
 Fig. 2 — Plot of  $\log(-d[M]/dt)$  versus  $\log[\text{catalyst}]$ 

 TABLE 2 — EFFECT OF VARYING WATER CONTENT OF THE REACTION MEDIUM ON THE RATE OF  $\text{Rh}^{3+}$ -CATALYSED POLYMERIZATION OF MMA

{[Monomer]=2 ml ( $1.253 \text{ mole litre}^{-1}$ ); time of reaction=1 hr; [Catalyst]=1.5 ml of  $1 \times 10^{-2} \text{ mole litre}^{-1}$ ; solution ( $1 \times 10^{-3} \text{ mole litre}^{-1}$ ); temp.= $60^\circ$ ; total vol=15 ml}

Water ml	Ethanol ml	$-d[M]/dt \times 10^6$ (moles $\text{litre}^{-1} \text{ sec}^{-1}$ )	$\log -d[M]/dt + 6$	Chain length "
0.5	11.0	0.47	0.6721	—
1.0	10.5	1.39	1.1431	1081
1.5	10.0	1.36	1.1335	1096
2.0	9.5	1.88	1.2967	1273
2.5	9.0	2.09	1.3201	2458
3.0	8.5	2.39	1.3784	1909
3.5	8.0	2.22	1.3464	1445
4.0	7.5	1.99	1.2989	2186
5.0	6.5	1.51	1.1790	1808
6.0	5.5	1.66	1.2201	2094

a gradual increase in the rate was observed up to a composition of 33.3% water (maximum rate) after which the rate dropped down gradually (Table 2). Chain lengths of the PMMA samples increased with an increase in the monomer concentration and decreased with the catalyst concentration, in the manner expected from the rate equation.

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## Kinetics of $\text{Ag(I)}$ Catalysed Oxidation of Isoamyl Alcohol by Peroxydisulphate

R. N. SINGH, L. N. SINGH & H. S. SINGH

Department of Chemistry, University of Allahabad, Allahabad

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Kinetics of  $\text{Ag(I)}$ -ion catalysed oxidation of isoamyl alcohol by peroxydisulphate has been studied in aqueous medium. The reaction shows first order kinetics with respect to peroxydisulphate and zero order with respect to isoamyl alcohol. The effect of varying  $[\text{Ag}^+]$  on the reaction rate indicates the direct proportionality on  $[\text{Ag}^+]$  even at different temperatures. A probable mechanism has been suggested.

THE kinetics of oxidation of isoamyl alcohol has been studied by a number of workers using oxidants such as potassium permanganate<sup>1</sup>, potassium dichromate<sup>2</sup>, cobalt bromide<sup>3</sup>, nitric acid<sup>4</sup>, *tert*-butyl chromate<sup>5</sup> and chromic acid<sup>6</sup>. The present note deals with the results of kinetics of silver(I)-ion catalysed oxidation of isoamyl alcohol by peroxydisulphate in aqueous medium.

All the chemicals (Analar or GR) were procured from either BDH or E. Merck.

The progress of reaction was followed by estimating unreacted  $\text{K}_2\text{S}_2\text{O}_8$  iodometrically<sup>7</sup> at various intervals of time in pyrex glass bottle, coated on the outside with black Japan and wrapped with black cloth.

The results given in Table 1 indicate the first order kinetics with respect to peroxydisulphate. The overall first order velocity constant ( $k_a$ ), velocity constant ( $k_d$ ) for the decomposition of the peroxydisulphate and first order velocity constant ( $k$ ) for the oxidation of isoamyl alcohol at different [peroxydisulphate] are also given in Table 1. The order of reaction with respect to isoamyl alcohol has been found to be zero (Table 2). A perusal of Fig. 1 clearly demonstrates the direct proportionality of the reaction rate on  $[\text{Ag}^+]$  even at different temperatures.

 TABLE 1 — EFFECT OF VARYING  $[\text{S}_2\text{O}_8^{2-}]$  ON THE REACTION RATE

{[Isoamyl alcohol]= $2.87 \times 10^{-2} M$ ;  $[\text{Ag}^+]=1.0 \times 10^{-3} M$ ; temp.= $55^\circ$ }

$[\text{S}_2\text{O}_8^{2-}] \times 10^2 M$	0.5	1.0	1.5	2.0	2.5
$k_a \times 10^3 \text{ min}^{-1}$	27.10	26.26	26.10	25.80	25.21
$k_d \times 10^3 \text{ min}^{-1}$	6.07	5.81	5.34	4.66	4.50
$k \times 10^3 \text{ min}^{-1}$	21.03	20.45	20.76	21.14	20.71

TABLE 2 — EFFECT OF VARYING [ISOAMYL ALCOHOL] ON THE REACTION RATE

{ $[\text{S}_2\text{O}_8^{2-}]=1.0 \times 10^{-2} M$ ;  $[\text{Ag}^+]=1.0 \times 10^{-3} M$ ; temp.= $55^\circ$ }

(Isoamyl alcohol) $\times 10^2 M$	1.435	2.870	4.305	5.740
$k_a \times 10^3 \text{ min}^{-1}$	27.03	26.26	26.77	26.85
$k_d \times 10^3 \text{ min}^{-1}$	5.81	5.81	5.81	5.81
$k \times 10^3 \text{ min}^{-1}$	21.22	20.45	20.96	21.04

