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KINETIC STUDY OF CARBONYLATION OF n-BUTYLAMINE USING HOMOGENEOUS WATER SOLUBLE Ru^{II}–EDTA–CO CATALYST

M M TAQUI KHAN*, S B HALLIGUDI, SUMITA SHUKLA and S H R ABDI

Discipline of Coordination Chemistry and Homogeneous Catalysis Central Salt and Marine Chemicals Research Institute, Bhavnagar 364002 (India)

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Summary

The kinetics of carbonylation of n-butylamine catalyzed by $[Ru^{II}(EDTA–H)CO]^-$ in aqueous solution to give n-butylformamide (70%) and *N,N'*-dibutylurea (30%) is reported. The optimum conditions of the reaction are 140 °C and 30 atm of CO

The effect of ruthenium catalyst, CO pressure and n-butylamine concentrations on the initial rates of carbonylation were investigated. It was found that the rate of carbonylation has a first order dependence with respect to catalyst, CO pressure and substrate concentrations, respectively. A polar solvent such as water, used in our study, was found to enhance the rate of carbonylation of the primary amine in comparison with nonaqueous solvent systems. The effect of temperature on the rate of n-butylamine carbonylation was also investigated and the activation energy evaluated is 21.6 kcal mol^{-1}.

Introduction

The importance of C_1 chemistry using CO or its source (natural gas/syn gas) has considerably increased in recent years [1]. This is mainly due to the reactivities of many transition metal complexes of the platinum group series, which have been designed specially to activate small molecules such as CO, H_2, olefin, O_2 and NO under milder reaction conditions. The use of these complexes in industrially important reactions such as carbonylation, oxidation and hydroformylation of olefins and other substrates has made a definite impact [1]. One of the important CO insertion reactions is the carbonylation of amines, catalyzed by soluble metal complexes, to give formamides and ureas depending on the nature of the substrates and the catalytic systems involved [2].

The aliphatic amines yield mainly *N*-formyl derivatives as CO insertion products, whereas aromatic amines give diarylureas [2, 3], due to the dif-

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*Author to whom correspondence should be addressed

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ferences in the basicities of the starting amines. Diarylureas are formed by a hydrogen transfer mechanism involving two moles of the reactant during CO insertion; such a reaction is favoured by low basicity of the reactants. The aromatic amines therefore give diarylureas as the carbonylation products [4].

Metal carbonyls [5 - 10] catalyze the carbonylation of amines in the temperature range 150 - 270 °C and CO pressures between 100 - 300 atm. In our studies we have found that the ruthenium complex $[Ru^{II}(EDTA—H)(CO)]^-$ catalyzes the carbonylation of diethyl and triethylamine in aqueous medium to give *N*-formyl derivatives as main products at the comparatively mild conditions of temperature ~80 - 100 °C and CO pressure in the range 5 - 30 atm [11]

The present work reports the detailed kinetics of the carbonylation of the primary amine, n-butylamine, catalyzed by $[Ru^{II}(EDTA—H)(CO)]^-$ in aqueous solution. The above catalyst is formed *in situ* by the carbonylation of $K[Ru^{III}(EDTA—H)(H_2O)]$, and has been found to be an excellent catalyst system for many carbonylation reactions in aqueous or mixed solvent systems [11 - 14].

Experimental

Materials

n-Butylamine, supplied by S.D.S. Laboratory Chemicals, Bombay was purified according to the procedure described [15]. $RuCl_3 \cdot 3H_2O$ was obtained from Johnson Matthey (U.S A.) and Na_2EDTA (disodium salt of ethylenediaminetetraacetic acid) was of AR grade. The complex $K[Ru^{III}(EDTA—H)Cl] \cdot 2H_2O$ 1 was prepared according to the procedure described elsewhere [16]. The carbon monoxide gas used in this study was obtained from B.O.C., U.K. and its purity was >99.96%.

Apparatus and procedure

The carbonylation experiments were carried out in a 300 ml stainless steel pressure reactor procured from Parr Instrument Co. U.S.A. The details of this reactor and the procedure adopted are described in our earlier publication [11].

The analysis of liquid samples withdrawn at different time intervals from the reactor was done using a Shimadzu GC-9A gas chromatograph with a 2 m long S.S. column packed with 10% Apiezon-L impregnated on 90/100 mesh Anankrom (ABS). The other conditions of GLC analysis were carrier gas N_2, flow rate 30 ml min^{-1}, column temperature programmed between 100 - 150 °C, injection temperature 250 °C and detector (FID) temperature 350 °C.

