

ALLYLIC AND VINYLIC CARBOXYLATION OF CYCLOHEXENE CATALYSED BY $[\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})(\text{CO})]$

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Summary

The complex $[\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})(\text{CO})]$ (EDTA = ethylenediamine-tetraacetic acid) catalyses the carbonylation of cyclohexene in alcohol:water (80:20) mixture to give cyclohexene-1-carboxaldehyde, cyclohexene-3-carboxaldehyde and cyclohexane-carboxaldehyde. The optimum conditions of the reaction are 120 °C and 20 atm CO partial pressure. The effect of catalyst, CO pressure and cyclohexene concentration on the initial rates of carbonylation was investigated. The rate of carbonylation exhibits first-order dependence with respect to catalyst, CO pressure and substrate concentration. The effect of temperature on the rate of cyclohexene carbonylation was studied and the activation energy, E_a , evaluated at $16 \pm 1 \text{ Kcal mol}^{-1}$.

Carbonylations of 1-methyl-, 3-methyl- and 4-methylcyclohexenes conducted at 160 °C and 20 atm CO partial pressure gave the corresponding alcohols.

Introduction

The importance of C_1 chemistry and its source (natural gas/syn gas) has considerably increased in recent years [1]. This is mainly due to the reactivity of platinum group metal ions as catalysts designed to activate small molecules such as CO, H_2 , olefins, O_2 and NO under milder conditions. The industrially important organic reactions such as carboxylation, hydroformylation and oxidation of olefins and other organic substrates have made a large [1] impact recently.

Though there are numerous studies involving the activation of olefins by metal complexes under hydroformylation conditions to give the corresponding aldehydes [2-5], most of the reactions are associated with some unresolved problems of isomerisation of the substrate, inhibitory effects of α, β -unsaturated aldehydes formed as intermediates or products during the reaction, and thermal instability of the catalyst. There are reports [6] in

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which these problems have been greatly reduced, however the yields are poor. Further, all these reactions reported have yielded saturated aldehydes, *i.e.* carbonylation is always associated with the hydrogenation of the double bond.

In this paper we report the kinetics of the carbonylation of cyclohexene in alcohol:water (80:20) mixture catalysed by $[\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})(\text{CO})]$ at 120 °C and 20 atm CO partial pressure to give vinylic aldehyde-cyclohexene-1-carboxaldehyde (20%), allylic cyclohexene-3-carboxaldehyde (20%) and saturated aldehyde-cyclohexane carboxaldehyde (60%). We also report the carbonylation of 1-methylcyclohexene, 3-methylcyclohexene and 4-methylcyclohexene at 160 °C and 20 atm CO partial pressure to give 1-(2-methylcyclohexene)methanol, 1-(4-methylcyclohexene)methanol and 1-(5-methylcyclohexene)methanol as major carbonylated products. In the case of 1-methylcyclohexene, formation of small amounts of 2-(1-cyclohexene)ethanol was also seen.

Experimental

Materials

Cyclohexene used was prepared according to the procedure described in the literature [7]. 1-Methylcyclohexene, 3-methylcyclohexene and 4-methylcyclohexene were obtained from Aldrich Chemicals and were used without further purification. The complex $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}] \cdot 2\text{H}_2\text{O}$ (EDTA = ethylenediaminetetraacetic acid) was prepared by the known procedure [8]. High purity carbon monoxide (99.6%) was obtained from B.O.C., U.K.

Apparatus and procedure

The carbonylation experiments were conducted in a 300 ml stainless steel pressure reactor procured from Parr Instrument Co. The analysis of liquid samples withdrawn at fixed time intervals was carried out on a Shimadzu GC-9A gas chromatograph with an S.S. column of 10% Carbowax 20 M on 60/100 mesh Anakrom-SD. The other conditions of GLC analysis were: carrier gas N_2 , flow rate 25 ml min^{-1} , column temperature programmed between 60–150 °C, injection temperature 200 °C and F.I.D. detector. The products were characterised by ^{13}C NMR spectroscopic studies (Jeol FX-100 FT-NMR).

