KINETICS AND MECHANISM OF THE REDUCTIVE CARBONYLATION OF NITROBENZENE CATALYZED BY DICHLOROBIS(SALICYLALDEHYDE)-*o*-PHENYLENEDIIMINATORUTHENATE(III)

M. M. TAQUI KHAN*, S. B. HALLIGUDI, SUMITA SHUKLA and Z. A. SHAIKH

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

Summary

The complex [Ru(saloph)Cl$_2$] (saloph = bis(salicylaldehyde)-*o*-phenylenediimine) catalyzes the reductive carbonylation of nitrobenzene in ethanol to one exclusive product, phenylurethane. The reaction proceeds at mild conditions of 15 atm CO and 160 °C with a turnover rate of 80 mol product per mol catalyst per hour. The rates of carbonylation of nitrobenzene measured at 160 °C and 3 - 15 atm CO partial pressure were found to exhibit first-order dependences with respect to catalyst, dissolved CO and nitrobenzene concentrations. The rates of the reductive carbonylation of nitrobenzene were measured in the temperature range 140 - 160 °C and the activation energy E_a was calculated as 38 kcal mol^{-1}.

Introduction

The reductive carbonylation of nitrobenzene to phenylurethane is a very important reaction from the viewpoint of production of polyurethane foam and fibers [1]. The reductive carbonylation of nitrobenzene in the presence of a transition metal catalyst [2 - 7] offers a convenient non-corrosive route for the synthesis of phenylurethane. Various transition metal catalysts have been reported [8 - 10] for the reductive carbonylation of nitrobenzene to phenylurethane. In the pressure range 60 - 100 atm CO and at ~200 °C, the turnover rates in most cases are in the range 10 - 30 mol product per mol catalyst per hour.

In an earlier paper [11] we have reported the turnover rates of the reductive carbonylation of nitrobenzene with a variety of Ru(III)–Schiff base complexes at the relatively mild conditions of 15 atm CO and 160 - 200 °C. A maximum turnover rate of 80 mol product per mol catalyst per hour was obtained [11] from [Ru(saloph)Cl$_2$] 1.

---

*Author to whom correspondence should be addressed.

The present paper describes the kinetics and mechanism of the reductive carbonylation of nitrobenzene catalyzed by 1. In the CO pressure range of 3 - 15 atm, the rate of carbonylation of nitrobenzene by 1 is first order with respect to CO partial pressure, catalyst and nitrobenzene concentrations. The reaction was studied in the temperature range 140 - 160 °C and the activation energy is reported. A mechanism for the reaction based on the kinetic observations is proposed.

Experimental

The preparation of [Ru(saloph)Cl$_2$] has been reported in our earlier publication [11].

The reductive carbonylation of nitrobenzene was conducted in a 300 ml stainless steel pressure reactor (Parr Instruments Co., USA). In a typical experiment, the carbonylation runs were carried out in 100 ml ethanol by charging the substrate (nitrobenzene) and the catalyst over a wide range of concentrations. The CO pressure was varied from 3 - 15 atm.

The bomb was pressurized by CO to the desired value when the required temperature was attained. The reaction was initiated by starting the agitation. Liquid samples were withdrawn from the reactor at different time intervals to monitor the progress of the reaction. The reaction mixture was analyzed for phenylurethane by GLC (Shimadzu, GC-9A) with a stainless steel column comprising 5% SE-30 supported on Carbowax 80/100 mesh (2.5 m length) and a FID detector. The column temperature was programmed in the range 120 - 250 °C with an injector temperature of 275 °C. Nitrogen carrier gas was used with a flow rate of 30 ml min^{-1}.

Results and discussion

The kinetics of the reductive carbonylation of nitrobenzene in ethanol solvent to give exclusively phenylurethane was studied using the complex catalyst [Ru(saloph)Cl$_2$] 1. The effects of catalyst concentration, substrate concentration, dissolved CO concentration and temperature on the initial rates of carbonylation of nitrobenzene were determined from the plots of moles of nitrobenzene consumed *vs.* time. The CO solubility data required under the reaction conditions were determined separately [12] and used in kinetic interpretation.

