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STOICHIOMETRIC REDUCTION OF CARBON DIOXIDE TO HCHO AND HCOOH BY $K[Ru^{III}(EDTA{-}H)Cl]\cdot 2H_2O$

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Summary

The stoichiometric reduction of carbon dioxide by soluble $K[Ru^{III}(EDTA{-}H)Cl]\cdot 2H_2O$ complex at CO_2 pressures in the range of 5 - 70 atm and temperatures 40 - 80 °C gave formic acid and formaldehyde as the reaction products. The rates of formation of formic acid and formaldehyde were found to have first order dependence with respect to catalyst and dissolved CO_2 concentrations. Activation energies of 3.5 kcal mol^{-1} for formaldehyde and 4.8 kcal mol^{-1} for formic acid were obtained by studying the temperature dependence of the rates of formation of both the products. Based on the products formed and kinetic observations, a possible mechanism is proposed.

Introduction

Carbon dioxide and water are the end products of many chemical and biological processes. The utilization of CO_2 to synthesize value-added chemicals is, therefore, of much importance in industry. CO_2 is used industrially in large quantities for the preparation of urea [1] and inorganic compounds such as carbonates and bicarbonates. Activation of CO_2 by transition metal complexes to form adducts is an active area of investigation [2 - 8]. The synthesis of methyl formate by the reaction of CO_2, H_2 and CH_3OH catalyzed by $Ru(PPh_3)_3Cl_2$ is a good example of the reductive fixation of CO_2 [9]. $CO_2 + H_2$ have been used in place of $CO + H_2$ in the synthesis of homologous alkanes, alkenes, alcohols and amines in the presence of NH_3 [10 - 12]. The rhodium complex $Rh(diphos)(BPh_4)$ catalyzes the co-oligomerization of CO_2 and methyl acetylene to give cyclic compounds [13].

The present paper reports the reduction of CO_2 to formic acid and formaldehyde by the water soluble $K[Ru^{III}(EDTA)Cl]\cdot 2H_2O$ system under mild reaction conditions (40 - 80 °C, 5 - 70 atm). The system suggests the

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possibility for a catalytic cycle for the fixation of CO_2 to value-added products.

Experimental

The CO_2 fixation experiments were performed in a 300 ml pressure reactor (Parr Instrument Co., USA). The operating procedure and other details of the reactor have been described in our earlier publication [14].

Carbon dioxide gas with a purity greater than 99.5% was obtained from Industrial Gas Suppliers, Bhavnagar. The complex $K[Ru^{III}(EDTA—H)Cl]\cdot 2H_2O$ **1** (EDTA—H = protonated ethylenediamine-tetraacetic acid) was prepared using $RuCl_3\cdot 3H_2O$ and the disodium salt of EDTA, according to the procedure described elsewhere [15]. Acetyl acetone, acetic acid and ammonium acetate required to prepare Nash's reagent [16, 17] for the analysis of HCOOH and HCHO were of AR grade. Water used for these experiments was double distilled.

In a sample run, a known amount of complex **1** was dissolved in 100 ml of distilled water and placed in the pressure reactor. The bomb was pressurized by CO_2 to the required value when the desired temperature was attained. The progress of the reaction was monitored by analyzing liquid samples withdrawn at different intervals of time for HCOOH and HCHO contents. The concentrations of HCHO and HCOOH present in the liquid samples were estimated spectrophotometrically by monitoring the peak at 412 nm using Nash's reagent [16, 17]. From the graphs of time *vs.* amount of HCHO or HCOOH formed, the rates of formation of both the products were evaluated. Gaseous samples were also withdrawn at suitable intervals of reaction time and analysed for CO_2 and CO contents using a GLC (Shimadzu GC-9A). The column used for the analysis of gases was a 2.5 m long s.s Porapak-Q-80/100 mesh with a TC detector (150 °C), column temperature 40 °C, injector temperature 50 °C and H_2 carrier gas with a flow rate of 30 ml min^{-1}.

