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Kinetics of Oxidation of 2,4 Dinitrophenol by Cerium (IV)

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The oxidation of 2,4 dinitrophenol (DNP) by cerium (IV) in aqueous H_2SO_4 medium is first order each in [oxidant] and [DNP] and fractional order in $[H^+]$. Activation parameters are evaluated and a suitable mechanism is proposed.

INTRODUCTION

Extensive studies have been carried out[1–6] on the oxidation kinetics of different phenols with various oxidants, but no unequivocal conclusion has been drawn regarding the reaction mechanism. The meagre information and controversy regarding the mechanism of oxidation of nitrophenols prompted us to undertake this investigation.

EXPERIMENTAL

All the chemicals were of AR grade. Doubly distilled water was used for preparing the solutions. Due to low solubility of 2,4-dimitrophenol (DNP) in water, its standards solution was prepared in 0.0033 mol dm^{-3} NaOH solution.

The reaction was initiated by the addition of requisite quantities of Ce(IV) solution to (DNP) solution after thermostating the two solutions separately for 1 hr. at constant temperature (± 0.1 K) in reaction flasks blackened from outside. The reaction was monitored by estimating volumetrically the unconsumed oxidant by a standard mohr's salt solution using ferroin as redox indicator.

Under the conditions of [Ce(IV)] >> [DNP], cerium(IV) was allowed to react with (DNP) for 48 hrs and the excess of oxidant was estimated. Value of Δ [Ce(IV)]/Δ [DNP] revealed 2:1 stoichiometry (oxidant: substrate) according to the following equation:

$$(NO_2)_2C_6H_3OH + 2Ce(IV) + H_2O \rightarrow (NO_2)_2C_6H_2O_2 + 2Ce(III) + 4H^+$$

However, the product of oxidation could not be isolated.

Positive polymerisation tests were obtained by methyl-methacrylate and

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acrylamide as described by us earlier[7,8], showing that the oxidation process involves a free radical mechanism.

RESULTS AND DISCUSSION

The kinetic investigations were carried out at several initial concentrations of Ce(IV) and [DNP]. It was found that the experimental results were **best-fit** to the first order kinetic expression:

$$k_1 = 2.303/t \log a/(a - x)$$

The k_1 values were found to be constant and a plot of log a/(a–x) vs time gave a straight line with a slope equal to 2.303/k. The effect of varying [DNP] in the range $1.00 - 1.42 \times 10^{-3}$ M did not produced any significant change to the reaction rate suggesting first order behaviour with respect to the substrate. Similarly, the effect of varying [oxidant] in the range $1.82 - 2.50 \times 10^{-2}$ M, the plot of log k vs log [oxidant] was found to be linear with a unit slope suggesting that the order with respect to the oxidant is also one.

To study the effect of $[H^+]$ ions on rate of reaction, experiments were conducted in the range 0.25–1.50 mol dm^{-3} H_2SO_4. The log-log plots were linear having slope less than 0.5 indicating fractional order dependence of rate on $[H^+]$. The rate of reaction was found to decrease on increasing the sulphuric acid concentration, Table-1.

TABLE 1

RATE DEPENDENCE ON SULPHURIC ACID CONCENTRATION AT 303 K

$[DNP] = 1.25 \times 10^{-3}$ mol dm^{-3}; $[Ce(IV)] = 2.00 \times 10^{-2}$ mol dm^{-3}

$[NaOH] = 0.33 \times 10^{-2}$ mol dm^{-3}

$[H_2SO_4]$ mol dm^{-3}	1.50	1.00	0.50	0.25
$10^4 k_1 (sec^{-1})$	2.38 ± 0.01	2.88 ± 0.01	3.22 ± 0.02	3.90 ± 0.02

The decrease in rate with increasing $[H_2SO_4]$ is due to the existence of various complex in solution as described in our earlier paper[9]. Since the rates were not influenced by added salts, no attempt was made to maintain the ionic strength constant during the rate measurements.

Activation parameters

To determine activation parameters, the reaction velocities were studies at four temperatures (298–313 K). The values of activation parameters are given in Table 2.

TABLE 2
ACTIVATION PARAMETERS

$[Ce(IV)] = 2.00 \times 10^{-2}$ mol dm^{-3}; $[H_2SO_4] = 1.00$ mol dm^{-3}

$[DNP] = 1.25 \times 10^{-3}$ mol dm^{-3}; $[NaOH] = 0.33 \times 10^{-2}$ mol dm^{-3}

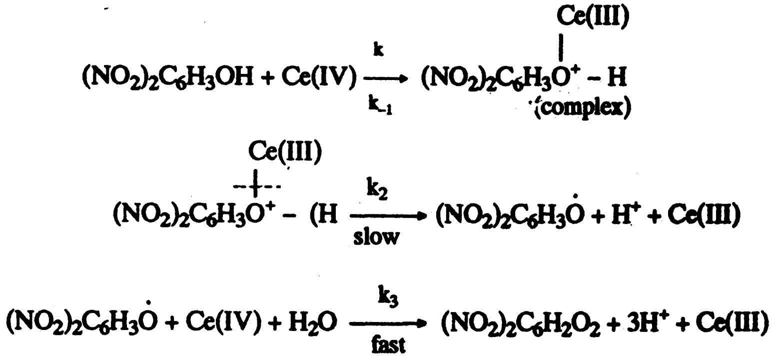
Temp K	10^4 k_1 sec^{-1}	$-\Delta S^*$	10^{-2} pZ sec^{-1}	ΔH^*	ΔF^*	E_a
298	2.57	41.88	0.638	90.00	94.09	92.45
303	2.89	37.38	0.627	89.96	95.41	
308	3.24	33.08	0.640	89.92	96.72	
313	8.62	36.28	0.636	89.88	95.73	

ΔH^*, ΔF^*, E_a are in k J mol^{-1} while ΔS^* is in JK^{-1} mol^{-1}

Reaction rates were found to increase with temperature. The entropy of activation (ΔS^*) is negative suggesting the rigid nature of the transition state. The plot of k^{-1} vs $[DNP]^{-1}$ is also linear with a positive intercept suggesting Michaelis-Mention type of kinetics i.e. (DNP) forms a complex with Ce(IV), which decomposes to form the product through free radical.

Mechanism

Based on the above experimental observations, the following probable mechanism is proposed:



$$(NO_2)_2C_6H_3OH + Ce(IV) \underset{k_{-1}}{\overset{k}{\longrightarrow}} (NO_2)_2C_6H_3\overset{\overset{\displaystyle Ce(III)}{|}}{O^+} - H \text{ (complex)} \quad (i)$$

$$(NO_2)_2C_6H_3\overset{\overset{\displaystyle Ce(III)}{|}}{O^+} - (H \xrightarrow[slow]{k_2} (NO_2)_2C_6H_3\dot{O} + H^+ + Ce(III) \quad (ii)$$

$$(NO_2)_2C_6H_3\dot{O} + Ce(IV) + H_2O \xrightarrow[fast]{k_3} (NO_2)_2C_6H_2O_2 + 3H^+ + Ce(III) \quad (iii)$$

$$(NO_2)_2C_6H_3OH + 2Ce(IV) + H_2O \rightarrow (NO_2)_2C_6H_2O_2 + 4H^+ + Ce(III)$$

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