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Oxidation of *s*-Butyl Alcohol by Cerium(IV)

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The oxidation of *s*-butyl alcohol by Ce(IV) in dilute nitric acid medium has been studied. The reaction is of first order with respect to Ce(IV)but of fractional order with respect to *s*-butyl alcohol. A plot of inverse of alcohol concentration against inverse of observed first order rate constant gave a straight line which did not pass through the origin. This suggests an intermediate Ce(IV)-alcohol complex formation. By repeating this procedure at different temperatures the formation constants of the complex and the thermodynamic parameters for the complex formation process have been evaluated. Hydrogen, nitrate, and sulphate ions decrease the rate of oxidation. The results have been explained on the basis of equilibrium $Ce^{4+}+H_2O \overset{K_h}{\rightleftarrows} Ce(OH)^{3+}+H^+$ and assuming $Ce(OH)^{3+}$ as the reactive species of Ce(IV). From the slope-intercept of straight line obtained between inverse of observed rate constant and [H$^+$], value of $K_h=6.19$ at 35°C has been evaluated in dilute nitric acid at $\mu=2.55$ M. A mechanism in which the first step is the rapid reversible formation of a complex between Ce(IV) and Substrate followed byα-C-H bond rupture in the rate determining step has been suggested.

The oxidation of *s*-butyl alcohol by ceric salts in dilute nitric acid has been examined by Sethuram and Muhammad.[1] The present paper reports some additional data on the oxidation of *s*-butyl alcohol by cerium(IV) in nitric acid to elucidate the mechanism of oxidation.

Experimental

Material. B.D.H. "Analar" *s*-butyl alcohol was used after distillation. Ceric ammonium nitrate A.R. (Atomic Energy Commission, India) and Nitric acid A.R. (Oster, India) were used. All other chemicals used were of analytical grade. All solutions for kinetic studies were prepared in doubly distilled water.

Kinetic Measurements. The reactions were carried out at constant temperature (±0.05°C) with the reaction vessel covered with black paint. The reaction system consisted of ceric ammonium nitrate [$\sim 4.0\times10^{-3}$ M], alcohol [$\sim 5.0\times10^{-2}$ M] and nitric acid [$\sim$1.08 M] with a total volume of 100 m*l* and at an ionic strength $\mu=1.13$. The ionic strength was kept constant by the addition of sodium perchlorate. It was found that the change in ionic strength ($\sim$1.13 to 2.63) does not appreciably change the rate of oxidation. Nitric acid was used as a source of hydrogen ions and nitrate ion concentration was adjusted with potassium nitrate solution.

The rate of oxidation was followed by withdrawing aliquots at appropriate intervals of time and quenching the latter in known excess of ferrous ammonium sulphate, back titrating the excess of the latter by standard ceric sulphate using ferroin as an indicator. Reactions were usually conducted for 50—60% conversion of ceric ion.

Results and Discussion

Rate Laws. When *s*-butyl alcohol was in excess, the rate at which cerium(IV) disappears followed the first order rate law, agreeing with the findings of Sethuram and Muhammad.[1] The graphical method was generally used to derive the rate constants.

Table 1. Variation of rate with concentration of *s*-butyl alcohol

[Ce(IV)]: 4.0×10^{-3} M; [HNO_3]: 1.08 M; Temp.: 25°C. $\mu=1.13$ M

[Alcohol] $\times10^2$ mol/*l*	5.0	10.0	15.00	20.0	25.0
$k_1\times10^3$ min^{-1}	2.23	4.06	5.15	6.66	7.69

In a constant cerium(IV) concentration, it was found that the rate of oxidation rises with increase in alcohol concentration but tends to reach a limiting value at high concentrations of alcohol (Table 1). A plot of the inverse of alcohol concentration against that of observed rate constants gave a straight line. The result suggests that the oxidation proceeds through

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[1] B. Sethuram and S. S. Muhammad, *Acta Chim. Hung.*, **46**, 115, 125 (1965).

