



Ruthenium(III) Catalyzed Oxidation of Fumaric Acid by Cerium(IV): A Kinetic and Mechanistic Approach

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Kinetics of ruthenium(III) catalyzed oxidation of fumaric acid by acidic cerium(IV) has been studied by the rate of disappearance of [Ce(IV)]. The reaction is zero order with respect to [Ce(IV)] and unity with respect to both [fumaric acid] and [catalyst]. Negative effect of [H⁺] and inverse first order with respect to [Cl⁻] was observed while negligible effect of variation of [HSO₄⁻] and ionic strength was observed. The result suggest the formation of a complex between substrate and hydroxylated species of ruthenium(III) in a fast step. This complex yields the product in a rate determining step. The complex reacts further with the acidic cerium(IV) species in a rate determining step to yield the products. The reaction constants involved in the mechanism and the activation parameters have been calculated. There is a good agreement between observed and calculated rate constants under different experimental conditions. Formic acid was detected as end product.

Key Words: Kinetics, Reaction mechanism, Oxidations, Cerium(IV) sulphate, Fumaric acid, Thermodynamic parameters.

INTRODUCTION

Transition metals in the higher oxidation state generally can be stabilized by chelation with suitable complex agent¹⁻⁴. Metal complexes¹⁻⁴ are good oxidants in acid or alkaline media under appropriate reaction conditions. However, our preliminary observations indicate that the oxidation of some organic compounds by Ce(IV) in aqueous sulphuric acid is kinetically sluggish and the process can be efficiently catalyzed by various metal ions even at trace concentration. Different metal ions catalysts⁵⁻⁹ have been used in the oxidation by cerium(IV). Among the different metal ions, ruthenium(III) and iridium(III) are highly efficient.

Reaction mechanism of various elementary reactions must be investigated to analyze the factors effecting the selectivity. Therefore, the basic study of catalytic reaction will provide the basis for improving catalyst selectivity and making high-efficiency catalyst. Absence of studies on the oxidation of fumaric acid by Ce(IV) has encouraged us to investigate the kinetic behaviour of the oxidation of fumaric acid by Ce(IV). Recently, ruthenium(III) catalyzed oxidation of methacrylic acid and maleic acid by tetravalent cerium in aqueous sulphuric acid medium by Singh *et al.*¹⁰⁻¹².

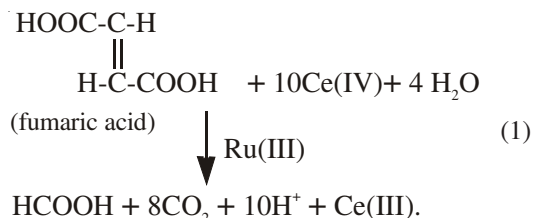
EXPERIMENTAL

Ceric sulphate solution was prepared by warming it in sulphuric acid and double distilled water. The strength of sulphuric acid was maintained at least 0.5 N. The ceric sulphate solution was standardized against ferrous ammonium sulphate using ferroin as indicator. Ceric sulphate, ferrous ammonium sulphate and ferroin were all B.D.H. while sulphuric acid was of A.R. Merck. Aqueous solutions of fumaric acid (B.D.H. Chemical Ltd. Poole England) were prepared by dissolving a weighed quantity of the sample in doubly distilled water. Stock solution of ruthenium trichloride was prepared by dissolving the sample (Johnson & Matthey Chemical Ltd.) in a solution of hydrochloric acid. The final concentrations of HCl and RuCl₃ were 4.00×10^{-3} and 4.76×10^{-3} mol dm⁻³, respectively. Other chemicals used were either AnalaR grade or chemically pure.

Kinetic studies: The reactants *i.e.* cerium(IV), sulphuric acid and catalyst [ruthenium(III)], were mixed in a black coated conical flask. The fumaric acid solution at 35 °C was then rapidly poured into the reaction mixture and the reaction was started with vigorous shaking of the reaction mixture and its progress was followed by titrating it against ferrous ammonium sulphate solution using ferroin as indicator and from these values the concentrations of remaining cerium(IV) were calculated at different intervals of time. The titre values of cerium

sulphate were directly proportional to the amount of ceric sulphate consumed in the mixture.