Effect of catalyst concentration

The catalyst concentration was varied from 0.2 to 1.0 mmol at a nitrobenzene concentration of 0.04 M, dissolved CO concentration of 0.28 M and at 160 °C. The initial rates of carbonylation of nitrobenzene exhibit a first-order dependence with respect to the catalyst concentration, as shown in Fig. 1.
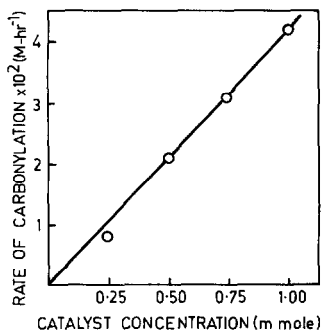
Fig. 1. Effect of catalyst concentration on the rate of carbonylation of nitrobenzene.
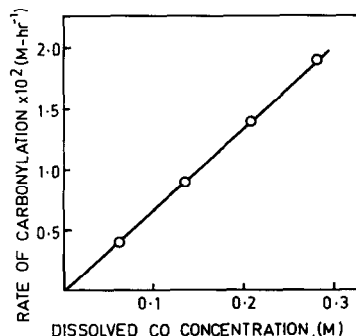
Fig. 2. Effect of CO pressure on the rate of carbonylation of nitrobenzene catalyzed by complex 1.

Effect of dissolved CO concentration

The effect of dissolved CO concentration on the rate of carbonylation was studied with nitrobenzene concentration of 0.04 M and catalyst concentration of 0.5 mmol at 160 °C by varying the CO concentration in the range 0.10 to 0.28 M (3 - 15 atm CO). The plot of the rate of carbonylation *vs.* dissolved CO concentration (Fig. 2) shows a first-order dependence of the rate of reductive carbonylation of nitrobenzene with respect to dissolved CO concentration.

Effect of nitrobenzene concentration

Figure 3 shows the dependence of the rate of carbonylation of nitrobenzene with respect to initial nitrobenzene concentration. The concentration of nitrobenzene was varied in the range 0.01 - 0.04 M, keeping other conditions constant, *i.e.* a dissolved CO concentration of 0.28 M and catalyst concentration of 0.5 mmol at 160 °C. The reaction is first order with respect to nitrobenzene concentration.

Effect of temperature

The effect of temperature on the rate of carbonylation of nitrobenzene was studied in the temperature range 140 - 160 °C for concentrations of nitrobenzene at 0.04 M, catalyst at 0.5 mmol and dissolved CO 0.28 M. A plot of $-\ln$ rate *vs.* $1/T$ is shown in Fig. 4, from which the value of the activation energy E_a was evaluated as 38.0 kcal mol^{-1}.

Mechanism

The reductive carbonylation of nitrobenzene catlayzed by complex 1 gave only phenylurethane. Based on the product formed and from the kinetic parameters, *i.e.* first-order dependences on substrate, catalyst and CO concentration, the following mechanism is proposed for the reaction (Scheme 1).
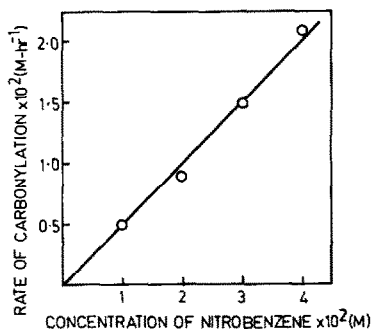
Fig. 3. Effect of initial concentration of nitrobenzene on the rate of carbonylation catalyzed by complex 1.
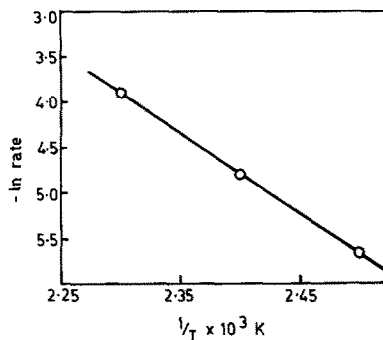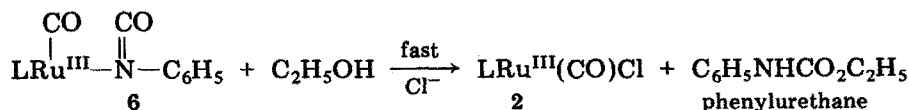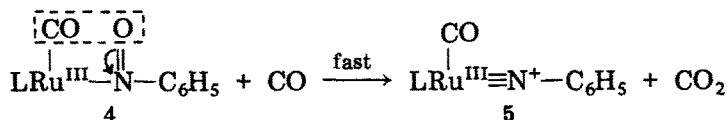
Fig. 4. Effect of temperature on the rate of carbonylation of nitrobenzene catalyzed by complex 1.

