SULFATE FREE RADICALS –A KINETIC APPROACH FOR OXIDATION OF L-ASCORBIC ACID IN AQUEOUS ACID MEDIUM

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The kinetics of oxidation of L-ascorbic acid in absence and presence of silver(I) as catalyst has been studied in aqueous acid medium. The stoichiometry corresponds to the reaction as represented by eqn: $S_2O_8^{2-} + C_6H_8O_6 \rightarrow 2SO_4^{2-} + C_6H_6O_6 + 2H^+$. The order with respect to ascorbic acid is unity in uncatalyzed reaction where as it is zero order in silver (I) catalyzed reaction. The reaction mechanism has been suggested in both the conditions delineating the role of sulfate radical ion.

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Introduction

Numerous studies on uncatalyzed and silver(I) catalyzed oxidations of various types of substrates by peroxodisulfate have been reported.[1-11] The rate of silver(I) catalyzed reactions was generally found to be independent of substrate(s) concentration in oxidation reactions of persulfate. However, certain questions still remain to be replied.

The thermal decomposition of peroxodisulfate is first order whereas the reaction is second order in the presence of certain substrate(s). Therefore, such observations are not only interesting but help in understanding chemistry of the oxidant owing to the formation of sulfate free radicals.

Similar is the situation in silver(I) catalyzed oxidation of the substrate which is also a second order reaction and the rate is still controlled by the interaction of catalyst and oxidant. However, no firm evidence is provided to discriminate between catalyst redox cycles viz. Ag^{I}/Ag^{II} or Ag^{I}/Ag^{III}.

Ascorbic acid (vitamin C) has played an essential role as a water soluble vitamin in diet. Survey is developed in a person due to its deficiency vitamin C is also known to help in cardiovascular and cancer diseases.[12] Interestingly plants and some animals make their own vitamin C but it is not in case of human bodies and is, therefore, sought from other sources.[13] It is added as a supplementary source in pharmaceutical preparations. Also, it is a known anti-oxidant in large number of biological processes. The kinetic based determinations in analytical chemistry have been exploited owing to its strong reducing properties.[14] The spectrofluorometric methods are based on vanadium(V) catalysed and ascorbic acid activated oxidation of rhodamine[15,16] or Saframine T[17] by bromate. Such were the observations that tempted us to undertake the title study to gain detailed insight of the reaction events *viz.* to *viz*. the role of sulfate free radicals in both silver (I) catalyzed and uncatalyzed oxidations of l-ascorbic acid by peroxodisulfate.

Experimental

Material and method

All the reagents employed in the kinetics study were either of AnalaR or guaranteed reagent grade and were employed as supplied. Silver nitrate (BDH) solution was prepared by dissolving requisite amount of the salt in doubly distilled water. The solution of silver nitrate, however, was kept in bottles painted black from the outside at refrigerated temperature (~ 5 ˚C) to check photochemical decomposition. Nevertheless, afresh solution of the catalyst was employed.

Twice distilled water was employed throughout the study; the second distillation was from an alkaline potassium permanganate solution in an all glass apparatus. Other reagents were employed as received.

Kinetic procedure

The reaction was conducted in Corning glass vessels painted black from the outside. These flasks were immersed in a water-bath thermostated at ± 0.1 °C unless stated otherwise. All other reaction ingredients of requisite concentrations except peroxodisulfate were taken in these flasks, the reaction was initiated by adding temperature pre-equilibrated peroxodisulfate solution and the time of initiation of the reaction was recorded when the pipette was half-emptied. An aliquot sample (5 cm^3) of the reaction mixture was withdrawn at different time intervals and then discharged into an ice-cold dil. H_2SO_4 (~1.0 mol dm^{-3}), the remaining ascorbic acid was then estimated by titrating

against cerium(IV) solution using n-phenylanthranilic acid as an indicator. The results in triplicate were reproducible within ± 6 %. Initial rates (k_i, mol dm^3 s^{-1}) were computed by employing plane mirror method.

