

Fig. 1. Arrhenius plots for the oxidation of carbon monoxide over $\text{LaMn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ catalysts.
(—○— $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$; —▽— $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$;
—△— $\text{LaMn}_{0.3}\text{Co}_{0.7}\text{O}_{3-\delta}$; —□— LaCoO_3)

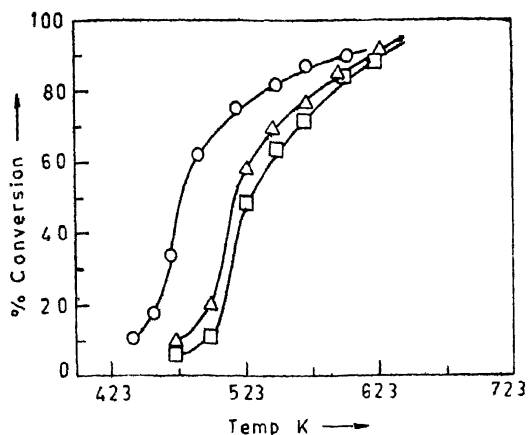


Fig. 2. Percentage conversion of carbon monoxide vs temperature over $\text{LaMn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ catalysts, at a flow rate of 8000 ml/hr.
(—□— $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$; —△— $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$;
—○— LaCoO_3)

catalytic activity decreased from about 90% at 350° to nearly 50% at 250°. The results can be discussed on the basis of spin states of the concerned transition metal ions and non-stoichiometry resulting from variations in the proportion of cation/anion vacancies.

Lanthanum manganite is oxygen excess especially when prepared in oxygen atmosphere and reported to have Mn^{3+} and Mn^{4+} ions, the concentrations of which are very much dependent on the preparative conditions⁴. In this 'hopping' type material the presence of Mn^{3+} or Mn^{4+} or cation vacancies in the La(A) site apparently do not contribute to catalytic activity, as experimentally observed. On the other hand, lanthanum cobaltite is oxygen deficient⁸ and known to contain

cobalt ions in multivalent states⁶, viz., Co^{3+} , Co^{4+} (high spin), Co^{3+} (low spin) and Co^{4+} in the temperature region where catalytic activity was studied. Presence of the transition metal ions in different oxidation states viz., Mn^{4+} , Mn^{3+} , Co^{3+} and Co^{4+} in the system $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ has also been suggested by Jonker⁷. Since one may expect a decrease in the oxygen vacancies with increase in manganese content in the solid solutions between LaCoO_3 and LaMnO_3 , the negligible activity shown by the compositions of $x > 0.6$ may be attributed to the oxygen vacancies in the compound.

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Ruthenium(III) Catalysed Oxidation of Chalcones by Ce(IV) in H_2SO_4 -HOAc Mixtures: A Kinetic Study

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IN an earlier communication¹ we reported the kinetics of oxidation of chalcone (benzalacetophenone) and its substituted analogues by Ce(IV) in H_2SO_4 -HOAc mixtures. This reaction, which is extremely slow at room temperature, was found to be catalysed by as small amounts of Ru(III) as 10^{-4} M. For example, under similar conditions the rate constant values (k'') for uncatalysed and catalysed reactions are 3.2×10^{-6} and 4.07×10^{-4} $\text{lit.mol}^{-1}.\text{sec}^{-1}$, respectively at 300 K. Ru(III) was employed as a homogeneous catalyst in Ce(IV) oxidation of a variety of compounds and various mechanisms were proposed²⁻⁴. Since chalcone

contains two functional groups viz., >C=C< and >C=O in conjugation, it is of interest to find out the type of mechanism when it reacts with Ce(IV) in the presence of Ru(III) . It is therefore worth considering (i) whether the presence of Ru(III) ion results in a change in the mechanism, (ii) the nature of the radicals or ions formed and (iii) the effect of substituents on rate of reaction. The present study is a step in this direction.

Experimental

Ruthenium(III) chloride solution was prepared and standardised by the methods reported earlier³. The method of following the rate of reaction was the same as reported earlier¹.

Results and Discussion

Acetic acid, which is used as a cosolvent, was not oxidised under the conditions employed. The stoichiometry of the reaction was 2 moles of Ce(IV) to one mole of chalcone and the products identified were phenylacetaldehyde and benzoic acid. The order in [Ce(IV)] was found to be unity as observed from the linear plot of $\log(a/a-x)$ vs time under the conditions [Ce(IV)] \ll [chalcone] where 'a' is the initial concentration and (a-x) is the concentration at time 't' of Ce(IV) (Fig. 1A). This was found to be true with all the chalcones studied. The order in [chalcone] changed from unity in the absence of catalyst to fraction (0.6) in the presence of catalyst indicating that it might be involved in complexation either with Ce(IV) or with Ru(III) (Fig. 1B). Spectral studies in the present investigation indicated the absence of complex formation between Ce(IV) and chalcone in H_2SO_4 -HOAc mixtures. It is well known that Ru(III) forms complexes with organic compounds containing double bonds⁵. The effect of variation of [Ru(III)] shows fractional order in [Ru(III)] (Fig. 1C). It is, therefore, assumed that a complex might be formed between Ru(III) and chalcone in a fast step before it is oxidised in a slow step by Ce(IV) to give Ru(IV)-complex which collapses in a fast step to give products. Formation of such a type of complex was also confirmed by Michaelis-Menten reciprocal plots which gave straight lines with intercept on $1/k'$ axis.

