

## OXIDATIVE CARBONYLATION OF CYCLOHEXYLAMINE TO CYCLOHEXYLURETHANE CATALYSED BY DICHLOROBIS-(SALICYLALDEHYDE)-*o*-PHENYLENEDIIMINATO RUTHENATE(III)

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### Summary

The complex  $[\text{Ru}(\text{saloph})\text{Cl}_2]$  (saloph = bis(salicylaldehyde-*o*-phenylenediimine)) catalyses the oxidative carbonylation of cyclohexylamine in ethanol medium to cyclohexylurethane selectively at 160 °C and CO + O<sub>2</sub> (1:0.50) pressure of 21 atm. A turnover number of 30 mol per mol catalyst per hour was observed in this reaction. The rate of oxidative carbonylation of cyclohexylamine measured at 160 °C in the range 7–21 atm is first order with respect to catalyst, cyclohexylamine and dissolved CO concentrations and one-half order with respect to dissolved O<sub>2</sub> concentration. The effect of temperature on the rate of oxidative carbonylation was studied in the temperature range 150–170 °C and the activation energy evaluated as 21.0 kcal mol<sup>-1</sup>.

### Introduction

The oxidative carbonylation of cyclohexylamine to cyclohexylurethane is an important reaction from the view point of production of polyurethane foams and fibres [1]. Urethanes find application in agriculture as pesticides and as precursors of isocyanates by thermal decomposition. Urethanes are usually prepared by the phosgenation of an amine, and the drawbacks of this route are well known [2]. Use of the low cost reactant carbon monoxide is more convenient and has several advantages over the conventional phosgenation method.

The oxidative carbonylation of different primary and secondary amines catalysed by Co(salen) complex has been described [3, 4]. The yields reported for the urethanes are, however, poor (30–60%) and the turnover number based on the amount of amine converted was found to be 0.50–2.0. Palladium catalysts with iodide promoters were reported to catalyse the oxidative carbonylation of amines to urethanes [5]. Though high tempera-

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ture and pressure are required for the reaction [3, 5, 6], oxidative carbonylation of amines is found to have certain advantages over the reductive carbonylation of nitro compounds [7].

In this paper we report the kinetics and suggested mechanism for the oxidative carbonylation of cyclohexylamine catalysed by  $[\text{Ru}(\text{saloph})\text{Cl}_2]$  (saloph = bis(salicylaldehyde)-*o*-phenylenediimine) to give urethanes. In the  $\text{CO} + \text{O}_2$  (1:0.5) partial pressure range of 7–21 atm, the rate of this reaction was found to be first order with respect to catalyst, cyclohexylamine and dissolved CO concentrations and one-half order with respect to dissolved  $\text{O}_2$  concentration. The reaction was studied in the temperature range 150–170 °C and the activation energy is reported. The turnover number obtained in our case is 30 mol product per mol catalyst per hour, which is ten-fold greater than the turnover numbers for the oxidative carbonylation of various primary and secondary amines catalysed by Co(salen) complex [3, 4]. A probable mechanism, based on kinetic observations involving a ruthenium(V)-oxo species as an intermediate, is proposed for the oxidative carbonylation of cyclohexylamine.

## Experimental

### Materials

Cyclohexylamine procured from S.D.S. Fine Chemicals, Bombay was distilled before use. The catalyst  $\text{K}[\text{Ru}^{\text{III}}(\text{saloph})\text{Cl}_2]$  (saloph = bis(salicylaldehyde)-*o*-phenylenediimine) was prepared according to a known procedure [8]. The NMR of the product, cyclohexylurethane, was taken on a Jeol FX-100 FT-NMR spectrometer.

The oxidative carbonylation of cyclohexylamine was conducted in a 300 ml stainless steel pressure reactor (Parr Instrument Co., USA). In a typical experiment, the carbonylation run was carried out by charging the substrate (cyclohexylamine) in 100 ml of ethanol along with a known amount of catalyst. The  $\text{CO} + \text{O}_2$  (1:0.5) pressures were varied between 7–21 atm at 160 °C.

The bomb was pressurized by  $\text{CO} + \text{O}_2$  to the desired value when the desired temperature was attained. Liquid samples were withdrawn from the reactor at fixed time intervals to monitor the progress of the reaction. The reaction mixture was analysed for cyclohexylamine and cyclohexylurethanes using GLC (Shimadzu, GC, 9A) with a S.S. column containing 5% SE-30 supported on Carbowax 80/100 mesh (2.5 m length) using a FID detector. The column temperature was programmed in the range 120–170 °C with an injection temperature of 250 °C. Nitrogen carrier gas was used with a flow rate of 30 ml  $\text{min}^{-1}$ . The product, cyclohexylurethane, was identified and characterised by  $^{13}\text{C}$  NMR.