Stoichiometry

The stoichiometry was determined by conducting reactions taking excess of ascorbic acid (H_2A) over peroxodisulfate (heretofore written as PDS) in glass stoppered vessels along with other reaction ingredients. The reaction mixtures were thermostated in a water-bath maintained at 40 ± 0.1 °C for ca. 4 h. The excess ascorbic acid was determined ceremetrically. The results correspond to the stoichiometry of the reaction as represented by Eqn. 1.

$$S_2O_8^{2-} + C_6H_8O_6 \xrightarrow{Ag^I} 2SO_4^{2-} + C_6H_6O_6 + 2H^+ \quad (1)$$

where $C_6H_6O_6$ is dehydroascorbic acid. Similar stoichiometry has earlier been reported.[18,19]

Results

Peroxodisulfate dependence

The concentration of peroxodisulfate varied fixing constant concentrations of other reaction ingredients. Initial rates (k_i, mol dm^{-3} s^{-1}) were calculated and a plot of initial rate against the concentration of the oxidant [PDS] yielded a straight line passing through the origin conforming first order with respect to peroxodisulfate in uncatalyzed and catalyzed reactions respectively.

L-Ascorbic acid dependence

The concentration of l-ascorbic acid also varied at constant concentrations of other reaction ingredients under pseudo first order conditions ([H_2A] << 10 [PDS]) and pseudo first order plots were made. However, rate was independent of gross initial concentrations of ascorbic acid in silver(I) catalyzed reaction ascribing rate to be first order with respect to substrate concentrations. Nevertheless, rate exhibited first order dependence with respect to ascorbic acid also in uncatalyzed reaction.

Silver(I) dependence

The concentration of silver (I) varied from 1.0x10^{-4} to 1.0x10^{-3} mol dm^{-3} at fixed concentrations of other reaction ingredients. A plot of initial rate against [Ag(I)] yielded a straight line passing through the origin conforming first order with respect to the catalyst.

If one takes into account these kinetic orders with respect to peroxodisulfate, ascorbic acid (H_2A) in uncatalyzed and silver(I) in catalyzed reactions respectively, following empirical rate Eqns. 2 and 3 are obeyed.

$$-\frac{d\left[S_2O_8^{2-}\right]}{dt} = k\left[S_2O_8^{2-}\right]\left[H_2A\right] \quad (2)$$

$$-\frac{d\left[S_2O_8^{2-}\right]}{dt} = k_{Ag}\left[S_2O_8^{2-}\right]\left[Ag^I\right] \quad (3)$$

where k and k_{Ag} are the second order rate constants in uncatalyzed and catalysed reactions respectively.

Hydrogen ion dependence

The concentration of hydrogen ion varied by employing perchloric acid at fixed concentrations of other reaction ingredients and also at constant ionic strength (I). (Ionic strength (I) was adjusted to be 0.5 mol dm^{-3} by employing lithium perchlorate). The rate, however, remains unchanged on varying ionic strength. The rate decreases with increasing hydrogen ion concentration in uncatalyzed reaction whereas rate is independent of hydrogen ion concentration in silver(I) catalyzed reactions.

Persulfate reactions normally show the presence of free radicals if the oxidant interacts with one-equivalent substrate. Free radicals were, therefore, tested in the reaction mixture by adding acrylic acid during the progress of the reaction. The monomer of this unsaturated acid changes to polymer yielded white solid material which after some time settles. This conforms participation of $SO_4^{\bullet -}$ free radicals. However, none of the reactants polymerized when the monomer was added in these reactant solutions respectively under identical experimental conditions of the reaction.

Discussion

Mechanism of uncatalyzed reaction

An important observation in uncatalyzed oxidation of L-ascorbic acid is the retardation of the rate by the addition of acrylic acid with the formation of white precipitate. Acrylic acid is known to be an efficient scavenger of sulfate free radicals in reactions of peroxodisulfate. Whether it is the initial interaction of the oxidant and the substrate to generate free radicals or simply the latter is generated by thermal decomposition of persulfate. Since the reaction is second order *viz*. first order with respect to each reactant, following mechanism consisting of Eqns. 4-9 can be envisaged involving role of free radicals.

$$H_2A \underset{}{\overset{K}{\rightleftharpoons}} HA^- + H^+ \quad (4)$$

$$S_2O_8^{2-} + HA^- \xrightarrow{K_1} SO_4^{2-} + SO_4^{\bullet -} + HA \quad (5)$$

$$SO_4^{\bullet -} + HA^- \xrightarrow{K_2} SO_4^{2-} + HA \quad (6)$$

$$HA + HA \xrightarrow{K_3} \text{Products} \quad (7)$$

$$SO_4^{\bullet -} + H_2O \xrightarrow{K_4} HSO_4^- + OH \quad (8)$$

$$OH + HA^- \xrightarrow{K_5} H_2O + A^{\bullet -} \quad (9)$$

where HA is the ascorbate radical.

