Kinetic Studies of the Oxidation Reaction of Arsenic(III) to Arsenic(V) by Peroxodisulphate Ion in Aqueous Alkaline Media

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The arsenic(III) ion was oxidized to arsenic(V) by the peroxodisulphate ion in aqueous alkaline solutions of various pH (>8.6) at 20—40 °C. The only reactive species at pH 8.6—11.6 was the deprotonated species $H_2AsO_3^-$; the mechanisms (i) and (ii) and the rate law (iii) are proposed to

$$H_3AsO_3 \overset{K_a}{\rightleftharpoons} H_2AsO_3^- + H^+ \qquad \text{(i)}$$

$$H_2AsO_3^- + S_2O_8^{2-} \xrightarrow[H_2O]{k} HAsO_4^{2-} + 2SO_4^{2-} + 3H^+ \qquad \text{(ii)}$$

$$-\frac{d[S_2O_8^{2-}]}{dt} = \frac{kK_a[OH^-][S_2O_8^{2-}][As^{III}]}{K_a[OH^-] + K_w} \qquad \text{(iii)}$$

account for the results obtained. The first acid dissociation constant K_a of H_3AsO_3 and the rate constant k for the reaction between the $S_2O_8^{2-}$ and $H_2AsO_3^-$ ions were determined under various conditions. The activation enthalpy and entropy, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, for the reaction of $H_2AsO_3^-$ with $S_2O_8^{2-}$ were 47.6 kJ mol^{-1} and −130.4 J K^{-1} mol^{-1}, respectively, whereas ΔH_a and ΔS_a for the acid dissociation of H_3AsO_3 were 2.8 kJ mol^{-1} and −171.4 J K^{-1} mol^{-1}, respectively. The addition of acrylamide and acrylonitrile as radical scavengers produced no polymer and did not affect the reaction rate. The radicals $SO_4^{\bullet -}$ and As^{IV}, the expected reaction intermediates, could not be detected by the addition of acrylamide and acrylonitrile monomers, and thus, the reaction between $S_2O_8^{2-}$ and As^{III} is considered to be a two-electron transfer reaction. In strong basic medium ($pH \geqslant 12.0$), the $HAsO_3^{2-}$ ion as well as $H_2AsO_3^-$ reacted with the peroxodisulphate ion with the rate constant $(1.6 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at an ionic strength of 0.1 mol dm^{-3}, at 30 °C.

Kinetic studies of the oxidation of arsenic(III) by several oxidants in acidic media have been made by several investigators.[1–6] However, there are few studies on the oxidation of arsenic(III) in alkaline media,[7] considering the reactivity of various deprotonated species of arsenious acid. The peroxodisulphate ion ($S_2O_8^{2-}$) is thermodynamically a strong oxidant, but oxidation by this ion occurs only slightly or only at an extremely slow rate at the ordinary temperatures without addition of catalyst. Gupta *et al.*[8–10] studied the oxidation reaction of arsenic(III) ion by the peroxodisulphate ion in neutral and acidic solutions at 45 °C and indicated that the reaction rate was first order with respect to the peroxodisulphate ion concentration, and independent of the arsenic(III) concentration, and that this reaction was catalyzed by silver(I) and copper(II) ions. Woods *et al.*[11] also indicated that the oxidation reaction of arsenic(III) by $S_2O_8^{2-}$ was induced by the addition of iron(II) ion. The present paper shows that, even in the absence of any catalysts, at ordinary temperatures, the oxidation reaction of arsenic(III) by peroxodisulphate proceeds at a moderate rate in alkaline solutions of pH > 8.6; the mechanism of the reaction is presented to account for the results obtained.

Experimental

Chemicals.—Reagent grade potassium peroxodisulphate (Wako Pure Chemicals Co.) was recrystallized twice from redistilled water and dried at room temperature in a vacuum desiccator. The sodium perchlorate used for adjusting ionic strength was recrystallized twice from redistilled water. All other chemicals were of guaranteed reagent grade and used without further purification.

The oxidation reaction using $S_2O_8^{2-}$ is very susceptible to impurities in the solution. Gupta *et al.*[8–10] observed that the results were only reproducible if the same stock solution of arsenic(III) was used throughout. In this paper, the arsenic(III) solution was always freshly prepared by direct weighing of As_2O_3, dissolving in sodium hydroxide solution, and adjusting the pH with perchloric acid. The rate constants obtained were reproducible to within ±2%.