Stoichiometry and product analysis: The stoichiometry of fumaric acid and Ce(IV) sulphate reaction was determined by allowing the Ru(III) catalyzed oxidation to go to completion at room temperature by maintaining fumaric acid and Ce(IV) sulphate in 1:10 molar ratio. The observed stoichiometry was found to be:



Oxidation product of fumaric acid was detected as formic acid by thin layer spot test, using butan-1-ol-ethyl acetate-water (4:1:5 v/v/v) as the solvent⁷ and iodine as detecting agent ($R_f = 0.86$). The reported R_f value is consistent with the value of authentic sample as the reference one. In a typical experiment the solution of fumaric acid (0.02 M), Ce(IV) (0.2 M), Ru(III) (5×10^{-7} M) and H_2SO_4 (1.18 M) were allowed to stand for *ca.* 24 h in a thermostate to ensure completion of the reaction. The unreacted oxidant was assessed iodometrically. The result showed a mole ratio of consumption of Ce(IV) to reductant fumaric acid of 1:10.

RESULTS AND DISCUSSION

A kinetic study of oxidation of fumaric acid by cerium(IV) sulphate in presence of ruthenium(III) was investigated at several initial concentrations of the reactants. The zero order kinetics with respect to cerium(IV) was verified by the constant values of $(-dc/dt)$, obtained at various initial concentrations of cerium(IV) (Fig. 1). The reaction was observed to show linear relationship between $(-dc/dt)$ and [fumaric acid] (Fig. 2) indicating first order kinetics with respect to fumaric acid. Variation of initial concentration of ruthenium(III) increased the rate of oxidation of fumaric acid in direct proportionality,

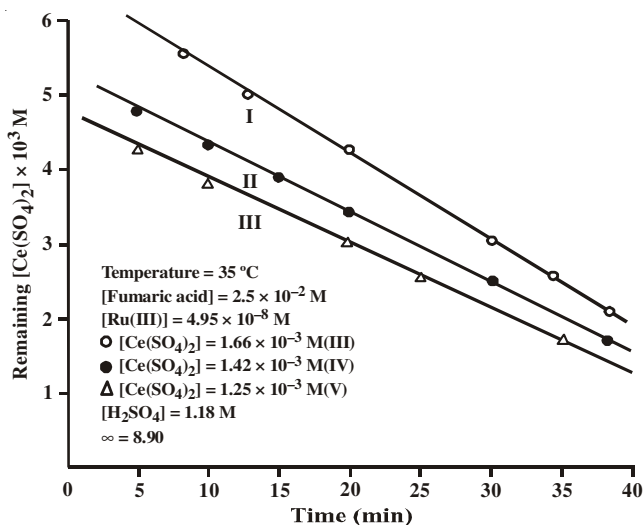


Fig. 1.

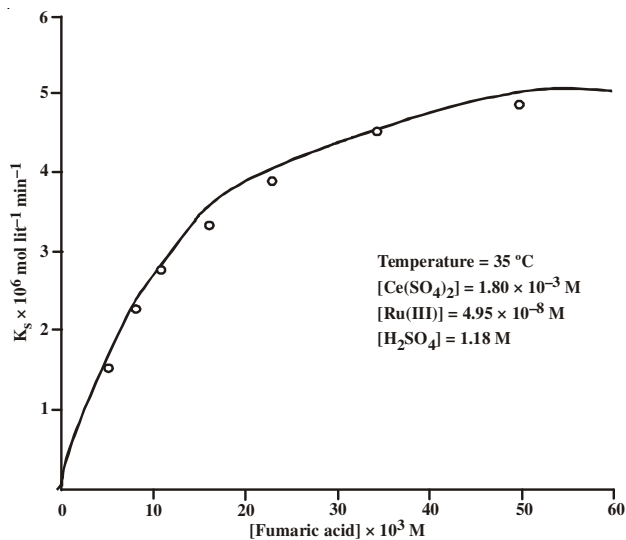


Fig. 2.

Showing first order kinetics with respect to [Ru(III)] (Fig. 3).