Applying steady state to free radicals such as $SO_4^{\bullet -}$, HA and OH respectively which are in steady-state concentrations, Eqns. 10, 11 and 12 are obtained.

$$\frac{d\left[SO_4^{\bullet -}\right]}{dt} = k_1\left[S_2O_8^{2-}\right]\left[HA^-\right] - k_2\left[HA^-\right]\left[SO_4^{\bullet -}\right] - k_4\left[SO_4^{\bullet -}\right] = 0 \quad (10)$$

$$\frac{d\left[HA\right]}{dt} = k_1\left[S_2O_8^{2-}\right]\left[HA^-\right] - k_2\left[HA^-\right]\left[SO_4^{\bullet -}\right] - k_5\left[OH\right]\left[HA^-\right] - k_3\left[HA^-\right]^2 = 0 \quad (11)$$

and

$$\frac{d\left[OH\right]}{dt} = k_4\left[SO_4^{\bullet -}\right] - k_5\left[OH\right]\left[HA^-\right] = 0 \quad (12)$$

The rate of the reaction is given by Eqn. 13

$$-\frac{d\left[H_2A\right]}{dt} = k_3\left[HA\right]^2 \quad (13)$$

Eqn. 14 is obtained from Eqns. 11 and 13,

$$\frac{d\left[H_2A\right]}{dt} = k_1\left[S_2O_8^{2-}\right]\left[HA^-\right] - k_2\left[HA^-\right]\left[SO_4^{\bullet -}\right] - k_5\left[OH\right]\left[HA^-\right] \quad (14)$$

The concentrations of free radicals ($SO_4^{\bullet -}$) and (OH) are obtained from Eqns. 10 and 12 as in Eqns. 15 and 16 respectively

$$\left[SO_4^{\bullet -}\right] = \frac{k_1\left[S_2O_8^{2-}\right]\left[HA^-\right]}{k_2\left[HA^-\right] + k_4} \quad (15)$$

and

$$\left[OH\right] = \frac{k_4\left[SO_4^{\bullet -}\right]}{k_5\left[HA^-\right]} \quad (16)$$

If Eqns. 14, 15 and 16 are simultaneously considered, Eqn. 17 or 18 is obtained after accounting for an inequality $k_2[HA^-] >> k_4$.

$$\frac{d\left[H_2A\right]}{dt} = 2k_1\left[S_2O_8^{2-}\right]\left[HA^-\right] \quad (17)$$

or

$$-\frac{d\left[H_2A\right]}{dt} = \frac{2k_1K\left[S_2O_8^{2-}\right]\left[H_2A\right]}{\left[H^+\right]} \quad (18)$$

where $k=2k_1K$ is an observed composite second order rate constant.

The rate Eqn. 18 is in agreement with the rate equation obtained earlier[18] but slightly differing from other.[19] A plot of $(-d[H_2A]/dt)[S_2O_8^{2-}][H_2A] = k_{obs}$ was made against $[H^+]^{-1}$ that yielded a straight line passing through the origin (Fig 1).

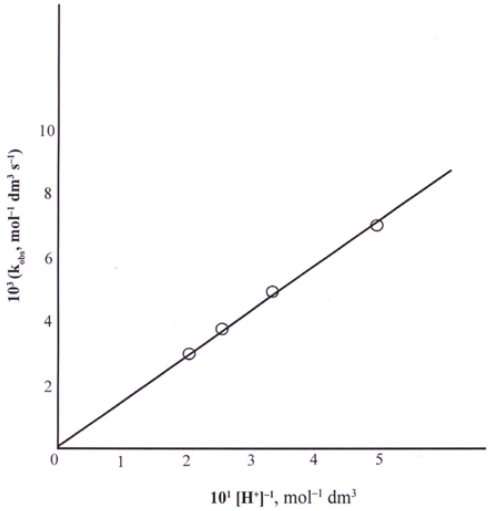

Figure 1. Plot of k_{obs} versus $[H^+]$ in ascorbic acid and peroxodisulphate reaction, [PDS]=5.0x10^{-2} M; [H_2A]=2.0x10^{-3} M; I=0.5 M; 40 °C