Redistilled water was prepared from anion–cation exchange resin water first by successive distillation from alkaline permanganate solution and finally without addition of any reagents in a glass still. Redistilled water was also used for washing the glassware.

Procedures.—The reaction vessel was coated with black tape to eliminate any photochemical effect. All the experiments were carried out with nitrogen gas bubbling through the solutions. Aliquot samples were removed at appropriate times, neutralized with perchloric acid, and mixed with anion-exchange resin (Dowex 1-X8:50—100 mesh, Cl form, washed well with redistilled water) in order to remove $S_2O_8^{2-}$. The As^{III} species was not adsorbed on the anion-exchange resin in the neutral and acidic solutions. After filtration, the concentration of the arsenic(III) ion remaining was determined by polarography at −0.15 V *vs.* a saturated calomel electrode (s.c.e.) in oxygen-free solutions of 0.5 mol dm^{-3} potassium hydroxide and 0.01% gelatine at 25 °C. The concentration of $S_2O_8^{2-}$ remaining was determined by polarography at 0.1 V *vs.* s.c.e. in a solution of 0.01 mol dm^{-3} perchloric acid, 0.1 mol dm^{-3} sodium perchlorate, and 0.01% gelatine at 25 °C.

Results and Discussion

Stoicheiometry.—The stoicheiometry of the reaction was studied under various hydroxide ion concentrations (pH 9, *ca.*

Table 1. Values of k, K_a/K_w, and K_a under various conditions

I/mol dm^{-3}	Temp. (°C)	10^3k/ dm^3 mol^{-1} s^{-1}	$\frac{10^{-4}K_a}{K_w}$	$10^{10}K_a$/ mol dm^{-3}
0.10	30	5.35	1.61	
0.15	30	7.08	1.74	
0.20	30	7.66	1.63	
0.25	30	8.57	1.68	
0.10	40	12.7	0.84	
0.10	25	4.80	2.12	3.52[a]
0.10	20	3.22	3.77	4.23[b]

[a,b] Values calculated with $K_w = 10^{-13.78}$ and $10^{-13.95}$ mol^2 dm^{-6} at I = 0.1 mol dm^{-3}, at 25 and 20 °C, respectively.[13]

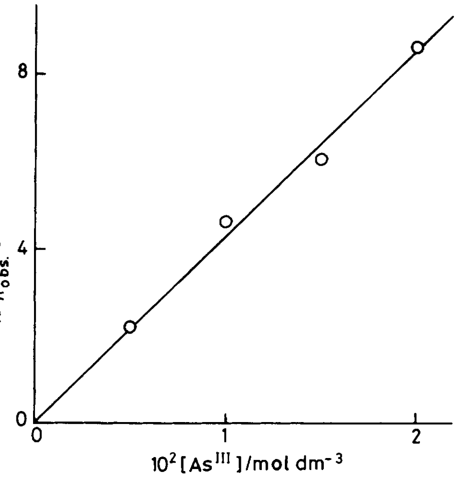

Figure 1. Plots of pseudo-first-order rate constants *vs.* arsenic(III) concentrations. Conditions: 5 × 10^{-3} mol dm^{-3} $K_2S_2O_8$, I = 0.1 mol dm^{-3}, pH 10.0, 30 °C, nitrogen-gas saturated

0.05 mol dm^{-3} NaOH). The results were $[S_2O_8^{2-}]_r/[As^{III}]_r$ = 1.01 ± 0.02 (r = reacted) as an average of seven runs. Thus, the stoicheiometry is as described in equation (1).

$$S_2O_8^{2-} + As^{III} \longrightarrow 2SO_4^{2-} + As^{V} \qquad (1)$$

Reaction Order.—The kinetic studies of reaction were made at the various concentrations of the peroxodisulphate ion at a constant arsenic(III) concentration of 0.015 mol dm^{-3}, pH 10.0, I = 0.1 mol dm^{-3}, and 30 °C. The plots of ln $[S_2O_8^{2-}]$ *vs.* t were linear and the observed rate constants ($k_{obs.}$) were 5.87 × 10^{-5}, 5.95 × 10^{-5}, 6.02 × 10^{-5}, and 5.50 × 10^{-5} s^{-1} at peroxodisulphate concentrations of 2.9 × 10^{-3}, 3.9 × 10^{-3}, 5 × 10^{-3}, and 6.7 × 10^{-3} mol dm^{-3}, respectively. Therefore $k_{obs.}$ is effectively independent of the $S_2O_8^{2-}$ concentration and the reaction rate is first order with respect to $[S_2O_8^{2-}]$.

