

REDUCTION OF CO₂ BY MOLECULAR HYDROGEN TO FORMIC ACID AND FORMALDEHYDE AND THEIR DECOMPOSITION TO CO AND H₂O

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

*Discipline of Coordination Chemistry and Homogeneous Catalysis,
Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002 (India)*

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Summary

The reduction of carbon dioxide by hydrogen is catalyzed by K[Ru^{III}-(EDTA-H)Cl]·2H₂O in aqueous medium at milder pressures (1 - 4 atm CO₂ or H₂) and 40 °C. The reduction of CO₂, gives formic acid and formaldehyde as the initial reaction products, which later decompose to give CO and H₂O as the final products.

The rates of formation of formic acid and formaldehyde exhibited first-order dependence with respect to catalyst and dissolved CO₂ and H₂ concentrations, respectively. The rates of decomposition of formic acid and formaldehyde studied under the same reaction conditions also showed first-order dependence with respect to catalyst and substrate concentrations, respectively. The effect of temperature on the rates of formation and decomposition of formic acid and formaldehyde was also studied in the temperature range 30 - 50 °C, and from the Arrhenius plots activation energies were evaluated.

Based on the kinetic data, a mechanism is proposed for the formation of formic acid and formaldehyde and their decomposition to CO and H₂O, the end products of the reverse water-gas shift reaction.

Introduction

With a variety of industrial processes, large amounts of CO₂ are released into the atmosphere, causing pollution and ecological problems [1]. CO₂ is widely used for the large scale preparation of urea and certain inorganic chemicals such as carbonates and bicarbonates [2]. Carbon dioxide being an abundant source of carbon, many options are available for converting this valuable C₁ synthetic block into industrial organic chemicals.

* Author to whom correspondence should be addressed.

There have been many studies on the development of homogeneous catalysts for water-gas shift reaction [3 - 12]. In contrast, only a few examples of the homogeneously catalyzed transformations of CO_2 and H_2 into CO and H_2O have been reported [2, 13 - 15]. Many transition metal hydrides interact with CO_2 to give metal formates and bicarbonates, which then decompose to release CO [13, 14]. In an earlier paper [16], we reported the stoichiometric reduction of CO_2 catalyzed by $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ in aqueous medium to give formic acid and formaldehyde as the liquid phase products.

In this paper we report the results of $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ -catalyzed liquid phase reduction of CO_2 by H_2 into HCOOH and HCHO , and the decomposition of the latter to give CO and H_2O under the same reaction conditions.

Experimental

The experiments were conducted in a 300 ml stainless steel autoclave (Parr Instrument Co., USA) which has all the provisions for automatic operations. Carbon dioxide and hydrogen gas (purity > 99.9%), obtained from Industrial Oxygen Company, Bhavnagar, were directly used in the experiments without further purification. The water used in this study was double distilled. The chemicals required for the preparation of Nash's reagent were of A.R. grade. The catalyst precursor complex $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ 1 was prepared by known methods [17, 18] using $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$ and the disodium salt of EDTA. The products were analyzed with a Shimadzu gas chromatograph model GC-9A. The spectrophotometric measurements were conducted on a Shimadzu UV-160 spectrophotometer.

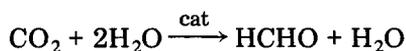
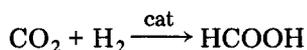
In a sample run, the experiment was conducted by charging the autoclave with known amounts of catalyst, water, CO_2 and H_2 at the desired temperature and pressure. The run conducted with 1 mmol of the catalyst in 100 ml water at $\text{CO}_2 + \text{H}_2$ (1:1) pressure of 34 atm and 40 °C gave CO as a gaseous product, and formic acid and formaldehyde as the products in the liquid phase. The gaseous samples were analyzed by GLC for CO content using a Porapak-Q 80/100 mesh stainless steel column (2.5 m in length), column temperature 40 °C and H_2 as carrier gas (flow rate 30 ml min^{-1}). The liquid samples withdrawn at different time intervals were analyzed for formic acid and formaldehyde spectrophotometrically, using Nash's reagent [19, 20], by monitoring the peak at 412 nm. The rates of formation and decomposition of formic acid and formaldehyde were obtained by knowing the amounts of both the liquid phase products formed to the maximum concentration (formation kinetics) and decomposed (decomposition kinetics) in a contact time range of 40 - 90 min under the same reaction conditions. The total contact time required for the evaluation of rates of formation of formic acid and formaldehyde determined by altering the reaction conditions was in the range of 20 - 40 min, after which the decomposition

reaction predominates. The CO_2 and H_2 solubility data required to calculate the dissolved gas concentrations were taken from the published literature [21].