The required solubility data of CO_2 in water at different temperatures and pressures were taken from the reported values [18], and the total dissolved CO_2 concentration needed to interpret the kinetic data was calculated.

Results and discussion

In order to fix the conditions for kinetic study, the experiment was conducted with 1 mmol of complex **1**, a CO_2 partial pressure of 68.0 atm and at 80 °C. The yields of HCOOH and HCHO formed as a function of time are shown in Fig. 1. It is clear from the graph that the concentrations of both HCHO and HCOOH increase with time, reaching a maximum in 3 - 4 h; later both the products tend to dissociate, resulting in a decrease in their concentrations. The reduction in the concentration of HCHO is more pronounced than that of HCOOH. Therefore, the rates of formation of

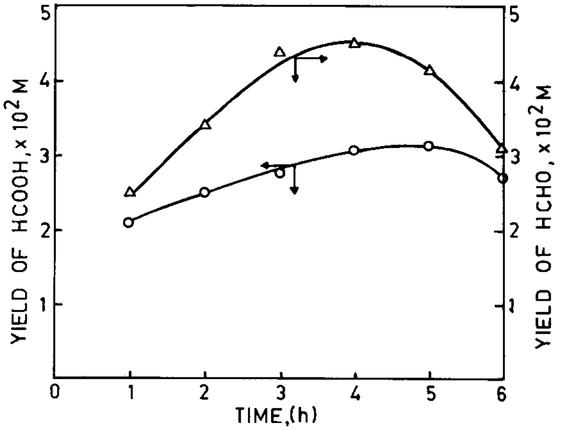


Fig. 1. The yields of HCOOH (○) and HCHO (△) in CO_2 reduction by $K[Ru^{III}(EDTA-H)Cl]\cdot 2H_2O$.

HCHO and HCOOH were evaluated in the interval between 1 - 3 h, which ensured a linear dependence. The decay rate of HCHO was evaluated in the declining portion of the curve after 3.5 h.

Kinetics

The kinetic experiments on CO_2 reduction were conducted by varying the concentrations of CO_2, and rates of formation of HCHO and HCOOH were evaluated.

Effect of complex concentration

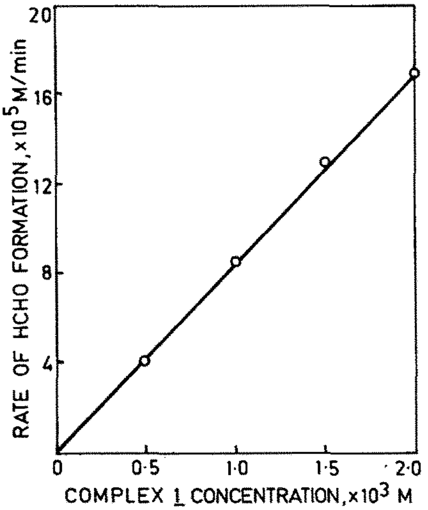
The concentration of complex 1 was varied from 0.5 - 2 × 10^{-3} M with a constant dissolved CO_2 concentration of 3.9 × 10^{-2} M and temperature of 80 °C for all the runs. The dependence of rates of formation of HCHO and HCOOH on the concentration of complex 1 are shown in Figs. 2 and 3, respectively. Both HCHO and HCOOH rates show a first order dependence with respect to complex 1 concentration.

Effect of dissolved CO_2 concentration

Figures 4 and 5 show the plot of rates of formation of HCHO and HCOOH *vs.* dissolved CO_2 concentration. The experiments were performed keeping a constant complex concentration of 1 × 10^{-3} M, 80 °C and varying the dissolved CO_2 concentration from 1.98 × 10^{-2} M to 7.73 × 10^{-2} M (17 - 68 atm CO_2). The rates of formation of both HCHO and HCOOH show a linear dependence on CO_2 concentration.