In a typical experiment, the carbonylation of cyclohexene using complex 1 was carried out under optimised conditions in different alcohol:water (80:20) mixtures to give cyclohexene-1-carboxaldehyde (20%), cyclohexene-3-carboxaldehyde (20%) and cyclohexane carboxaldehyde (60%) as carbonylation products. The products and their percentage distribution were found to be nearly the same in all the alcohol:water systems studied, although the percentage conversion of cyclohexene in each case was found to differ with the alcohol used, *e.g.* methanol (6.6%), ethanol (6.8%), propanol (4.9%) and isopropanol (4%).

^{13}C NMR spectra of cyclohexene in alcohol:water mixture were recorded before and after the carbonylation reaction and were compared. The spectrum of the sample withdrawn at a fixed time interval showed the peaks corresponding to cyclohexene-1-carboxaldehyde ($\delta = 205$ ppm for $\text{C}=\text{O}$, 156 and 130 ppm for alkene carbons and 25–30 ppm for $-\text{CH}_2$ carbons), cyclohexene-3-carboxaldehyde ($\delta = 200$ ppm for $\text{C}=\text{O}$; 124 and 122 ppm for alkene carbons and 25–30 ppm for alkane carbons) and cyclohexane carboxaldehyde ($\delta = 200.2$ ppm for $\text{C}=\text{O}$, 20–40 ppm for CH_2 carbons).

Runs were also carried out under identical conditions without cyclohexene to study the participation of alcohols in this reaction. The ^{13}C NMR and GC analysis of the reaction mixture did not show any peaks corresponding to the carbonylated products of alcohol such as carboxylic acids/esters, thereby eliminating the possibility of carbonylation of the solvent. This fact was also established in our earlier work on the carbonylation of ethanol [9].

Carbonylation of substituted cyclohexenes such as 1-methylcyclohexene, 3-methylcyclohexene and 4-methylcyclohexene conducted under identical conditions showed neither carbonylated product nor olefin isomerisation product. However, on increasing the temperature to 160°C , 1-methylcyclohexene, 3-methylcyclohexene and 4-methylcyclohexene gave 1-(2-methylcyclohexene)methanol (^{13}C NMR, $\delta = 97$ ppm for $-\text{CH}_2\text{OH}$, 137 and 121 ppm for olefinic carbons and 20–30 ppm for methylene carbons), 1-(4-methylcyclohexene)methanol (^{13}C NMR, $\delta = 95$ ppm for $-\text{CH}_2\text{OH}$, 133 and 127 ppm for olefinic carbons and 20–30 ppm for methylene carbons) and 1-(5-methylcyclohexene)methanol ($\delta = 95$ ppm for $-\text{CH}_2\text{OH}$, 131 and 127 ppm for olefinic carbons and 20–30 ppm for methylene carbons). In the case of 1-methylcyclohexene formation, a small amount of 2-(1-cyclohexene)ethanol ($\delta = 49$ ppm for $-\text{CH}_2\text{OH}$ of the ethanolic group, 129 and 127 ppm for olefinic carbons and 20–30 ppm for methylene carbons) was also found. The formation of the corresponding alcohols as the final products in carbonylation of olefins at higher temperatures is reported in the literature [10, 11].

Results and discussion

The effect of catalyst concentration, cyclohexene concentration, dissolved CO concentration and temperature on the initial rates of carbonylation of cyclohexene was investigated. For each variable, the initial rates were calculated from the plots of cyclohexene consumed *vs.* time.

The CO solubility data required under the reaction conditions were independently determined [12].

Effect of catalyst concentration

The effect of catalyst concentration (varied in the range 0.5–2.0 mM) on the reaction rate was studied at 120°C , 0.987 M cyclohexene concentration

and 0.45 M dissolved CO concentration. The results are shown in Fig. 1, which indicates 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 13–20 atm) was studied at 0.987 M cyclohexene concentration, 2 mM catalyst and at 120 °C. A plot of rate of carbonylation *vs.* dissolved CO concentration is presented in Fig. 2, which indicates a first-order dependence of the reaction with respect to dissolved CO concentration.