The effect of $[H^+]$, $[HSO_4^-]$ and [HOAc] were found to be similar to those observed in the uncatalysed reaction and hence neutral $Ce(SO_4)_2$ is believed to be the reactive species in this case also⁶. The catalysed reaction induces polymerization of acrylonitrile and the ir spectrum of polymer formed gave a sharp peak at 1640 cm^{-1} indicating the presence of $C_6H_5-CH=CH$ in the polymer chain⁷.

It is known that aquation of $RuCl_3$ takes place only in a few seconds^{8,9}. Therefore Ru^{3+}_{aq} is assumed as reactive species in the present study.

Based on the above experimental observations, the following mechanism is proposed for the oxidation of benzalacetophenone:

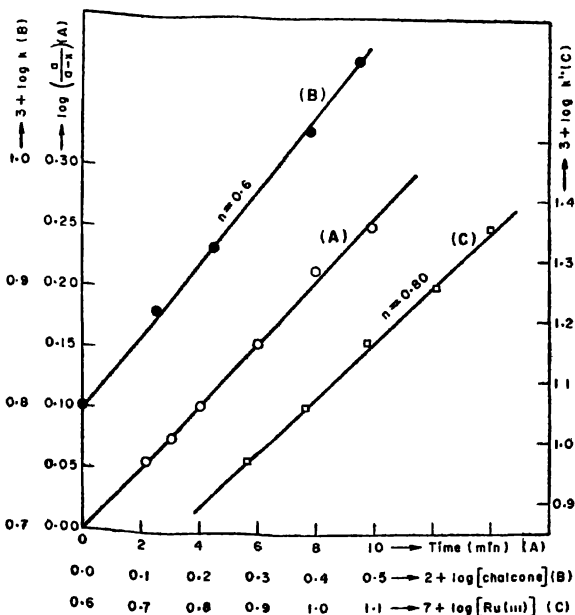
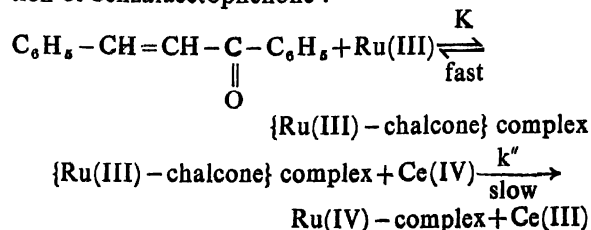


Fig. 1. A. Plot of $\log(a/a-x)$ vs time.

[Ce(IV)] = 0.002 M; [chalcone] = 0.02 M; [HOAc] = 70.0% (v/v); $[H_2SO_4] = 1.0$ M; $[Ru(III)] = 7.60 \times 10^{-7}$ M; Temp = 27°.

B. Plot of $\log k'$ vs \log chalcone.

[chalcone] = 0.01 to 5.052 M; other conditions are same as in A.

C. Plot of $\log k'$ vs $\log [Ru(III)]$. $[Ru(III)] = 7.60 \times 10^{-7}$ to 3.40×10^{-6} M. Other conditions are same as in A.

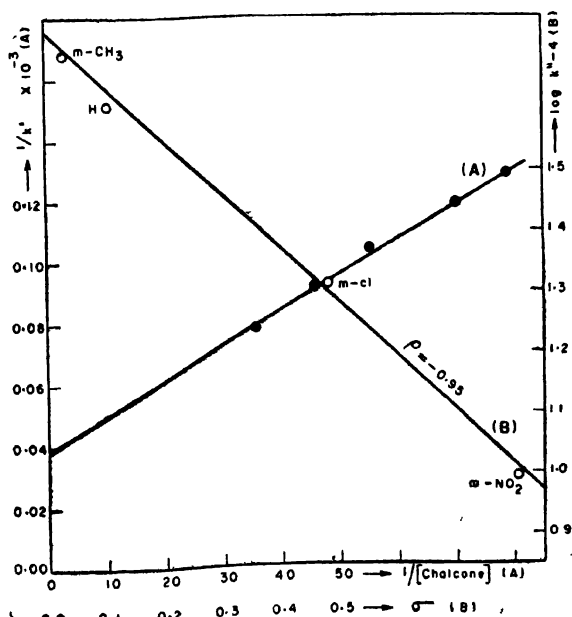
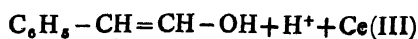
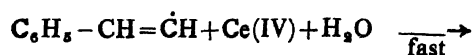
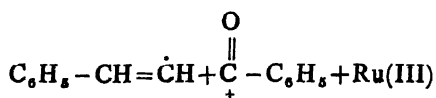
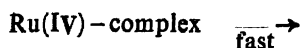


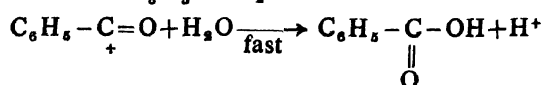
Fig. 2. A. Plot of $1/k'$ vs $1/[chalcone]$.