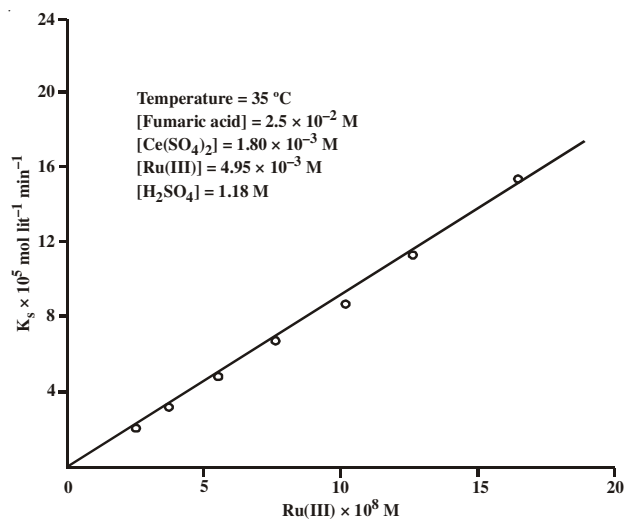


Fig. 3.

The rate of reaction was decreased on increasing the concentration of KCl (Fig. 4).

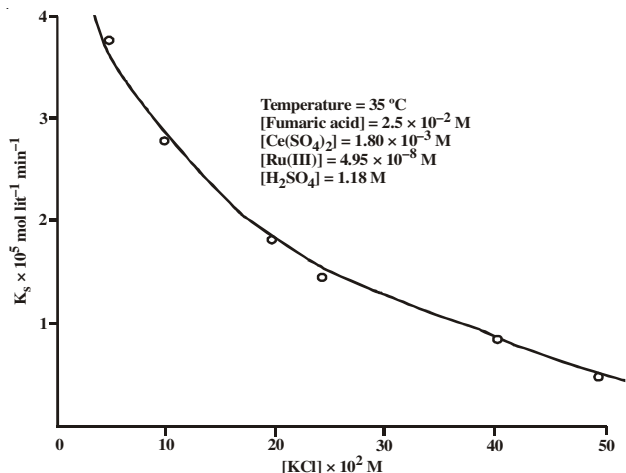


Fig. 4.

At constant $[Ce(IV)]$, $[fumaric\ acid]$ and $[Ru(III)]$ with an increase in $[H_2SO_4]$, decreased the rate of oxidation. Similar effects of $[KHSO_4]$ were reported in earlier studies (Fig. 5) and the literature is also reporting as well¹⁰⁻¹². Similarly, a graph is being plotted between K_s values and concentration of potassium hydrogen sulphate as shown in Fig. 5.

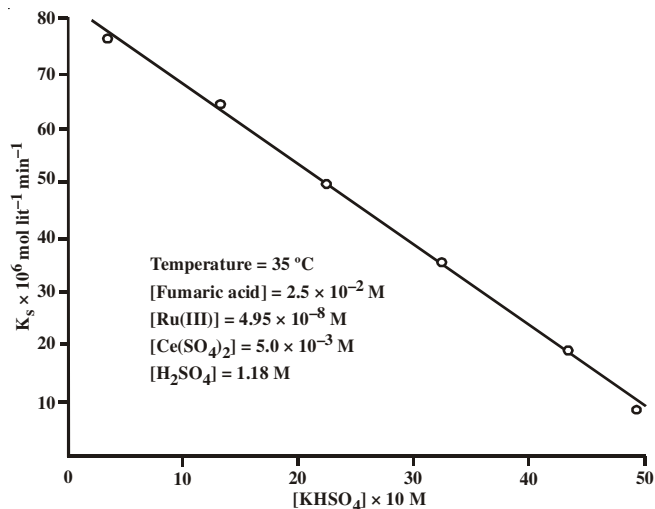


Fig. 5.

A close examination of Fig. 5 shows that as the concentration of H^+ ions decreases, the rate of reaction also decreases.

A perusal of the Fig. 6, clearly indicates that rate of reaction decreases on increasing the concentrations of sodium bisulphate. At higher concentration of $NaHSO_4$, it showed a linear decrease of reaction rate.

