SO$_2$ OXIDATION BY HETEROPOLYACIDS (HPA) AND DIOXYGEN IN HPA PRESENCE IN AQUEOUS SOLUTIONS

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Summary

It is shown that under mild conditions sulphur dioxide is stoichiometrically oxidized to H$_2$SO$_4$ by aqueous solutions of phosphomolybdenum-vanadic heteropolyacids (HPA) and dioxygen in the presence of HPA as a catalyst. The reaction proceeds according to the mechanism of oxidative sulphurization of water in separate stages of HPA reduction by sulphur dioxide and H$_2$HPA oxidation by dioxygen.

Introduction

In aqueous solution, sulphur dioxide is easily oxidized to H$_2$SO$_4$ by compounds of copper(II), iron(III), Cu(II)—Fe(III) synergistic system [1] or other metal ions or organic radicals [2]:

$$SO_2 + 2H_2O + Ox \longrightarrow H_2SO_4 + 2H^+ + Red \qquad (1)$$
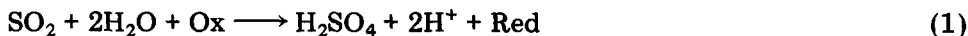
where Ox is Cu(II), Fe(III), Mn(VII), V(V), Phen$^-$.

In practice, the most prevalent cases are those when Red is easily oxidized to Ox by oxygen of the air. This property is possessed by, *e.g.* phosphomolybdenum-vanadic heteropolyacids of H$_{3+n}$PMo$_{12-n}$V$_n$O$_{40}$ type which have been used as Ox in reaction (1) and as catalysts in reaction (2):

$$SO_2 + \tfrac{1}{2} O_2 + H_2O \xrightarrow{\text{HPA–H}_2\text{HPA}} H_2SO_4 \qquad (2)$$
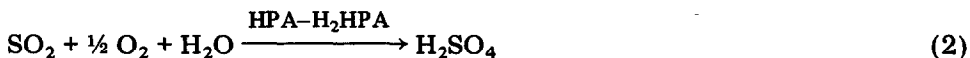
Experimental

The kinetics of reactions (1) and (2) were studied chromatographically [3]. This included periodic (each 3 min) chromatographic analyses of gas at the inlet and outlet of the reactor (LXM 8 MD chromatograph, helium gas carrier, 1 m column, silica gel support). Argon was used as an inert diluent of SO$_2$. The diluted SO$_2$ (0.5 - 1.25 vol.%) was stored over a 20% solution of H$_2$SO$_4$.

The thermostatted shaking reactor ensured that the reaction proceeded in the kinetic regime. Changes in the HPA and H_2HPA concentrations were monitored simultaneously by measuring the redox potential (φ) of the system in time. φ values are cited with respect to the normal hydrogen electrode.

Results and discussion

It was found that sulphur dioxide non-catalytically reduces the heteropolyacid-5 (*i.e.* $n = 5$) solution by two electrons:

$$H_8PMo_7V_5O_{40} + SO_2 + 2H_2O \longrightarrow H_{10}PMo_7V_5O_{40} + H_2SO_4 \qquad (3)$$

By analogy with CO oxidation [4], reaction (3) is expected to cause 2 V^V reduction to 2 V^{IV} (or $V^V_2 \to V^{IV}_2$).

The study of the kinetics of reaction (3) in phosphomolybdenum-vanadic HPA-5 solution has shown the reaction rate to be a complicated function of all concentrations of the components, and of temperature: $W \sim f(C_{HPA}, C_{H_2SO_4}, C_{KI}, P_{SO_2}, T)$.

Figure 1a presents typical kinetic $(W \sim \tau)$ and potentiometric $(\varphi \sim \tau)$ curves for different concentrations of HPA-5. The reaction rate decreases with heteropolyacid reduction, and the redox system potential is shifted to the cathode side, confirming the $V^V \to V^{IV}$ transition.

With increasing HPA-5 concentration from 1×10^{-2} to 2.5×10^{-2}, the initial rate constant grows (Fig. 1). Within this concentration range, the
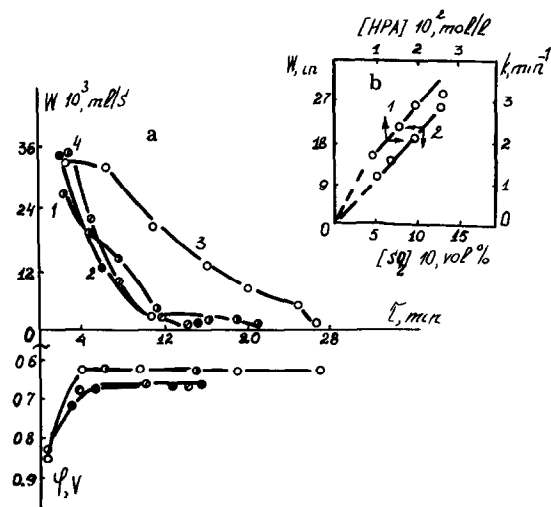