[Ce(IV)] = 0.002 M; $[Ru(III)] = 7.6 \times 10^{-7}$ M; $[H_2SO_4] = 1.00$ M; [HOAc] = 70.0%; Temp. = 27°.

B. Plot of $\log k'' + 4$ vs σ . Conditions same as in A.



⇌ keto-enol tautomerism



In the proposed oxidation scheme, the further oxidation of Ru(IV)-complex is ruled out based on the strict first order dependence of rate on [Ce(IV)]. Alternatively, it can be assumed that Ru(IV), which is formed by direct oxidation of Ru(III) by Ce(IV) in the reaction $\text{Ru(III)} + \text{Ce(IV)} \xrightleftharpoons{K'} \text{Ru(IV)} + \text{Ce(III)}$ can oxidise the chalcone. This possibility is ruled out as it could not explain the experimentally observed fractional order in [chalcone] and [Ru(III)] and unit order in [Ce(IV)].

From the above mechanism, the rate law comes out to be

$$\begin{aligned} -\frac{d[\text{Ce(IV)}]}{dt} &= \frac{k'K[\text{chalcone}][\text{Ce(IV)}][\text{Ru(III)}]}{1+K[\text{chalcone}]+K[\text{Ru(III)}]} \quad \dots (1) \end{aligned}$$

or

$$\begin{aligned} -\frac{2.303 d \log [\text{Ce(IV)}]}{dt} &= k' \\ &= \frac{k'K[\text{chalcone}][\text{Ru(III)}]}{1+K[\text{chalcone}]+K[\text{Ru(III)}]} \end{aligned}$$

where k' is the observed pseudo first order-rate constant, k'' the bimolecular rate constant for the slow step and K the formation constant. Equation (1) explains well all the experimental results obtained.

Taking the reciprocal of the above eq. (1) we get

$$\begin{aligned} \frac{1}{k'} &= \frac{1}{[\text{chalcone}]} \left[\frac{1}{k''K[\text{Ru(III)}]} + \frac{1}{k''} \right] + \\ &\quad \left[\frac{1}{k''[\text{Ru(III)}]} \right] \quad \dots (2) \end{aligned}$$

It is clear from eq. (2) that the plot of $1/k'$ vs $1/[\text{chalcone}]$ at constant ruthenium(III) chloride should be linear. Such plots were obtained in the present work for all the chalcones studied confirming the validity of the derived rate law. From the intercept and slope values the bimolecular rate constants for slow step (k'') and the

formation constant of the complex (K) were evaluated (Table 1).

TABLE 1—ACTIVATION PARAMETERS FOR Ru(III) CATALYSED OXIDATION OF CHALCONES BY Ce(IV) AT 300K

Substi- tuent	$k'' \times 10^{-4}$ $\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$	K $\text{dm}^3 \text{mol}^{-1}$	E_{exp}	ΔH^\ddagger kJ.mol^{-1}	ΔG^\ddagger	ΔS^\ddagger $\text{J.deg}^{-1} \text{mol}^{-1}$
<i>p</i> -CH ₃	5.41	48.2	25.0	22.6	45.9	-77.7
<i>m</i> -CH ₃	4.96	42.5	41.3	38.8	46.0	-24.0
H	4.07	41.0	56.8	54.3	46.7	25.3
<i>p</i> -Cl	3.05	40.7	49.3	46.8	47.3	-1.67
<i>m</i> -Cl	2.08	40.1	51.8	49.3	48.2	3.67
<i>m</i> -NO ₂	1.00	38.6	53.0	50.5	50.1	1.33
<i>p</i> -NO ₂	0.42	38.9	66.8	64.3	52.2	40.3

The effect of substituents on rate was studied using chalcone and six substituted chalcones and the reactivity was in the order $p\text{-CH}_3 > m\text{-CH}_3 > \text{H} > p\text{-Cl} > m\text{-Cl} > m\text{-NO}_2 > p\text{-NO}_2$. The Hammett plot was linear with a slope of (ρ) -0.95 indicating the radical nature of the reaction.

The E_{exp} values calculated from Arrhenius plot and other thermodynamic parameters are presented in Table 1. From these results it is evident that both the parameters (ΔH^\ddagger and ΔS^\ddagger) are important in controlling the rates of reaction, though the enthalpy factor seems to be predominating. This point was also verified by calculating the isokinetic temperature (β) from the slope of the plot of ΔH^\ddagger vs ΔS^\ddagger . The β value (350 K) was found to be well above the temperature range used in the present work. Constancy of calculated ΔG^\ddagger values for all chalcones indicates that probably the same mechanism operates in all the cases. The large negative values for entropy of activation indicate that the activated complex is more rigid.

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