

Kinetics of the Oxidation Reaction of Arsenious Acid by Peroxodisulfate Ion, Induced by Irradiation with Visible Light of Aqueous Solutions Containing Tris(2,2'-bipyridine)ruthenium(II) Ion

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Abstract

The oxidation reaction of arsenious acid (H_3AsO_3) by the peroxodisulfate ion ($\text{S}_2\text{O}_8^{2-}$) is greatly accelerated by irradiation with visible light of aqueous acid solutions containing the tris(2,2'-bipyridine)ruthenium(II) ion ($[\text{Ru}(\text{bpy})_3]^{2+}$). The $[\text{Ru}(\text{bpy})_3]^{2+}$ ion acts as a photocatalyst during the reaction. The mechanism of the reaction consists of a chain reaction being initiated by the quenching reaction of the photoexcited ruthenium(II) complex ion ($[\text{Ru}(\text{bpy})_3]^{2+*}$) with $\text{S}_2\text{O}_8^{2-}$ ion, followed by the oxidation reaction of arsenious acid by the SO_4^- radical and $[\text{Ru}(\text{bpy})_3]^{3+}$. The rate law is expressed by $-\text{d}[\text{S}_2\text{O}_8^{2-}]/\text{d}t = k_q I_a \phi [\text{S}_2\text{O}_8^{2-}] / (k_0 + k_q [\text{S}_2\text{O}_8^{2-}])$ and the bimolecular quenching rate constants k_q are determined by kinetic experiments under various conditions. The rate constants of the reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and arsenious acid are evaluated at 25 °C and ionic strength of 0.05 mol dm^{-3} with stopped-flow method to be 6.3 , 1.2×10^3 , 2.2×10^3 and $1.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 2.6, 4.0, 6.5 and 8.1, respectively.

Introduction

A kinetic study of the oxidation of arsenic(III) by several oxidants has been carried out by several investigators [1–11]. In the previous work [12], we demonstrated that the peroxodisulfate ion could oxidize the deprotonated species H_2AsO_3^- and HAsO_3^{2-} at $\text{pH} > 8.6$, but could hardly oxidize the species of H_3AsO_3 in acidic solutions. In the present study, it was found that the reaction between H_3AsO_3 and $\text{S}_2\text{O}_8^{2-}$ proceeded at a moderate rate by the addition of tris(2,2'-bipyridine)ruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}$) with irradiation of visible light. The mechanism of this photo-induced reaction will be presented to account for the experimental results obtained.

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Experimental

Chemicals

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8$ and NaClO_4 were obtained as described in the previous paper [13]. Arsenic(III) solution was always freshly prepared by direct weighing of arsenious trioxide (As_2O_3), dissolving in sodium hydroxide solution and adjusting the pH with perchloric acid. All other chemicals used were of guaranteed reagent grade without further purification. 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.

Procedure

The reaction vessel, a colorless glass bottle (capacity 0.5 dm^3 , diameter 80 mm, thickness 1 mm with 10 mm neck), was placed in a thermostatted water bath made of colorless glass ($2 \times 3 \times 3 \text{ dm}$, thickness 6 mm). Unless otherwise stated, the sample solution was irradiated with light from two 100-W tungsten lamps that were placed 3 dm to the right- and left-hand sides from the center of the reaction vessel. Irradiation was continued throughout the reaction. Oxygen was removed by bubbling pure nitrogen gas through the solution. Aliquot samples were withdrawn at appropriate times and mixed with a cation-exchange resin (Dowex 50W-X8, 200–400 mesh, hydrogen form, washed well with distilled water) in order to remove $[\text{Ru}(\text{bpy})_3]^{2+}$ from the reaction solution and to stop the reaction. After filtration, the concentration of the peroxodisulfate ion remaining was determined polarographically at +0.1 V versus SCE under the conditions of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$, $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$ and 0.1% gelatin at 25 °C. The concentration of the arsenic(III) ion remaining was also determined polarographically at -0.15 V versus SCE in 0.1 mol dm^{-3} sodium hydroxide after removal of the peroxodisulfate ion by mixing the sample solution with anion-exchange

