RUTHENIUM(III) CATALYZED OXIDATION OF HEXACYANOFERRATE(II) BY PERIODATE IN AQUEOUS ALKALINE MEDIUM

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Abstract
Ruthenium(III) catalyzed oxidation of hexacyanoferrate(II) by periodate in alkaline medium is assumed to occur via substrate-catalyst complex formation followed by the interaction of oxidant and complex in the rate-limiting stage and yield the products with regeneration of catalyst in the subsequent fast step. The reaction exhibits fractional order in hexacyanoferrate(II) and first-order unity each in oxidant and catalyst. The reaction constants involved in the mechanism are derived.

Keywords: Ru(III) catalysis, hexacyanoferrate(II), periodate

INTRODUCTION

Periodate ion has been used extensively in oxidations of organic compounds, particularly in the oxidations of glycols [1,2]. The oxidation of 1,2-diols by periodate has been shown to proceed by way of a cyclic intermediate [3]. This corresponds to an inner/sphere mechanism. However, the literature on the mechanism of oxidation reactions of inorganic materials by periodates is scanty.

The hexacyanoferrate(II) ion is a one-electron reducing agent with a relatively stable octahedral coordination sphere [4]. Its oxidation by various oxidizing agents, however, has rarely produced simple kinetics [5].

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Ruthenium(III) catalysis in redox reactions involves complexities due to the formation of different intermediates and oxidation states of Ru, etc. Hence, the title reaction has been studied in order to interpret the mechanism.

EXPERIMENTAL

Reagent grade chemicals were used. A stock solution of KIO\textsubscript{4} was prepared and kept in dark since periodate solutions are known to undergo photochemical decomposition \[6\]. Hexacyanoferrate(II) solutions were used immediately after they were prepared. The main products were found to be hexacyanoferrate(III) and iodate. Stoichiometry was found to be 1:2 as observed by measuring the amount of hexacyanoferrate(III) produced at infinite time. The concentrations of the remained oxidant \[7\] and the reductant \[8a\] were ascertained by standard methods. The concentration of the catalyst, Ru(III), was unchanged at the end of the reactions as found by the EDTA method \[8b\]. Activation parameters were evaluated in the range of 25-45°C.

The reaction path was followed by monitoring the absorbance of the product hexacyanoferrate(III) at 420 nm on a Hitachi 150-20 spectrophotometer (\(\varepsilon = 1060\pm10\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)). The ionic strength was maintained constant with potassium nitrate. Initial rates were calculated by using the plane mirror method \[9\] and were reproducible to within ±4%. Temperature was maintained within ±0.1°C. The uncatalyzed reaction studied earlier is very slow under the present experimental conditions.

RESULTS AND DISCUSSION

All the experiments were carried out under second-order conditions. The orders in oxidant, reductant and catalyst were determined from log-log plots of initial rates against concentration at constant alkali and ionic strength. The order in both [IO\textsubscript{4}\textsuperscript{-}] and [Ru(III)] was unity, while that in [hexacyanoferrate(III)] was fractional (0.8) (Table 1). Increase in alkali concentration and also ionic strength decreases the rate of reaction. It was also observed that added products Fe(CN)\textsubscript{6}\textsuperscript{3-} and IO\textsubscript{3}\textsuperscript{-} were without effect. The title reaction follows the approximate rate law,

\[-d[IO_4^-]/dt = k[Fe(CN)_6^{4+}]^{0.8}[IO_4^-][Ru(III)][OH^-]^{0.3}\]

The foregoing observations in the study of stoichiometry are consistent with