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Oxidation of aspirin by a new oxidant diperiodatoargentate(III) in aqueous alkaline medium

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The kinetics of oxidation of aspirin by diperiodatoargentate(III) (DPA) in alkaline medium at a constant ionic strength of 1.0 mol dm^{-3} has been studied spectrophotometrically. The reaction between DPA and aspirin in alkaline medium exhibits 1: 2 stoichiometry (aspirin: DPA). The reaction is of first order in [DPA] and has less than unit order in both [ASP] and [alkali]. However, the order in [ASP] and [alkali] changes from first order to zero order as the concentration changes from lower to higher concentration. A decrease in the dielectric constant of the medium increases the rate of the reaction. The effect of added products and ionic strength of the reaction medium have been investigated and a mechanism is proposed.

Keywords: kinetics, aspirin, oxidation, diperiodatoargentate(III)

Aspirin (acetylsalicylic acid)(ASP) is a non-steroidal analgesic, anti-inflammatory and anti-pyretic agent. It is used in acute conditions such as headache, arthralgia, myalgia and other cases requiring mild analgesia. It is widely studied in medicine and several methods are suggested in the literature for its determination.[1]

Diperiodatoargentate(III) (DPA) is a powerful oxidising agent in alkaline medium with the reduction potential[2a] (1.74V). It is widely used as a volumetric reagent for the determination of various organic and inorganic species.[3] Jaya Prakash Rao, *et al.*[4] have used DPA as an oxidising agent for the kinetics of oxidation of various organic substrates. They normally found that the order with respect to both oxidant and substrate was unity and $[OH^-]$ was found to enhance the rate of reaction. They also considered the possible active species of DPA in alkali and they proposed mechanisms by generalising the DPA as $[Ag(HL)L]^{(x+1)-}$. However, Kumar[5] *et al.* produced evidence for the reactive form of DPA on the large scale, at alkaline pH. In the present investigation, we have obtained evidence for the reactive species for DPA in alkaline medium. A literature survey reveals that is no report on the kinetics of oxidation of aspirin by any oxidant. Hence, it was important and interesting for the detailed investigation of oxidation of ASP by DPA in aqueous alkaline medium.

Experimental

Materials and reagents

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of aspirin (M/s. S.S. Antibiotics Pvt. Ltd.,) was prepared by dissolving an appropriate amount of a recrystallised sample in double-distilled water. The purity of the ASP sample was checked by comparing its IR spectrum with literature data and with its m.p.136°C. The required concentration of ASP was used from its aqueous stock solution. KNO_3 and KOH were used to maintain ionic strength and alkalinity of the reaction respectively. An aqueous solution of $AgNO_3$ was used to study the product effect, Ag(I).

Preparation of DPA

DPA was prepared by oxidising Ag(I) in presence of KIO_4 as described elsewhere:[6] a mixture of KOH (28 g) and of KIO_3 (23 g) of water (100 cm^3) along with $AgNO_3$ (8.5 g) was heated just to boiling and $K_2S_2O_8$ (20 g) was added in several lots with stirring then the mixture was allowed to cool. It was filtrated through a medium porosity fritted glass filter and NaOH (40 g) was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerate. The precipitate was filtered as above and washed three to four times with cold water. The pure crystals were dissolved in water (50 cm^3) and warmed to 80°C with constant stirring thereby some solid was dissolved to give a red solution. The resulting solution was filtered when it was hot and on cooling at room temperature, orange crystals separated out and were recrystallised from water.

The complex was characterised from its UV spectrum; it exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported earlier for DPA.[6] The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analysed[7] for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess KI was added to the filtrate for IO_4^-. The aqueous solution of DPA was used for the required [DPA] in the reaction mixture. During the kinetics a constant concentration *viz.* 1×10^{-4} mol dm^{-3} of KIO_4 was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of ASP by periodate was tested and found that there was no significant interference due to KIO_4 under experimental conditions. Precautions were also taken to avoid the dissolution of O_2 and CO_2 in the solution by maintaining an inert atmosphere with N_2 throughout the study.