The dependence on arsenic(III) concentration was examined under the same conditions, with $[S_2O_8^{2-}]$ = 5 × 10^{-3} mol dm^{-3}. As seen in Figure 1, the value of $k_{obs.}$ was proportional to the initial concentration of arsenic(III) ion. Therefore, the rate law is given by equation (2). Hereafter, all the experiments were

$$-d[S_2O_8^{2-}]/dt = k_2[As^{III}][S_2O_8^{2-}] \qquad (2)$$

carried out under the same initial concentrations of both reactants: *i.e.*, $[As^{III}]_i = [S_2O_8^{2-}]_i$, and the second-order rate constants (k_2) were determined from the slope of plots of $[S_2O_8^{2-}]^{-1}$ *vs.* t.

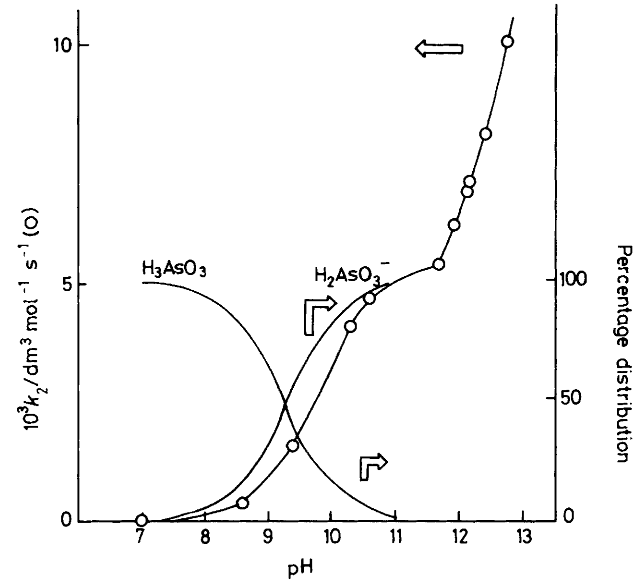

Figure 2. Effect of pH on the second-order rate constants (k_2). Conditions are the same as in Figure 1, except for 2.5 × 10^{-3} mol dm^{-3} As_2O_3 and variable hydroxide ion concentration (○). Other solid curves indicate the distribution of H_3AsO_3 and $H_2AsO_3^-$ calculated with the dissociation constant of ref. 15

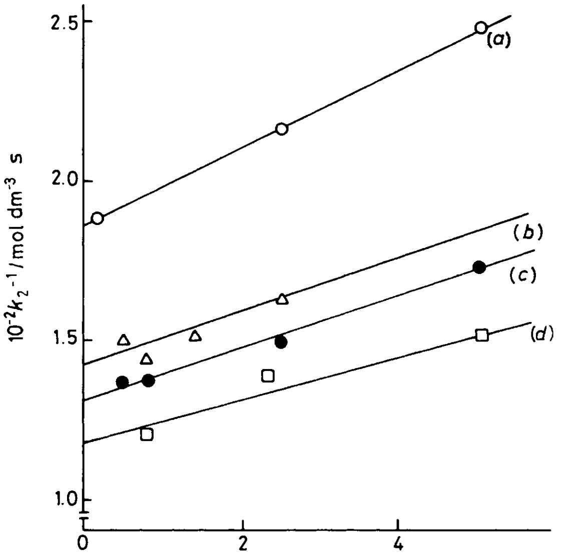

Figure 3. Ionic strength dependence. Conditions are the same as in Figure 2, except for I = 0.10 (*a*), 0.15 (*b*), 0.20 (*c*), and 0.25 mol dm^{-3} (*d*). The data at pH 8.6 and 9.4 in Figure 2 also lie on the straight line (*a*)

pH Dependence.—The oxidation of the arsenic(III) ion by $S_2O_8^{2-}$ hardly occurred at pH ≤ 7. The values of k_2 in equation (2) increased gradually with increasing pH over the range of 8.6—11.6, and then increased remarkably with increasing pH at values >11.9 (see Figure 2). Plots of k_2^{-1} *vs.* $[OH^-]^{-1}$ were rectilinear at pH 8.6—11.6 [Figure 3(*a*)], and the data at pH ≥ 11.9 deviated from the straight line.