Temperature

The temperature of the experiments for reduction of CO_2 by complex 1 was varied between 40 - 80 °C, with other conditions constant such as catalyst concentration of 1 × 10^{-3} M and dissolved CO_2 concentration of



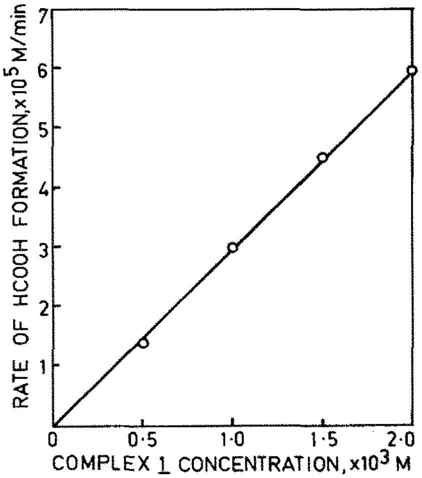


Fig. 2. Effect of complex 1 concentration on the rate of HCHO formation.

Fig. 3. Effect of complex 1 concentration on the rate of HCOOH formation.

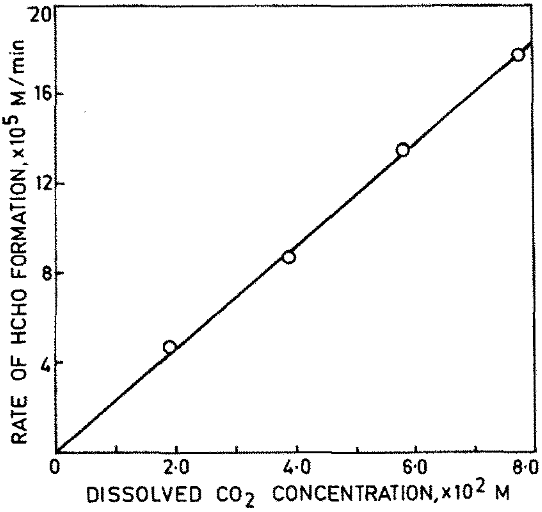


Fig. 4. Effect of dissolved CO_2 concentration on the rate of HCHO formation.

3.9×10^{-2} M. Figure 6 shows the graph of $-\ln$ rate *vs.* $1/T$. From the slopes of both the straight lines, the activation energies evaluated for HCOOH and HCHO are 4.8 kcal mol^{-1} and 3.5 kcal mol^{-1}, respectively.

Mechanism

The reduction of CO_2 by complex 1 gave two products, namely HCHO and HCOOH. The rates of formation of both the products have a first-order dependence with respect to catalyst and dissolved CO_2 concentrations.

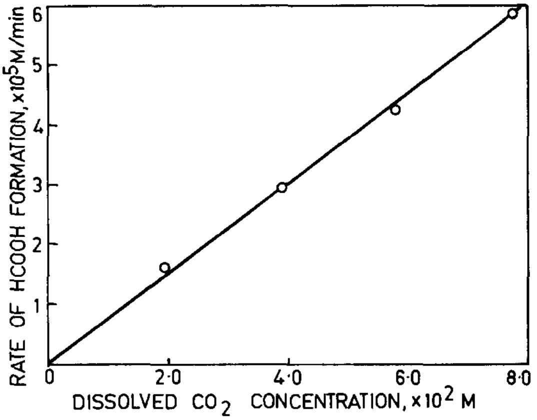


Fig. 5. Effect of dissolved CO_2 concentration on the rate of HCOOH formation.