In a typical experiment, the carbonylation of n-butylamine using complex 1 was carried out for complete conversion at optimised reaction conditions. The products of carbonylation of n-butylamine were separated by TLC technique and identified by their usual physicochemical properties as n-butylformamide (70%) and *N,N′*-dibutylurea (30%).

Results and discussion

The effect of the catalyst K[Ru^{III}(EDTA−H)Cl]·2H$_2$O 1 concentration, n-butylamine concentration, dissolved CO concentration and temperature on the initial rate of carbonylation of n-butylamine was investigated. For each variable, the initial rates were calculated from the plots of the quantity of CO absorbed *vs.* time Since the reaction under consideration is a gas–liquid reaction, it is important to ensure that the rate data is obtained under conditions such that diffusional resistance is negligible. The reaction mixture was thoroughly agitated at a speed of 600 rpm in all experiments, which ensured that the gas–liquid mass transfer resistance is negligible and the rates are determined under purely kinetically controlled conditions

The CO solubility data required under the reaction conditions are independently determined [17] and used to interpret the kinetic data of this reaction.

Effect of catalyst concentration

The effect of catalyst concentration on the reaction rate was studied at 140 °C and 0.101 M n-butylamine concentration and dissolved CO concentration of 4.7×10^{-3} M. The results are shown in Fig. 1, which indicate that the reaction is first order with respect to catalyst concentration.

Effect of dissolved CO concentration

The effect of dissolved CO concentration (CO partial pressure varied between 5 - 30 atm) has been studied at 0.101 M n-butylamine concentration, catalyst concentration of 2.0 mmol l^{-1} and at 140 °C. A plot of rate of carbonylation *vs* dissolved CO concentration is presented in Fig 2,

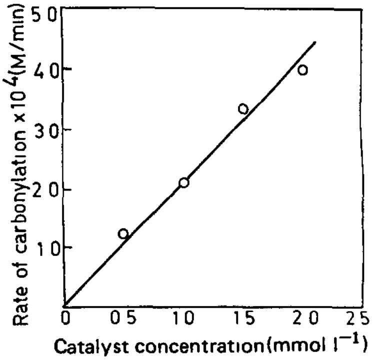


Fig 1 Effect of catalyst concentration on the rate of n-butylamine carbonylation

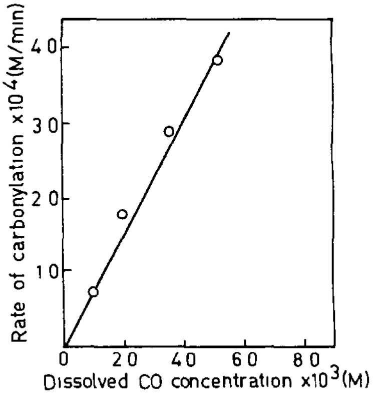
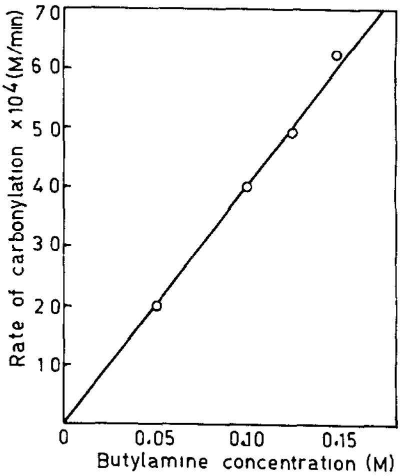


Fig 2 Effect of dissolved CO concentration on the rate of n-butylamine carbonylation



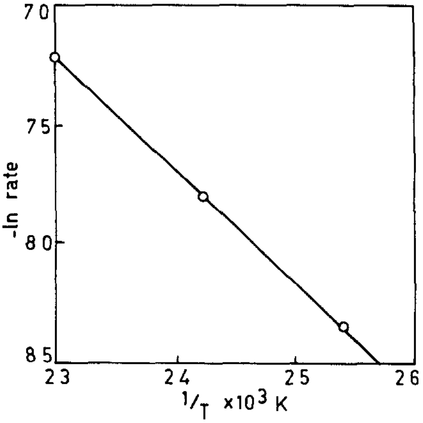


Fig 3 Effect of n-butylamine concentration on the rate of carbonylation

Fig 4 Effect of temperature on the rate of n-butylamine carbonylation

which indicates a first-order dependence of the reaction on CO concentration.