Ionic Strength Dependence.—Plots of k_2^{-1} *vs.* $[OH^-]^{-1}$ at various ionic strengths (I) are given in Figure 3. The values of k

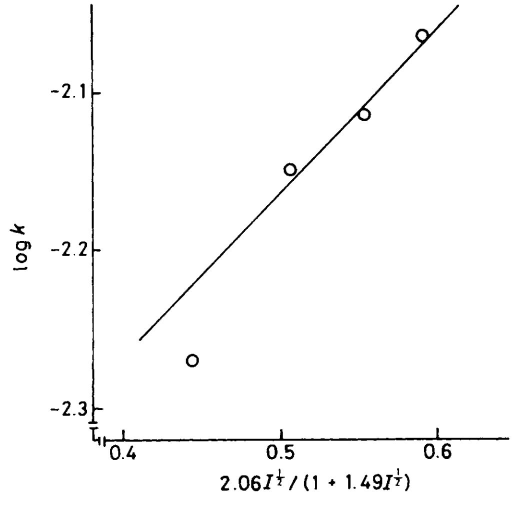

Figure 4. Plots of equation (3): open circles indicate the experimental data and the slope of the straight line is unity

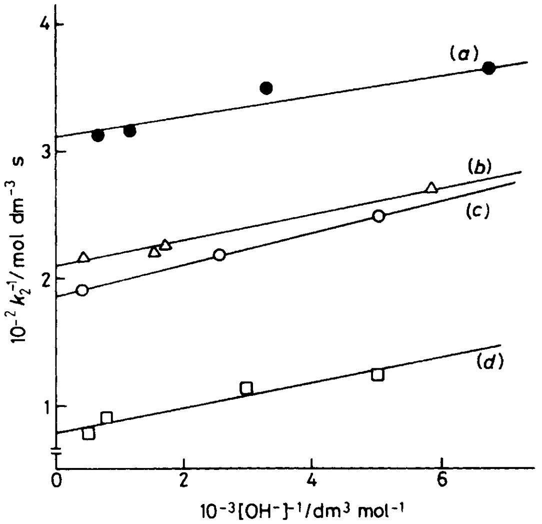

Figure 5. Temperature dependence. Conditions are the same as in Figure 2, except for $T = 20$ (*a*), 25 (*b*), 30 (*c*), and 40 °C (*d*)