Results and discussion

The thermal reduction of CO_2 by H_2 catalyzed by complex 1 gives formic acid and formaldehyde as the initial products, which later decompose under the same reaction conditions catalytically to give CO and H_2O , the final products of reverse water-gas shift reaction. For the evaluation of kinetic parameters, the reaction was considered to occur in two stages:

(A) Formation kinetics



(B) Decomposition kinetics



Formation kinetics

The rates of formation of formaldehyde and formic acid were determined at different reaction conditions by varying the concentration of catalyst, partial pressures of CO_2 and H_2 and temperature. Since the rates of formation of the products were faster than the rates of decomposition, the liquid samples were analyzed at 5 min time intervals until the maximum concentration of the products was reached, and thereafter at longer intervals after the initiation of decomposition, shown by a decrease in the concentration of HCOOH and HCHO .

Effect of catalyst concentration

The catalyst concentration was varied in the range 0.25 to 1.0 mmol, maintaining 34 atm $\text{CO}_2 + \text{H}_2$ (1:1) pressure and 40 °C. The rates of formation of HCOOH and HCHO shown were found to be first order with respect to their dependence on catalyst concentration, as in Fig. 1. The maximum rates of formation of HCOOH and HCHO , observed with 1 mmol catalyst, 34 atm $\text{CO}_2 + \text{H}_2$ (1:1) and at 40 °C, are 5.45×10^{-3} (M min^{-1}) and 4.65×10^{-4} (M min^{-1}), respectively. Therefore, a comparison of formation rates under the identical reaction conditions, mentioned above, indicates that the rate of HCOOH formation (ratio of HCOOH to HCHO rates) is 11.72 times

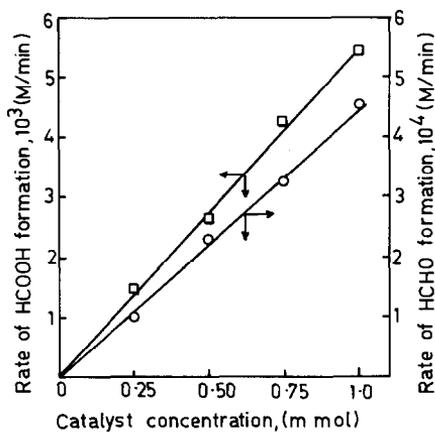


Fig. 1. Effect of catalyst concentration on the rates of formation of HCOOH (□) and HCHO (○).

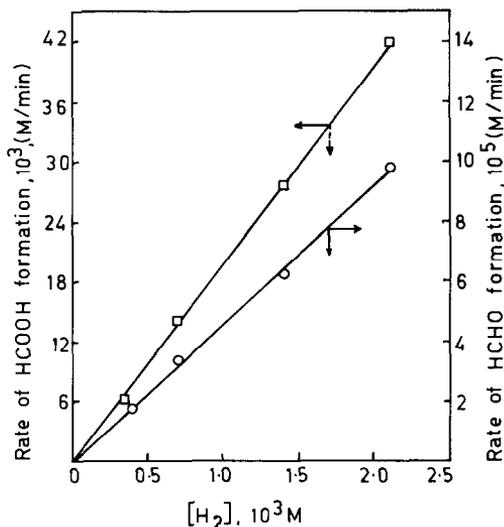


Fig. 2. Effect of [H₂] on the rates of HCOOH (□) and HCHO (○) formation.

faster than that of HCHO. This also indicates that formic acid is a major product of the reduction of CO₂ by H₂ catalyzed by complex 1.

Effect of hydrogen pressure

The hydrogen pressure was varied in the range 0.5 to 3 atm (0.35 × 10⁻³ - 2.10 × 10⁻³ M dissolved H₂ concentration) keeping CO₂ at 17 atm (0.35 M) and the catalyst at 1 mmol at 40 °C. The rates of formation of formic acid and formaldehyde were found to have a first-order dependence (Fig. 2) with respect to dissolved H₂ concentration. It is very interesting to note here that the rates of formation of HCOOH are significantly enhanced (300 - 400 fold) in comparison with HCHO using a ratio of H₂/CO₂ in the range 9.4 × 10⁻⁴ to 60 × 10⁻⁴. With 1 mmol of catalyst concentration and 17 atm CO₂, the rates for the formation of HCOOH and HCHO are 2 × 10⁻² M min⁻¹ and 0.05 × 10⁻³ M min⁻¹, respectively. Thus the rate of HCOOH formation is about 400 times faster than that of HCHO. Therefore, lower H₂ pressures, up to 3 atm, and higher CO₂ pressures, around 17 atm, are favourable conditions to obtain a maximum yield of HCOOH at 40 °C.

