

NOTE

Mechanism of Ru(VI) Catalysis in Potassium Bromate Oxidation of Cyclopentanol in Alkaline Media

DARSHANA SINGH, SHASHI BHUSHAN SINGH, VED PRAKASH SAHAY,
MANJU PRASAD and JANAK PRASAD*
Chemistry Department
Magadh University, Bodh Gaya-8j24 234 India

The kinetic data obtained in Ru(VI) catalysed oxidation of cyclopentanol by alkaline solution of potassium bromate in the presence of mercuric acetate as bromide ions scavenger have been reported. First order kinetics with respect to each of bromate ion, Ru(VI) and cyclopentanol was observed. Zero order dependence on $[\text{OH}^-]$ and negligible effect of variation of ionic strength of the medium were observed while successive addition of mercuric acetate shows zero effect on the reaction velocity. Mechanistic aspects are discussed.

Scant attention has been paid to the activity of potassium bromate in the presence of a catalyst in alkaline or acidic media¹ and no attempt has been made, so far, to explain the catalytic role of Ru(VI) with potassium bromate as an oxidant in alkaline media. This prompted us to undertake the present investigation which deals with kinetics and mechanism of Ru(VI) catalysed oxidation of cyclopentanol by alkaline solution of potassium bromate.

All the reagents used were of highest purity available. Solutions of potassium bromate (E. Merck), cyclopentanol (BDH, AR grade), sodium perchlorate (E. Merck), mercuric acetate (E. Merck) were prepared by dissolving their weighed samples in doubly distilled water. The kinetic procedure employed was the same as reported by Mukherjee *et al.*² The reaction was studied for two half lives. Cyclopentanone was analysed as final product.

Spectra of Ru(VI) in different concentrations of NaOH were taken in UV Model Beckman 26 spectrophotometer. It was found that near 1×10^{-2} M NaOH, Ru(VI) exists at 460 nm. Hence all experiments were performed near about 1.00×10^{-2} M NaOH in order to realise Ru(VI) catalysis in the present study.

The reaction was investigated at several concentrations of reactants (Table 1). The kinetic data on negligible effect of ionic strength of the medium, mercuric acetate and $[\text{OH}^-]$ are reported in Table-2. The value of energy of activation was calculated from the rate measurements at 30, 40 and 45°C and it was found to be 16.48 kcal/mole. The function of mercuric acetate is thus limited to elimination

of parallel oxidation by bromine which would have been formed as a result of interaction between bromide ion and bromate³ ion.

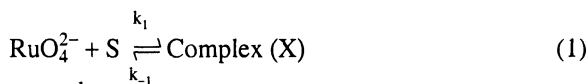
TABLE-1
EFFECT OF VARIATION [REACTANTS] ON THE REACTION RATE AT 35°C
[Hg(OAc)₂] = 3.00 × 10⁻³ M

^a [KBrO ₃] × 10 ⁴ M	1.10	1.40	1.80	2.60	3.34	5.60
k ₁ × 10 ⁴ s ⁻¹	16.00	16.00	15.89	17.16	15.82	15.28
a → [Cyclopentanol] = 5.00 × 10 ⁻² M, [NaOH] = 1.00 × 10 ⁻² M, [Ru(VI)] = 5.00 × 10 ⁶ M and						
^b [Cyclopentanol] × 10 ² M	1.00	2.00	3.00	4.00	5.00	6.00
k ₁ × 10 ⁴ s ⁻¹	3.06	5.89	9.25	12.24	15.82	18.96
k ₂ × 10 ² M ⁻¹ L s ⁻¹	3.06	2.94	3.08	3.06	3.16	3.16
b → [KBrO ₃] = 3.34 × 10 ⁻⁴ M, [NaOH] = 1.00 × 10 ⁻² M, [Ru(VI)] = 5.00 × 10 ⁻⁶ M						
^c [Ru(VI)] × 10 ⁶ M	1.25	2.50	3.75	5.00	6.25	7.50
k ₁ × 10 ⁴ sec ⁻¹	3.88	8.25	12.50	16.00	20.12	24.25
k ₂ × 10 ⁻² M ⁻¹ L s ⁻¹	3.10	3.30	3.33	3.20	3.22	3.23
c → [KBrO ₃] = 1.40 × 10 ⁻⁴ M, [Cyclopentanol] = 5.00 × 10 ⁻² M, [NaOH] = 1.00 × 10 ⁻² M						

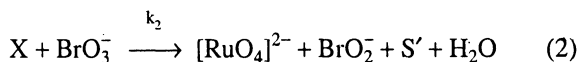
TABLE-2
EFFECT OF VARIATION OF [NaOH], [Hg(OAc)₂] AND IONIC STRENGTH (μ) OF THE
MEDIUM ON REACTION RATE AT 35°C, [KBrO₃] = 1.8 × 10⁻⁴ M
[Cyclopentanol] = 5.00 × 10⁻² M, [Ru(VI)] = 5.00 × 10⁻⁶ M

[NaOH] × 10 ² M	k ₁ × 10 ⁴ s ⁻¹	Ionic strength (μ) × 10 ³ M	k ₁ × 10 ⁴ s ⁻¹	[Hg(OAc) ₂] × 10 ³ M	k ₁ × 10 ⁴ s ⁻¹
0.50	1.63	10.18	15.89	1.00	1.52
1.00	1.58	18.18	15.45	1.50	1.54
1.50	1.62	22.18	16.71	2.00	1.52
2.00	1.58	30.18	16.07	2.50	1.51
2.50	1.65	40.18	15.71	3.00	1.53
3.00	1.63	50.18	15.09	4.50	1.52

The reactive species of potassium bromate in alkaline medium is reported⁴ as BrO₃⁻. Ruthenate ions, *i.e.*, RuO₄²⁻ obtained from dissolution of RuO₄ in NaOH solution, is a reactive species of Ru(VI) as further coordination of RuO₄²⁻ with OH⁻ forms unstable species⁵ [RuO₄(OH)³⁻]. Hence on the basis of the above statement and kinetic data, the following mechanistic steps are suggested.

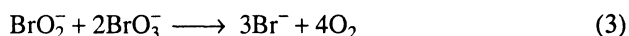


where S stands for cyclopentanol.



where S' stands for cyclopentanone.

Step (2) is slow and rate determining step.



Considering above steps (1)–(2) and applying steady state approximation to [X], we get a rate law (4) in terms of rate of loss of concentration of bromate ion.

$$\frac{-d[\text{BrO}_3^-]}{dt} = \frac{k_1[\text{BrO}_4^-][\text{RuO}_4^{2-}][\text{S}]}{k_{-1} + k_2[\text{BrO}_3^-]} \quad (4)$$

Since step (2) is slow, hence k_2 is small. Therefore on assuming $k_1 \gg k_2[\text{BrO}_3^-]$, the equation (4) may be written as equation (5):

$$\frac{-d[\text{BrO}_3^-]}{dt} = K[\text{BrO}_3^-][\text{RuO}_4^{2-}][\text{Cycloheptanol}] \quad (5)$$

where

$$K = k_1/k_{-1}$$

The rate law (5) explains all kinetic results. Hence the proposed mechanism is valid.

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