## Results and discussion

The kinetics of the oxidative carbonylation of cyclohexylamine in ethanol to give exclusively cyclohexylurethane was studied using the complex  $[\text{Ru}(\text{saloph})\text{Cl}_2]$  **1**. The effect of catalyst, substrate, dissolved  $\text{CO} + \text{O}_2$  (1:0.5) concentration and temperature on the initial rates of oxidative carbonylation of cyclohexylamine were evaluated from plots of moles of cyclohexylamine converted *vs* time. The  $\text{CO}$  solubility data required under the reaction conditions was determined separately [9] and used in kinetic interpretation. The oxygen solubility data required under the reaction conditions was calculated via a temperature-dependent exponential form of the solubility equation, using the known value at the specified temperature [10].

### *Effect of catalyst concentration*

The catalyst concentration was varied from 0.25 to 1.0 mM at a cyclohexylamine concentration of 0.035 M, dissolved  $\text{CO}$  concentration of 0.50 M and dissolved  $\text{O}_2$  concentration of 0.056 M at 160 °C. The effect of catalyst on the initial rates of oxidative carbonylation of cyclohexylamine is shown in Fig. 1, which shows first-order dependence with respect to catalyst concentration.

### *Effect of dissolved CO concentration*

Figure 2 shows the dependence of the rate of oxidative carbonylation on the concentration of dissolved  $\text{CO}$ . The concentration of dissolved  $\text{CO}$  was varied over the range 0.10 M to 0.50 M, keeping other parameters constant: catalyst concentration 1 mM, cyclohexylamine concentration 0.035 M and dissolved  $\text{O}_2$  concentration 0.056 M at 160 °C. The reaction shows a first-order dependence with respect to dissolved  $\text{CO}$  concentration.

### *Effect of dissolved $\text{O}_2$ concentration*

The concentration of dissolved  $\text{O}_2$  was varied from 0.03 M–0.01 M at a cyclohexylamine concentration of 0.035 M, catalyst concentration of 1 mM

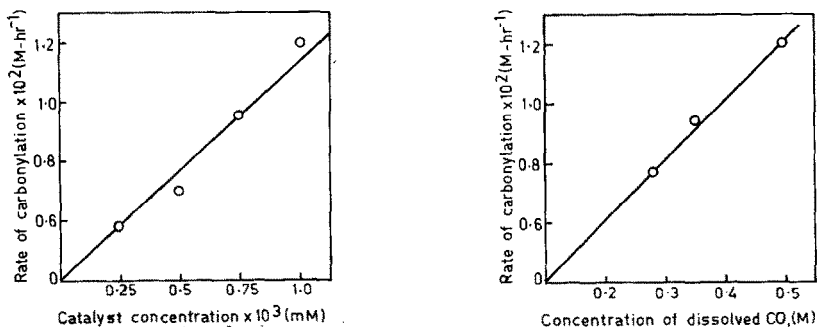


Fig. 1. Effect of catalyst concentration on the rate of oxidative carbonylation of cyclohexylamine.  
 Fig. 2. Effect of dissolved  $\text{CO}$  concentration on the rate of oxidative carbonylation of cyclohexylamine.

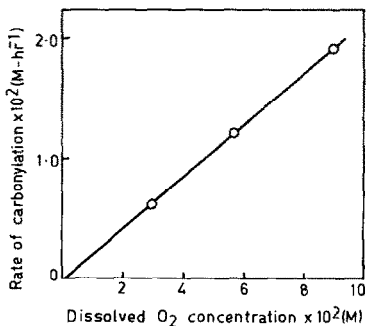


Fig. 3. Effect of dissolved O<sub>2</sub> concentration on the rate of oxidative carbonylation of cyclohexylamine.

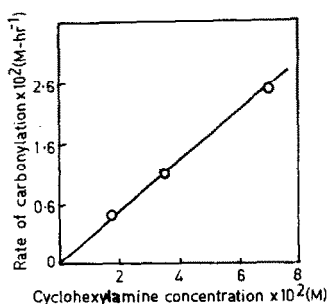


Fig. 4. Effect of cyclohexylamine concentration on the rate of oxidative carbonylation of cyclohexylamine.

and dissolved CO concentration 0.50 M at 160 °C. The plot of the rate of oxidative carbonylation *vs.* dissolved O<sub>2</sub> concentration (Fig. 3) shows one-half order dependence with respect to dissolved O<sub>2</sub> concentration.

#### *Effect of cyclohexylamine concentration*

The effect of cyclohexylamine concentration (varied from 0.01 to 0.07 M) on the initial rate of oxidative carbonylation was studied under constant reaction conditions of 1 mM catalyst concentration, dissolved CO concentration 0.50 M and dissolved O<sub>2</sub> concentration 0.056 M at 160 °C. Figure 4 shows a first-order dependence of the rate of oxidative carbonylation with respect to cyclohexylamine concentration.

