 35 | 19·5<br>(2) | 83·7<br>(8·6) | 45·8<br>(59·5) | 43·2<br>(57) | 76<br>(81·9) | −110<br>(−90) |
| 40 | 26·9<br>(3) | 115·4<br>(12·9) | | | | |
| 45 | 34·6<br>(3·9) | 148·5<br>(16·7) | | | | |

Values in parentheses correspond to the UV measurements, $k = k_0/[S_2O_8^{2-}]$.

Table 2. Observed rate constant dependence on the SDS concentration. [$p$-$NH_2$-DPA] = $1{\cdot}66 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = $3{\cdot}33 \times 10^{-3}$ M. $T = 30$ °C

| $10^4$[SDS] (M) | $10^2 \times k_0$ ($s^{-1}$) |
|---|---|
| 0 | 2·53 |
| 2·5 | 2·4 |
| 5 | 2·31 |
| 10 | 2·28 |
| 15 | 2·25 |

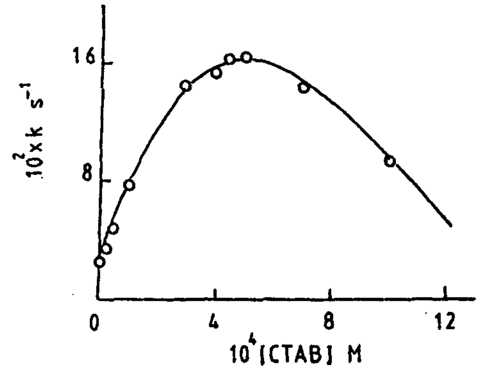


Figure 5. Variation of rate constant with CTAB concentration at 30 °C. [$p$-NH2-DpA] = $5 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = $2 \times 10^{-3}$ M

CTAB as cationic micelles, an enhancement was observed in the reaction rate followed by an inhibition through a maximum value at CTAB concentration of around $5 \times 10^{-4}$ M (Figure 5).

## pH Dependence

Universal buffer was utilized to study the effect of pH variation on the reaction rate. The variation of the observed rate constant with pH is given in Figure 6. The figure demonstrates a sharp increase in the rate constant as the pH rises from 4·2 to 6·5. Below and above this range a slow increase was observed. Retardation of the reaction rate in media with a pH of 4 may be attributed to the formation of unreactive protonated substrate species. Similar pH dependence has been observed in the peroxydisulphate oxidation of several organic reductants.[8,9]

## Effect of radical scavenger

Allyl acetate as a free-radical-sensitive monomer inhibited the reaction rate when added to the reaction mixture. (Table 3). The rate constant of the reaction in the absence of allyl acetate was 19·6 $s^{-1}$ and in the presence of scavenger the rate constant decreased with increasing concentration of allyl acetate, i.e. it reached 15·4 $s^{-1}$ when the concentration of scavenger was $9{\cdot}2 \times 10^{-3}$ M. This indicates the *in situ* formation of free radicals or radical ions that are involved in the reaction mechanism.

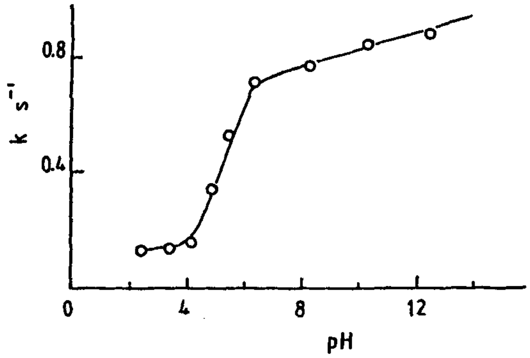


Figure 6. Effect of pH on the rate of oxidation. [$p$-$NH_2$DPA] = $1{\cdot}66 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = 0·05 M; $T = 30$ °C

Table 3. Effect of allyl acetate on the observed rate constant, $k_0$, for the oxidation reaction of $p$-$NH_2$-DPA with $S_2O_8^{2-}$. [$p$-$NH_2$-DPA] = $1{\cdot}66 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = 0·05 M. $T = 30$ °C

| $10^3$[allyl acetate] (M) | $k_0$ ($s^{-1}$) |
|---|---|
| 0 | 19·6 |
| 0·37 | 18·14 |
| 0·74 | 17·9 |
| 0·92 | 17·4 |
| 1·11 | 16·9 |
| 1·48 | 16·3 |
| 1·85 | 15·9 |
| 5·55 | 15·6 |
| 9·21 | 15·4 |