Mechanism of silver(I) catalyzed oxidation of ascorbic acid

The role of silver(I) as a catalyst in peroxodisulfate reactions is reported through the catalyst redox cycle of either Ag^I/Ag^{II} or Ag^I/Ag^{III}. Since the rate is independent of the substrate concentration, there is every possibility that higher valent silver(III) is obtained through the interaction of silver(I) and peroxodisulfate that oxidizes substrate in a fast step. An interaction of Ag(I) with persulfate to form Ag(II) is probably responsible for formation of sulphate free radical. Moreover, if the redox potential of Ag(II)/Ag(I) or Ag(III)/Ag(I) redox couples is any guide, the reactions of Ag(II) or Ag(III) with ascorbic acid must be very fast.

Considering these aspects, a plausible reaction mechanism for Ag(I) catalyzed oxidation of ascorbic acid can be envisaged as follows:

$$S_2O_8^{2-} + Ag(I) \xrightarrow{K_1} SO_4^{2-} + SO_4^{\bullet -} + Ag(II) \quad (19)$$

$$Ag(II) + H_2A \xrightarrow{K_2} HA + Ag(I) + H^+ \quad (20)$$

$$SO_4^{\bullet -} + H_2A \xrightarrow{K_3} HSO_4^- + HA \quad (21)$$

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$$HA + HA \xrightarrow{K_4} \text{Product} \quad (22)$$

$$SO_4^{\bullet -} + H_2O \xrightarrow{K_5} HSO_4^- + OH \quad (23)$$

$$OH + H_2A \xrightarrow{K_6} H_2O + HA \quad (24)$$

Applying steady – state treatment to all intermediates such as $SO_4^{\bullet -}$, Ag^{II}, OH and HA, the following Eqns. 25-28 are obtained

$$\frac{d\left[SO_4^{\bullet -}\right]}{dt} = k'_1\left[S_2O_8^{2-}\right][Ag(I)] - k_3\left[SO_4^{\bullet -}\right][H_2A] - k_5\left[SO_4^{\bullet -}\right] = 0 \quad (25)$$

$$\frac{d\left[Ag(II)\right]}{dt} = k'_1\left[S_2O_8^{2-}\right][Ag(I)] - k_2\left[Ag(II)\right][H_2A] = 0 \quad (26)$$

$$\frac{d\left[(OH)\right]}{dt} = k_5\left[SO_4^{\bullet -}\right] - k_6\left[(OH)\right][H_2A] = 0 \quad (27)$$

$$\frac{d\left[HA\right]}{dt} = k'_2\left[Ag(II)\right][H_2A] - k_3\left[SO_4^{\bullet -}\right][H_2A] - k_6\left[OH\right][H_2A] - k_4\left[HA\right]^2 = 0 \quad (28)$$

The rate of the reaction is represented by Eqn. 29

$$\frac{d\left[(H_2A)\right]}{dt} = k'_2\left[Ag(II)\right][H_2A] + k_3\left[SO_4^{\bullet -}\right][H_2A] - k_6\left[(OH)\right][H_2A] \quad (29)$$

Combining Eqn. 29 with Eqns. 26 and 27, Eqn. 30 is obtained:

$$\frac{d\left[H_2A\right]}{dt} = k'_1\left[S_2O_8^{2-}\right][Ag(I)] \quad (30)$$

Such a rate Eqn. 30 accounts for first order dependence with respect to persulfate and silver(I) respectively and rate independence of ascorbic acid concentration.