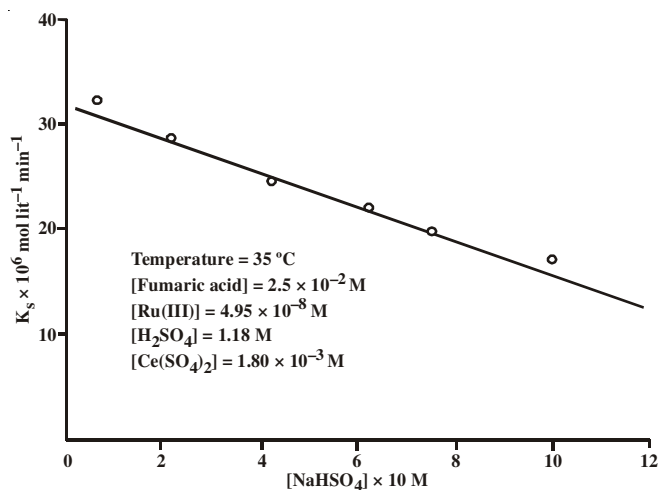
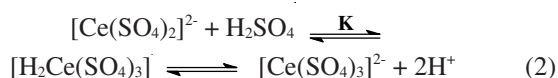


Fig. 6.

These results could be explained by proposing the following equilibrium in which $[Ce(SO_4)_3]^{2-}$ was assumed to be the main reactive species.



It is assumed that the rate could be increased with increase in $[H^+]$ as it will influence the existence of oxidant reactive species. It is well known from the literature that $Ru(III)$ in aqueous acid medium exists in various forms, but $[Ru(H_2O)_5Cl]^{2+}$ is considered to be the reactive species

because a reaction of $RuCl_3$ takes place in a few seconds to form $[Ru(H_2O)_5Cl_3]$ and $[Ru(H_2O)_5Cl]^{2+}$ while the conversion to $[Ru(H_2O)_6]^{3+}$ takes place in a very long period.

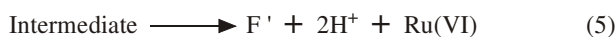
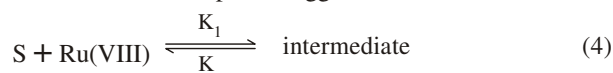
On the basis of above experimental findings a probable scheme is proposed for the oxidation of fumaric acid. Since the rate of oxidation of fumaric acid decreases with the increase in the concentration of H_2SO_4 , known acidic species of fumaric acid is involved in the rate determining steps. When $Ru(III)$ is mixed with excess of $Ce(IV)$, it is oxidized¹⁰⁻¹² rapidly to $Ru(VIII)$ by $Ce(IV)$ as shown in eqn. 3.



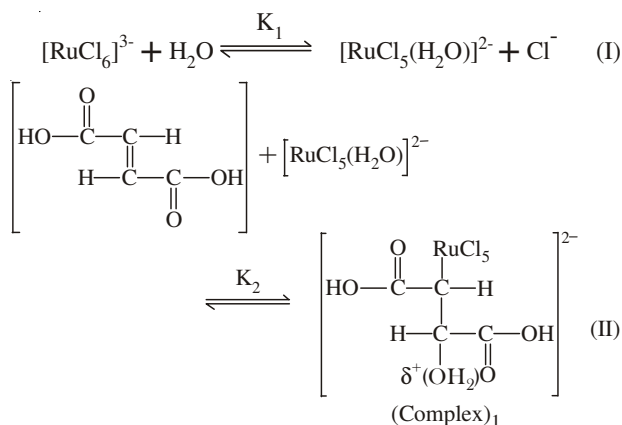
It appears that the conversion of $Ru(III)$ to $Ru(VIII)$ takes place more rapidly than the oxidation of fumaric acid. Hence, it is reasonable to postulate that $Ru(VIII)$ is the species responsible for the catalysis. Reports⁵ are available in the literature that in the acid medium, $Ru(VIII)$ is present in the form of H_2ORuO_5 or $RuO_3(OH)_2$. In order to explain the kinetic results, it is proposed that an intermediate is formed in the rate determining step between H_2RuO_5 and fumaric acid. The electron transfer probably takes place *via* $Ru(III)$ center which abstracts electrons from the fumaric acid in fast step forming $Ru(VI)$ which is rapidly oxidized by $Ce(IV)$ to $Ru(VIII)$. Thus the present redox system becomes $Ru(VIII)$ catalyzed.