Effect of CO₂ pressure

Figure 3 shows the graph of rates of formation of HCOOH and HCHO vs. dissolved CO₂ concentration. The CO₂ concentration is varied from 1 × 10⁻² M to 6 × 10⁻² M (0.5 to 3 atm), keeping other parameters constant, i.e. 1.25 × 10⁻² M H₂ concentration (17 atm), 1 mmol catalyst and 40 °C. The rates of formation of HCOOH and HCHO are linear, indicating a first-order dependence with respect to dissolved CO₂ concentration. The rates of

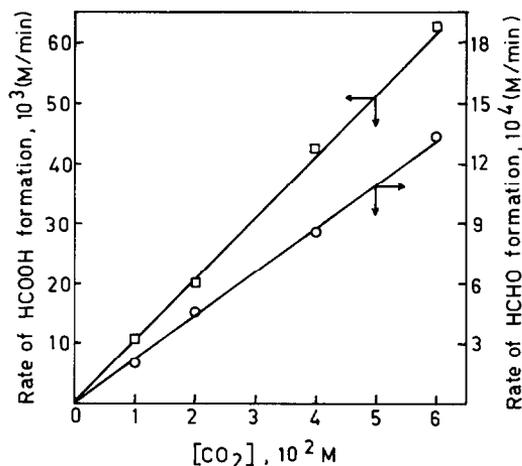


Fig. 3. Effect of dissolved CO_2 concentration on the rates of HCOOH (\square) and HCHO (\circ) formation.

formation of HCOOH ($62.5 \times 10^{-3} \text{ M min}^{-1}$) and HCHO ($13.5 \times 10^{-4} \text{ M min}^{-1}$) observed at 40°C and 1 mmol catalyst concentration with a CO_2/H_2 ratio of 4.8 (highest studied) indicates that the rate of HCOOH formation is about 46 times higher than that of HCHO, showing a preference for HCOOH formation in the reduction of CO_2 by H_2 . The rates for HCOOH and HCHO formation (Fig. 3) are $1.04 \times 10^{-3} \text{ M min}^{-1}$ and $0.023 \times 10^{-3} \text{ M min}^{-1}$, respectively, which are in the ratio 46 (HCOOH/HCHO) in comparison with a ratio of specific rate constants of 400 with a CO_2/H_2 concentration of $10^3 - 10^2$. Our investigations confirm that excess hydrogen retards the rate of formation of HCOOH and helps increase HCHO yield under the same reaction conditions. Thus H_2 has a dominant role in the reduction of CO_2 to give HCOOH and HCHO.

Effect of temperature

The rates of formation of HCOOH and HCHO were studied in the temperature range $20 - 40^\circ\text{C}$. Above 40°C , decomposition rates of these products become significant, therefore experiments were conducted keeping $\text{CO}_2 + \text{H}_2$ (1:1) at 34 atm, catalyst concentration 1 mmol , while the temperature was varied between $20 - 40^\circ\text{C}$. Figure 4 shows the graphs of $-\ln$ rate vs. $1/T$ for the formation of both HCOOH and HCHO. From this Arrhenius plot, the activation energies for the formation of HCOOH and HCHO were evaluated as $7.4 \text{ kcal mol}^{-1}$ and $8.3 \text{ kcal mol}^{-1}$, respectively.

Decomposition kinetics

The rates of decomposition of formic acid and formaldehyde were measured under the same reaction conditions used for their formation. The decrease in the concentrations of formic acid and formaldehyde were monitored with time after the products had attained their maximum

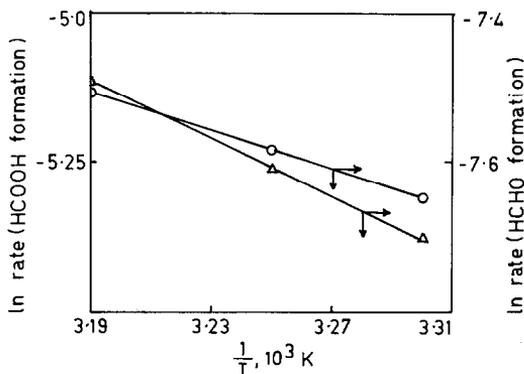


Fig. 4. Effect of temperature on the rates of formation of HCOOH (○) and HCHO (△).

concentration. This concentration was taken as the starting point for the calculation of the total rates of formation and decomposition under constant catalyst concentration and temperature. The rates of formation of formic acid and formaldehyde r_1 and r_2 were subtracted from the overall rates to get the rates of decomposition r_3 and r_4 of the two products, respectively.