Kinetic measurements

Since the initial reaction was too fast to be monitored by usual methods, kinetic measurements were performed on a Varian CARY 50 Bio UV–Vis Spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12)

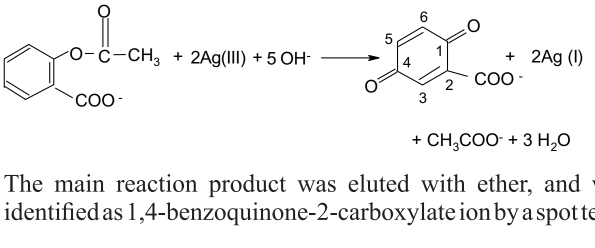
The kinetics was followed under pseudo-first order condition where [ASP] > [DPA] at least 10 times at 30 ± 0.1°C, unless specified. The reaction was initiated by mixing the DPA to an ASP solution which also contained the required concentration of KNO_3, KOH and KIO_4; and the progress of reaction was followed spectrophotometrically at 360 nm by monitoring the decrease in absorbance due to DPA with the molar absorbancy index, 'ε' to be 13900 ± 100 dm^3 mol^{-1} cm^{-1}. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength.

The pseudo-first order rate constants, 'k_{obs}', were determined from the log(absorbance) *vs* time plots. The plots were linear up to 90% completion of reaction under the range of $[OH^-]$ used. The orders for various species were determined from the slopes of plots of log k_{obs} *vs* respective concentration of species except for [DPA] in which non variation of 'k_{obs}' was observed as expected to the reaction condition.

Results

Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPA to aspirin in the presence of a constant amount of OH^- and KNO_3 were kept for 6 h in a closed vessel under N_2. The remaining concentration of DPA was estimated spectrophotometrically at 415 nm. The results indicated a 1: 2 stoichiometry as given in reaction (1):



(1)

The main reaction product was eluted with ether, and was identified as 1,4-benzoquinone-2-carboxylate ion by a spot test.[8]

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The nature of the 1,4-benzoquinone-2-carboxylate ion was confirmed by its IR spectrum which showed a C=O stretching at 1633 cm^{-1} indicating the presence of the C=O group of the 1,4-benzoquinone moiety, the bands at 1588 cm^{-1} and at 1364 cm^{-1} also indicate the presence of this group. The product was also characterised by NMR spectra ($CDCl_3$, δ ppm): chemical shifts at 6.73 (s, 1H, C_2-H), 6.80 (s, 1H, C_5-H) 7.28 (s, 1H, C_6-H). It was further confirmed by its melting point 206°C (lit. m.p. 205–207°C). Further, 1,4-benzoquinone-2-carboxylate ion was subjected to GC-Mass spectral analysis. GC–MS data was obtained on a 17 A Shimadzu gas chromatograph with a QP-5050A shimadzu mass spectrometer using the EI ionisation technique. The mass spectrum showed a molecular ion peak at 152 amu confirming the 1,4-benzoquinone-2-carboxylate ion. All other peaks observed by GC–MS can be interpreted in accordance with the observed structure of the product (Fig.1). Sodium acetate was identified by a spot test.[8] The formation of free Ag^+ in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to the formation of AgCl. It was observed that 1,4-benzoquinone-2-carboxylate ion does not undergo further oxidation under the present kinetic conditions.

Reaction orders

The reaction orders were determined from the slopes of log k_{obs} *vs* log (concentration) plots by varying the concentration of the reductant and alkali in turn while keeping other conditions constant. The DPA concentration was varied in the range of 5.0×10^{-6} to 8.0×10^{-5} mol dm^{-3} and the linearity of the plots of log absorbance *vs* time up to 90% completion of the reaction (Fig. 2) indicates a reaction order of unity in [DPA]. This is also confirmed by varying [DPA], which did not result in any change in the pseudo first order rate constants, k_{obs} (Table 1). The aspirin concentration was varied in the range 0.5×10^{-3} to 4.0×10^{-3} mol dm^{-3} at 30°C while keeping other reactant concentrations and conditions constant. The k_{obs} values increased with the increase in concentration of aspirin indicating an apparent less than unit order dependence on [ASP] [order 0.45] under the conditions of experiment (Table 1). This is also confirmed in the plots of k_{obs} *vs* $[\text{ASP}]^{0.45}$ in which it is linear rather than the direct plot of k_{obs} *vs* [ASP] (Fig. 3).The effect of alkali on the reaction has been studied in the range of 0.10 to 1.0 mol dm^{-3} at constant concentrations of aspirin, DPA and a constant ionic strength of 1.0 mol dm^{-3}. The rate constants increased with increasing [alkali] and the order was found to be less than unity (Table 1). However, at lower concentration of aspirin, the reaction was first order in aspirin and at high concentration of aspirin, the reaction was independent of [aspirin]. The order in aspirin changes from first order to zero order as [aspirin] varies. Similarly, the order in alkali changes from first order to zero order as [alkali] varies.