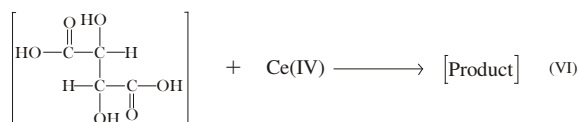
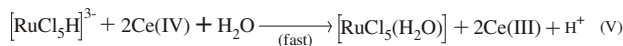
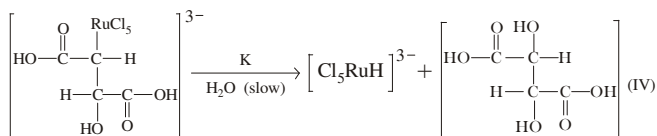
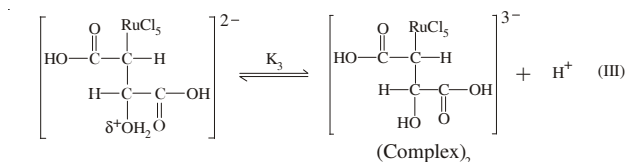
The conversion of unstable species of $Ru(VI)$ and $Ru(VII)$ back to $Ru(VIII)$ with oxidant $Ce(IV)$ in the fast step which has already been reported in the literature¹³. It is interesting to note that a similar mechanism of electron transfer *via* $Ru(VIII)$ center was proposed by Awasthi and Upadhyay¹⁴ for the $Ru(III)$ catalyzed oxidation of amino alcohols by $Ce(IV)$.

The mechanistic steps are suggested as:-



On the basis of final oxidation products of fumaric acid following mechanistic steps can be proposed.





The rate law equation for oxidation of fumaric acid under experimental conditions may thus be represented as:

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{KK_1K_2K_3[\text{Ru(III)}]_T[\text{S}]}{[\text{H}^+][\text{Cl}^-] + K_1[\text{H}^+] + K_1K_2[\text{H}^+] + K_3K_1K_2[\text{S}]} \quad (9)$$

At constant $[\text{Ru(III)}]$, the plot of $1/d[(\text{Ce(IV)})]/dt$ versus $1/[\text{FA}]$ was found to be linear. The straight line with +ve intercept at $1/d/dt[\text{Ce(IV)}]$ axis clearly indicates the validity of rate law as shown in Fig. 7.

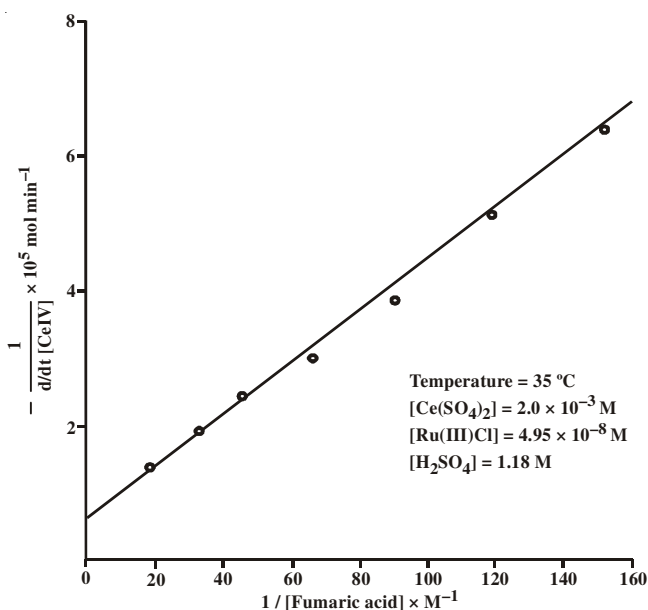


Fig. 7.

From the intercept of straight line the values of were also calculated and on the basis of aforesaid statements, the proposed reaction mechanism is quite valid in the range of concentration studied. The observed values were also calculated which are relatively large and negative. These values are not uncommon in literature³. It can easily be guessed that the fraction of collisions that have proper molecular orientations become more stringent and may lead to slow rate even though the activation energy is relatively low and the concentrations are enough to ensure many collisions.

Conclusion

From the above results and discussions, it is clear that the kinetics of ruthenium(III) catalyzed oxidation of fumaric acid by cerium(IV) in sulphuric acid medium is typical in nature and is studied for the first time. The study of intermediate complexes formed furnishes the information about non-covalent intermolecular forces binding the "host-guest" molecules. The negative ΔG , ΔH and ΔS values support the formation of such complexes.

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