Effect of cyclohexene concentration

The reaction was studied at 120 °C as a function of cyclohexene concentration (varied from 0.5–0.987 M) at a catalyst concentration of 2 mM and dissolved CO concentration of 0.45 M. Figure 3 shows a plot of rate of carbonylation *vs.* cyclohexene concentration, which indicates first-order dependence with respect to cyclohexene concentration.

Effect of temperature

The effect of temperature on the rate of carbonylation of cyclohexene was studied in the temperature range 100–140 °C at constant conditions of catalyst concentration 2 mM, cyclohexene concentration of 0.987 M and dissolved CO concentration of 0.45 M. From the plot of $-\ln$ rate *vs.* $1/T$ (Fig. 4), the activation energy, E_a , is evaluated at 16 ± 1 kcal mol⁻¹.

Mechanism

Based on the products formed and kinetics of cyclohexene carbonylation catalysed by complex **2**, the mechanism shown in Scheme 1 is proposed.

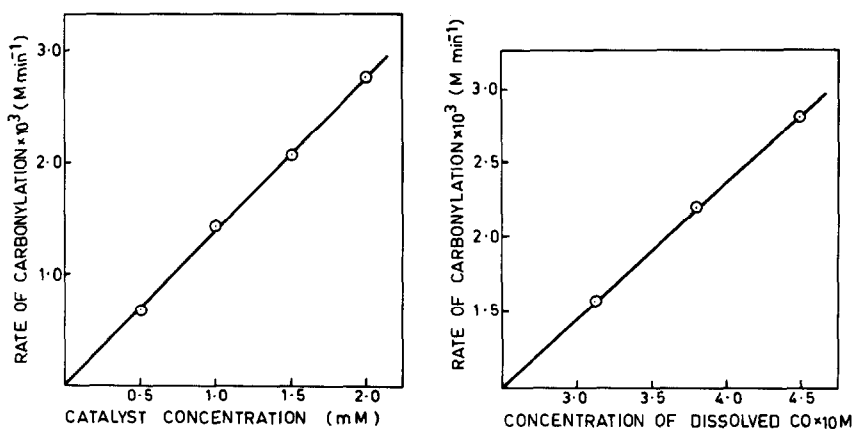


Fig. 1. Effect of catalyst concentration on the rate of carbonylation of cyclohexene.

Fig. 2. Effect of CO concentration on the rate of carbonylation of cyclohexene.

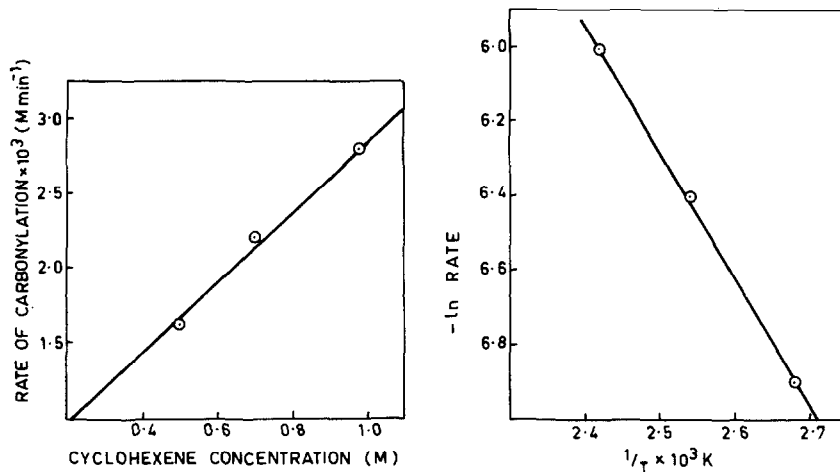
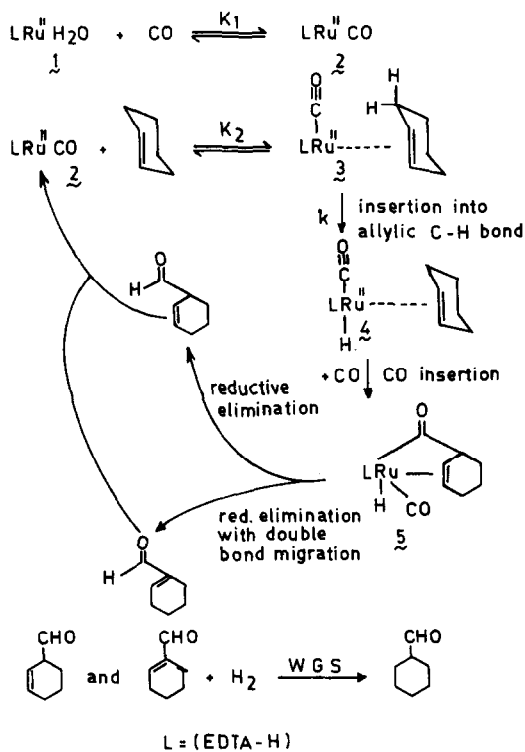