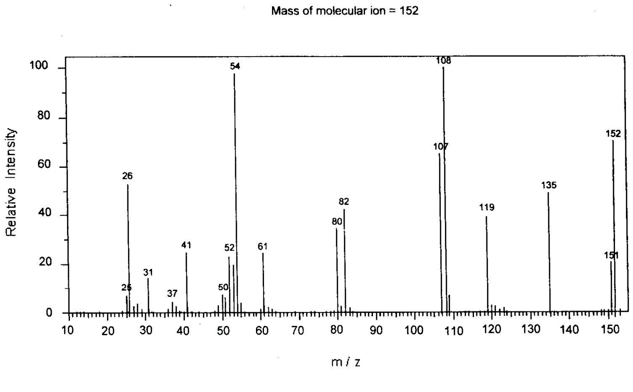


Fig. 1 GC-mass spectrum of 1,4benzoquinone2-carboxylate ion with its molecular ion peak at 152 amu.

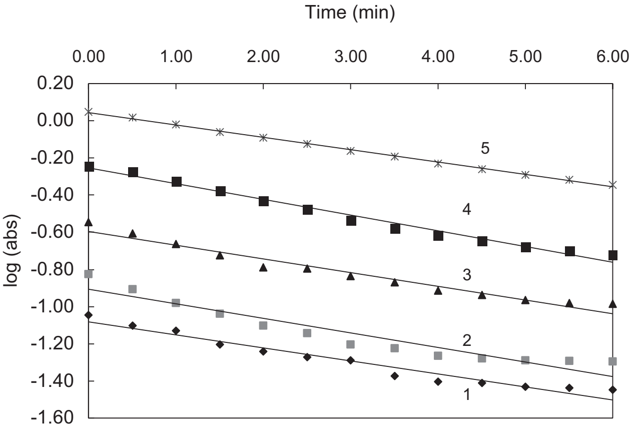


Fig. 2 First-order plots for oxidation of aspirin by DPA in aqueous alkaline medium at 30 °C. 10^5 [DPA] (mol dm^{-3}); (1) 0.5; (2) 1.0; (3) 2.0; (4) 5.0; (5) 8.0 (10^3 [ASP] = 1.0, $[\text{OH}^-]$ = 0.50 and I = 1.0 mol dm^{-3}).

Effect of [periodate]

Periodate was varied from 1.0×10^{-4} to 5.0×10^{-4} at constant [DPA], [ASP] and ionic strength. It was observed that the rate constants decreased by increasing $[\text{IO}_4^-]$ (Table 1).

The experimental rate law under the conditions studied is given by:

$$-d[\text{DPA}]/dt = k[\text{ASP}]^{0.45}\,[\text{OH}^-]^{0.55}\,[\text{IO}_4^-]^{-0.43}$$

Effect of products

Initially added products, Ag(I), acetic acid and 1,4-benzoquinone2-carboxylate ion did not have any significant effect on the rate of reaction.

Effect of ionic strength (I) and dielectric constant of the medium (D)

The addition of KNO_3, to increase the ionic strength of the reaction, increased the rate of reaction at constant [DPA], [ASP], $[\text{OH}^-]$ and $[\text{IO}_4^-]$; the plot of log k_{obs} *vs* $\sqrt{I}$ was found to be linear with positive slope of 0.8 (Fig. 4).

Table 1 Effect of [DPA], [ASP], $[\text{IO}_4^-]$ and $[\text{OH}^-]$ on diperiodatoargentate(III) oxidation of aspirin in alkaline medium at 30°C, I = 1.0 mol dm^{-3}

$[\text{DPA}]\times10^5$ /mol dm^{-3}	$[\text{ASP}]\times10^3$ /mol dm^{-3}	$[\text{IO}_4^-]\times10^4$ /mol dm^{-3}	$[\text{OH}^-]$ /mol dm^{-3}	$k_{obs}\times10^3$ (s^{-1})
0.5	1.0	1.0	0.5	3.2
1.0	1.0	1.0	0.5	3.7
2.0	1.0	1.0	0.5	3.8
5.0	1.0	1.0	0.5	3.2
8.0	1.0	1.0	0.5	2.9
5.0	0.5	1.0	0.5	2.1
5.0	0.8	1.0	0.5	2.9
5.0	1.0	1.0	0.5	3.2
5.0	2.0	1.0	0.5	4.3
5.0	4.0	1.0	0.5	5.6
5.0	1.0	1.0	0.5	3.2
5.0	1.0	2.0	0.5	2.2
5.0	1.0	3.0	0.5	1.6
5.0	1.0	4.0	0.5	1.3
5.0	1.0	5.0	0.5	1.2
5.0	1.0	1.0	0.1	1.6
5.0	1.0	1.0	0.2	2.2
5.0	1.0	1.0	0.4	3.0
5.0	1.0	1.0	0.5	3.2
5.0	1.0	1.0	0.8	3.8
5.0	1.0	1.0	1.0	3.9