Fig. 1. SO_2 oxidation by heteropolyacid-5 in aqueous solution at 298 K. (a) kinetic (W) and potentiometric (φ) curves. $[SO_2]$, vol.%: (1) 0.50, (2) 0.63, (3) 0.92, (4) 1.25, $[HPA] = 10^{-2}$ mol l^{-1}, (b) $W_{in} \sim f(C_{HPA})$ (1) and $W_{in} \sim f(C_{SO_2})$ (2) relations.

reaction order for HPA is 0.4. Calculation of absorbed SO_2 confirms the two-electron reduction of HPA-5 in the pH range 2.4 to 0.5.

By varying SO_2 concentration from 0.5 to 1.25 vol.%, the rate constant of sulphur dioxide oxidation is found to increase with increasing concentration of this component in the gaseous phase. The reaction order for $[SO_2]$ is about 1 (Fig. 1b).

It is known that the reaction rate of SO_2 in aqueous solution increases owing to complexing with OH^- (from H_2O), I^-, Br^- and Cl^- ions [5]. We have tested I^- and Cl^- ions as catalysts (modifiers) of reaction (3). In Fig. 2, a maximum $k \sim f(C_{KI})$ is observed in the 0 to 3×10^{-3} mol l^{-1} concentration range, whereas any modification effect of Cl^- ions is observed only at high concentrations. A similar relation $W \sim f(C_{KX})$, where $X = Cl^-$, I^-, is observed also in $SO_2 \rightarrow H_2SO_4$ oxidation by Cu(II) compounds in aqueous solution [6].

Palladium(II) compounds — catalysts of CO oxidation by hereropolyacids [4] — accelerate the reaction with SO_2 slightly. The relation $W \sim f(C_{H^+})$ has a maximum at $[H^+] = 2.4$ g-ion l^{-1}. Apparently, the proton acidity effect is determined also by the concentration of HSO_4^- ion in solution. The equilibrium (4) suggests that with variation of the solution acidity $[HSO_4^-] \sim f(C_{H^+})$ function also passes through a maximum. The activation energy is 52.5 kJ mol^{-1}; $\Delta S^* = -18.6$ J $(mol\text{-}deg)^{-1}$.
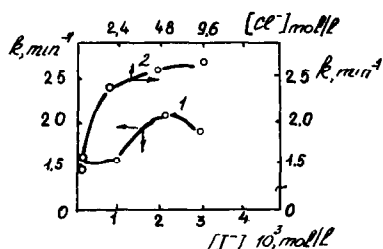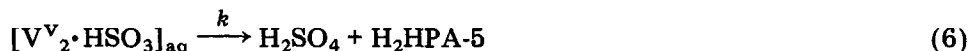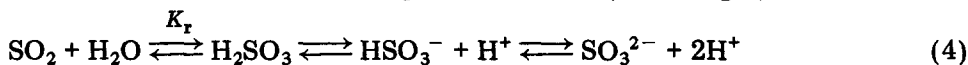

Fig. 2. Dependence of reaction (3) rate constant on concentration of I^- (1) and Cl^- (2) ions, 298 K, [HPA] = 10^{-2} mol l^{-1}, C_{SO_2} is reduced to 1 vol.%.

The following scheme of HPA-5 reduction (we consider here only the $V^V{}_2$ part from HPA) by sulphur dioxide in aqueous solution can be proposed on the basis of literature and experimental data (basic stages):

$$SO_2 + H_2O \overset{K_r}{\rightleftharpoons} H_2SO_3 \rightleftharpoons HSO_3^- + H^+ \rightleftharpoons SO_3^{2-} + 2H^+ \qquad (4)$$

$$V^V{}_2 + HSO_3^- \rightleftharpoons [V^V{}_2 \cdot HSO_3]_{aq} \qquad (5)$$

$$[V^V{}_2 \cdot HSO_3]_{aq} \overset{k}{\longrightarrow} H_2SO_4 + H_2HPA\text{-}5 \qquad (6)$$

Assuming the reaction of intrasphere redox decomposition, i.e. the transfer of two electrons from $HSO_3^-{}_{aq}$ to $V^V{}_2$, to be the limiting step in a large excess of water, the kinetic equation of the rate of HPA-5 reduction by sulphur dioxide takes the form:

$$W = k_{eff}[HPA\text{-}5][SO_2],$$

where $k_{eff} = 0.67 \times 10^2 \text{ mol}^{-1} \text{ l min}^{-1}$.

