

KINETIC STUDY OF THE CARBONYLATION OF DIETHYLAMINE AND TRIETHYLAMINE CATALYZED BY THE WATER-SOLUBLE $K[Ru^{III}(EDTA-H)Cl] \cdot 2H_2O$ COMPLEX IN AQUEOUS MEDIUM

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Summary

The carbonylations of diethylamine and triethylamine were conducted in a pressure reactor using $K[Ru^{III}(EDTA-H)Cl] \cdot 2H_2O$ as catalyst at a CO pressure of 5 - 26 atm and temperature in the range 80 - 100 °C in aqueous medium. The products of carbonylation of diethylamine were *N,N*-diethylformamide (80%) and *N,N*-tetraethylurea (20%), whereas triethylamine gave 100% *N,N*-diethylpropionamide. The observed rates for the carbonylation of diethylamine and triethylamine show first order dependence with respect to catalyst, substrates and dissolved CO concentrations. The effect of temperature was also studied on the rate of carbonylation, and from the graph of $-\ln \text{ rate vs. } 1/T$, the activation energies were evaluated. Mechanisms are proposed for $K[Ru^{III}(EDTA-H)Cl] \cdot 2H_2O$ -catalyzed carbonylation of diethylamine and triethylamine.

Introduction

In recent years considerable attention has been given to carbonylation reactions catalyzed by transition metal complexes [1 - 8] which give many value-added chemicals by the insertion of CO into simple substrates. The insertion of carbon monoxide in the M-N bond of amines catalyzed by metal carbonyls to give *N*-formyl derivatives and substituted ureas is known [4, 5, 8]. Manganese, cobalt and nickel carbonyl derivatives have been mainly used as catalysts in these reactions in the temperature range 150 - 270 °C and CO pressures between 100 to 300 atm [6]. A complete survey of the carbonylation reactions has been published by Bird [7]. The selective formation of formamides or ureas depends on the nature of the metal ion catalyst used and also on the presence of ancillary ligands.

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The catalyst system $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ **1** can combine with π -acids such as PPh_3 [9] and SnCl_3^- [10] and CO [11] to form thermodynamically stable mixed ligand complexes of the composition $\text{Ru}^{\text{III}}(\text{EDTA})(\text{L})$ ($\text{L} = \text{PPh}_3, \text{SnCl}_3^-, \text{CO}$). We have earlier reported the carbonylation of benzyl chloride catalyzed by **1** [12]. Since water-soluble metal complex catalysts for CO insertion reactions and carbonylation are less well known, we considered extending the carbonylation studies in aqueous system to other substrates. The present paper reports the kinetic data on the $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ -catalysed carbonylation of diethylamine and triethylamine.

Experimental

Materials

Ruthenium(III) chloride was obtained from Johnson Matthey Inc. and the disodium salt of ethylenediaminetetraacetic acid (EDTA) was of A.R. grade. The complex **1** $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ was prepared by known method [13]. Diethylamine and triethylamine were of reagent grade and were twice distilled before use. Carbon monoxide gas was procured from BOC, UK.

A pressure reactor of 300 ml capacity (Parr Instrument Co., USA) made of stainless steel was used to conduct carbonylation experiments. The operating procedure has been described in our earlier communication [12].

Several exploratory carbonylation experiments with diethylamine and triethylamine using catalyst **1** were conducted at the CO pressure of 26 atm and at 100 °C. Samples of the reaction mixture were withdrawn from the reactor at different time intervals and analyzed for reactants and products of carbonylation using GLC (Shimadzu, GC-9A, Japan). The column used for the analysis were 2.0 m long Porapak-Q with a carrier gas (H_2) flow rate of 30 ml min^{-1} in the temperature programming range 60 - 180 °C. A TCD (thermal conductivity detector) maintained at 250 °C and an injection temperature at 200 °C were used for the analysis. The progress of the reactions was monitored by the decrease in the area of the peaks of diethylamine or triethylamine substrates in the respective carbonylation experiments. The reactions were continued till the peaks corresponding to the substrates disappeared in the GLC chromatogram. The product peaks that appeared in the GLC analysis were identified later by separating them with the help of TLC, and were characterized by spectroscopic techniques. The carbonylation of diethylamine gave two products namely, *N,N*-diethylformamide (80%) and *N,N*-tetraethylurea (20%). Triethylamine however gave only one product *N,N*-diethylpropionamide.

