Oxidation of Catechol with Ceric Ammonium Sulphate

(MS.) REKHA SHARMA[a], ARVIND KUMAR[a] and R. K. PRASAD[b]*

[a]Department of Chemistry, M. I T., Muzaffarpur-842 003

[b]Department of Chemistry, L S. College Muzaffarpur-842 001

Yadav and Verma reported the oxidation of catechol by cerium(IV)[1]. In view of the fact that their results widely differ from ours[2], a detailed study of the oxidation of catechol by Ce^{IV} in sulphuric acid medium has been made.

Results and Discussion

Salient features of the stoichiometry of the reaction are presented in Table 1.

TABLE 1

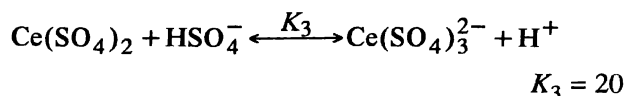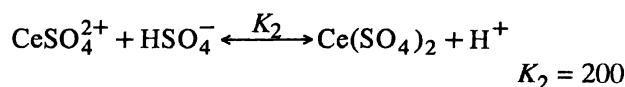| Method	Titrant	No. of moles of Ce^{IV} per mole of catechol	Product
Back titration with Ce^{IV}	Reaction mixture with excess of Ce^{IV}	2	o-Benzo-quinone
Potentiometric titration with Ce^{IV}	Fixed volume of catechol	2	o-Benzo-quinone
Potentiometric titration with order of addition changed		14	CO

The results of kinetic investigations are given in Table 2. From the measurements of k_1 at four different temperatures (298, 303, 308 and 313 K), activation energy ($E^{\dagger}$) and activation entropy ($\Delta S^{\#}$) are found to be 51.18 kJ mol^{-1} (13.67 kcal mol^{-1}) and -103.83 JK^{-1} mol^{-1} (-24.84 e.u.) respectively. Based on the kinetic results the following tentative mechanism is proposed,

$$Ce^{4+} + S \longrightarrow R + Ce^{3+} + H^+$$

$$Ce^{4+} + R \longrightarrow P_1 + Ce^{3+} + H^+ \qquad (1)$$
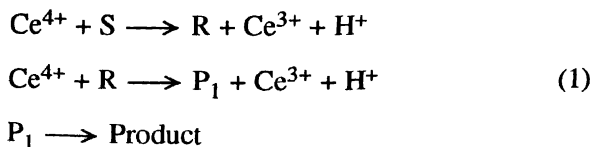
$$P_1 \longrightarrow Product$$

where S is catechol, R the intermediate free radical and P_1 intermediate product (o-benzoquinone). This leads to the following rate law,

$$\frac{-d[Ce^{IV}]}{dt} = k[S][Ce^{IV}] = k_1[Ce^{IV}] \qquad (2)$$

where, $k_1 = k[S]$, and $k = k (H^+, HSO_4^+)$. The nature of the function can be determined from the reactive forms of Ce^{IV}. In H_2SO_4 medium, Hardwick and Robertson[3] established the following equilibria among the various Ce^{IV} species,

$$Ce^{4+} + HSO_4^- \xrightarrow{K_1} CeSO_4^{2+} + H^+ \qquad K_1 = 3500$$

$$CeSO_4^{2+} + HSO_4^- \xrightarrow{K_2} Ce(SO_4)_2 + H^+$$
$$K_2 = 200$$

$$Ce(SO_4)_2 + HSO_4^- \xrightarrow{K_3} Ce(SO_4)_3^{2-} + H^+$$
$$K_3 = 20$$

Calculations using these equilibria would show that at a fixed $[HSO_4^-]$, as $[H^+]$ increases the relative concentration of $Ce(SO_4)_3^{2-}$ decreases while those of the other species increase. In the range of $[H^+]$ used here $[Ce^{4+}]$ and $[CeSO_4^{2+}]$ are negligibly small and

$$[Ce^{4+}]_T = [Ce(SO_4)_2] + [Ce(SO_4)_3^{2-}] \qquad (4)$$

Now, we assume that both $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ react with the substrate and the former is more reactive. For low $[H^+]$ (< 1 M) the $[Ce(SO_4)_2]$ is relatively small and therefore the reaction with $[Ce(SO_4)_3^{2-}]$ dominates. As $[H^+]$ increase, the $[Ce(SO_4)_2]$ increases and even though $[Ce(SO_4)_3^{2-}]$ remains larger, the reaction with the former dominates due to its greater reac-