When SO_2 is present in the gaseous phase simultaneously with dioxygen, V^{IV} is oxidized to V^V:

$$V^{IV}_2 + \tfrac{1}{2} O_2 + 2H^+ \longrightarrow V^V_2 + H_2O \qquad (7)$$

i.e. the catalytic cycle closes and reaction (2) proceeds.

Under these conditions, the kinetic curves are found to consist of two parts: non-stationary and stationary (st) (Fig. 3a). In the first part, reaction (3) proceeds until a certain ratio of $HPA:H_2HPA$ is reached, the reaction rate decreasing. In the stationary part, equilibrium is reached between reactions (3) and (1). As follows from the kinetic curves, $k_{st} \sim f(C_{HPA}, C_{O_2})$, the reaction order for the catalyst and oxidant is ~ 1, within the concentration ranges studied.
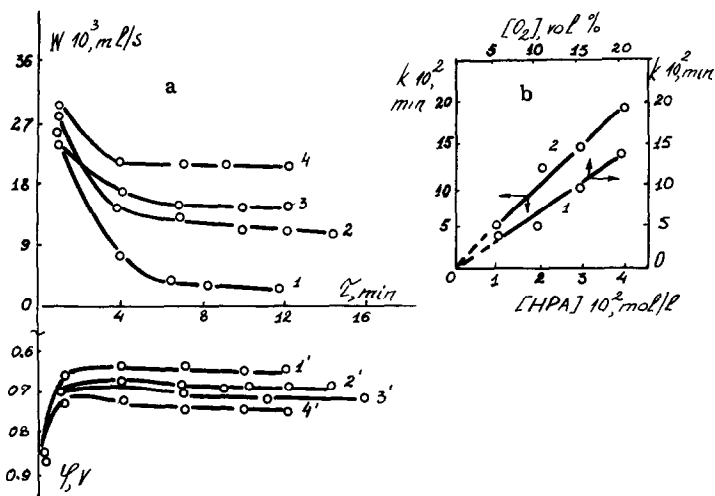

Fig. 3. SO_2 oxidation by dioxygen in HPA-5 presence. 298 K, (a) kinetic (W) and potentiometric (φ) curves, [HPA-5] mol l^{-1}· (1) 0.01, (2) 0.02, (3) 0.03, (4) 0.04, [SO_2], vol.%: (1) 0.47, (2) 0.76, (3) 0.75, (4) 0.85, (b) $W \sim f(C_{HPA})$, [O_2] = 21 vol.% and $W \sim f(C_{O_2})$ relations, [HPA] = 10^{-2} mol l^{-1}, (2), SO_2 is reduced to 1 vol.%.

The calculation based on φ values shows the portion of H_2HPA in the 0 - 20 vol.% [O_2] range to be 0 - 65% with respect to the initial HPA concentration.

Varying the [SO_2] content in the gaseous phase from 0.75 to 1.75 vol.% at constant HPA concentration in the solution increases both the stationary (W_{st}) and non-stationary rates; reaction orders in both regions are equal to 1.

In the 1.2 - 4.8 mol l^{-1} H_2SO_4 concentration range, the reaction rate constant decreases. This is related to the fact that, according to potentiometric data, increasing the solution acidity leads to a decrease in the HPA reduction rate, which affects W_{st}.

In the stationary part, the activation energy of the reaction is 52.1 kJ mol^{-1}; $\Delta S^* = -14.6$ J mol^{-1} deg^{-1}.

Based on experimental and literature data [7], the reaction of SO_2 oxidation by dioxygen in HPA aqueous solutions can be presented by a Scheme including states (4 - 6) and stage (7).

As follows from Fig. 3a, stage (7) — H_2HPA-5 oxidation — is the limiting step, which is evidenced also by the first-order reaction of O_2. As a consequence, the HPA $\rightleftarrows$ H_2HPA-5 equilibrium is shifted during the reaction to the side of H_2HPA because of the higher rate of HPA reduction by sulphur dioxide. So long as H_2HPA concentration depends also on the HPA amount, the reaction order for HPA is determined to be close to 1.

The process can be described by the following equation:

$$W = k_{eff}'[SO_2][O_2]$$

where $k_{eff}' = 2.2 \times 10^3$ mol^{-1} l min^{-1}, $k_{eff}' = k[HPA]$.

Hence, we have found that phosphomolybdenum-vanadic heteropolyacids can be used under mild conditions to oxidize sulphur dioxide to sulphuric acid.

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