Kinetic measurements of the carbonylation of diethylamine and triethylamine were obtained by gas absorption techniques. In a sample run, known quantities of substrate and catalyst were dissolved in 100 ml distilled water and placed in the reactor. The reaction solution was agitated and

flushed with CO twice to ensure that the reaction mixture was free from any dissolved oxygen. When the desired temperature was attained, the reactor was pressurized to the required CO pressure. The progress of the reaction was monitored by recording the drop in CO pressure shown on the pressure gauge with time. The initial rates of carbonylation were calculated by knowing the moles of CO absorbed with time. Data on the solubility of CO to calculate the dissolved CO concentration in the reaction medium under reaction conditions were determined separately [14] and used in the calculation of kinetic data.

Results and discussion

Carbonylation of diethylamine

Under the reaction conditions studied, the carbonylation of diethylamine catalyzed by complex 1 in aqueous medium gave two products, namely *N,N*-diethylformamide (80%) and *N,N*-tetraethylurea (20%). The effect of catalyst, diethylamine, dissolved CO concentration and temperature on the rate of reaction was determined.

Effect of catalyst concentration

The concentration of catalyst 1 was varied from 0.5×10^{-3} M to 3×10^{-3} M, keeping the concentrations of diethylamine 1.93 M and dissolved CO 5.894×10^{-2} M constant at 100 °C. The initial rates of carbonylation obtained at different catalyst concentrations were plotted as the rate of carbonylation *vs.* catalyst concentration. The data are shown in Fig. 1. The rate of carbonylation of diethylamine has a first order dependence with respect to the catalyst concentration.

Effect of diethylamine concentration

The rate of carbonylation measured by varying the concentration of diethylamine at 100 °C, keeping the other parameters constant, reflects a

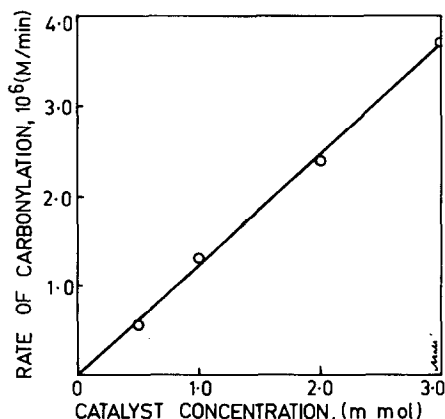


Fig. 1. Effect of catalyst concentration on the rate of carbonylation of diethylamine.

first order dependence on diethylamine concentration. The concentration of diethylamine was varied from 0.483 M to 1.933 M, maintaining the catalyst concentration at 3.0×10^{-3} M. The plot of rate of carbonylation *vs.* diethylamine concentration shown in Fig. 2 is a straight line passing through the origin, indicating a linear first order dependence with respect to diethylamine concentration.

Effect of dissolved CO concentration

The concentration of CO was varied from 1.29×10^{-2} M to 5.89×10^{-2} M while keeping the catalyst and substrate concentrations fixed at 3×10^{-3} M and 1.933 M, respectively. The rates of carbonylation of diethylamine were studied at 100 °C. The kinetics of the reaction indicates first order dependence with respect to dissolved CO concentration. Figure 3 shows the effect of the variation of CO concentration on the rate of carbonylation of diethylamine.