## Effect of ionic strength

Variable amounts of $K_2SO_4$ were used to study the reaction at different ionic strengths. The reaction rate was found to decrease slightly with increasing ionic strength. The plot of ln $k_0$ versus $\sqrt{\mu}/(1+\sqrt{\mu})$ (Figure 7) is linear with a slope of 0·625. The product $Z_A Z_B$ thus equals −0·267, which is nearly approaching zero. This is in accordance with the theoretical value ($Z_a Z_B = 0$), which thereby confirms that the reaction proceeds between an anion and a neutral molecule. The rate constant at infinite dilution obtained from Figure 7 is 0·167 $s^{-1}$.

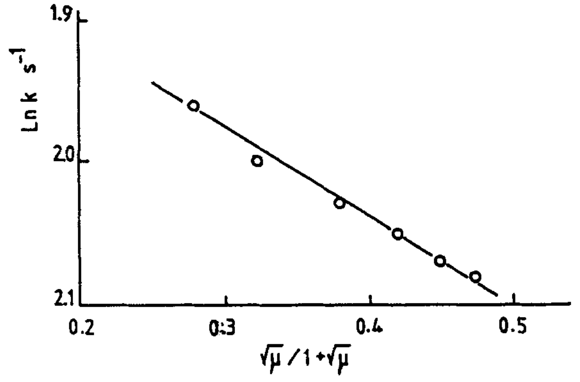


Figure 7. Correlation between ln $k$ and $\sqrt{\mu}/1+\sqrt{\mu}$ at varying ionic strengths maintained by $K_2SO_4$ at 30 °C. [$p$-$NH_2$-DPA] = $1{\cdot}66 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = 0·05 M

### Effect of solvent

The reaction was studied in different aquo-organic mixtures in order to explore the role of solvent in the current ion–dipole interaction. The organic component was methanol, ethanol, 1-propanol, 2-propanol and ethylene glycol; it was always present in 33% v/v. The variation of the rate constant with the dielectric constant is linear for some of the reaction mixtures (Figure 8). The dielectric constant dependence of ln $k$ should obey the equation:[10]

$$\ln k = \ln k_\infty + 1/4\pi D_0(Ze\mu N/RTr^2)1/D \qquad (2)$$

where $k$ and $k_\infty$ are the rate constants in media with dielectric constant $D$ and dielectric constant of infinite magnitude. $N$ is the Avogadro constant, $Ze$ is the ionic charge of the ion and $\mu$ is the dipole moment of the neutral molecule. $D_0$ is the dielectric constant of vacuum, and $r$ is the distance between the reacting species. Since the slope of the plot is negative, then $Ze$ must be negative. This conforms with the rate-determining step lying between that of the negatively charged $S_2O_8^{2-}$ ion and the dipolar substrate.

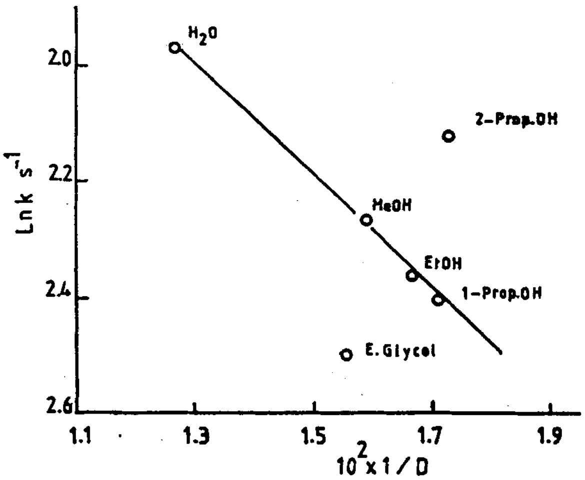
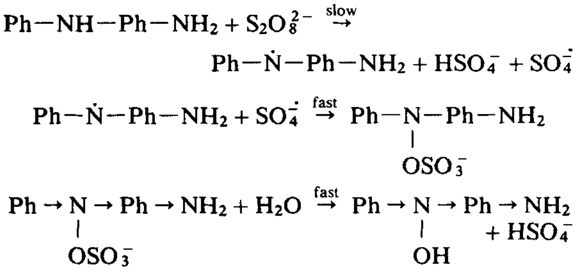


Figure 8. Correlation between ln $k$ and $1/D$ in different aquo-organic solvent mixtures at 30 °C. [$p$-$NH_2$-DPA] = $1{\cdot}66 \times 10^{-4}$ M; [$S_2O_8^{2-}$] = 0·05 M

## DISCUSSION

In the present system, the oxidation of $p$-$NH_2$-DPA with peroxydisulphate is accompanied by the appearance of a wine-red colour which changes to become colourless.