Effect of catalyst concentration

The effect of catalyst concentration on the rates of decomposition of formic acid and formaldehyde is shown in Fig. 5. The catalyst concentration was varied between 0.25 and 1.0 mmol, using 34 atm $\text{CO}_2 + \text{H}_2$ (1:1) at 40 °C. It was found that the rates of decomposition of formic acid and formaldehyde have a first-order dependence with respect to catalyst concentration. The rate for formic acid decomposition (Fig. 5) ($2.35 \times 10^{-3} \text{ M min}^{-1}$) is nearly one-half (0.44) that for formic acid formation (Fig. 1) ($5.4 \times 10^{-3} \text{ M min}^{-1}$), indicating that the decomposition rates are slower than formation rates under identical reaction conditions. The rate of decomposition of formaldehyde r_4 was, however, found to be faster than its formation. This explains the higher concentration build-up of formic acid as compared to formaldehyde in the reaction products.

Effect of substrate concentration

Figure 6 shows the effect of initial formic acid and formaldehyde concentrations on their rates of decomposition. The formic acid concentration (0.028 - 0.109 M) and formaldehyde concentration (0.0023 - 0.0093 M) were varied, keeping catalyst concentration 1 mmol and temperature at 40 °C. It was found that the rates of decomposition of formic acid and formaldehyde have a first-order dependence with respect to their initial concentrations.

Effect of temperature

The effect of temperature on the rates of decomposition of formic acid and formaldehyde was studied in the range 20 - 40 °C, using both formic

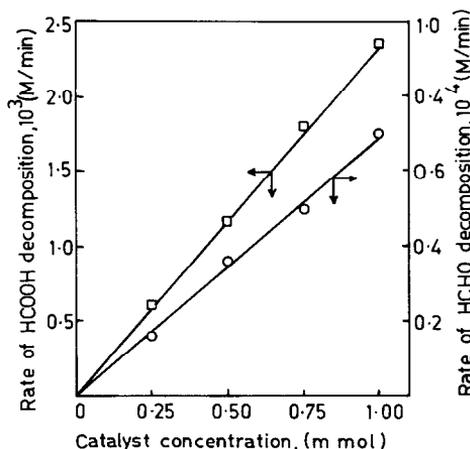


Fig. 5. Effect of $K[Ru^{III}(EDTA-H)Cl] \cdot 2H_2O$ on the decomposition rates of HCOOH (\square) and HCHO (\circ).

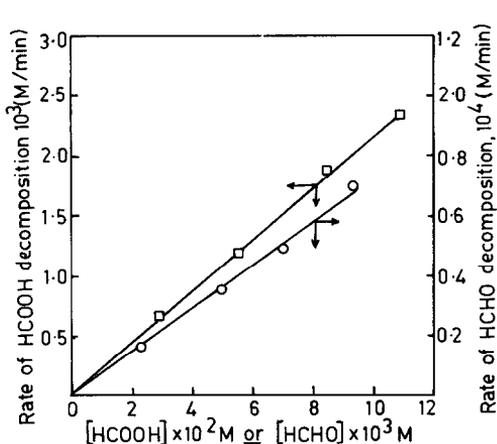


Fig. 6. Effect of initial concentration of HCOOH (\square) and HCHO (\circ) formed on their rate of decomposition.