the complex between the alcohol and cerium(IV) as has been suggested by Ardon.[2]

$$\text{Cerium(IV)} + s\text{-butyl alcohol} \overset{K}{\rightleftarrows} \text{complex}$$

$$\text{Complex} \xrightarrow[\text{slow}]{k_s} \text{Cerium(III)} + \text{Free radical} + \text{H}^+$$

$$\text{Free radical} + \text{Cerium(IV)} \xrightarrow{\text{fast}} \text{Ketone} + \text{Cerium(III)} + \text{H}^+$$

The variation of rate of oxidation with concentration of alcohol is given by the expression

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{k_s[\text{Alcohol}][\text{Ce(IV)}]}{1/K + [\text{Alcohol}]}$$

From the slope-intercept ratio, $K=2.50$ and $K_s = 3.34\times 10^{-4}\,\text{sec}^{-1}$ at 25°C have been obtained.

By repeating the procedure at various temperatures, the formation constants (K) have been calculated at different temperatures (Table 2). The thermodynamic data on the cerium(IV)-alcohol complex are listed in Table 3.

TABLE 2. EFFECT OF TEMPERATURE ON FORMATION OF CERIUM(IV)-*s*-BUTYL COMPLEX

[Ce(IV)]: 4.0×10^{-3} M; [HNO$_3$]: 1.08 M, $\mu=1.13$ M

Temp., °K	298	303	308
K, l/mol	2.50	1.97	1.62

TABLE 3. THERMODYNAMIC CONSTANTS OF THE CERIUM(IV) - *s*-BUTYL ALCOHOL COMPLEX

Property	By Sethuran and Muhammad[1] at 22°C	Present work at 25°C and [H$^+$]: 1.08, μ: 1.13 M
K l/mol	2.213	2.50
$-\Delta H$ kcal/mol	6.75	7.66
$-\Delta F$ cal/mol	465.8	540.8
$-\Delta S$ e. u.	-23.06	-23.90

The difference in the values reported by Sethuram and Muhammad[1] and those obtained in the present investigation might be due to different experimental conditions. The value of the formation constant of the Ce(IV) -alcohol complex probably depends upon hydrogen ion concentration used. The authors[1] gave no idea of the hydrogen ion concentration used by them.

The variation of rate constants with temperature is shown in Table 4.

TABLE 4. EFFECT OF TEMPERATURE ON THE RATE OF REACTION

[Ce(IV)]: 4.0×10^{-3} M: [Alcohol]: 5.0×10^{-2} M; [HNO$_3$] = 1.08 M

Temp., °K	298	303	308	313
$k_1\times 10^5$ sec^{-1}	3.71	6.83	10.4	21.6

The apparent energy of activation E was calculated to be 22.0±1.0 kcal by plotting $\log k_1$ *vs.* $1/T$.

At constant nitrate ion concentration increase in hydrogen ion concentration causes a slight but distinct decrease in the rate of oxidation. (Table 5).

TABLE 5. VARIATION OF RATE WITH CONCENTRATION OF HYDROGEN IONS

[Ce(IV)]: 4.0×10^{-3} M, [Alcohol]: 5.0×10^{-2} M; Temp.: 35°C; [NO$_3^-$]: 2.5 M; $\mu=2.55$ M

[H$^+$] mol/l	0.50	0.90	1.50	2.0	2.5
$k_1\times 10^3$ min^{-1}	7.17	6.76	6.07	5.81	5.48

The effect of hydrogen ion concentration may be explained on the basis of the equilibrium

$$\text{Ce}^{4+} + \text{H}_2\text{O} \rightleftarrows \text{Ce(OH)}^{3+} + \text{H}^+ \qquad (1)$$

If it is assumed that Ce(OH)$^{3+}$ is a more powerful oxidant than Ce^{4+}, then an increase in the concentration of hydrogen ions should decrease the concentration of Ce(OH)$^{3+}$ and hence the rate of oxidation. The small effect of the concentration of hydrogen ions on the rate of oxidation suggests that the value of the equilibrium constant for reaction (1) is small. At the total concentration of cerium(IV) used, cerium exists mostly as Ce(OH)$^{3+}$ or Ce^{4+}, concentration of the dimer (Ce–O–Ce)$^{6+}$ being negligibly small.