Fig. 3. Effect of cyclohexene concentration on the rate of carbonylation of cyclohexene.

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



Scheme 1.

In the proposed mechanism, the active catalytic species $[\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})(\text{CO})]$ **2** is formed *in situ* by the reduction of $[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})(\text{H}_2\text{O})]$ to $[\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})(\text{H}_2\text{O})]$ **1** by CO. $[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})(\text{H}_2\text{O})]$ is formed in solution by rapid aquation [13] of the starting material $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})(\text{Cl})]\cdot 2\text{H}_2\text{O}$. Species **1** reacts with CO in a pre-equilibrium step K_1 to form the active catalytic species **2** by the displacement of a water molecule. In the second pre-equilibrium step K_2 , the substrate cyclohexene reacts with complex **2** to form the mixed ligand η^2 -olefin complex **3**. The rate-determining step is considered to be the insertion of Ru catalyst in the allylic C—H bond to form an allylic intermediate **4**. The next step, CO insertion (or alkyl migration), which is a well-known step in homogeneous catalysis, affords an acyl species **5** which, on reductive elimination and simultaneous double bond migration, gives cyclohexene-1-carboxaldehyde and cyclohexene-3-carboxaldehyde, regenerating species **2** by reaction with CO. Cyclohexane carboxaldehyde is formed via the hydrogenation of cyclohexene-1-carboxaldehyde and cyclohexene-3-carboxaldehyde by hydrogen gas released from the water-gas-shift reaction. The occurrence of the water-gas shift reaction under the reaction conditions has been established in our earlier studies [14].

The products observed in the case of carbonylation of substituted cyclohexenes can also be accounted for in terms of the mechanism shown in Scheme 1. However, the product analysis suggests that at higher temperatures only vinylic products are favoured.

Rate law for cyclohexene carbonylation

Based on the kinetic observations for the carbonylation of cyclohexene, the rate law can be written as:

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

where $[\text{CAT}]_{\text{T}}$ = total $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ concentration, $[\text{CO}]$ = dissolved CO concentration, $[\text{S}]$ = cyclohexene 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) can be rearranged into slope and intercept form as:

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

From the slope and intercept obtained by plotting a graph of $[\text{CAT}]_{\text{T}}/\text{rate}$ vs. $1/[\text{S}]$, the values of K_2 and k , calculated respectively from the known value of K_1 [15], are as follows:

$$K_1 = 4.9 \text{ M}^{-1}$$

$$K_2 = 1.9 \text{ M}^{-1}$$

$$k = 1.43 \text{ min}^{-1}$$

The activation parameters calculated for the carbonylation of cyclohexene at 120 °C and 20 atm CO partial pressure are: $E_a = 16.0 \text{ Kcal mol}^{-1}$, $\Delta H^\ddagger = 15.0 \text{ Kcal mol}^{-1}$, $\Delta S^\ddagger = +35 \text{ e.u.}$

The positive enthalpy value observed in this case ($\Delta H^\ddagger = 15.0 \text{ Kcal mol}^{-1}$) indicates that the reaction is exothermic in nature, which may be due to the energy needed for the insertion of the CO molecule into the allylic C—H bond of cyclohexene to form the allylic intermediate **3**. The more positive value of ΔS^\ddagger ($\Delta S^\ddagger = +35 \text{ e.u.}$) supports the associative mechanism wherein intramolecular insertion of CO takes place in species **4**.

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