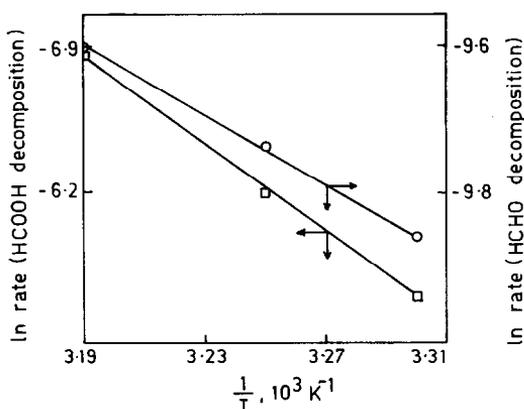
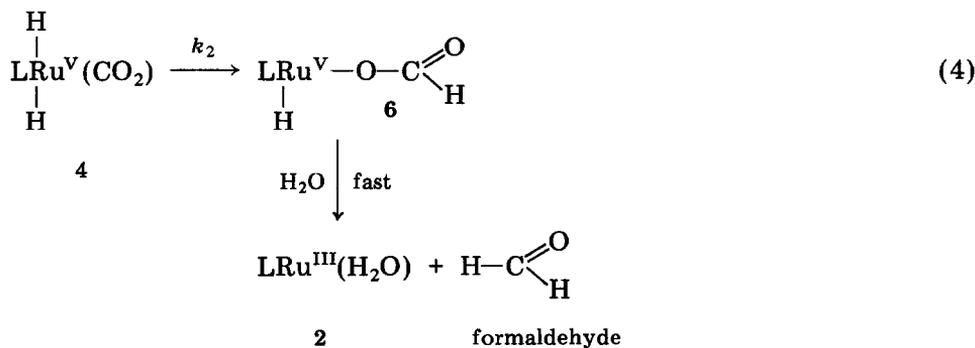
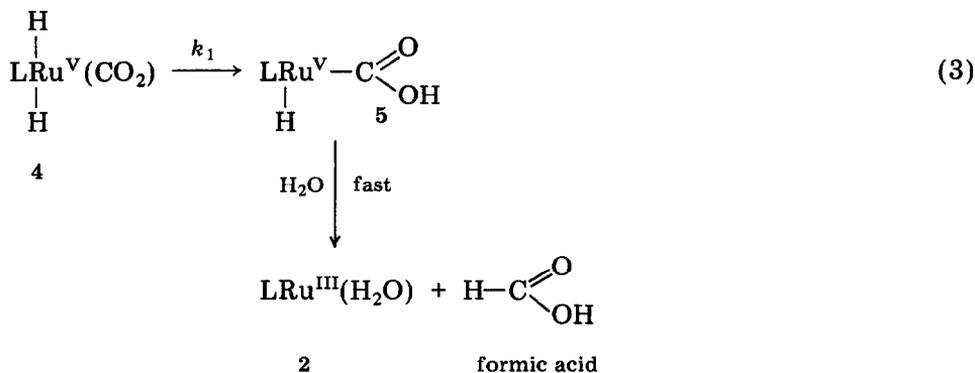
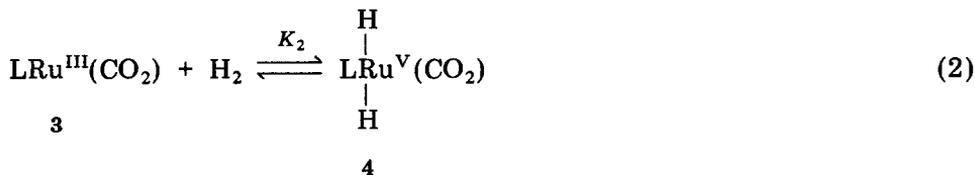
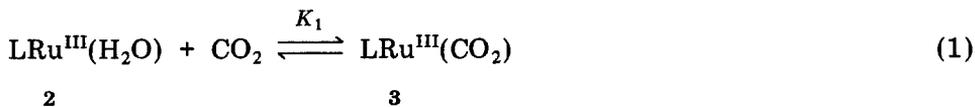


Fig. 7. Effect of temperature on the rates of decomposition of HCOOH (\square) and HCHO (\circ).

acid (0.109 M) and formaldehyde (0.0093 M) with 1 mmol catalyst concentration. It was found from Fig. 7 that the rates of decomposition of formic acid and formaldehyde increased considerably with increasing temperature. The energy of activation evaluated for decomposition is $12.0 \text{ kcal mol}^{-1}$ for formic acid and $10.7 \text{ kcal mol}^{-1}$ for formaldehyde.

Mechanism

The reduction of CO_2 by H_2 catalyzed by complex 1 in aqueous medium gave formic acid and formaldehyde as the initial liquid phase products, which on decomposition give CO and H_2O , the final products of



L = EDTA-H (protonated ethylenediaminetetraacetic acid)

Scheme 1.

reverse water-gas shift reaction. Based on these observations, a plausible mechanism is proposed as shown in Scheme 1.

The catalyst precursor complex 1, upon rapid hydrolysis in the presence of water, gives Ru^{III} aquo species 2 [17]. The aquo species 2 interacts with CO_2 to form species 3 [16] in a pre-equilibrium step 2. In step 2, the oxidative addition of hydrogen to complex 3 gives an intermediate mixed ligand species 4. The rate-determining insertion of CO_2 into the Ru-H bond of 4 in both steps 3 and 4 simultaneously results in the formation of unstable η^1 -formate species 5 and η^1 -carboxylate species 6, respectively.

The η^1 -formate species 5 undergoes proton transfer in a fast reductive elimination step, resulting in the formation of formic acid and species 2. Such transformation of metalloformate complexes has already been reported [15, 22]. Formic acid thus formed undergoes catalytic decomposition to give the final reverse water-gas shift reaction products CO and H_2O in step 5.

