

HYDRATION OF ACETYLENE TO ACETALDEHYDE USING $K[Ru^{III}(EDTA-H)Cl]2H_2O$

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 364002 (India)

(Received March 13, 1989; accepted June 21, 1989)

Summary

The hydration of acetylene catalyzed by water-soluble $K[Ru^{III}(EDTA-H)Cl]2H_2O$ at 80° and 1 atm gave a clean product, acetaldehyde. Under the reaction conditions studied, the rate of hydration of acetylene exhibits a first-order dependence with respect to both catalyst and dissolved acetylene concentrations. Based on our observations, a mechanism has been proposed involving a π -complex intermediate with a water molecule coordinated to the metal ion. From the study of rate of hydration of acetylene as a function of temperature, the activation energy evaluated for the reaction is 33.4 kcal mol⁻¹.

Introduction

Acetylene is an important hydrocarbon source for the large-scale preparation of oxygenated products such as acetaldehyde, acetone and acetic acid [1]. The hydration of acetylene giving rise to oxygenated products is carried out industrially using heterogeneous catalyst systems consisting of metal oxides, phosphates and silicates at 1 atm of acetylene and temperatures in the range 250–500°C [1–3]. Though the yields reported for the oxygenated products are in the range 40–95%, the heterogeneous catalyst system is energy-intensive and found to be non-selective to the specific products [4–7].

Budde and Dessy [8] have reported the liquid phase hydration of phenylacetylene with $Hg^{II}ClO_4$ as catalyst in a water–dioxane–perchloric acid medium and observed that increasing the ratio of phenylacetylene to $Hg(II)$ ion decreases the rate of acetophenone formation. Halpern *et al.* [9] have reported $Ru(III)$ chloride-catalyzed hydration of acetylene to acetaldehyde with small amounts of crotonaldehyde. The rate of hydration of acetylene decreased with increasing HCl concentration.

Recalling the catalytic activity of $K[Ru^{III}(EDTA-H)Cl]2H_2O$ 1 in our earlier studies in carbonylation [10, 11], hydroformylation [12, 13] and

*Author to whom correspondence should be addressed.

hydration of CO [14] at milder reaction conditions, we considered it important to extend our studies to the activation of acetylene by complex 1. The present investigation reports the kinetics of the $K[Ru^{III}(EDTA-H)Cl]2H_2O$ -catalyzed hydration of acetylene to give acetaldehyde at 80 °C and 1 atm of acetylene.

Experimental

Material

Ruthenium(III) chloride was obtained from M/s. Arora Mathey Ltd., Calcutta, and the disodium salt of ethylenediaminetetraacetic acid (EDTA) of A.R. grade was supplied by M/s. Sarabhai Chemicals, Baroda. The complex $K[Ru^{III}(EDTA-H)Cl]2H_2O$ 1 was prepared by a known procedure [15]. Acetylene gas was used after purifying the commercial gas according to the procedure described elsewhere [16], and its purity as verified by GLC was 99.8%. Doubly distilled and degassed water was used in this study.

Procedure

Acetylene hydration experiments were conducted in a 50 ml double-walled stirred glass cell maintained at the desired temperature by circulating water from a thermostatted bath controlled to an accuracy of ± 0.1 °C. A known amount of distilled water was placed in the cell maintained at the desired temperature. Acetylene gas was bubbled for *ca.* 10–15 min while agitation was in progress. The reaction was started by adding the required amount of catalyst, after ensuring that the distilled water was saturated with acetylene. For this purpose acetylene was bubbled continuously until the end of the experiment.

An aliquot was withdrawn from the cell to monitor the rate of formation of acetaldehyde. Samples withdrawn at different time intervals were analyzed for acetaldehyde by monitoring the peak at 480 nm using a UV-160 model Shimadzu spectrophotometer according to the procedure described elsewhere [17]. The initial rates of acetaldehyde formation were evaluated from the graphs of the amount of acetaldehyde formed *vs.* time in different experiments. The acetaldehyde present in the reaction mixture was also confirmed by preparing its 2,4-dinitrophenylhydrazine derivative and by its ^{13}C NMR spectrum (Jeol FX-100, FT-NMR) which showed a —CHO peak at 199 ppm and —CH₃ peak at 30.7 ppm.