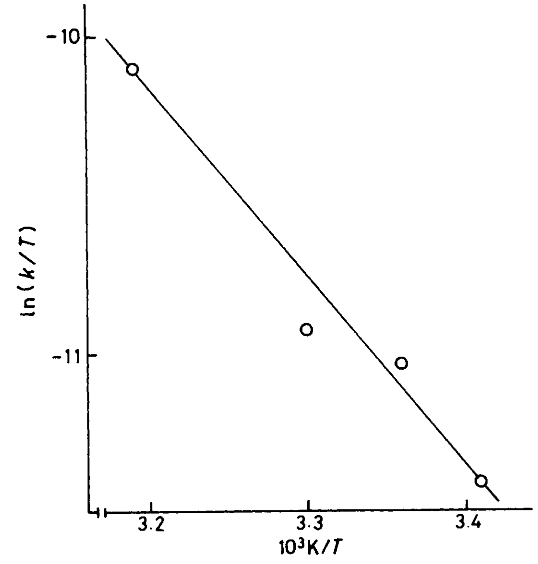

Figure 6. Plots of ln (k/T) *vs.* T^{-1}. Conditions are the same as in Figure 5

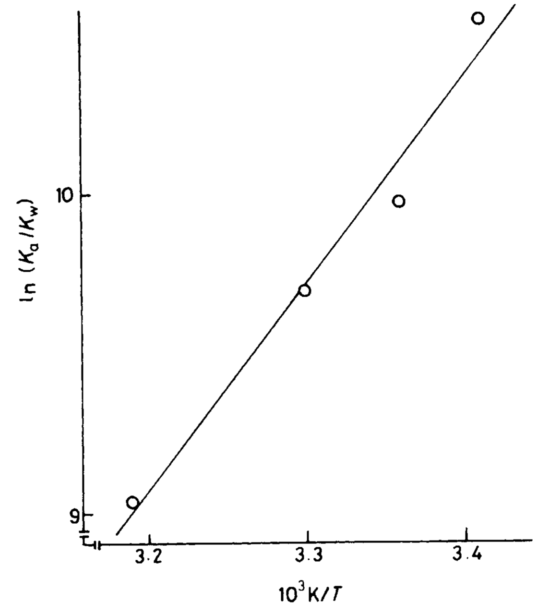

Figure 7. Plots of ln (K_a/K_w) *vs.* T^{-1}

can be evaluated by using equation (7) (see below) and are given in Table 1. The rate constant k increased on increasing the ionic strength. Applying the rate constants (k) at 30 °C and various ionic strengths to the Debye-Hückel equation (3), the distance

$$\log k = \log k_0 + 1.03\, Z_A Z_B I^{\frac{1}{2}}/(1 + 0.33aI^{\frac{1}{2}}) \qquad (3)$$

of closest approach (a/Å) between $S_2O_8^{2-}$ and $H_2AsO_3^-$ can be calculated as 4.5 Å. Plots of equation (3) are shown in Figure 4. The ion size parameter of $S_2O_8^{2-}$ is reported to be 4.0 Å,[12] and thus, that of $H_2AsO_3^-$ can be calculated to be 5.0 Å. This value is reasonable compared with the reported value for $H_2AsO_4^-$ (4—4.5 Å).[12]*

Temperature Dependence.—The temperature dependence was examined under the same conditions as in Figure 2, with various temperatures over the range 20—40 °C. The results are given in Figure 5 and Table 1. The rate constant (k) and the first acid dissociation constant (K_a) of H_3AsO_3 were calculated from the intercept and the slope in Figure 5 [see equation (7), below]. The enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the reaction step (5) (see below) were calculated from plots of ln (k/T) *vs.* T^{-1} (Figure 6) to be 47.6 kJ mol^{-1} and -130.4 J K^{-1} mol^{-1}, respectively. These values are reasonable for a bimolecular reaction between charged species of the same sign. The negative value of $\Delta S^{\ddagger}$ is due to the increased charge on the activated complex.

The enthalpy and entropy change associated with the equilibrium step (4) were also calculated from the plot of

$$H_3AsO_3 \xrightleftharpoons{K_a} H_2AsO_3^- + H^+ \qquad (4)$$

$$H_2AsO_3^- + S_2O_8^{2-} \xrightarrow[H_2O]{k} HAsO_4^{2-} + 2SO_4^{2-} + 3H^+ \qquad (5)$$

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* The application of the Debye-Hückel equation (3) at ionic strengths above 0.1 mol dm^{-3} is inappropriate, but the results are reasonable, and thus, the variation of the rate constants k with ionic strength are probably due to the coulombic forces of the ionic species in the reaction.

Table 2. Effect of radical scavenger*

Additive	10^3k_2/dm^3 mol^{-1} s^{-1}
1.5% Acrylamide	4.21
2.5% Acrylamide	4.03
2.0% Acrylonitrile	3.91
None	4.29

* Conditions are the same as in Figure 1.

ln (K_a/K_w) *vs.* T^{-1} (Figure 7): $\Delta H_a = (\Delta H_w - 5.39 \times 10^4)$ J mol^{-1} and $\Delta S_a = (\Delta S_w - 97.3)$ J K^{-1} mol^{-1}, respectively. Here, ΔH_w and ΔS_w are the enthalpy and entropy changes for water dissociation and are taken as 56.7 kJ mol^{-1} and -74.1 J K^{-1} mol^{-1},[13] respectively. Thus, the values of ΔH_a and ΔS_a were evaluated to be 2.8 kJ mol^{-1} and -171.4 J K^{-1} mol^{-1}, respectively. Such a negative entropy for the dissociation reaction (4) is due to hydration of the dissociated products H^+ and $H_2AsO_3^-$. The negative entropy value is not unusual for the dissociation of a neutral molecule to give charged ions.