If reaction (1) is valid and [Ce(IV)] represents the total concentration of cerium(IV), we have

$$[\text{Ce(OH)}^{3+}] + [\text{Ce}^{4+}] = [\text{Ce(IV)}]$$

$$\text{and}\quad K_h = \frac{[\text{Ce(OH)}^{3+}][\text{H}^+]}{[\text{Ce}^{4+}]}$$

$$= \frac{[\text{Ce(OH)}^{3+}][\text{H}^+]}{[\text{Ce(IV)}] - [\text{Ce(OH)}^{3+}]}$$

$$\text{or}\quad K_h[\text{Ce(IV)}] = [\text{Ce(OH)}^{3+}]\{[\text{H}^+] + K_h\}$$

$$\text{or}\quad [\text{Ce(OH)}^{3+}] = \frac{K_h[\text{Ce(IV)}]}{[\text{H}^+] + K_h}$$

The rate of oxidation will be given by the equation

$$\frac{-d[\text{Ce(IV)}]}{dt} = K'\frac{K_h}{[\text{H}^+] + K_h}\cdot[\text{Ce(IV)}]$$

$$= k_1[\text{Ce(IV)}]$$

$$\text{hence}\quad k_1 = \frac{K'K_h}{[\text{H}^+] + K_h}$$

where K_h is the equilibrium constant for reaction (1), k_1 is the observed first order rate constant, and K' is a constant which includes the concentration of alcohol (which is kept constant). Hence we have

$$\frac{1}{k_1} = \frac{1}{K'K_h}\cdot[\text{H}^+] + \frac{1}{K'}$$

A plot of $1/k_1$ against [H$^+$] gave a straight line in the case of *s*-butyl alcohol. The value of K_h was found to be 6.19 at 35°C. The value of K_h found spectrophotometrically by Hardwick and Robertson[3] in HClO$_4$ for reaction (1) was 5.2 at 25°C. This supports the view that in the present investigation Ce(OH)$^{3+}$ may probably be the active species.

It may, however, be pointed out that Sethuram and Muhammad[1] observed that at constant nitrate

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[2] M. Ardon, *J. Chem. Soc.*, **1957**, 1811.

[3] T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

ion concentration, the increase in the H^+ ion concentration was found to accelerate the rate of oxidation. They suggested $[Ce(H_2O)_2(NO_3)_4]$ as the neutral active species. We have not been able to confirm this result.

Table 6. Effect of nitrate ion on the rate of oxidation

[Ce(IV)]: 4.0×10^{-3} M; [Alcohol]: 5.0×10^{-2} M; [HNO]: 0.50 M; Temp.: 35°C.

$[KNO_3]$ mol/l	0.00	0.20	0.40	0.60	0.80	1.00
$k_1\times10^4$ min^{-1}	7.13	6.98	6.71	6.58	6.20	6.01

The nitrate ion was found to inhibit oxidation to a small extent (Table 6). The retardation caused by nitrate ions has also been indicated by Sethuram and Muhammad[1] who observed a linear relationship between observed rate constant and the square of the nitrate ion concentration. The retardation caused by nitrate ions is not so strong as indicated by them. The small retarding effect observed by us can not be attributed to the effect of the ionic strength as well. Shorter[4] explains this inhibiting action of nitrate ions during the oxidation of acetone by ceric ammonium nitrate in nitric acid, by conversion of $Ce(OH)^{3+}$ into a much less reactive species $[Ce(OH)NO_3]^{2+}$:

$$Ce(OH)^{3+} + NO_3^- \rightleftharpoons [Ce(OH)NO_3]^{2+} \qquad (2)$$

Addition of sulphate ion retarded the rate of oxidation considerably. The results on the effect of addition of sulphate ions on the rate of oxidation are given in Table 7.