$$LRu^{III}Cl_2 + CO \underset{}{\overset{K_1}{\rightleftharpoons}} LRu^{III}(CO)Cl + Cl^-$$
$$\quad\quad\ 1 \quad\quad\quad\quad\quad\quad\quad\quad\quad\ 2$$

$$LRu^{III}(CO)Cl + C_6H_5NO_2 \underset{}{\overset{K_2}{\rightleftharpoons}} LRu^{III}(CO)(C_6H_5NO_2) + Cl^-$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 3$$
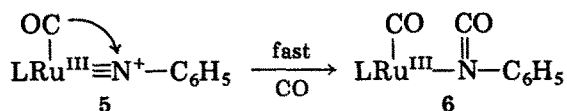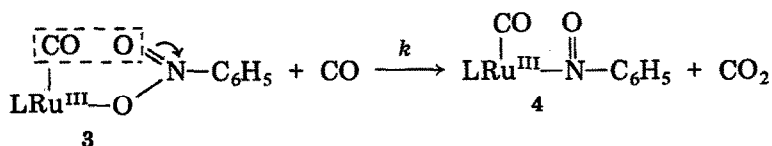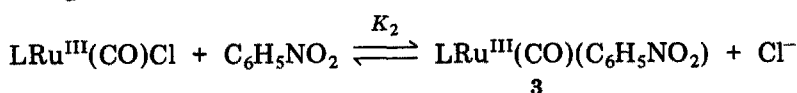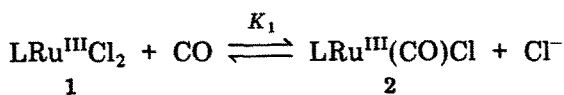
L = bis(salicylaldehyde)-o-phenylenediimine (saloph)

Scheme 1.

In the proposed mechanism (Scheme 1), complex 1 reacts with a molecule of CO to give [LRu^{III}(CO)Cl] species 2 in a pre-equilibrium step. The solution spectra of the carbonylation experiment conducted in the absence of substrate nitrobenzene showed a peak at 370 nm which is attributed to the LMCT band of the carbonyl complex 2 [13 - 15]. In a second pre-equilibrium step, nitrobenzene forms a mixed ligand complex 3 which reacts with another molecule of CO in a rate-determining step to give the Ru(III)–nitroso complex 4 by deoxygenation of –NO$_2$ group of nitrobenzene and the release of CO$_2$. The solution spectra of reaction mixture withdrawn while the reaction was in progress showed a characteristic peak of the Ru–NO bond at 316 nm [13, 16]. The nitroso complex 4 quickly takes up one more molecule of CO in a fast step to give a nitride intermediate species 5 via deoxygenation of the nitroso –NO group. Migration of CO of the electrophilic nitrogen atom of the M≡N$^+$–R intermediate gives the coordinated phenylisocyanate complex 6, which reacts with ethanol in the presence of CO in a fast step to give phenylurethane, simultaneously regenerating the active catalytic species 2.

Rate law

Based on the kinetic study, the rates of carbonylation of nitrobenzene catalyzed by complex 1 were found to exhibit first-order dependences with respect to catalyst, dissolved CO and initial substrate concentrations. Taking into consideration the total catalyst concentration present in the form of different species *in situ* at steady-state conditions, the final rate law can be written as:

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

where [CAT]$_T$ = total catalyst concentration of complex 1, [CO] = dissolved CO concentration, [S] = nitrobenzene concentration, K_1 and K_2 are the pre-equilibrium constants and k is the rate constant.