The thermal decomposition of the peroxydisulphate is characterized by an activation energy in the range 110–120 kJ mol$^{-1}$,[11] which is nearly twice the value of the activation energy obtained in the present work, (Table 1). This suggests a substantial contribution by the amine-induced oxidation mechanism rather than the initial thermal decomposition of the peroxydisulphate ion. Furthermore, the entropies of activation determined for the present reactions are strongly negative compared with that reported[11] for the $S_2O_8^{2-}$ dissociation (104·6 J mol$^{-1}$ K$^{-1}$). These facts therefore made it safe to infer that the rate-determining step is based on a bimolecular interaction between the substrate and the oxidant. An overall mechanism accounting for the kinetic findings may thus be suggested (Scheme 1). The results from measurements of the rate constant, the activation parameters and the effect of radical scavenger clearly support the outlined mechanism.



$$\text{Ph-NH-Ph-NH}_2 + S_2O_8^{2-} \xrightarrow{\text{slow}} \text{Ph-}\dot{\text{N}}\text{-Ph-NH}_2 + HSO_4^- + SO_4^{\dot{-}}$$

$$\text{Ph-}\dot{\text{N}}\text{-Ph-NH}_2 + SO_4^{\dot{-}} \xrightarrow{\text{fast}} \text{Ph-}\underset{\displaystyle OSO_3^-}{\underset{|}{\text{N}}}\text{-Ph-NH}_2$$

$$\text{Ph} \rightarrow \underset{\displaystyle OSO_3^-}{\underset{|}{\text{N}}} \rightarrow \text{Ph} \rightarrow \text{NH}_2 + H_2O \xrightarrow{\text{fast}} \text{Ph} \rightarrow \underset{\displaystyle OH}{\underset{|}{\text{N}}} \rightarrow \text{Ph} \rightarrow \text{NH}_2 + HSO_4^-$$

Scheme 1.

This mechanism is consistent with the fact that the reactions are first-order dependent on the concentration of the substrate and the oxidant, and consistent with the mechanism shown in Ref. 6.

With SDS there is a general inhibition in the oxidation rate (Table 2). If the inhibition is due to the formation of micellar aggregates, which squeeze the substrate molecules and protect them from electrophilic attack by peroxydisulphate, then the SDS concentration employed to show such effect should be similar to or greater than its c.m.c. ($8 \times 10^{-3}$ M). This is not our finding; the maximum amount of SDS utilized was $1{\cdot}5 \times 10^{-3}$ M (Table 2), which is about five times less than the corresponding c.m.c. The observed decrease in the reaction rate in the presence of this surfactant may therefore be attributed to unfavourable electrostatic interactions[12] between the negatively charged head groups of SDS and $S_2O_8^{2-}$.

The dependence of the rate constant on the cationic surfactant concentration (Figure 5) shows a maximum at a CTAB concentration of $5 \times 10^{-4}$ M, before the c.m.c. A maximum at a CTAB concentration of $1{\cdot}2 \times 10^{-3}$ M was also found in the rate constant–surfactant concentration profile of the hydroxide ion-catalysed hydrolysis of benzylidine acetophenone.[13] The catalysing property of CTAB, which exists, not unexpectedly, in the case of anion–molecule reactions may be interpreted in Figure 5 in terms of electrostatic interactions.[13] The observed retardation of reaction rate (Figure 5) associated with the increased CTAB concentration may be attributed to a low level of molecular aggregation at concentrations well below its c.m.c., during which dimers, tetramers and other 'premicellar' aggregates are formed.[14] Such aggregates may interact electrostatically with $S_2O_8^{2-}$ in the bulk solution leading to a decrease in the oxidant mobility and also a consequent decrease in the reaction rate. At the c.m.c. ($9 \times 10^{-4}$ M) and above, the inhibition is due to the formation of micellar aggregates which squeeze the substrate molecules and protect them from electrophilic attack by peroxydisulphate.

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