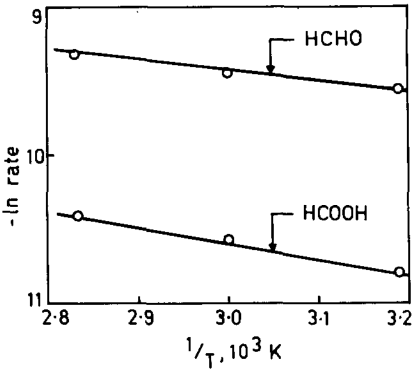
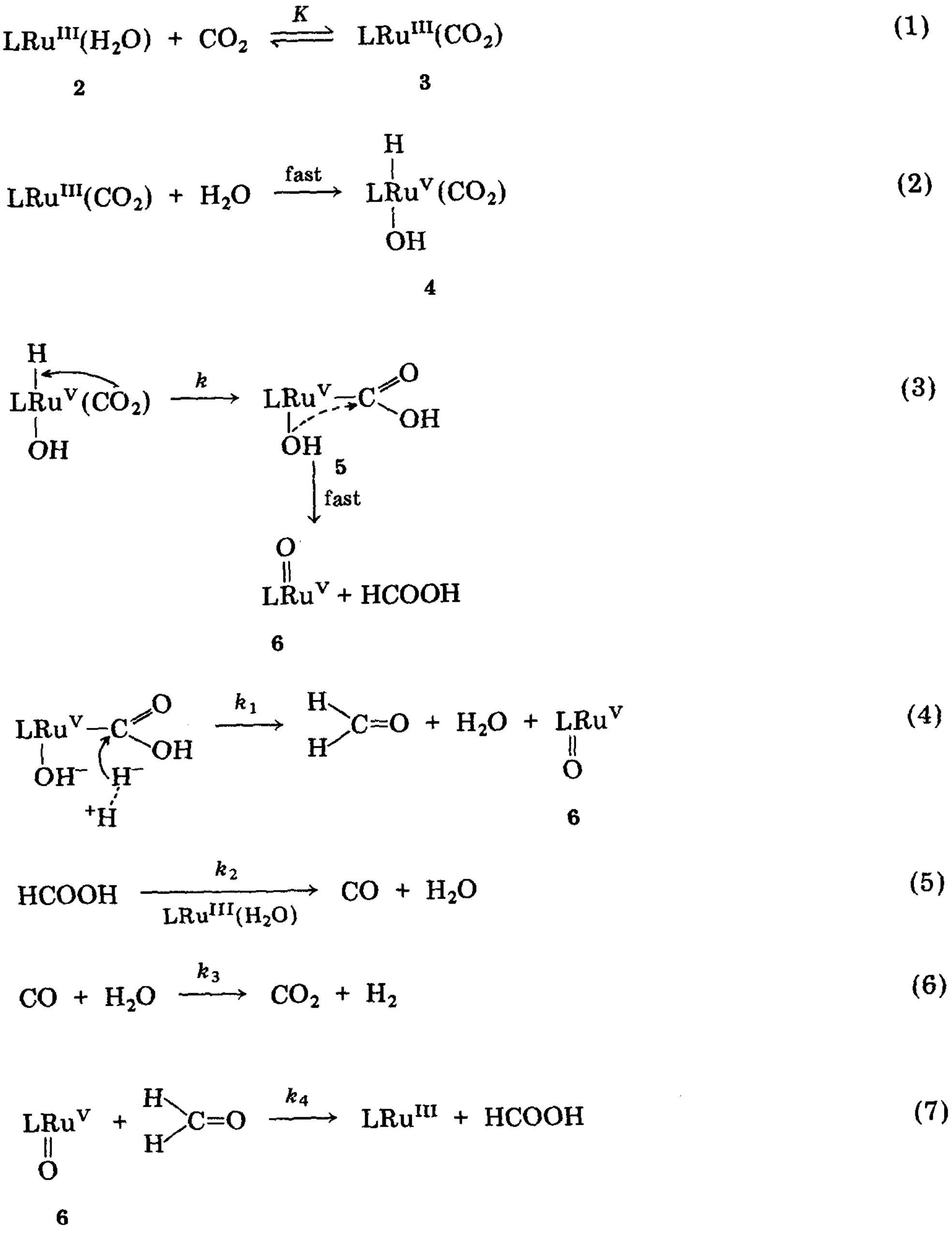


Fig. 6. Effect of temperature on the rates of formation of HCOOH and HCHO.