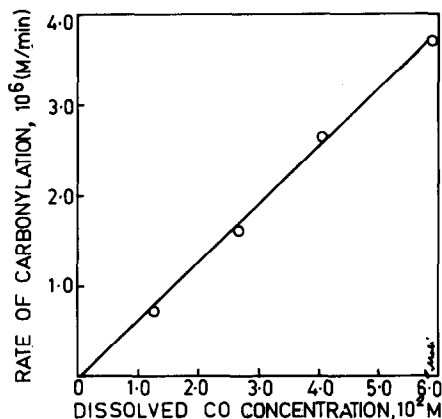
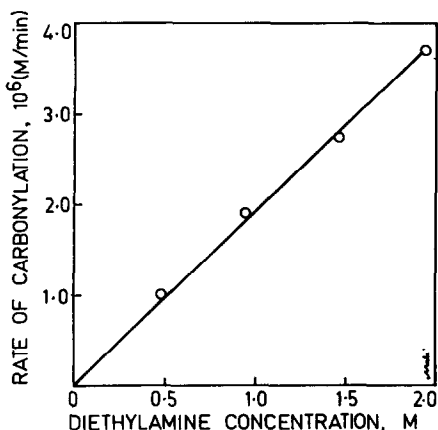


Fig. 2. Effect of diethylamine concentration on the rate of carbonylation of diethylamine.

Fig. 3. Effect of dissolved CO concentration on the rate of carbonylation of diethylamine.

Effect of temperature

The effect of temperature on the rate of carbonylation was studied by varying the temperature from 80 to 100 °C, keeping other parameters, *viz.* catalyst 3×10^{-3} M, diethylamine 1.933 M and dissolved CO 5.89×10^{-2} M concentrations, constant. From the slope of the graph of $-\ln$ rate *vs.* $1/T$ shown in Fig. 4, the activation energy for the carbonylation reaction was calculated as $4.34 \text{ kcal mol}^{-1}$.

Based on the kinetic observations and products of carbonylation of diethylamine catalyzed by complex 1, the probable mechanism of carbonylation is proposed as shown in Scheme 1.

The mechanism suggested for the carbonylation of diethylamine involves the initial formation of carbonyl complex 3. Complex 2 is obtained by

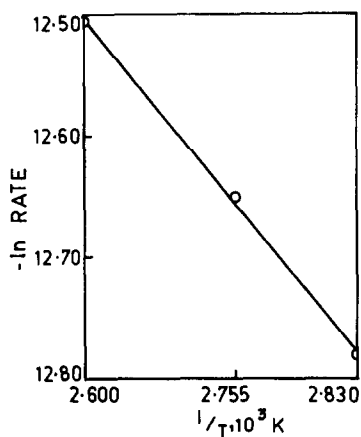
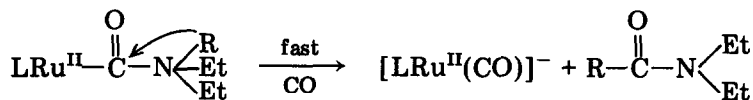
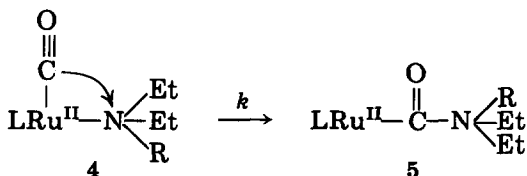
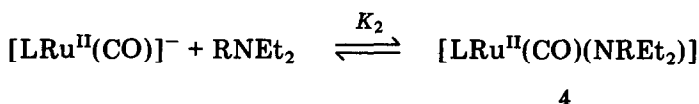
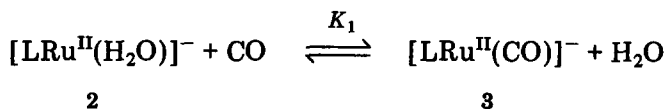
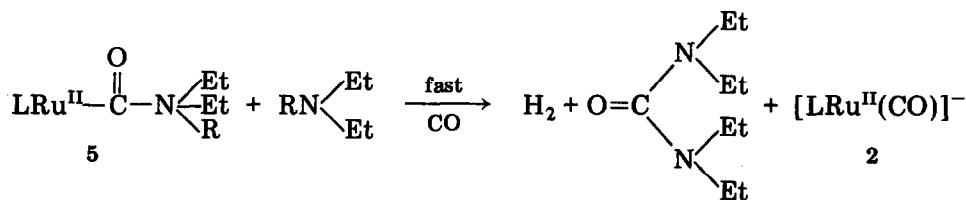


Fig. 4. Effect of temperature on the rate of carbonylation of diethylamine.