#### *Effect of temperature*

The effect of temperature on the rate of oxidative carbonylation of cyclohexylamine was studied in the temperature range 150–170 °C at a catalyst concentration of 1 mM, cyclohexylamine concentration 0.035 M and dissolved CO and O<sub>2</sub> concentrations of 0.5 M and 0.056 M, respectively. A plot of  $-\log \text{rate}$  *vs.*  $1/T$  is shown in Fig. 5, from which the value of activation energy,  $E_a$ , was evaluated as 21 kcal mol<sup>-1</sup>.

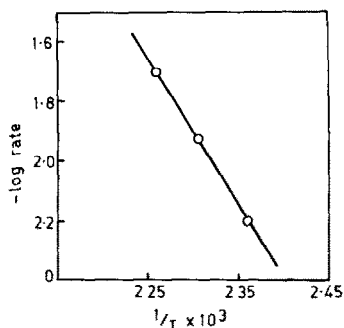
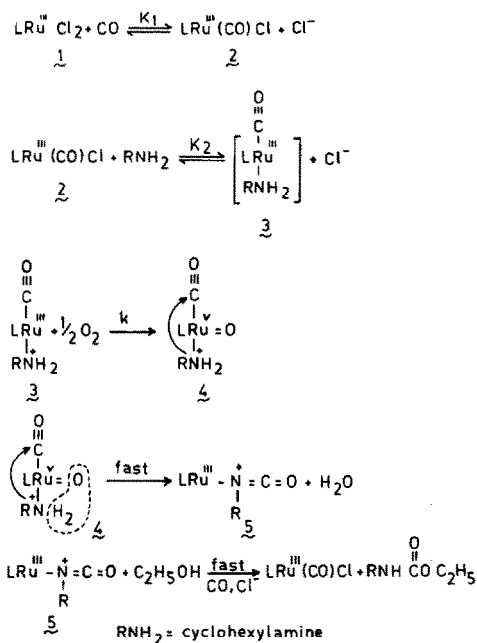


Fig. 5. Effect of temperature on the rate of oxidative carbonylation of cyclohexylamine.

## Mechanism

The oxidative carbonylation of cyclohexylamine catalysed by complex **1** gave cyclohexylurethane. Based on the product formed and from the kinetic data, a mechanism proposed for the reaction is shown in Scheme 1.

In the proposed mechanism, complex **1** reacts with a molecule of CO to give  $[\text{LRu}^{\text{III}}(\text{CO})\text{Cl}]$  **2** in a pre-equilibrium step. The solution spectrum of the carbonylation species in the absence of the substrate showed a peak at 370 nm, which is attributed to the LMCT band of the carbonyl complex **2** [11–13]. In a second pre-equilibrium step, carbonyl complex **2** reacts with cyclohexylamine to form a mixed ligand complex **3**. The rate-determining step is considered as the interaction between species **3** and oxygen to form an intermediate  $\text{Ru}^{\text{V}}$ -oxo complex **4**. The reactive  $\text{Ru}^{\text{V}}$ -oxo species readily dehydrogenates the primary amine to form a reactive  $\text{R}-\text{N}^+$  moiety, which is inserted in the  $\text{Ru}-\text{C}$  bond in a fast step to form the coordinated cyclohexylisocyanato complex **5**. The dehydrogenation of primary amines to imines or nitriles in the presence of  $\text{Ru}(\text{III})$  complexes and molecular  $\text{O}_2$  was reported by Diamond *et al.* [14] and to imine and alkylideneamido complexes by Adcock *et al.* [15]. The presence of CO in the coordination sphere of the metal ion promotes this dehydrogenation by a facile  $\text{Ru}^{\text{V}}/\text{Ru}^{\text{III}}$  conversion. The coordinated nitrene  $\text{RN}^+$  is a strong electrophile which is readily inserted into the  $\text{Ru}-\text{C}$  bond by an attack on the nucleophilic CO centre. Species **5** reacts with ethanol in the presence of CO in a fast step to give cyclohexyl-urethane, regenerating the active catalytic species **2**.



Scheme 1.

*Rate law*

Based on the kinetic study, the rate of oxidative carbonylation of cyclohexylamine catalysed by complex **1** exhibits first-order dependence with respect to catalyst, substrate and dissolved CO concentrations, and one-half-order dependence with respect to dissolved O<sub>2</sub> concentration. Based on the kinetic study, the final rate law can be written as:

$$\text{rate} = \frac{kK_1K_2[\text{Cat}]_T[\text{CO}][\text{S}][\text{O}_2]^{1/2}}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{S}]} \quad (1)$$

where [Cat]<sub>T</sub> = total catalyst concentration, CO = dissolved CO concentration, [S] = cyclohexylamine concentration, K<sub>1</sub> and K<sub>2</sub> are equilibrium constants and *k* is the rate constant.

