OXIDATION OF ETHANOL BY Ce(IV) IN ACID NITRATE MEDIUM

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The oxidation kinetics of ethanol by Ce(IV) has been studied as a function of pH, nitrate and water concentration. Even at high concentration of $\text{H}^+$ and $\text{NO}_3^-$ several species appear to exist. The oxidation is fastest in strongly acidic medium without added nitrate ions.

INTRODUCTION

Recently, a kinetic and mechanistic study with Ce(IV) in an acidic sulfate medium has been published /1/. Also perchlorate media are frequently used /2/, whereas some kinetic studies were performed in both nitric acid medium /3–4/ and mixtures of nitric acid and acetonitrile, although this may result in simultaneous oxidation of the solvent, complicating the calculation of reaction parameters /5/.

A frequently used /6–8/ and readily available Ce(IV) salt is CAN, ammonium-hexanitratocerate(IV). In using this reagent for the oxidation of alcohols, we found that it appeared to be very difficult to obtain a solution in which a single Ce(IV) species predominates during the reaction. Even when using acidic media and excess nitrate, several Ce(IV) species (formed by ligand exchange and/or hydrolysis and dimer formation) seem to be present.
A previous study dealing with CAN oxidation of methanol /6/, used only conversion degrees up to 50% (with $[\text{Ce}] = 2 \times 10^{-2} \text{M}$ and aqueous systems. The present paper describes the reaction between CAN and ethanol with special attention given to the variation in the concentration of the reagents.

**EXPERIMENTAL**

Ammoniumhexanitratocerate(IV) (Merck, purity $\geq 99\%$), ethanol (Baker), nitric acid (Merck, 65%), perchloric acid (Baker, 70.1%) and ammonium nitrate (Fischer) were all used without further purification. In a few experiments ethanol was further dried on molecular sieves, type 3A (Merck).

The spectrophotometric and kinetic experiments were performed with a Varian-Techtron 658 double beam spectrophotometer (200–500 nm). 1.0 mm cells (Hellma, 110-QS) and 10.0 mm cells (Hellma, 160-B-QS) were used. The 10.0 mm cells were double walled and kept at a constant temperature ($\pm 0.05 ^\circ \text{C}$) by a thermostat.

Usually all reactants (except CAN) were mixed at room temperature. Then the calculated amount of solid CAN was added to the reaction mixture in the dark, in most cases it took less than 2 minutes to dissolve the CAN. Then the solution was transferred to the thermostated cell.

Because ethanol is applied in excess, calculations concerning the values of the pseudo n-th order rate constants $k$, and the overall reaction order $n$, were based on the equation

$$-\frac{dE}{dt} = k(E - E_\infty)^n,$$  \hspace{1cm} (1)

in which $E$ is the extinction measured at time $t$, and $E_\infty$ the value of $E$ at infinite time.

After integrating eq. (1) by the method of Runge-Kutta /9/, the parameters $k$, $n$, $E_\infty$ and $E_0$ ($E$ at $t = 0$) were determined by a Marquardt optimization technique /10/.