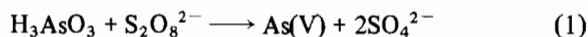
resin (Dowex 1-X8, 50–100 mesh, chloride form, washed well with distilled water). The arsenic(III) species was not adsorbed at all to the anion-exchange resin in neutral and acidic solutions. The rate constants of the redox reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and As(III) species were determined with a Union RA-401 stopped flow spectrophotometer. The solution of $[\text{Ru}(\text{bpy})_3]^{3+}$ was prepared by oxidizing $[\text{Ru}(\text{bpy})_3]^{2+}$ with lead dioxide (PbO_2) in 0.5 mol dm^{-3} sulfuric acid. Immediately after removal of PbO_2 and PbSO_4 by filtration, the $[\text{Ru}(\text{bpy})_3]^{3+}$ solution was used for the experiments.

Results and Discussion

It was confirmed spectrophotometrically that the concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ ion remained constant during the reaction under any conditions employed.

Stoichiometry

The stoichiometry for the light-induced reaction was determined under various conditions. The ratio of $[\text{As(III)}]_{\text{reacted}}/[\text{S}_2\text{O}_8^{2-}]_{\text{reacted}}$ was 1.01 ± 0.07 as an average of seven runs. This indicates that the stoichiometry is expressed by eqn. (1).



where H_3AsO_3 is the predominant species over the pH range 1.3–8.2 and As(V) represents H_3AsO_4 , H_2AsO_4^- and HAsO_4^{2-} .

Effect of Hydrogen Ion Concentration

The effect of the hydrogen ion concentration on the reaction rates ($-\text{d}[\text{S}_2\text{O}_8^{2-}]/\text{d}t$) was examined over the pH range 1.3–11.4. As seen in Fig. 1, the

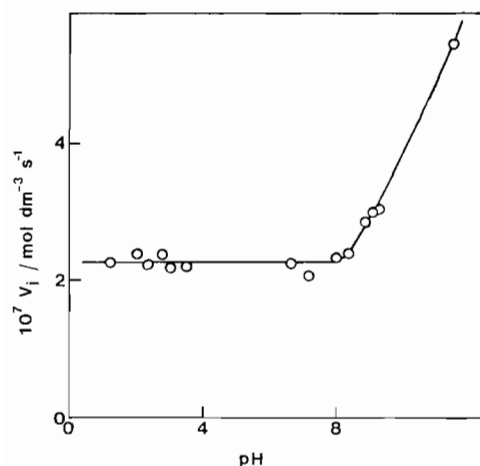


Fig. 1. Effect of pH on the reaction rate (V_i): 5×10^{-5} mol dm^{-3} $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 4×10^{-3} mol dm^{-3} $\text{K}_2\text{S}_2\text{O}_8$, 30°C , 5×10^{-3} mol dm^{-3} As_2O_3 , N_2 -saturated, $\mu = 0.1$ mol dm^{-3} , two lamps irradiated.

initial rate of the reaction $V_i (= -\Delta[\text{S}_2\text{O}_8^{2-}]_i/\Delta t)$ was independent of the hydrogen ion concentrations over the pH range 1.3–8.2, and increased remarkably at $\text{pH} > 8.4$ due to the occurrence of the reaction between the peroxodisulfate ion and the deprotonated species H_2AsO_3^- [12]. Hereafter, all the experiments were carried out at pH 4.

Effect of Concentrations of Reactants

The rates of the reaction (V_i) were independent of the initial concentrations of H_3AsO_3 over the range 0.005–0.03 mol dm^{-3} , but were dependent on those of peroxodisulfate ion. As seen in Fig. 2, the plots of V_i^{-1} versus $[\text{S}_2\text{O}_8^{2-}]_i^{-1}$ showed a straight line with an intercept, and the slope of the plot was dependent on the ionic strengths (μ). Thus, the empirical rate law can be written as follows.

$$V_i^{-1} = \alpha + \beta[\text{S}_2\text{O}_8^{2-}]_i^{-1} \quad (2)$$

The values of α and β in eqn. (2) obtained at various ionic strengths are given in Table 1 together with the rate constants.