TABLE 2

Analysis	Observation	Inference
k_1 vs [Ce^{IV}]	Insensitive	First order w.r.t. Ce^{IV}
log k_1 vs log [catechol]$^{-1}$	Linear	First order w.r.t. catechol
k_1^{-1} vs [catechol]$^{-1}$	No intercept on ordinate axis	No complex formation
UV-spectra of reaction mixture neutralised with NaOH	No new peak	No complex formation
Effect of [H$_2$SO$_4$] and [HSO$_4^-$]	Rate of reaction reduced	
log k_1 vs log [H$^+$]	Curve with slope changing from +ve to –ve	Reactive form of Ce^{IV} in the low and high [H$^+$] are different
Effect of Ce^{III} sulphate	No effect	Slow step of reaction is not reversible
Acrylonitrile	Viscous liquid	Free radical intermediate

tivity. This leads to two rate laws

$$k_1 = \frac{k'[S]\left[H^+\right]}{K_3\left[HSO_4^-\right]+\left[H^+\right]} \text{ and}$$

$$k_1 = \frac{k''K_3[S]\left[HSO_4^-\right]}{K_3\left[HSO_4^-\right]+\left[H^+\right]}$$

A plot of k_1^{-1} vs [H$^+$]$^{-1}$ in low [H$^+$] and that of k_1^{-1} vs [H$^+$] in higher [H$^+$] are linear. This is in conformity with the suggested mechanism. From the slopes and intercepts of these plots we have, at [S] = 4 × 10^{-2} M and [HSO$_4^-$] = 0.25 M, $k' = 1.56$, $k'' = 0.33$ and $k_3 = 14$.

The activation energy value is consistent with oxidation via splitting of the O–H bond and the large negative activation entropy indicates a mechanism involving H$^+$, Ce^{4+} species and the substrate in the activated complex.

Experimental

Stock solutions of ceric ammonium sulphate and

TABLE 3 – EFFECT OF [REACTANT]$_O$ ON THE PSEUDO-FIRST ORDER RATE CONSTANT $(k_1)^*$

[H$_2$SO$_4$] = 0.25 mol dm^{-3}, temp. = 308 K, λ = 360 nm

× 10^3 [Ce^{IV}]$_o$ mol dm^{-3}	× 10^2 [Catechol]$_o$ mol dm^{-3}	× 10^3 k_1 (s^{-1})
2.02	1.5	1.45
2.02	2.0	2.10
2.02	3.0	2.80
2.02	4.0	4.14
1.01	4.0	4.10
0.05	4.0	4.15

*Reproducibility, ± 4%.

TABLE 4 – EFFECT OF [HSO$_4^-$] AND [H$^+$] ON k_1

[Ce^{IV}] = 2.02 × 10^3 mol dm^{-3}, [Catechol] = 4.0 × 10^2 mol dm^{-3}, [H$_2$SO$_4$] = 0.25 mol dm^{-3}, temp. = 308 K

[HSO$_4^-$] mol dm^{-3}	[H$^+$] mol dm^{-3}	× 10^3k_1 s^{-1}
0.25	0.25	4.14
0.35	0.25	3.57
0.45	0.25	2.90
0.25	0.50	7.70
0.25	1.5	13.33
0.25	1.5	8.60
0.25	2.0	7.14
0.25	3.0	6.25
0.25	4.0	5.40

catechol (both B.D.H.) were prepared in 0.5 M H$_2$SO$_4$ and the solutions were standardised with Mohr's salt and KBrO$_3$–KBr mixture respectively.

Potentiometric titrations were carried out with a Systronics 355 pH meter using Pt-saturated calomel electrode combination. The uv absorbance was measured on a SICO-SPEC GL 200 spectrophotometer. Constant temperature was maintained in a thermostat (± 0.05°).

References

1. R. L. YADAV and R. G. VERMA, *I. Indian Chem. Soc.*, 1981, **58**, 768.

2. R. S. SINGH, P. N. JHA and R. K. PRASAD, *Proc. Nat. Scad. Sci.*, 1985, **57**, 271.

3. T. J. HARDWICK and E. ROBERTSON, *Can. J. Chem.*, 1951, **29**, 828.