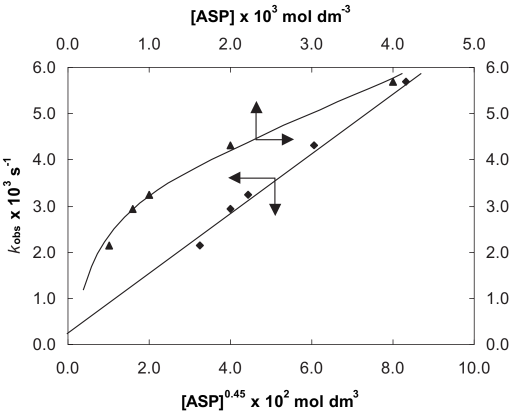


Fig. 3 Plot of k_{obs} *vs* $[\text{ASP}]^{0.45}$ and k_{obs} *vs* [ASP].

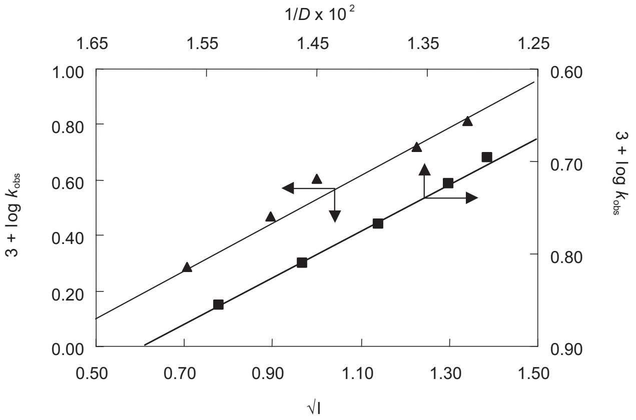


Fig. 4 Effect of ionic strength and dielectric constant of the medium on oxidation of aspirin by diperiodatoargentate(III) in aqueous alkaline medium at 30°C.

The dielectric constant of the medium, '*D*' was varied by varying the *t*-butyl alcohol and water percentage. The *D* values were calculated from the equation $D = D_{\text{w}} V_{\text{w}} + D_{\text{B}} V_{\text{B}}$, where D_{w} and D_{B} are dielectric constants of pure water and *t*-butyl alcohol respectively and V_{w} and V_{B} are the volume fractions of components water and *t*-butyl alcohol respectively in the total mixture. The decrease in dielectric constant of the reaction medium, increase the rate and the plot of log k_{obs} *vs* $1/D$ was linear with positive slope (Fig. 4).

Effect of temperature (T)

The influence of temperature on the k_{obs} values were studied at 30, 35, 40 and 45°C. The rate constants, *k*, of the slow step of Scheme 1 were obtained from the intercepts of $1/k_{obs}$ *vs*1/[ASP] plots at four different temperatures. The values are given in Table 2. The activation parameters for the rate determining step were obtained by the least square method of plot of log *k vs* $1/T$ and are presented in Table 2.

Test for free radicals

The intervention of free radicals was examined as follows, the reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 1 h. Upon diluting the reaction mixture with methanol, no precipitate resulted, suggesting there is no participation of free radicals in the reaction.

Discussion

In the later period of the 20th century the kinetics of oxidation of various organic and inorganic substrates by Ag(III) species have been studied due to the strong versatile nature of the two electrons oxidant. Among the various species of Ag(III), the complex species $Ag(OH)_4^-$ diperiodatoargentate(III) and ethylenebis (biguanide), (EBS), silver(III) are of maximum interest due to their relative stability.[9] The stability of $Ag(OH)_4^-$ is very sensitive towards traces of dissolved oxygen and other impurities in the reaction medium therefore it had not drawn much attention. However, the other two forms of Ag(III)[4,5,10] are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

Table 2 Thermodynamic activation parameters for the oxidation of aspirin by DPA in aqueous alkaline medium with respect to the slow step of Scheme 1

(A) Effect of temperature

Temperature/*K*	10^3 *k*/s^{-1}
303	6.96
308	7.05
313	7.15
318	7.25

(B) Activation parameters (Scheme 1)