Effect of Temperature

The rate of the reaction (V_i) was hardly dependent on temperature 20 – 40°C .

Effect of Incident Light

No appreciable decomposition of $\text{S}_2\text{O}_8^{2-}$ ions was found in the dark under the conditions given. The initial rate of the reaction was found to be proportional to the number of lamps used (see Fig. 3).

Effect of Concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$

The initial rate increased with concentrations of $[\text{Ru}(\text{bpy})_3]^{2+}$ and then reached a limiting value (see

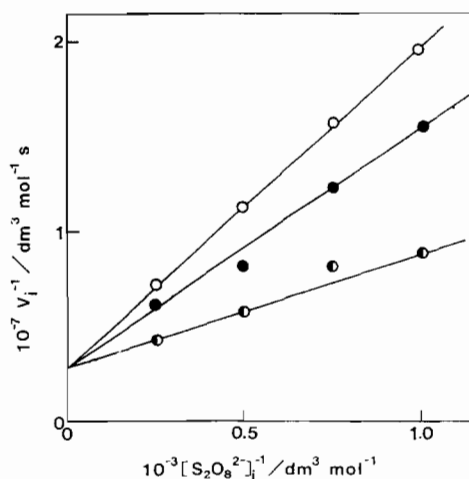


Fig. 2. Plots of V_i^{-1} vs. $[\text{S}_2\text{O}_8^{2-}]_i^{-1}$. Conditions are the same as in Fig. 1, except for pH 4 and ionic strength (μ) = 0.5 (○), 0.3 (●), 0.1 (◐) mol dm^{-3} .

TABLE 1. Values of α , β , k_q/k_0 , and k_q under various conditions^a

Temperature (°C)	μ (mol dm ⁻³)	$10^{-6} \times \alpha$ (dm ³ mol ⁻¹ s)	$10^{-3} \times \beta$ (s)	k_q/k_0 (dm ³ mol ⁻¹)	$10^{-8} \times k_q$ (dm ³ mol ⁻¹ s ⁻¹)	
30	0.1	2.83	6.38	444	6.72	7.00 ^b
30	0.3	2.55	12.8	199	3.02	3.26 ^b
30	0.5	2.71	17.5	155	2.35	2.02 ^b
20	0.1	3.12	6.76	462		
40	0.1	2.99	6.57	455		
		Av. 2.84 ± 0.17				

^aConditions are the same as in Fig. 1, except for pH 4.

^bValues obtained from the Stern–Volmer plots of the quenching of the luminescence from $[\text{Ru}(\text{bpy})_3]^{2+}$ by $\text{S}_2\text{O}_8^{2-}$ [13].

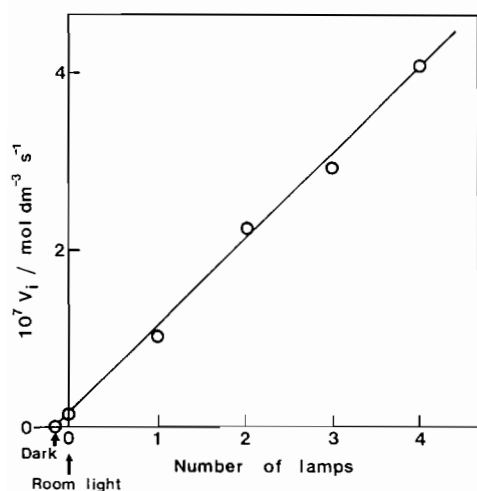


Fig. 3. Effect of light intensity. Conditions are the same as in Fig. 1, except for pH 4.