The η^1 -carboxylate species 6 formed in step 4 gives formaldehyde and complex 2 in the presence of H_2 . The formaldehyde later decomposes to give CO and H_2 in step 6.

Rate laws

In the $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}] \cdot 2\text{H}_2\text{O}$ catalyzed reduction of CO_2 by H_2 , the rates of formation of formaldehyde and formic acid are first order with respect to catalyst, CO_2 and H_2 concentrations. The rates of decomposition of formic acid and formaldehyde, however, were found to have linear first-order dependences with respect to catalyst concentration and concentrations of substrates, respectively. Based on the mechanism in Scheme 1 and on kinetic observations, the following four rate equations can be derived for the formation and decomposition kinetics of both formic acid and formaldehyde.

$$\frac{[\text{Cat}]_{\text{T}}}{r_1} = \left(\frac{1}{k_1 K_1 K_2 [\text{CO}_2]} + \frac{1}{k_1 K_2} \right) \frac{1}{[\text{H}_2]} + \frac{1}{k_1} \quad (1)$$

$$\frac{[\text{Cat}]_{\text{T}}}{r_2} = \left(\frac{1}{k_2 K_1 K_2 [\text{CO}_2]} + \frac{1}{k_2 K_2} \right) \frac{1}{[\text{H}_2]} + \frac{1}{k_2} \quad (2)$$

$$\frac{[\text{Cat}]_{\text{T}}}{r_3} = \left(\frac{1}{k_1 k_3} \right) \frac{1}{[\text{HCOOH}]} + \frac{1}{k_3} \quad (3)$$

$$\frac{[\text{Cat}]_{\text{T}}}{r_4} = \left(\frac{1}{k_2 k_4} \right) \frac{1}{[\text{HCHO}]} + \frac{1}{k_4} \quad (4)$$

where r_1 = rate of HCOOH formation, r_2 = rate of HCHO formation, r_3 = rate of HCOOH decomposition, r_4 = rate of HCHO decomposition, $[\text{Cat}]_{\text{T}}$ = total concentration of complex 1, $[\text{CO}_2]$ = dissolved CO_2 concentration, $[\text{H}_2]$ = dissolved H_2 concentration, $[\text{HCOOH}]$ = initial concentration of HCOOH,

[HCHO] = initial concentration of HCHO, k_1 = HCOOH formation rate constant, k_2 = HCHO formation rate constant, k_3 = HCOOH decomposition rate constant and k_4 = HCHO decomposition rate constant.

Equations (1) and (2) represent formic acid and formaldehyde formation kinetics, respectively. From the slopes and intercepts obtained by plotting the graphs of $1/[H_2]$ vs. $[Cat]_T/r_1$ and $1/[H_2]$ vs. $[Cat]_T/r_2$, the values of K_2 , k_1 and k_2 were obtained by using the known value of K_1 [16]. Equations (3) and (4) represent the kinetics of formic acid and formaldehyde decomposition, respectively. From the slopes and intercepts obtained by plotting the graphs of $1/[HCOOH]$ vs. $[Cat]_T/r_3$ and $1/[HCHO]$ vs. $[Cat]_T/r_4$, the values of k_3 and k_4 were calculated. Equilibrium and kinetic constants obtained at 40 °C for the reduction of CO₂ by H₂ are:

$$K_1 = 6.6 \text{ M}^{-1}$$

$$K_2 = 0.24 \text{ M}^{-1}$$

$$k_1 = 25.0 \text{ min}^{-1}$$

$$k_2 = 0.67 \text{ min}^{-1}$$

$$k_3 = 14.3 \text{ min}^{-1} \text{ and}$$

$$k_4 = 1.2 \text{ min}^{-1}$$

It is clear from the above rate constant values that the reduction of CO₂ by H₂ catalyzed with complex 1 at milder pressures (1 - 4 atm) and 40 °C gives more formic acid ($k_1 = 25 \text{ min}^{-1}$) and 40 times less formaldehyde ($k_2 = 0.67 \text{ min}^{-1}$). The decomposition rate constants under the reaction conditions of formation indicate that the rate of formic acid decomposition ($k_3 = 14.3 \text{ min}^{-1}$) is only half as fast as its formation rate ($k_1 = 25.0 \text{ min}^{-1}$), and that of formaldehyde decomposition is 1.8 times faster than its formation. Thus, the two-electron reduction product of CO₂ and H₂ (formic acid) is formed more easily than the four-electron reduction product (formaldehyde), while the decomposition rate (decarbonylation) follows the reverse trend.