Parameters	Values
$\Delta H^{\#}$/kJ mol^{-1}	23 ± 1
$\Delta S^{\#}$/JK mol^{-1}	–213 ± 20
$\Delta G^{\#}$/kJ mol^{-1}	88 ± 4
log *A*	2.1 ± 0.02

(C) Effect of temperature to calculate K_1, K_2 and K_3 for the oxidation of aspirin by diperiodatoargentate(III) in alkaline medium

Temperature/K	K_1 /dm^3 mol^{-1}	K_2 x 10^4 /mol dm^{-3}	K_3 x 10^{-3} /dm^3 mol^{-1}
303	0.52 ± 0.03	1.94 ± 0.10	2.91 ± 0.14
308	0.69 ± 0.03	2.24 ± 0.12	1.49 ± 0.06
313	0.78 ± 0.04	2.41 ± 0.12	1.24 ± 0.05
318	0.95 ± 0.05	2.61 ± 0.14	1.18 ± 0.03

(D) Thermodynamic quantities using K_1, K_2 and K_3

Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3
ΔH/kJ mol^{-1}	32 ± 1	17 ± 1	–67 ± 3
ΔS/JK^{-1} mol^{-1}	100 ± 4	–14 ± 1	–155 ± 5
ΔG_{303}/kJ mol^{-1}	1.0 ± 0.05	22 ± 1	–19 ± 1

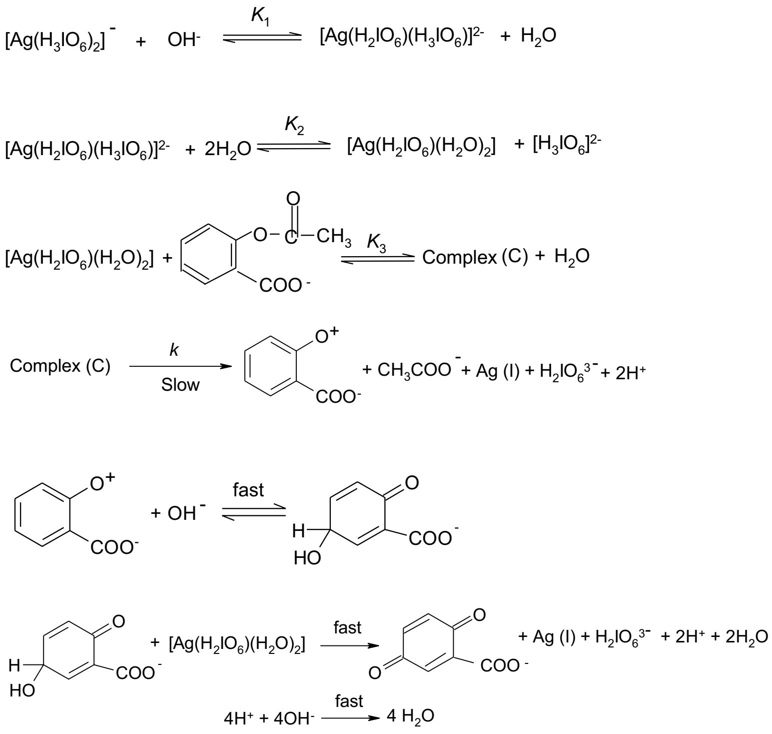
A literature survey[6] reveals that the water-soluble species diperiodatoargentate(III) (DPA) has a formula $[Ag(IO_6)_2]^{7-}$ with a square planar structure. When the same molecule is used in alkaline medium, it is unlike to exist as $[Ag(IO_6)_2]^{7-}$, as periodate is known to be in various protonated forms[11] depending on the pH of the solution, as given in the following multiple equilibria (2)–(4).

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \qquad (2)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \qquad (3)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \qquad (4)$$

Periodic acid (H_5IO_6) exists in acid medium and also as $H_4IO^-_6$ at pH 7. Thus, under the present alkaline conditions, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise.[2b] On the contrary, the authors[4] in their previous studies have proposed DPA to be $[Ag(HL)_2]^{x-}$, in which 'L' is a periodate with uncertain number of protons and 'HL' is a protonated periodate of uncertain number of protons. This can be ruled

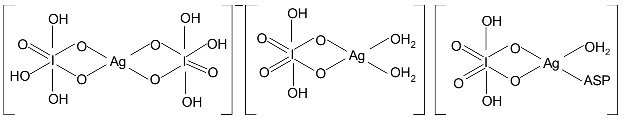


Scheme 1

out by considering the alternative form[11] of IO_4^- at pH > 7 which is in the form $H_3IO_6^{2-}$ or $H_2IO_6^{3-}$. Hence, DPA could be as $[Ag(H_3IO_6)_2]^-$ or $[Ag(H_2IO_6)_2]^{3-}$ in alkaline medium. Therefore, under the present condition, diperiodatoargentate (III), may be depicted as $[Ag(H_3IO_6)_2]^-$. The similar speciation of periodate in alkali was proposed[12] for diperiodatonickelate (IV).