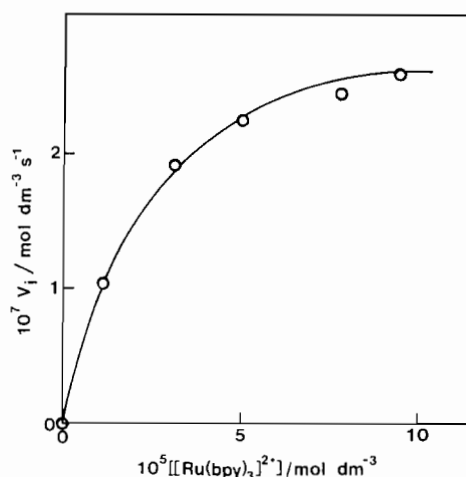


Fig. 4. Effect of the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion concentration. Conditions are the same as in Fig. 1, except for pH 4.

Fig. 4). This behavior is due to the change of the amount of light absorbed according to the concentration change of $[\text{Ru}(\text{bpy})_3]^{2+}$ and can be explained by eqn. (3), although eqn. (3) is derived for irradiation with monochromatic light.

$$I_a = I_0(1 - \exp(-A [[\text{Ru}(\text{bpy})_3]^{2+}])) \quad (3)$$

where I_0 is the intensity of the incident light, I_a is the amount of light absorbed by $[\text{Ru}(\text{bpy})_3]^{2+}$ and A is an empirical constant comprising the length of light path and the molar absorption coefficient of $[\text{Ru}(\text{bpy})_3]^{2+}$. The rate of reaction (V_i) is proportional to I_a (see eqn. (12)), and thus, the curve shown in Fig. 4 coincides with the expression of eqn. (3).

Determination of the Rate Constants (k_3)

The second-order rate constant k_3 for the reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and $\text{As}(\text{III})$ was determined with a stopped-flow spectrophotometer and is given in Fig. 5. The k_3 value decreased remarkably with the decrease of pH of the solution.

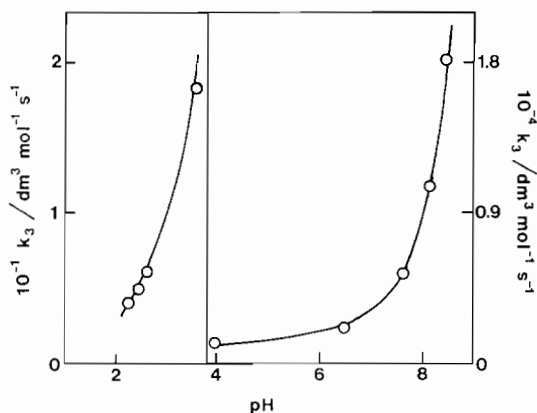


Fig. 5. Effect of pH on the rate constant k_3 : 5×10^{-6} mol dm⁻³ $[\text{Ru}(\text{bpy})_3]^{3+}$, $\mu = 0.05$ mol dm⁻³, 25 °C, $[\text{As}(\text{III})] = 5 \times 10^{-3}$ mol dm⁻³.

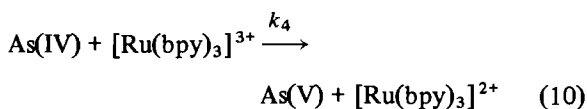
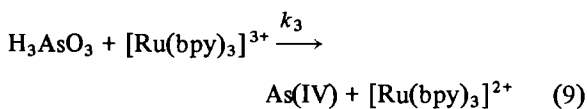
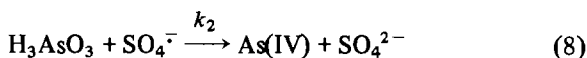
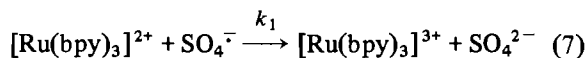
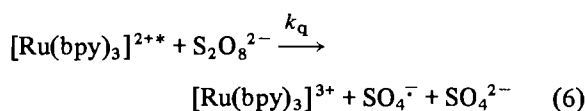
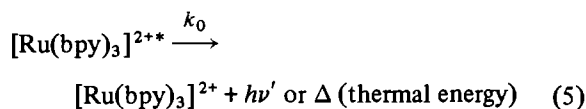
Effect of Radical Scavengers