The rate constants evaluated in our studies of the 1-catalyzed formation and decomposition of liquid phase products formic acid and formaldehyde with different gaseous reactant systems in aqueous solution such as (a) CO (spin-off products of the water-gas shift reaction [7]), (b) stoichiometric CO₂ reduction [16] and the present system (c), reduction of CO₂ by H₂, are presented in Table 1. It is seen from the data presented in Table 1 that the rate constant evaluated for different systems with respect to formic acid formation is orders of magnitude higher for the (CO₂ + H₂) system in comparison with the (i) CO + H₂O [7] or (ii) CO₂ + H₂O [16] system. This strongly suggests that the presence of H₂ as electron donor in the system considerably enhances the rate of formic acid formation. This idea is further supported by the difference in the mechanistic steps involved in the three

TABLE 1

Formation and decomposition rate constants of HCOOH and HCHO in $K[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ -catalyzed reduction systems of CO, CO₂ and CO₂ + H₂ in water

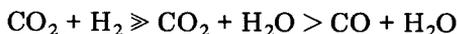
Reduction system	Rate constants (min ⁻¹)			
	Formation		Decomposition	
	HCOOH	HCHO	HCOOH	HCHO
^a CO	5.56×10^{-3}	1.39×10^{-3}	—	—
^b CO ₂	0.33	3.03	^b 1.2	—
^c CO ₂ + H ₂	25.0	0.67	14.3	1.2

^aFrom [7], at 80 °C.

^bFrom [16], at 80 °C.

^cData at 40 °C.

reactions. The oxidative addition of water to Ru(II) and Ru(III) complexes in the cases of systems (i) and (ii) results in the formation of hydrido-hydroxy Ru(IV) and Ru(V) complexes respectively [7, 16]. In the case of the present system, oxidative addition of H₂ to Ru(III) to form a Ru(V) dihydrido complex is proposed. The oxidative addition of H₂ to Ru(III) seems to be more facile than the oxidative addition of H₂O to Ru(III), which requires a higher temperature. The CO or CO₂ insertion in Ru—H bond, resulting in the formation of η^1 -formate and η^1 -metallocarboxylate to give formic acid and formaldehyde, respectively, becomes a crucial step in all three systems (mechanisms), and hence depends on factors such as thermodynamic stability and redox potential of the electron donor species obtained in the oxidative addition steps. The formation of formic acid seems to be more facile with $[\text{Ru}^{\text{V}}(\text{H})_2(\text{CO}_2)]$ complex, due to the stereochemistry of the dihydride and the presence of two H atoms in the coordination sphere of the metal ion, factors favourable for the formation of formic acid. In the oxidative addition of H₂O to $[\text{Ru}^{\text{II}}(\text{EDTA})(\text{CO})]$ and $[\text{Ru}^{\text{III}}(\text{EDTA})(\text{CO}_2)]$, the intermediate species formed are the ruthenium complexes $[\text{Ru}^{\text{IV}}(\text{H})(\text{OH})(\text{CO})]$ [7] and $[\text{Ru}^{\text{V}}(\text{H})(\text{OH})(\text{CO}_2)]$ [16], respectively. In these cases after the insertion of CO₂ or CO in Ru—H bond, attack from the other H atom requires the dissociation of the O—H bond. This is less facile as compared to transfer of the other H atom in the dihydrido complex $[\text{Ru}^{\text{V}}(\text{H})_2(\text{CO}_2)]$. The rate constants for the formation of formic acid catalyzed by complex 1 decrease in the order:



The rate constant for formaldehyde formation (Table 1), with CO₂ + H₂ system at 40 °C (0.67 min⁻¹) is about fifty times higher than CO + H₂ (1.39×10^{-3} min⁻¹) at 80 °C. The rate of formation of HCHO in the CO₂ + H₂ system at 40 °C cannot be compared with that of the CO₂ + H₂O system [16] at 80 °C, since the measurements could not be conducted in the present

investigation at 80 °C. The rate of HCHO decomposition into CO + H₂O is higher than the rate of formation in system (b) as compared to the present system. As a result, the concentration of HCHO reaches about ten times that of the formic acid concentration.