Thus, the hydration of acetylene using complex 1 catalyst ensured the formation of a clean product, acetaldehyde, with no other side oxygenated products as reported earlier in the literature [9]. The solubilities of acetylene in water at the required temperatures were taken from reported data [18], and the total dissolved acetylene concentration was calculated using Henry's equation.

Results and discussion

The kinetic investigations of acetylene hydration to give acetaldehyde were conducted by varying the concentrations of catalyst and acetylene (the partial pressure was varied by mixing with nitrogen gas) at 80 °C. The effect of the reactant concentrations on the rates of acetylene hydration was evaluated from the graphs of the amount of acetaldehyde present as a function of time.

Effect of catalyst concentration

The catalyst concentration was varied from 0.5–2.0 mM at 1 atm of acetylene (0.015 M) and 80 °C. The initial rates of acetaldehyde formation observed at different catalyst concentrations were plotted as shown in Fig. 1, revealing that the rate of acetylene hydration has a first-order dependence with respect to catalyst concentration.

Effect of dissolved acetylene concentration

The partial pressure of acetylene was varied from 0.25–1.0 atm using nitrogen gas, keeping the catalyst concentration constant at 1.0 mM and 80 °C. Figure 2 shows the plot of the rate of acetyldehyde formed *vs.* acetylene concentration, which indicates that the rate of acetylene hydration has linear first-order dependence with respect to acetylene concentration.

Effect of temperature

The effect of temperature on the rate of acetylene hydration was studied in the temperature range 60–80 °C, keeping catalyst concentration constant at 1.0 mM and 1 atm acetylene (0.015 M). From the graph of $-\ln$ rate *vs.* $1/T$ shown in Fig. 3, the activation energy, E_a , was evaluated as 33.4 kcal mol⁻¹, indicating the highly endothermic nature of the reaction.

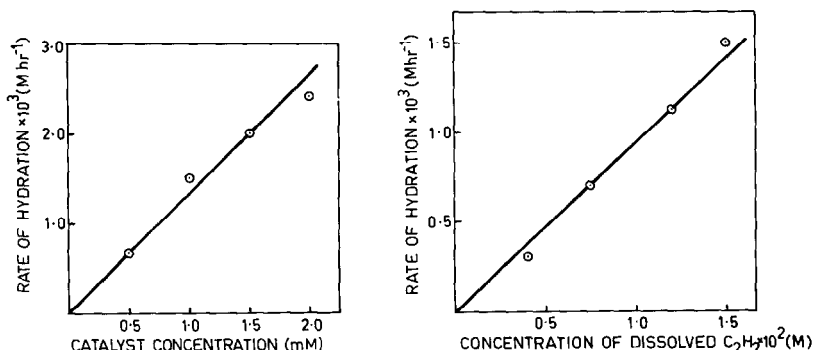


Fig. 1. Effect of catalyst concentration on the rate of acetylene hydration.

Fig. 2. Effect of dissolved acetylene concentration on the rate of acetylene hydration.