The addition of acrylonitrile and acrylamide into the reaction solution produced a polymer. This fact indicates that the light-induced reaction occurs via

the formation of radical species. The effect brought about by adding each radical scavenger was quite different. The white sediment of the polymer was found by the addition of acrylonitrile and some $[\text{Ru}(\text{bpy})_3]^{2+}$ was adsorbed onto the polymer. This caused the rate of the photo-catalytic reaction to decrease. On the other hand, the addition of acrylamide monomer considerably accelerated the reaction rate, which might be due to the reaction between the $\text{S}_2\text{O}_8^{2-}$ ion and the propagating radicals of the acrylamide polymer.

Mechanisms of the Reaction

The following mechanism of the reaction is presented to account for the results obtained.



It was reported that $[\text{Ru}(\text{bpy})_3]^{3+}$ is unstable in an aqueous solution at $\text{pH} > 4$ and an oxidative degradation of $[\text{Ru}(\text{bpy})_3]^{3+}$ to the destruction of bipyridine ligands was found in the absence of solid catalysts such as RuO_2 and IrO_2 which accelerate the reaction rate for the oxidation of water by $[\text{Ru}(\text{bpy})_3]^{3+}$ [14]. The rate of reactions (9) and (10) is much faster than that for the water oxidation by $[\text{Ru}(\text{bpy})_3]^{3+}$ and the steady state concentration of $[\text{Ru}(\text{bpy})_3]^{3+}$ is very small under the experimental conditions investigated. Thus, this might be the reason that no decomposition of the ruthenium(II) complex was found in the present work.

Assuming the steady state concentrations of SO_4^- , $[\text{Ru}(\text{bpy})_3]^{3+}$ and $[\text{Ru}(\text{bpy})_3]^{2+*}$, the rate law is expressed as eqns. (11) and (12).

$$-d[\text{S}_2\text{O}_8^{2-}]/dt = k_q I_a \phi [\text{S}_2\text{O}_8^{2-}] / (k_0 + k_q [\text{S}_2\text{O}_8^{2-}]) \quad (11)$$

$$V_i^{-1} = \frac{1}{I_a \phi} + \frac{k_0}{k_q I_a \phi} [\text{S}_2\text{O}_8^{2-}]^{-1} \quad (12)$$

where ϕ is the formation efficiency of the excited species, I_a is the amount of light absorbed by $[\text{Ru}(\text{bpy})_3]^{2+}$ (see eqn. (3)) and $I_a \phi$ corresponds to the formation rate of $[\text{Ru}(\text{bpy})_3]^{2+*}$. Equation (12) is equivalent to eqn. (2) obtained empirically, and thus, α and β values correspond to $(I_a \phi)^{-1}$ and $k_0/(k_q I_a \phi)$, respectively. The rate constants k_q calculated by α and β values according to the rate law (12) were in good agreement with those determined from the Stern–Volmer plots by the measurements of quenching luminescence (see Table 1). This fact supports the validity of the mechanism as well as the rate law proposed. The independence of the reaction rate on temperature could be ascribed to the independence of k_q/k_0 ($=\alpha/\beta$) values as shown in Table 1. The integral form of eqn. (11) is given by eqn. (13).

$$\alpha([\text{S}_2\text{O}_8^{2-}]_i - [\text{S}_2\text{O}_8^{2-}]) + \beta \ln([\text{S}_2\text{O}_8^{2-}]_i / [\text{S}_2\text{O}_8^{2-}]) = t \quad (13)$$

Using values of α and β , we can calculate a curve of the plots $[\text{S}_2\text{O}_8^{2-}]$ versus t . As seen in Fig. 6, the calculated curve is in good agreement with the plots obtained experimentally. This fact indicates that the mechanisms and the rate law proposed are valid at any stages as well as the initial period of the reaction.