Table 7. Effects of sulphate ions on the rate of oxidation

[Ce(IV)]: 4.0×10^{-3} M; [Alcohol]: 10.0×10^{-2} M [HNO_3]: 1.08 M; Temp.: 25°C.

$[Na_2SO_4]\times10^3$ mol/l	0.00	5.0	10.0	15.0	20.0	25.0
$k_1\times10^3$ min^{-1}	4.06	2.88	2.30	1.92	1.60	1.40

A plot of $1/k_1$ against $[SO_4^{2-}]$ gave a straight line.

The results find an explanation on the assumption that $Ce(OH)^{3+}$ forms complexes with SO_4^{2-} of the type (*cf.* Hargreaves and Sutcliff[5]),

$$Ce(OH)^{3+} + SO_4^{2-} \overset{k_b}{\rightleftharpoons} [Ce(OH)SO_4]^+ \qquad (3)$$

and that the complex $[Ce(OH)SO_4]^+$ is a poor oxidant as compared with $Ce(OH)^{3+}$.

If reaction (3) is valid, $[Ce(IV)]=[Ce(OH)^{3+}]+[Ce(OH)SO_4^+]$, the observed rate constant will be related to the concentration of sulphate ions by the expression

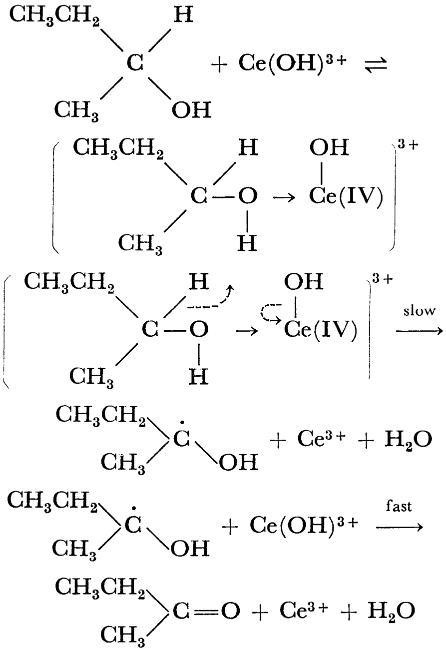
$$k_1 = \frac{K''}{1+K_b[SO_4^{2-}]}$$

$$\text{or}\quad \frac{1}{k_1} = \frac{K_b}{K''}\cdot[SO_4^{2-}] + \frac{1}{K''}$$

where k_1 is the observed rate constant and K'' is a constant which includes the concentration of alcohol. From the above relationship, the inverse of the observed rate constant plotted against concentration of sulphate ions should be a straight line as has been observed.

Our results suggest $Ce(OH)^{3+}$ as the reactive species. The colour change of the ceric solution from yellow to reddish brown when alcohol was added indicates the formation of an intermediate complex which has also been established spectrophotometrically.[1]

On the basis of the low value of $k_{CH}/k_{CD}=1.9$ for α-deuterioalcohol during the oxidation of deuterated cyclohexanol by ceric sulphate and $k_{OH}/k_{OD}=1.0$ for oxygen deuterium alcohol, Littler and Waters[6] and Littler[7] suggested that the α-carbon hydrogen fission might be preponderant, though Littler[8] suggested that a concerted mechanism involving both C–H and O–H fissions can not be ruled out. Thus, the mechanism for the oxidation of *s*-butyl alcohol by cerium (IV) in nitric acid may be written as



$Ce(OH)^{3+}$ is written as an oxidising species. The ligand groups like NO_3^-, H_2O, *etc.* have not been indicated for the sake of simplicity.

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4) J. Shorter, *J. Chem. Soc.*, **1962**, 1868.

5) G. Hargreaves and L. H. Sutcliff, *Trans. Faraday Soc.*, **51**, 1105 (1955).

6) J. S. Littler and W. A. Waters, *J. Chem. Soc.*, **1960**, 2767.

7) J. S. Littler, *ibid.*, **1959**, 4135.

8) J. S. Littler, *ibid.*, **1962**, 2190.