Since the catalysed reaction does not exhibit any hydrogen ion dependence, an important question in silver(I) catalysed oxidation of ascorbic acid is whether the catalyst operates via a Ag^I/Ag^{II} or Ag^I/Ag^{III} redox cycle and needs discrimination between Ag^{II} or Ag^{III}. Since an evidence for formation of complexes such as $[FeSO_4]^+$ and $[FeSO_4]^{2+}$ has been adduced[20] in the reaction of $[Fe(II)\text{-}SO_4^{\bullet -}]$

If a similar complex such as $[Ag^I\text{-}SO_4^{\bullet -}]$ is also a possibility between Ag^I and $SO_4^{\bullet -}$ as in Eqn. 31, Ag^{II} is expected to be formed in a one-equivalent reaction 32 through the redox rupturing of such a complex. Ag^{II} formation interacts with ascorbic acid in a fast step 33

$$Ag^I + SO_4^{\bullet -} \rightleftharpoons [Ag^I.\ SO_4^{\bullet -}] \quad (31)$$

$$[Ag^I.\ SO_4^{\bullet -}] \rightleftharpoons Ag^{II} + SO_4^{2-} \quad (32)$$

$$2Ag^{II} + C_6H_8O_6 \xrightarrow{fast} 2Ag^I + C_6H_6O_6 + 2H^+ \quad (33)$$

However, the possibility of formation of such a complex $[Ag^{II}.\ SO_4]^+$ and then to rupture oxidatively also cannot be ruled out as in Eqn. 34

$$[Ag^{II}.\ SO_4]^+ \rightleftharpoons Ag^{III} + SO_4^{2-} \quad (34)$$

$$Ag^{III} + C_6H_8O_6 \xrightarrow{fast} Ag^I + C_6H_6O_6 + 2H^+ \quad (35)$$

Such an alternative proposal explains the kinetics of the reaction but requires an evidence[21,22] for the formation of Ag^{III}. If redox potential[23] of this sulphate radical ion (2.5-3.1 V) is taken into account, Ag^{II} should further be oxidized to Ag^{III}. Nevertheless, addition of 2,2′-bipyridine in the reaction mixture exhibits an orange coloured species of transient life time that negates formation of Ag^{III}. Such a colored test might not be positive in the light of the fact that Ag^{III} as soon as is formed it is consumed by ascorbic acid oxidant leaving no chance for its indication. Nevertheless, following observations if taken into account, the formation of Ag^{III} can be ruled out.

The oxidation of Ag^I to Ag^{II} is energetically more facile as $SO_4^{\bullet -}$ radical ion is one electron oxidant. One electron transfer processes are more facile than two electron transfer process energetically.

Since ascorbic acid being a strong reducing agent, it will not allow $SO_4^{\bullet -}$ to interact with Ag^{II}. There is every possibility of competition between Ag^{II} and ascorbic acid for $SO_4^{\bullet -}$ in which ascorbic acid appears to score over. Ag^{II} minimising the chances of formation of Ag^{III} significantly.

If silver(III) is formed through fast disproportionation of initially formed silver(II) as in step 36 under experimental conditions, the presence of Ag(I)

$$2Ag(II) \rightleftharpoons Ag(I) + Ag(III) \quad (36)$$

will push back this equilibrium 36 significantly minimizing the chances of formation of Ag(III).

Also, Ag(III) is not stable in acid medium in absence of any complexing ligand. The complexing ligand even in alkaline medium is required to stabilize it.

Such arguments are logically and adequately account for the possibility of operation of Ag^{I}/Ag^{II} catalyst redox cycle in preference to Ag^{I}/Ag^{III} catalyst redox cycle in the oxidation of ascorbic acid by peroxodisulfate in the presence of silver(I).

Conclusions

Silver(I) catalyzed oxidation of ascorbic acid by peroxodisulfate is second order reaction. The rate in Ag^{I} catalyzed reaction does not show hydrogen ion dependence as in case of uncatalyzed oxidation of ascorbic acid by peroxodisulfate in a manner characterized in other oxidations. Since the rate in catalyzed reaction is independent of ascorbic acid, it is established that the rate dependence on hydrogen ion in uncatalyzed reaction comes from ascorbic acid. Since rate is independent of ascorbic acid, in silver(I) catalysed oxidation, silver(I) catalyst redox cycle operates via Ag^{II}/Ag^{I} in preference to Ag^{III}/Ag^{I}.

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