

results for oxidation of *n*-butanol as a typical alcohol. Oxidation of *n*-butanol by ceric perchlorate in the temperature range 10°–15° C,  $[\text{HClO}_4] = 0.5\text{--}2\text{ M}$ , ionic strength = 2.1 M in sodium<sup>+</sup> perchlorate both under deaerated and undeaerated conditions has been studied. The reaction has been followed by determining the rate of ceric disappearance by titrimetry with excess of ferrous ion and back titration with standard ceric ammonium sulphate. Concentrations of ceric ion, *n*-butanol and hydrogen ion, initially added cerous ion, ionic strength and temperature have been employed as variables. The rate is first-order with respect to ceric ion concentration. The pseudo first-order rate constant obtained under conditions of  $[\textit{n}\text{-butanol}] \gg [\text{Ce}^{4+}]$  gives an order of ca. 0.5 for butanol. On the other hand plots of  $1/\text{Rate}$  vs.  $1/[\textit{n}\text{-butanol}]$  as well as  $1/\text{Rate}$  vs.  $1/[\text{H}^+]$  are linear. Increase of ionic strength and initially added cerous ion have very little effect on the rate.

Our results may be explained on the basis of formation of ceric-butanol complex in 1:1 ratio and unimolecular decomposition of the complex as the rate-determining step. On the basis of the relationship

$$\text{Rate} = k_{\text{obs.}} [\text{Ce}^{4+}]_{\text{Total}} = k_t [\text{Complex}]$$

we get

$$\frac{1}{k_{\text{obs.}}} = \frac{1}{k_t} + \frac{1}{k_t K [\text{B}]} + \frac{K_h}{k_t K [\text{B}] [\text{H}^+]}$$

if  $k_t$  = theoretical rate constant;  $[\text{B}] = [\text{Butanol}]$ ;  $K$  is the equilibrium constant for ceric-butanol complex and  $K_h$  is the hydrolytic constant for  $\text{Ce}^{4+}$ . From plots of  $1/k_{\text{obs.}}$  vs.  $1/[\textit{n}\text{-butanol}]$  as well as  $1/k_{\text{obs.}}$  vs.  $1/[\text{H}^+]$  values of  $k_t$ ,  $K_h$  and  $K$  have been evaluated at temperatures 10–15° C. Values of  $\Delta H$  for  $K_h$  and  $K$  are 15.9 and 1.537 k. cal./mole respectively. The former value is in good agreement with that of 15.3 k. cal./mole reported by Hardwick and Robertson.<sup>13</sup> Values of  $\Delta S$  for  $K_h$  and  $K$  are 56.83 and 11.61 e.u. respectively. Further,  $k_t = 4.834 \times 10^{17} \text{ exp.}$

### OXIDATION OF *n*-BUTANOL BY CERIC IONS IN AQUEOUS SOLUTION

OXIDATIONS of various organic substrates—formaldehyde,<sup>1</sup> acetone and other ketones,<sup>2</sup> glucose and levulose,<sup>3</sup> mandelic,<sup>4</sup> lactic,<sup>5</sup> citric<sup>6</sup> and malonic acids,<sup>7</sup> ethanol,<sup>8</sup> methanol,<sup>9</sup> cyclohexanol,<sup>10</sup> glycerol<sup>11</sup> and polyvinyl alcohol<sup>12</sup>—by ceric ion have all been explained on the basis of homolytic fission of O–H or C–H bond in the substrate and electron transfer to ceric ion resulting in the formation of  $\text{H}^+$ ,  $\text{Ce}^{3+}$ , and substrate-free radical; further reactions of the latter radical with  $\text{Ce}^{4+}$  bring about degradation to stable products. We have studied oxidation of butanols and propanols and present our

$(-26,760/RT)$  sec.<sup>-1</sup> and  $A = (kT/h) e \exp. (20.46/R)$  sec.<sup>-1</sup> have also been obtained.

We wish to conclude that our results may be explained on the basis of  $Ce^{4+}$  (aq.) and not  $CeOH^{3+}$  (aq.) as the active species for oxidation; fission of O—H bond of alcohol accompanied by electron transfer to  $Ce^{4+}$  leads to formation of *n*-butyraldehyde which is rapidly oxidised to stable *n*-butyric acid. A detailed paper consisting of experimental results, mechanism, etc., for oxidation of various alcohols by ceric ion will appear elsewhere.

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