N,N-diethylformamide R = H
N,N-diethylpropionamide R = Et



N,N-tetraethylurea

L = EDTA-H, Et = C₂H₅-, R = H (diethylamine), R = Et (triethylamine)

Scheme 1. Mechanism for carbonylation of diethylamine and triethylamine.

the rapid aquation of chloro species 1 $K[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ [15]. The substrate diethylamine reacts with complex 3 in another pre-equilibrium step to give a mixed ligand complex 4. The rate-determining insertion of CO in the Ru-N bond in 4 gives rise to an intermediate complex 5. The migration of the ethyl group to nucleophilic CO in a fast step gives *N,N*-diethylformamide and the catalyst 2. In another fast step, complex 5 reacts with one more molecule of diethylamine to give an intermediate where the migration of a hydride to nucleophilic CO results in the formation of *N,N*-tetraethylurea, as shown in Scheme 1. This mechanism is similar to that suggested by Sternberg *et al.* [16] for the formation of *N,N*-dimethylformamide by CO insertion in the M-N bond of dimethylamine catalyzed by $\text{Co}_2(\text{CO})_8$.

From the proposed mechanism for the carbonylation of diethylamine and kinetic observations, the rate equation for the carbonylation of diethylamine can be written as:

$$\text{rate} = kK_1K_2[\text{Ru}^{\text{III}}(\text{EDTA})][\text{CO}][\text{S}_1] \quad (1)$$

Where $[\text{Ru}^{\text{III}}(\text{EDTA})]$ = catalyst concentration, $[\text{S}_1]$ = diethylamine concentration, K_1 , K_2 are equilibrium constants and k is the rate constant.

The total catalyst concentration involved in the two pre-equilibrium steps of Scheme 1 $[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}$ may be written as:

$$[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}} = [\text{Ru}^{\text{III}}(\text{EDTA})] + K_1[\text{Ru}^{\text{III}}(\text{EDTA})][\text{CO}] + K_1K_2[\text{Ru}^{\text{III}}(\text{EDTA})][\text{CO}][\text{S}_1] \quad (2)$$

$$[\text{Ru}^{\text{III}}(\text{EDTA})] = \frac{[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{S}_1]} \quad (3)$$

Substituting the value of catalyst concentration $[\text{Ru}^{\text{III}}(\text{EDTA})]$ in eqn. (1), the rate law becomes:

$$\text{rate} = \frac{kK_1K_2[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}[\text{CO}][\text{S}_1]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{S}_1]} \quad (4)$$

Equation (4) could be written in a slope intercept form in two ways as:

$$\frac{[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}}{\text{rate}} = \frac{1}{[\text{S}_1]} \left(\frac{1}{kK_1K_2[\text{CO}]} + \frac{1}{kK_2} \right) + \frac{1}{k} \quad (5)$$

$$\frac{[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}}{\text{rate}} = \frac{1}{[\text{CO}]} \frac{1}{kK_1K_2[\text{S}_1]} + \frac{1}{k} \left(1 + \frac{1}{K_2[\text{S}_1]} \right) \quad (6)$$