Based on these observations, the mechanism proposed for the reactions is shown in Scheme 1.

The complex 1 undergoes a rapid aquation in presence of water to give Ru(III) aquo species 2 [19], which reacts with CO_2 to form a CO_2 adduct 3. The formation of such CO_2 adducts were reported in the literature [3 - 5]. Species 3 activates water oxidatively in step (2) to form the Ru(V) species 4. The insertion of CO_2 into the Ru—H bond of 4 takes place in step (3) to form an η^1-formate species 5.

The metalloformate complex 5 undergoes a rapid intermolecular protonation resulting in the formation of formic acid and Ru^V–oxo species 6. Reductive elimination of metalloformate complexes to formate derivatives such as methyl formate from methanol, CO_2 and H_2 had been reported [9]. The electrons needed for the reduction of CO_2 to $HCOO^-$ in our case are obtained by the hydride insertion step (3). The formation of ruthenium(V) oxo species 6 is characterised by the appearance of a band at 390 nm. Species 6 also gives ν(Ru=O) at 810 cm^{-1}. In step (5), the formic acid formed in step (3) is catalytically decomposed to CO and H_2O by complex 2.



Scheme 1. Mechanism for the stoichiometric fixation of CO_2 by $LRu^{III}(H_2O)$.

The rate of decomposition of formic acid catalyzed by **1** was estimated in a separate experiment. It was confirmed by the analysis of both liquid as well as gas samples withdrawn at different time intervals that HCOOH decomposes into CO and H_2O. The CO obtained in step (5) is rapidly converted to CO_2 by the water–gas shift reaction [20].

The η^1-carboxylate species 5 reacts with H_2 in step (4) to give HCHO and Ru(V)–oxo species 6. Thus, the Ru(V)–oxo species is an end product of reduction of CO_2. In step (7), HCHO is oxidized to HCOOH by $LRu^V{=}O$ species regenerating species 2.

Rate laws

From the kinetic observations of the reduction of CO_2 to HCOOH and HCHO by $K[Ru^{III}(EDTA{-}H)Cl]\cdot 2H_2O$, the rate equation can be written as:

$$r_1 = \frac{kK[Ru^{III}(EDTA{-}H)(H_2O)]_T[CO_2]}{1 + [CO_2]} \tag{1}$$

$$r_2 = \frac{kk_1K[Ru^{III}(EDTA{-}H)(H_2O)]_T[CO_2]}{1 + [CO_2]} \tag{2}$$

where r_1 = rate of formation of HCOOH, r_2 = rate of formation of HCHO, $[Ru^{III}(EDTA{-}H)(H_2O)]_T$ = total complex 1 concentration, $[CO_2]$ = dissolved CO_2 concentration, K = equilibrium constant, k = rate constant for the formation of HCOOH, and k_1 = rate constant of HCHO formation.

Equations (1) and (2) can be rearranged in the following form to evaluate the kinetic constants.

$$\frac{[Ru^{III}(EDTA{-}H)(H_2O)]_T}{r_1} = \left(\frac{1}{kK} \times \frac{1}{[CO_2]}\right) + \frac{1}{k} \tag{3}$$

$$\frac{[Ru^{III}(EDTA{-}H)(H_2O)]_T}{r_2} = \left(\frac{1}{kk_1K} \times \frac{1}{[CO_2]}\right) + \frac{1}{kk_1} \tag{4}$$

From the intercepts and slopes of the above equations, the values of K, k and k_1 evaluated at 80 °C are:

$K = 7.46\ M^{-1}$

$k = 0.33\ min^{-1}$

$k_1 = 3.03\ min^{-1}$

The water–gas shift reaction occurring between CO and H_2O under the reaction conditions has a rate constant ($k_3 = 90.1\ min^{-1}$) reported in our earlier studies [20]. The values of k and k_1, the rate constants for formic acid and formaldehyde formation, respectively, are much smaller than k_3 and hence during the CO_2 reduction the CO generated by the decomposition of HCOOH participates rapidly in the water–gas shift reaction, giving CO_2 and H_2. The hydrogen produced by the water–gas shift reaction is utilized in the reduction of HCOOH and HCHO. The value of k_2 (rate constant for HCOOH decomposition), determined independently in the absence of CO_2 and in the presence of complex 1 at 80 °C, is $1.52\ min^{-1}$. The formic acid decomposition rate constant (k_2) is smaller than (k_3) (water–gas shift reaction rate constant) and much higher than (k) and (k_1), ensuring the complete conversion of CO generated into CO_2 and H_2 *in situ*.