The activation parameters E_a , ΔH^\ddagger and ΔS^\ddagger evaluated for the reduction of CO₂ by H₂ catalyzed by complex 1 in the present studies and the data taken from our earlier studies in systems (a) CO + H₂O [7] and (b) CO₂ + H₂O [16] are presented in Table 2. In the temperature range 40 - 60 °C, the enthalpies of activation ΔH^\ddagger (Table 2) for HCOOH formation are +6.8 kcal mol⁻¹ for (CO₂ + H₂), 4.2 kcal mol⁻¹ for (CO₂ + H₂O) [16] and 12.8 kcal mol⁻¹ for (CO + H₂O), respectively. The enthalpies are thus most endothermic for the CO + H₂O system [7]. The enthalpies of activation for the CO₂ + H₂O [17] and CO₂ + H₂ routes differ by about 2 kcal mol⁻¹, due to the difference in the active intermediates involved in the two reactions. The redox potentials of these intermediates seem to play an important role in the effective two-electron reduction of CO₂ by its insertion in the M-H bond. In the case of the hydrides of the monovalent metals, Cr, Mo and W of composition M(CO)₄LH (L = tertiary phosphine or CO), the insertion of CO₂ into the M-H bond is most favourable [15, 23] because of the more negative M¹⁺/M³⁺ redox potential of the system as compared to Ru³⁺/Ru⁵⁺ in the present investigation. The enthalpy for the CO₂ + H₂ system reported for the M(CO)₄LH hydrides is ~ -3.8 kcal mol⁻¹, or ~8 to 10 kcal mol⁻¹ more exothermic than the Ru(III) catalysts in the present investigation.

The enthalpies (ΔH^\ddagger) of activation for HCHO formation observed with the different systems are +7.6 kcal mol⁻¹ (CO₂ + H₂), +2.8 kcal mol⁻¹ (CO₂ + H₂O) [16] and 6.1 kcal mol⁻¹ (CO + H₂) [7], respectively. The enthalpy changes are well within the range 5.0 kcal mol⁻¹ observed in other studies [2, 24].

TABLE 2

Thermodynamic activation parameters for HCOOH and HCHO formation and decomposition catalyzed by K[Ru^{III}(EDTA-H)Cl]·2H₂O through different routes in aqueous medium

Parameter	CO ^a		CO ₂ ^b		(CO ₂ + H ₂)			
	Formation		Formation		Formation		Decomposition	
	HCOOH	HCHO	HCOOH	HCHO	HCOOH	HCHO	HCOOH	HCHO
E_a (kcal mol ⁻¹)	13.5	6.7	4.8	3.5	7.4	8.3	12.0	10.7
ΔH^\ddagger (kcal mol ⁻¹)	12.8	6.1	4.2	2.8	6.8	7.6	11.4	10.1
^c ΔS^\ddagger (e.u.)	+40.8	+19.3	+13.2	+8.9	+21.6	+24.2	+36.3	+32.1

^aFrom [7]: spin-offs of water-gas shift reaction.

^bFrom [16]: reduction by [Ru^V(EDTA)(OH)(H)].

^cEntropies calculated at 40 °C.

The entropies of activation (ΔS^\ddagger) for the formation of formic acid and formaldehyde are presented in Table 2. The entropies for HCHO formation in the present systems are slightly higher than HCOOH formation. This is due to the difference between the nature of the η^1 -formate 6 and η^1 -metallo-carboxylate 5 species involved as intermediate in the two reactions. The η^1 -formate species 6 is more of an ion pair type than η^1 -metallo-carboxylate, and hence the entropy of activation is more positive for HCHO formation through 6 than for HCOOH formation through 5. For systems (a) and (b), however, with a different transition state, the entropies for HCOOH formation are more positive than for HCHO formation. The highly favourable entropies for HCOOH and HCHO formation in the $\text{CO}_2 + \text{H}_2$ system more than compensate the endothermic enthalpies of the reaction, which may thus proceed catalytically.

The thermodynamic activation parameters for complex 1-catalyzed decomposition of formic acid and formaldehyde in the ($\text{CO}_2 + \text{H}_2$) system are presented in Table 2. The energy of activation E_a required for HCOOH decomposition at 40 °C is 12.0 kcal mol⁻¹, whereas for HCHO it is 10.7 kcal mol⁻¹. This indicates that HCOOH is more stable than HCHO towards decomposition, which is substantiated by their comparative rates of decomposition. The decomposition rate for formaldehyde is faster than its rate of formation. The E_a value for HCOOH decomposition (11.4 kcal mol⁻¹) is nearly one half that reported (22.0 kcal mol⁻¹) in the literature for decomposition catalyzed via Hg and Pd(II) salts [25, 26]. We were not able to compare the HCHO decomposition data with other studies, since catalytic decomposition studies similar to ours are not reported in the literature. As expected, the entropies of activation ΔS^\ddagger for HCOOH and HCHO decomposition are ~ 10 e.u. more positive than for their formation.

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