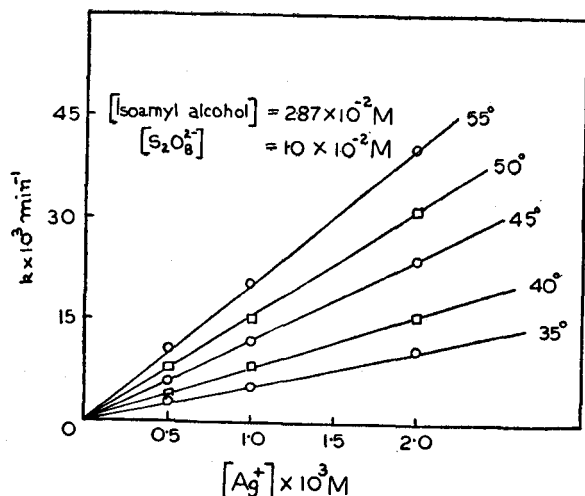


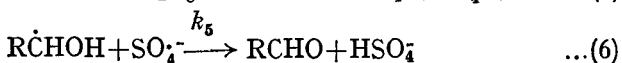
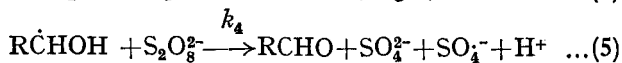
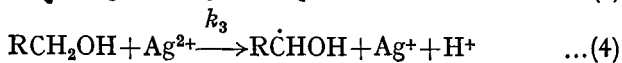
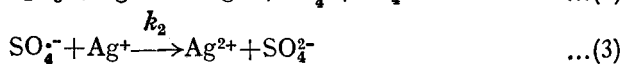
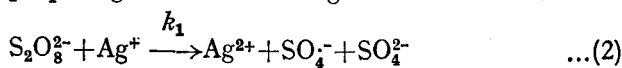
Fig. 1 — Effect of varying  $[Ag^+]$  on the reaction rate at different temperatures

On the basis of results the rate law may be represented by Eq. (1)

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_r[S_2O_8^{2-}][Ag^+] \quad \dots(1)$$

where  $k_r$  is the specific rate constant and comes out to be  $k/[Ag^+]$  litres mole<sup>-1</sup> min<sup>-1</sup>.

The results obtained might be explained on proposing the mechanism given in Scheme 1.



where  $(CH_3)_2CHCH_2 = R$

Scheme 1

This mechanism clearly explains the first order kinetics with respect to peroxydisulphate and  $Ag^+$  both. The various steps proposed are quite justified because in the  $Ag^+$ -catalysed oxidations,  $Ag^{2+}$  and a number of free radicals as intermediates have been reported by several workers<sup>8-14</sup>.

The rate of disappearance of peroxydisulphate may be given as,

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}][Ag^+] + k_4[R\dot{C}HOH][S_2O_8^{2-}] \quad \dots(7)$$

Considering the steady state conditions, the value of  $[R\dot{C}HOH]$  comes out to be

$$[R\dot{C}HOH] = \left( \sqrt{\frac{2k_1k_2}{k_4k_5} + \frac{k_2^2}{4k_5^2}} - \frac{k_2}{2k_5} \right) [Ag^+] \quad \dots(8)$$

Apparently Eq. (8) shows quite complicated feature but the close examination clearly reveals that the whole factor consists of various constants along with the  $[Ag^+]$  and hence it can be simplified as follows:

$$[R\dot{C}HOH] = \text{constant } [Ag^+] \quad \dots(9)$$

On substituting the value of  $[R\dot{C}HOH]$  in Eq. 7 we get

$$\begin{aligned} -\frac{d[S_2O_8^{2-}]}{dt} &= k_1[S_2O_8^{2-}][Ag^+] + k_4 \cdot \text{constant} \cdot [Ag^+] \\ &= k_r[S_2O_8^{2-}][Ag^+] \quad \dots(10) \end{aligned}$$

where  $k_r = (k_1 + k_4 \cdot \text{constant})$ .

The above equation clearly explains the experimental results obtained at different conditions. The oxidation product, isopentanal was estimated from the reaction mixture and confirmed by its characteristic NMR spectrum.

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#### Studies on Heteropoly Niobotungstate(VI)

G. C. BHATTACHARYA & SALIL KUMAR ROY

Department of Postgraduate Studies & Research in Chemistry  
Ranchi University, Ranchi 8

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The nature and conditions of formation of heteropoly niobotungstate(VI) have been established with the help of pH and thermometric titrations. Based on chemical and physical studies, the compound has been formulated as  $K_5Na_5[WNb_{12}O_{38}]11H_2O$ . The molecular weight (2380) for the compound, determined from the unit cell dimensions, tallies with the formula weight. The pressure-composition isothermals studied in the solid phase at 35° and 45° indicated  $K_5Na_5[WNb_{12}O_{38}]6H_2O$  to be the most stable form.

LAPITSKU and coworkers<sup>1</sup> reported a number of heteropoly niobate complexes of several transitional metal ions and also of Ce(III). Later Dale *et al.*<sup>2</sup> examined some of these complexes and in general found that the Russian work was not reproducible. In this note we report the results of