The mechanisms of the reaction show that the light-induced reaction proceeds essentially according to Scheme 1. We previously demonstrated that Scheme 1 also operated for the oxidation reaction of oxalate [13], formate [15] and ethylenediaminetetraacetatocobaltate(II) [16] with the peroxodisulfate ion, induced by the photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ ion.

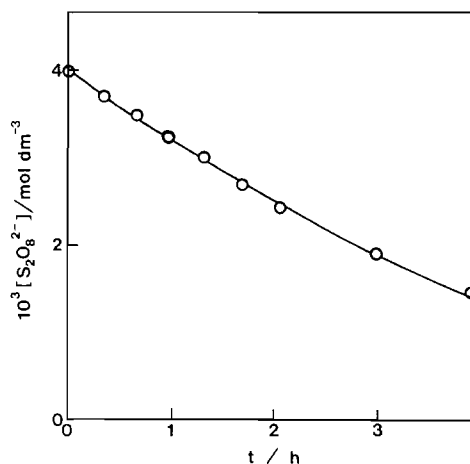
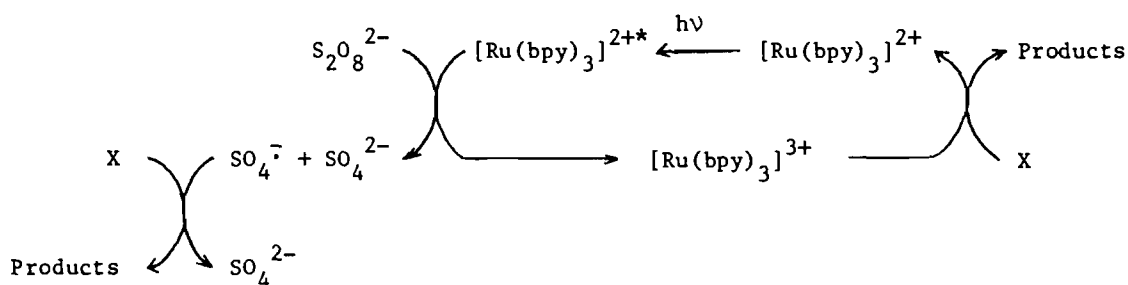


Fig. 6. Plots of $[\text{S}_2\text{O}_8^{2-}]$ vs. t . Conditions are the same as in Fig. 1, except for $\text{pH} 4$. The solid line indicate the calculated values using eqn. (13) with $\alpha = 2.83 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}$ and $\beta = 6.38 \times 10^3 \text{ s}$ at $\mu = 0.1 \text{ mol dm}^{-3}$ and 30°C .



Scheme 1.

When eqn. (14) can hold, the concentration of the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion remains constant during the reaction and $[\text{Ru}(\text{bpy})_3]^{2+}$ acts as a photocatalyst.

$$k_q [[\text{Ru}(\text{bpy})_3]^{2+*}] [\text{S}_2\text{O}_8^{2-}] + k_1 [[\text{Ru}(\text{bpy})_3]^{2+}] [\text{SO}_4^{2-}] = k_x [\text{X}] [[\text{Ru}(\text{bpy})_3]^{3+}] \quad (14)$$

The k_x value denotes the second-order rate constant for the reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and appropriate reductants (X) such as $\text{C}_2\text{O}_4^{2-}$, HCOO^- , $[\text{Co}(\text{edta})]^{2-}$ and H_3AsO_3 and the reaction conditions which satisfy the relationship of the eqn. (14) are different in each reaction system. However, under the reaction conditions where eqn. (14) holds, the reaction rate is expressed as eqn. (11), being utterly independent of the concentration of chemical species to be oxidized, pH and temperature of the reaction solution.

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