Effect of n-butylamine concentration

The reaction rate was studied at 140 °C as a function of n-butylamine concentration at a catalyst concentration of 2.0 mmol l^{-1} and dissolved CO concentration of 4 7 $\times$ 10^{-3} M. Figure 3 shows the plot of rate *vs* n-butylamine concentration. The reaction exhibits first-order dependence with respect to n-butylamine concentration.

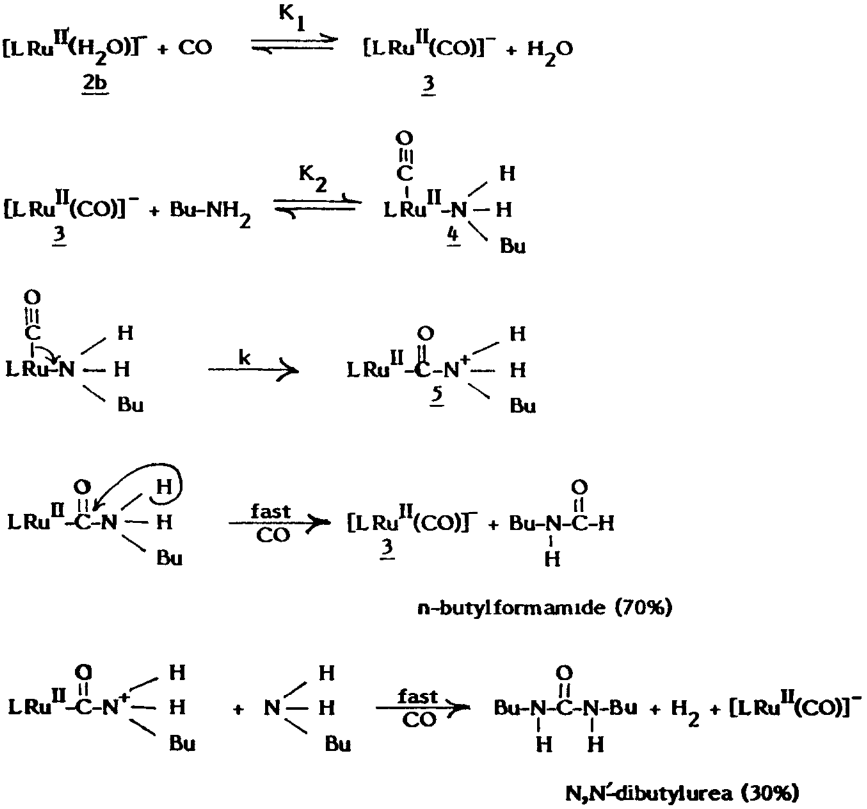
Effect of temperature

The effect of temperature on the rate of n-butylamine carbonylation was studied in the temperature range 120 - 160 °C at constant conditions of catalyst concentration of 2 mmol l^{-1}, n-butylamine concentration of 0.101 M and dissolved CO concentration of 4.7 $\times$ 10^{-3} M. From the graph of —ln rate *vs.* $1/T$ (Fig. 4), the activation energy E_a is evaluated as 21.6 kcal mol^{-1}

Mechanism and rate law

Based on the products formed and the kinetics of n-butylamine carbonylation catalyzed by complex 1, the mechanism shown in Scheme 1 is proposed

In the proposed mechanism, the active catalytic species $[Ru^{II}(EDTA{-}H)(CO)]^-$ 3 is formed *in situ* by the reduction of $[Ru^{III}(EDTA{-}H)(H_2O)]^-$ 2a in a fast reaction with CO. Species 2b is formed in solution by the rapid aquation of the starting material $K[Ru^{III}(EDTA{-}H)Cl]\cdot 2H_2O$ in aqueous solution [18]



L = EDTA—H (protonated ethylenediaminetetraacetic acid)
Bu = —$(CH_2)_3$—CH_3

Scheme 1

$$\underset{1}{K[Ru^{III}(EDTA{-}H)Cl]} + H_2O \xrightarrow{\text{fast}} \underset{2a}{[Ru^{III}(EDTA{-}H)(H_2O)]^-}$$

$$\underset{2a}{2[Ru^{III}(EDTA{-}H)(H_2O)]^-} + CO \xrightarrow[H_2O]{\text{fast}} \underset{2b}{2[Ru^{II}(EDTA{-}H)(H_2O)]^-} + CO_2 + 2H^+$$