It is well known that aspirin exists in the anionic form in basic medium.[13] Since the reaction was enhanced by $[OH^-]$, added periodate retarded the rate and the reaction shows first order dependency in [DPA] and fractional order in [ASP], the following mechanism has been proposed by considering ASP to be in the anionic form in alkaline medium, which explains all other experimental observations.

In the prior equilibrium step 1, the $[OH^-]$ deprotonates the DPA to give a deprotonated diperiodatoargentate(III) (DPA); in the second step, displacement of a ligand, periodate dissociates to give free periodate which is evidenced by decrease in the rate with increase in free [periodate] (Table 1). It may be expected that lower Ag (III) periodate species such as monoperiodatoargentate(III) (MPA) is more important in the reaction than the DPA. The inverse fractional order in $[H_3IO_6^{2-}]$ might also be due to this reason. In the pre-rate-determining stage, this monoperiodate (MPA), combines with a molecule of the anionic form of ASP to give an intermediate complex which decomposes in a slow step to give the intermediate species of aspirin, acetate ion and Ag(I) species by a two equivalent change of Ag(III) in a single step, as no intervention of free radical has been observed. This intermediate species reacts with one more molecule of MPA species in a fast step to yield the products. The plot of $1/[k_{obs}]$ *vs* 1/[ASP] proved the complex formation between oxidant and reductant, which explains less than unit order in [ASP]. Thus, in Scheme 1, the parallel reaction and involvement of two molecules of ASP in the intermediate complex are excluded. On the basis of the normal square planar geometry, structures of DPA, MPA and complex may be proposed as given below



DPA MPA Complex

The oxygen atom of the carboxyl group of the ASP is involved in the formation of the intermediate, as the molecular order in ASP and the absence of intervention of free radical raise such a possibility. Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from the UV-Vis spectra of aspirin (1.0 × 10^{-3}), DPA (5.0 × 10^{-5}, $[OH^-] = 0.50$ mol dm^{-3}) and mixture of both. A bathochromic shift of about 5 nm from 215 to 220 nm in the spectra of DPA was observed and hyperchromicity was observed at 220. The rate law for the Scheme 1 could be derived as

$$\text{rate} = -\frac{d[DPA]}{dt} = \frac{kK_1K_2K_3[Ag(III)]\,[ASP]\,[OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3\,[OH^-][ASP]}$$

$$k_{obs} = \frac{kK_1K_2K_3\,[ASP]\,[OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3\,[OH^-][ASP]} \qquad (5)$$

The rate law (5) can be rearranged into the following form for verification

$$\frac{1}{k_{obs}} = \frac{[H_3IO_6^{2-}]}{kK_1K_2K_3\,[OH^-][ASP]} + \frac{[H_3IO_6^{2-}]}{kK_2K_3\,[ASP]} + \frac{1}{kK_3[ASP]} + \frac{1}{k} \qquad (6)$$

The plots of $1/k_{obs}$ *vs* $[H_3IO_6^{2-}]$, $1/[OH^-]$ and 1/[ASP] were linear (Fig. 5). From the intercepts and slopes of such plots, the reaction constants K_1,K_2,K_3 and k were calculated as (0.52 ± 0.03) dm^3 mol^{-1}, (1.94 ± 0.10) × 10^{-4} mol dm^{-3}, (2.91 ± 0.14) × 10^3 dm^3 mol^{-1}, (6.96 ± 0.20) × 10^{-3} s^{-1} respectively. The value K_1 is in agreement with earlier reported value.[14]

The effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged

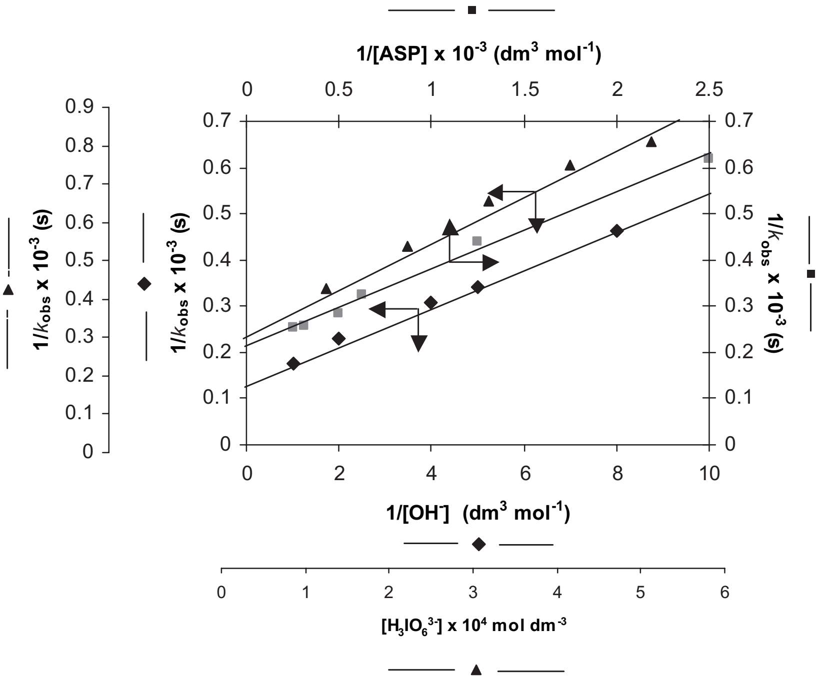


Fig. 5 Verification of rate law (5) on the oxidation of aspirin by diperiodatoargentate(III) in aqueous alkaline medium at 30°C.

ions, as seen in Scheme 1. The effect of solvent on the reaction rate has been described in detail in the literature.[15] Increasing the content of *t*-butyl alcohol in the reaction medium leads to an increase in the rate of reaction, which seems to be contrary to the expected reaction between neutral and anionic species in media of lower relative permittivity. However, an increase in the rate of the reaction with decreasing relative permittivity may be due to stabilisation of the complex (C) at low relative permittivity, which is less solvated than DPA at higher relative permittivity because of its larger size.

The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The aspirin and hydroxide ion concentrations (Table 1) were varied at different temperatures. The plots of $1/k_{obs}$ *vs* 1/[ASP] ($r \geq 0.9993$, $S \leq 0.00131$) and $1/k_{obs}$ *vs* 1/[OH$^-$] ($r \geq 0.9994$, $S \leq 0.00087$) should be linear as shown in Fig. 4. From the slopes and intercepts, the values of K_1 are calculated at different temperatures. A van't Hoff's plot was made for the variation of K_1 with temperature [*i.e.*, log K_1 *vs* $1/T$ ($r \geq 0.9993$, $S \leq 0.1107$)] and the values of the enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated. These values are also given in Table 2. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly slow and involves a high activation energy.[16] In the same manner, K_2 and K_3 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 2.

The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants.[17] The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations.[17.]