From eqn. (5), a plot of $[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}/\text{rate}$ vs. $1/[\text{S}_1]$ gives a straight line with an intercept from which the value of k was calculated. Similarly, from eqn. (6), a plot of $[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}/\text{rate}$ vs. $1/[\text{CO}]$ gives a straight line. On substituting the value of k in the values of the slope and intercept of this plot, the constants K_1 and K_2 were obtained. Thus the value of the constants k , K_1 and K_2 for the carbonylation of diethylamine catalyzed by complex 1 at 100 °C were found to be:

$$k = 5.88 \times 10^{-3} \text{ min}^{-1}$$

$$K_1 = 5.0 \pm 0.3 \text{ M}^{-1}$$

$$K_2 = 0.4 \text{ M}^{-1}$$

Carbonylation of triethylamine

The carbonylation of triethylamine catalyzed by complex 1 was studied in a manner similar to that of diethylamine. The carbonylation of triethylamine under the conditions studied gave exclusively *N,N*-diethylpropionamide as the product. The kinetics of this reaction using complex 1 was studied, and the details of the experimental condition and results are given in Table 1. The initial rates of carbonylation were obtained by monitoring CO absorption as described for the carbonylation of diethylamine. It was found that the rate of carbonylation catalyzed by complex 1 in aqueous medium has a first order dependence with respect to catalyst, substrate and dissolved CO concentrations, respectively.

From the observations made and the dependence of rate of carbonylation on the parameters involved in the reaction, the proposed mechanism for carbonylation of triethylamine is found to be similar to that suggested for diethylamine in Scheme 1, except for the last step of the urea-forming reaction for diethylamine. The rate data for the carbonylation of triethylamine were obtained in a manner similar to that of diethylamine, and the computed values of the constants k , K_1 and K_2 are:

TABLE 1

Experimental conditions and results of carbonylation of triethylamine catalyzed by complex 1

Run No.	[Ru ^{III} (EDTA)] ($\times 10^3$ M)	[Triethylamine] ($\times 10^2$ M)	[Dissolved CO] ($\times 10^2$ M)	Temperature (°C)	Rate of carbonylation ($\times 10^6$ M min ⁻¹)
<i>Effect of catalyst concentration</i>					
1	3.0	3.587	2.470	100	4.2758
2	2.0	3.587	2.470	100	2.7638
3	1.0	3.587	2.470	100	1.4252
4	0.5	3.587	2.470	100	0.6238
<i>Effect of triethylamine concentration</i>					
5	3.0	2.153	2.470	100	2.7720
6	3.0	1.435	2.470	100	1.7680
7	3.0	0.178	2.470	100	0.9312
<i>Effect of dissolved CO concentration</i>					
8	3.0	3.587	1.773	100	2.7953
9	3.0	3.587	1.148	100	1.8665
10	3.0	3.587	0.573	100	1.0032
<i>Effect of temperature</i>					
11	3.0	3.587	2.470	90	4.5965
12	3.0	3.587	2.470	80	4.2758

$$k = 12.5 \times 10^{-3} \text{ min}^{-1}$$

$$K_1 = 5.0 \pm 0.3 \text{ M}^{-1}$$

$$K_2 = 26 \text{ M}^{-1}$$

From the graph of $-\ln \text{ rate versus } 1/T$, the activation energy, the enthalpy and entropy of activation for the carbonylation of diethylamine and triethylamine were calculated, and are presented in Table 2.

TABLE 2

Thermodynamic quantities^a for the carbonylation of diethylamine and triethylamine at 100 °C

System	E_a (kcal mol ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal deg ⁻¹ mol ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)
diethylamine	4.3	3.6	-51.3	1.5
triethylamine	5.2	4.4	-47.6	0.3

^a E_a = activation energy, ΔH^\ddagger = enthalpy, ΔS^\ddagger = entropy, ΔG^\ddagger = free energy.

From the value of ΔG^\ddagger (Table 2) and the rate constants listed in Table 1, the carbonylation rate of triethylamine is about double that of diethylamine. The factor responsible seems to be the higher stability (by a factor of 60) of the mixed ligand Ru(III)-EDTA-triethylamine-carbonyl complex (K_2) as compared to the corresponding complex with diethylamine. The enthalpy of activation of the carbonylation of the two substrates are endoethermic and in line with the bond dissociations involved in the two reactions. The entropies are negative, in agreement with the highly associative transition state involving the metal ion, the substrate and coordinated CO [1].

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