Carbonylation of 2b takes place in a pre-equilibrium step K_1 to form the active catalytic species $[Ru^{II}(EDTA{-}H)(CO)]^-$ 3. In a second pre-equilibrium step, the substrate n-butylamine reacts with complex 3 to give the mixed ligand complex 4. The rate-determining step of the reaction is proposed to be the CO insertion in the Ru—N bond, giving rise to an unstable intermediate species 5. The migration of hydrogen to nucleophilic CO in a fast step gives the major carbonylation product n-butylformamide (70%), and the active complex 3 is generated in the presence of available CO. In a subsequent fast step, complex 5 reacts with one more molecule of n-butylamine to give the minor product *N,N'*-dibutylurea, a molecule of hydrogen and regenerates the active complex 3. This mechanism is similar to that proposed [11] earlier for the carbonylation of diethylamine and triethylamine. Intramolecular prototropic shift to the nucleophilic CO centre is more favourable for the primary amines because of their higher basicity and the resulting stabilization of intermediate species 3 Thus *N*-formyl derivatives are the major reaction products as compared to the ureas, which require a nucleophilic attack of the primary amine on the η^1-amide intermediate 5.

Based on the kinetic observations, the rate law can be written as.

$$\text{rate} = \frac{kK_1K_2[\text{CAT}]_\text{T}[\text{CO}][\text{S}]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{S}]} \tag{1}$$

where $[\text{CAT}]_\text{T}$ = total $K[\text{Ru}^{\text{III}}(\text{EDTA–H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ concentration, [CO] = dissolved CO concentration, [S] = n-butylamine concentration, K_1 and K_2 are equilibrium constants and k is the rate constant.

For the purpose of evaluating the kinetic constants, the above eqn. (1) could be rearranged in the following two ways as:

$$\frac{[\text{CAT}]_\text{T}}{\text{rate}} = \frac{1}{[\text{S}]}\left(\frac{1}{kK_1K_2[\text{CO}]} + \frac{1}{kK_2}\right) + \frac{1}{k} \tag{2}$$

and

$$\frac{[\text{CAT}]_\text{T}}{\text{rate}} = \frac{1}{[\text{CO}]}\left(\frac{1}{kK_1K_2[\text{S}]}\right) + \frac{1}{k}\left(1 + \frac{1}{K_2[\text{S}]}\right)$$

From the above eqns. (2) and (3), the values of k, K_1 and K_2, at 140 °C and 30 atm CO, as evaluated graphically are:

$k = 2.50\ \text{min}^{-1}$

$K_1 = 1.92\ \text{M}^{-1}$

$K_2 = 30.12\ \text{M}^{-1}$

The activation parameters of n-butylamine carbonylation were calculated in the temperature range 120 - 160 °C, and the average values are presented in Table 1. The activation energy of the carbonylation of n-butylamine is fairly endothermic, to the extent of about 17 kcal mol^{-1} as compared to those of diethylamine and triethylamine (Table 1) The reactivity order diethylamine < triethylamine < n-butylamine is in accord with the decreasing basicity of the amines. As the amine becomes more basic, the insertion of a nucleophilic CO in the M—N bond in the rate-determining step to form intermediate species 5 is retarded and the reaction slows down. The effect is more pronounced in n-butylamine, where the presence of the bulky n-butyl group considerably retards the insertion of CO in the M—N bond by a steric effect which raises the activation energy by ~17 kcal mol^{-1}

TABLE 1

Values of thermodynamic parameters of amine carbonylation

System	log K^a at 25 °C	E_a (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e u)	$\Delta G^{\ddagger}$ (kcal mol^{-1})
n-butylamine (120 - 160 °C)	10.64	21.6	20.8	+49.9	0.2
diethylamine^b (80 - 100 °C)	10.93	4.3	3.6	−51.3	1.5
triethylamine^b (80 - 100 °C)	10.72	5.2	4.4	−47.6	0.3

[a] [19]
[b] [11]

The reaction is however favoured by a positive entropy of activation which more than offsets the endothermic enthalpy of activation. Thus basicity seems to be the major factor in the reactivity of secondary and tertiary amines, whereas both basicity and steric effects operate in the reactivity of a bulky primary amine such as n-butylamine.

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