To evaluate the kinetic constants, the above eqn. (1) can be rearranged as:

$$\frac{[\text{CAT}]_T}{\text{rate}} = \frac{1}{[\text{CO}]}\left(\frac{1}{kK_1K_2[\text{S}]} + \frac{1}{kk_2}\right) + \frac{1}{k} \tag{2}$$

From eqn. (2), the value of k was calculated from the intercept obtained by plotting the graph of [CAT]$_T$/rate *vs.* 1/[CO]. The value of equilibrium constant K_1 was determined spectrophotometrically at room temperature by monitoring the peak at 370 nm (complex 2, Scheme 1) and extrapolated to 160 °C by multiplying with a temperature coefficient. Substituting the values of K_1, k and [S] in the value of the slope obtained in eqn. (2), the value of K_2 was evaluated. The kinetic constants determined for the complex 1-catalysed reductive carbonylation of nitrobenzene to give phenylurethane at 160 °C and 15 atm CO are:

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

$K_2 = 23.5 \ M^{-1}$

$k = 4.0 \ min^{-1}$

The activation energy E_a was calculated from the temperature dependence of the rate of carbonylation of nitrobenzene in the range 140 - 160 °C as 38 kcal mol^{-1}. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values calculated at 160 °C are 37.0 kcal mol^{-1} and +86.0 e.u., respectively. The $\Delta H^{\neq}$ value of 37.0 kcal mol^{-1} observed in this study indicates that the reductive carbonylation of nitrobenzene is highly endothermic in nature. This is expected because of the bond cleavage in the transition state. A high positive value of $\Delta S^{\neq}$ (+86.0 e.u.) reflects the various dissociative steps involved in the formation of the active intermediate. The catalytic activity of the Schiff base complex depends on the presence of labile axial chloride groups to facilitate such dissociation and the subsequent formation of a nitroso complex species 4. The driving force for the reaction is thus the high positive entropy of the reaction.

Conclusions

In comparison with similar studies in the literature, the turnover rates reported here are at least four times higher for the [Ru^{III}(saloph)Cl$_2$]-catalyzed reductive carbonylation of nitrobenzene to give exclusively phenylurethane at 160 - 200 °C and a low partial pressure of CO of 3 - 15 atm.

References

1 R. G. Arnold, J. A. Nelson and J. J. Verbanc, *Chem. Rev.*, *57* (1957) 47.
2 S. Cenini, M. Pizzotti, C. Crotti, F. Porta and G. L. Monica, *J. Chem. Soc., Chem. Commun.*, (1984) 1286.
3 A. Bontempi, E. Alessio, G. Chanos and G. Mestroni, *J. Mol. Catal.*, *42* (1987) 67.
4 Y. Watanate, Y. Tsuji and N. Suzuki, *Chem. Lett.*, (1982) 105.
5 *U.S. Pat. 3 531 512* (1970) to W. B. Hardy and R. P. Bennett.
6 A. L. Lapidus, S. D. Pirozhkov, Yu. V. Antipov, B. K. Nefedov and S. F. Politanskii, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, (1983) 1350.
7 P. Braunstein, R. Bender and J. Kerrennal, *Organometallics*, *1* (1982) 1236.
8 K. Univerferth, R. Hontsch and K. Schwetlick, *J. Prakt. Chem.*, *321* (1974) 86.
9 S. Fukuoka, M. Chono and M. Kohno, *Chemtech*, (1984) 670.
10 V. I. M. Yuvenskii and B. K. Nefedov, *Russ. Chem. Rev.*, *50* (1980) 470.
11 M. M. Taqui Khan, S. B. Halligudi, S. Shukla and Z. A. Shaikh, *J. Mol. Catal.*, *57* (1989) 9.
12 M. M. Taqui Khan, S. B. Halligudi and S. Shukla, *J. Chem. Eng. Data*, *34C* (1989) 353.
13 A. A. Diamantis and J. V. Dubrawski, *Inorg. Chem.*, *20* (1981) 1142.
14 A. D. Allen and J. R. Stevens, *Can. J. Chem.*, *50* (1972) 3093.
15 S. Pell and J. N. Armor, *Inorg. Chem.*, *12* (1973) 873.
16 J. V. Dubrawski and R. D. Felthan, *Inorg. Chem.*, *19* (1980) 355.