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References

1 S.M. Sultan, *Analyst.,*1987, **112**,1331; J. Anwar and T.A. Awan, *J. Chem. Soc. Pak.,* 1990, **12,** 30.
2 B. Sethuram, *Some Aspects of Electron Transfer Reactions Involving Organic Molecules* 2003; Allied Publishers (P) Ltd., New Delhi,; (a) p. 151; (b) p. 78.
3 P.K. Jaiswal and K.L. Yadava, *Talanta* 1970, **17**, 236; P.K. Jaiswal, *Analyst.,* 1972, **1,** 503.
4 P. Jayaprakash Rao, B. Sethuram and T. Navaneeth Rao, *React. Kinet. Catal.*, 1985, **29,** 289; K. Venkata Krishna and P. Jayaprakash Rao. *Ind. J. Chem.*, 1998, **37A,** 1106 and references therein.
5 Anil Kumar, Paresh Kumar and P. Ramamurthy, *Polyhedron.,* 1999, **18,** 773; Anil Kumar and Paresh Kumar, *J. Phy. Org. Chem.*, 1999, **12,** 79; Anil Kumar, Vaishali and P. Ramamurthy, *Int. J. Chem. Kinet.*, 2000, **32,** 286.
6 G.L. Cohen and G. Atkinson, *Inorg. Chem.*, 1964, **3,** 1741.
7 G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, Vogel's *Textbook of Quantitative Chemical Analysis* 5th edn; Longmans Singapore Publishers Pte Ltd., Singapore p.467, p.391.
8 F. Fiegl, *Spot Tests in Organic Analysis,* Elsevier, New York, 1975, p.333.
9 L.J. Krishenbaum and L. Mrozowski, *Inorg. Chem.*, 1978, **17,** 3718.
10 R. Banerjee, K. Das, A. Das and S. Dasgupta, *Inorg. Chem.,* 1989, **28,** 585; R. Banerjee, R. Das and S. Mukhopadhyay, *J. Chem. Soc. Dalton Trans.,* 1992, 1317.
11 C.E. Crouthamel, A.M. Hayes and D.S. Martin, *J. Am. Chem. Soc.,* 1951, **73,** 82; R.S Shetter and S.T. Nandibewoor, *J. Mol. Cat. A*. 2005, **238,** 137; Jr. J.C Bailar, H.J. Emeleus, S.R. Nyholm and A.F. Trotman- Dikenson. *Comprehensive Inorganic Chemistry.* Pergamon, Oxford 1975. **2,** 1456.
12 S. Bhattacharya, B. Saha, A. Datta and P. Banerjee, *Coord. Chem. Rev.*, 1988, 47, 170; R.I. Haines and A. McAuley, *Coord. Chem. Rev.,* 1981, 39, 77.
13 R.T. Mahesh, M.B. Bellakki and S.T. Nandibewoor, *J. Chem. Res.,* 2005, 13.
14 D.C. Hiremath, C.V. Hiremath and S.T. Nandibewoor, *E.J. Chem.,* 2006, **3**, 10.
15 E.A. Moelwyn-Hughes, *Physical Chemistry,* 2nd edn, Pergamon, New York, 1961; E. S. Amis, *Solvent Effects on Reaction Rates and Mechanisms,* Academic, New York, 1966.
16 K.S. Rangappa, M.P. Raghavendra, D.S. Mahadevappa and D. Channegouda, *J. Org. Chem.,* 1998, 63, 531.
17 M. Martinez, M.A. Pitarque and R.V. Eldik, *J. Chem. Soc. Dalton Trans.,* 1996, 2665; S.A. Farokhi and S.T. Nandibewoor, *Tetrahedron.,* 2003, 59, 7595.

Appendix A

According to Scheme 1

$$\text{Rate} = k[\text{C}] = \frac{kK_1K_2K_3[\text{Ag}(\text{H}_3\text{IO}_6)_2][\text{OH}^-][\text{ASP}]}{[\text{H}_3\text{IO}_6^{2-}]} \tag{I}$$

$$[\text{DPA}]_\text{T} = [\text{DPA}]_\text{f} + [\text{Ag}(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{2-} + [\text{Ag}(\text{H}_3\text{IO}_6)(\text{H}_2\text{O})_2] + [\text{C}]$$

$$[\text{DPA}]_\text{f} = \frac{[\text{DPA}]_\text{T}\,[\text{H}_3\text{IO}_6^{2-}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1\,[\text{OH}^-]\,[\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-]\,[\text{ASP}]} \tag{II}$$

$$[\text{OH}]_\text{T} = [\text{OH}]_\text{f} + [\text{Ag}(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{2-} + [\text{Ag}(\text{H}_3\text{IO}_6)(\text{H}_2\text{O})_2]$$

$$= [\text{OH}]_\text{f} + K1[\text{DPA}]\,[\text{OH}^-] + \frac{K_2\,[\text{DPA}]}{[\text{H}_3\text{IO}_6^{2-}]}$$

In view of the low concentration of [DPA] and $[\text{H}_3\text{IO}_6^{2-}]$ used,

$$[\text{OH}]_\text{T} = [\text{OH}]_\text{f} \tag{III}$$

$$[\text{ASP}]_\text{T} = [\text{ASP}]_\text{f} + [\text{C}]$$

$$= [\text{ASP}]_\text{f} + \frac{K_1K_2K_3[\text{DPA}]\,[\text{OH}^-]\,[\text{ASP}]}{[\text{H}_3\text{IO}_6^{2-}]}$$

$$= [\text{ASP}]_\text{f}\left(1 + \frac{K_1K_2K_3[\text{DPA}]\,[\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}]}\right)$$

In view of the low concentration of [DPA], $[\text{OH}^-]$ and $[\text{H}_3\text{IO}_6^{2-}]$ used,

$$[\text{ASP}]_\text{T} = [\text{ASP}]_\text{f} \tag{IV}$$

Substituting (II), (III) and (IV) in (I) and omitting the subscripts T and f, we get

$$\text{Rate} = \frac{k\,K_1\,K_2\,K_3\,[\text{DPA}][\text{ASP}]\,[\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1\,[\text{OH}^-]\,[\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-]\,[\text{ASP}]}$$