Because of the difference in the rates of formation of HCHO and HCOOH and the rate of decomposition of HCOOH, there is a slow increase in the concentration of HCOOH with time (Fig. 1). The HCHO concentration builds up faster than HCOOH and at any given instant is higher than that of HCOOH. After the first 3 h of reaction, however, there is a buildup in the concentration of the oxo species 6 because of reactions (3) and (4). The formaldehyde formed starts to interact with the oxo species 6 to form complex 1 and HCOOH. The rate constant (k_4) calculated for this reaction from the declining part of Fig. 1 is 3×10^{-3} min^{-1}. Thus, there is a fall in the concentration of HCHO after its maximum concentration is reached in 3 - 5 h, and after a period of 6 h the two products HCHO and HCOOH appear to attain their steady state concentration.

The rate constants for the water–gas shift reaction (k_3), formic acid decomposition (k_2) and CO_2 reduction to HCHO (k_1), formaldehyde formation (k_1), formate formation (k) and oxidation of HCHO by Ru(V)—oxo species (k_4) decrease in the order:

$$k_3 \gg k_2 > k_1 > k > k_4$$

The activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ for the reduction of CO_2 to HCOOH and HCHO are presented in Table 1. The data were obtained at 34 atm of CO_2 in the temperature range 40 - 80 °C. The activation parameters evaluated earlier [21] for CO hydration catalyzed by complex 1 to give HCOOH and its reduction to give HCHO at 40 - 80 °C are also presented in Table 1 for comparison. The enthalpies of activation $\Delta H^\ddagger$ for the formation of HCOOH and HCHO in CO_2 reduction are 4.25 and 2.82 kcal mol^{-1}, respectively, which are about three times less endothermic than the conversion of CO to HCOOH and HCHO, *i.e.* 13.5 and 6.7 kcal mol^{-1}, respectively. The lower order of endothermicity of CO_2 reduction products indicates that the formation of HCOOH and HCHO is more facile via CO_2 reduction than CO hydration and reduction.

TABLE 1

Thermodynamic parameters for HCHO and HCOOH formed by CO and CO_2 activation

Activation parameters	CO[a]		CO_2	
	HCHO	HCOOH	HCHO	HCOOH
E_a (kcal mol^{-1})	6.7	13.5	3.5	4.8
$\Delta H^\ddagger$ (kcal mol^{-1})	6.1	12.8	2.8	4.2
$\Delta S^\ddagger$ (e.u.)	+18.0	+38.0	+8.3	+12.3
$\Delta G^\ddagger$ (kcal mol^{-1})	+0.08	+0.14	+0.06	+0.05

[a] Data taken from [21].

The entropies of formation of HCOOH and HCHO from CO_2 reduction are +12.3 e.u. for HCOOH and +8.3 e.u. for HCHO. These entropies are considerably more negative than the entropies observed [21] for the conversion of CO to HCOOH and HCHO. This reflects the higher order of rearrangements in the coordination sphere of the metal ion in CO_2 insertion as compared to CO insertion. In general, the enthalpies and entropies are more negative in HCHO formation than HCOOH formation. Since a hydrogen molecule is needed for the reduction of coordinated η^1-formato or a formyl group, the transition state requires greater reorganisation in HCHO reaction as compared to HCOOH, hence a more negative entropy. The negative enthalpy reflects the higher bond strength in HCHO and HCOOH.

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