To evaluate the kinetic constants, the above eqn. (1) can be rearranged into slope and intercept form as:

$$\frac{[\text{Cat}]_T}{\text{rate}} = \frac{1}{[\text{S}]} \left( \frac{1}{kK_1K_2[\text{CO}][\text{O}_2]^{1/2}} + \frac{1}{kK_2[\text{O}_2]^{1/2}} \right) + \frac{1}{k[\text{O}_2]^{1/2}} \quad (2)$$

From eqn. (2), the value of *k* was calculated from the intercept obtained by plotting a graph of [Cat]<sub>T</sub>/rate vs. 1/[S]. The value of K<sub>1</sub> was determined spectrophotometrically by monitoring the peak at 370 nm (species **2**, Scheme 1). Substituting the values of *k*, K<sub>1</sub>, [CO], [O<sub>2</sub>]<sup>1/2</sup> in the slope from the values obtained from eqn. (2), the value of K<sub>2</sub> was calculated. The kinetic constants determined in the case of complex **1**-catalysed oxidative carbonylation of cyclohexylamine to give cyclohexylurethane are:

$$K_1 = 76.5 \text{ M}^{-1}$$

$$K_2 = 81.4 \text{ M}^{-1}$$

$$k = 17.6 \text{ min}^{-1}$$

The activation energy, *E<sub>a</sub>*, was calculated from the temperature dependence of the rate of carbonylation of cyclohexylamine as 21.0 kcal mol<sup>-1</sup> in the range 150–170 °C. The value of Δ*H*<sup>‡</sup> and Δ*S*<sup>‡</sup> calculated at 160 °C are 20 kcal mol<sup>-1</sup> and +46 e.u., respectively. The value of Δ*H*<sup>‡</sup> demonstrates the endothermicity of the reaction, which is probably due to cleavage of the N—H bond in Ru—NH<sub>2</sub><sup>+</sup> (in Scheme 1) with simultaneous insertion of the RN<sup>+</sup>

moiety into the Ru—C bond to form species **5** (Scheme 1) in the transition state. The more positive value of Δ*S*<sup>‡</sup> of +46 e.u. reflects the dissociative nature of the reactions leading to the formation of products.

It is of interest to compare the mechanism proposed for the oxidative carbonylation of cyclohexylamine catalysed by complex **1** to give cyclohexylurethane to that for the reductive carbonylation of nitrobenzene catalysed by complex **1** to give phenylurethane [16]. They differ in the mechanistic routes leading to the formation of the unstable coordinated isocyanate species **5**. In the oxidative carbonylation proposed in Scheme 1, species **5** is suggested to be formed by intramolecular oxygenation of the

primary amine by the  $\text{Ru}^{\text{V}}$ -oxo species **4** with the simultaneous elimination of a water molecule, whereas in the reductive carbonylation of nitrobenzene [16] the unstable coordinated isocyanate species **6** is formed by successive deoxygenation of both the oxygen atoms of the  $\text{NO}_2$  group by two molecules of CO, which are thus oxidised to  $\text{CO}_2$ . In addition to the above differences, the reactions also differ in the stoichiometry of CO required for the reaction. In the case of oxidative carbonylation, only 1 mol CO is required for the entire reaction (Scheme 1), whereas for reductive carbonylation 3 mol CO are required for the reaction.

The values of kinetic constants determined in the case of reductive carbonylation of nitrobenzene to phenylurethane catalysed by complex **1** are  $K_1 = 76.5 \text{ M}^{-1}$ ;  $K_2 = 23.5 \text{ M}^{-1}$ ;  $k = 4.0 \text{ min}^{-1}$ . The values of  $K_2$  and  $k$  obtained in the case of oxidative carbonylation of cyclohexylamine are nearly four times higher than the  $K_2$  and  $k$  values obtained in the case of reductive carbonylation of nitrobenzene. The difference is due to a stronger coordination of amine to the metal ion in the oxidative carbonylation than the nitro compound in reductive carbonylation. The dehydrogenation of the coordinated amine in the oxidative carbonylation seems to be more facile than the deoxygenation of the  $\text{NO}_2$  group in reductive carbonylation.

On comparing the values of activation parameters for the oxidative carbonylation of cyclohexylamine ( $E_a = 21 \text{ kcal mol}^{-1}$ ,  $\Delta H^\ddagger = 20 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 46 \text{ e.u.}$ ) with that of reductive carbonylation of nitrobenzene [16] ( $E_a = 38 \text{ kcal mol}^{-1}$ ,  $\Delta H^\ddagger = 37 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 86 \text{ e.u.}$ ), the oxidative carbonylation proceeds by a lower energy pathway than that of reductive carbonylation.

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