Effect of Radical Scavenger.—Waters[14] observed that the arsenic(III) ion was not oxidized by a one-electron-transfer oxidant in the absence of a catalyst, and that it was, however, readily oxidized by a two-electron-transfer oxidant. Some researchers[4,11] have reported that the oxidation of arsenic(III) to arsenic(V) proceeds *via* the tetravalent state of arsenic. The monomers of acrylamide as well as acrylonitrile are good scavengers of the radicals $SO_4^{\cdot -}$ and As^{IV}. In the present study, addition of acrylamide and acrylonitrile to the reacting solution produced no polymer and had no effect on the rate constants (Table 2). Thus, we could obtain no evidence for the formation of radicals and the peroxodisulphate ion appears to oxidize As^{III} to As^{V} as a two-electron-transfer oxidant.

The distribution of H_3AsO_3 and $H_2AsO_3^-$ at various pH was calculated using the dissociation constant (K_a)[15] and is given in Figure 2 together with the k_2 values. It is confirmed that only the deprotonated species $H_2AsO_3^-$ reacts with the $S_2O_8^{2-}$ ion under alkaline conditions at pH $\leqslant$ 11.6. Consequently, the mechanism of reaction in equations (4) and (5) is postulated to account for the results obtained. The rate of decrease of peroxodisulphate ion concentration and the second-order rate constant (k_2) in equation (2) are given by equations (6) and (7), respectively, where K_w is the ionic product of water. Equation (7) is in good agreement with the results at pH $\leqslant$ 11.6 and the

$$-\frac{d[S_2O_8^{2-}]}{dt} = \frac{kK_a[OH^-][S_2O_8^{2-}][As^{III}]}{K_a[OH^-] + K_w} \qquad (6)$$

$$1/k_2 = 1/k + K_w/(kK_a[OH^-]) \qquad (7)$$

values of the rate constant (k) and the first acid dissociation constant (K_a) are calculated from the intercept and slope of the plots of k_2^{-1} *vs.* $[OH^-]^{-1}$. The values of k and K_a obtained are summarized in Table 1 and the value of K_a coincides with those reported previously (2×10^{-10} to 9×10^{-10} mol dm^{-3}).[1,15]

The reaction rate increased remarkably with increasing pH over the alkaline concentration range 0.012—0.05 mol dm^{-3} NaOH (Figure 2). In such a strong basic region, not only the deprotonated species $H_2AsO_3^-$ but also the further deprotonated species $HAsO_3^{2-}$ react with the $S_2O_8^{2-}$ ion, equations (8) and (9). The second-order rate law of equation (2) always held

$$H_2AsO_3^- \overset{K_a'}{\rightleftharpoons} HAsO_3^{2-} + H^+ \qquad (8)$$

$$HAsO_3^{2-} + S_2O_8^{2-} \xrightarrow[H_2O]{k'} AsO_4^{3-} + 2SO_4^{2-} + 3H^+ \qquad (9)$$

even in such strong alkaline solutions and thus, the second-order rate constant (k_2) can be expressed as in equation (10).

$$k_2 = (kK_a[H^+] + k'K_aK_a')/([H^+]^2 + K_a[H^+] + K_aK_a') \qquad (10)$$

The values of the rate constant (k') and the second acid dissociation constant (K_a') are evaluated to be $(1.6 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $(1.7 \pm 0.7) \times 10^{-13}$ mol dm^{-3} ($K_w = 10^{-14}$ mol^2 dm^{-6}), respectively. Gupta *et al.*[8–10] reported that the rate of the reaction between As^{III} and $S_2O_8^{2-}$ was independent of the As^{III} concentration, their results being totally different from our own. Gupta *et al.*[8–10] studied the reaction at 45 °C in acidic media. Under such conditions, only the thermal decomposition of the peroxodisulphate ion to two sulphate radicals $(SO_4^{\cdot -})$ could be the rate-determining step and then the radical $SO_4^{\cdot -}$ reacted rapidly with H_3AsO_3. Although their reaction mechanisms were quite different from those obtained here, such a difference could be caused by the different conditions of temperature and acidity.

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