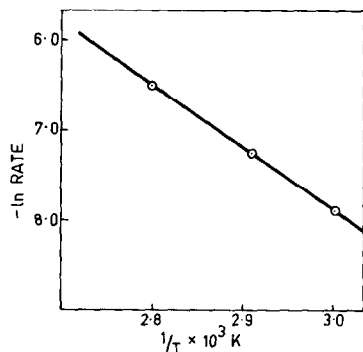
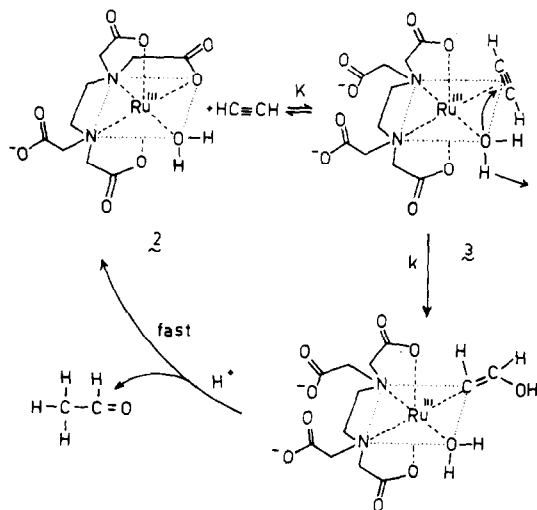


Fig. 3. Effect of temperature on the rate of acetylene hydration.

Mechanism and rate law

Based on kinetic data of the complex 1-catalyzed hydration of acetylene to acetaldehyde, the probable mechanism proposed for the reaction is shown in Scheme 1.

The mechanism suggested for the hydration of acetylene involves the initial formation of aquo species 2 by the rapid aquation of complex 1, which is well established [19]. This ensures the presence of at least one water molecule coordinated on the metal ion, as suggested by Halpern *et al.* [9] in their study on ruthenium(III) chloride-catalyzed acetylene hydration. The coordinated water molecule is found to increase the catalytic activity of metal ion during acetylene hydration; hence the present catalyst system, *i.e.* complex 1, is a suitable catalyst for the hydration of acetylene to acetaldehyde. It is suggested that the aquo species 2 reacts with a molecule of



Scheme 1.

acetylene to form a π -complex **3** in an equilibrium step. The complexation of acetylene to species **2** is supported experimentally by the appearance of a peak at 416 nm in the UV spectrum of the reaction mixture, which is attributed to the π -complexed acetylene complex **3**. The attack of the coordinated water molecule in **3** on coordinated acetylene results in the formation of Ru(III) α -complex **4** with the liberation of a proton. The formation of the Ru(III) σ -complex **4** from Ru(III) π -complex **3** is the suggested rate-determining step for the catalytic acetylene hydration. The reaction amounts to the insertion of acetylene in the M—OH bond. Species **4** then rapidly dissociates in a fast step, resulting in the formation of acetaldehyde, while the active Ru(III) catalytic species **2** is regenerated.

From the proposed mechanism for acetylene hydration and kinetic observations, the rate equation for acetaldehyde formation can be written as:

$$\text{rate} = k K [\text{Cat}] [\text{C}_2\text{H}_2] \quad (1)$$

where $[\text{Cat}]$ = complex **1** concentration, $[\text{C}_2\text{H}_2]$ = acetylene concentration, K = the equilibrium constant and k = the rate constant for the reaction.

By taking into account the total catalyst concentration $[\text{Cat}]_T$ present under steady state conditions in the form of different species (Scheme 1), the final rate law in the slope and intercept form may be written as:

$$\frac{[\text{Cat}]_T}{\text{rate}} = \frac{1}{k K [\text{C}_2\text{H}_2]} + \frac{1}{k} \quad (2)$$

From eqn. (2), a plot of $[\text{Cat}]_T/\text{rate}$ vs. $1/[\text{C}_2\text{H}_2]$ gives a straight line with an intercept from which the value of the rate constant k was calculated. From the slope, the value of the equilibrium constant K was evaluated. The values for k and K obtained for complex **1**-catalyzed hydration of acetylene at 80 °C to give acetaldehyde are:

$$k = 9.3 \times 10^{-4} \text{ min}^{-1}$$

$$K = 14.1 \text{ M}^{-1}$$

The rate of the hydration reaction catalyzed by Ru(III) chloride in 5 M HCl reported by Halpern *et al.* [9] at 50 °C is $6.7 \times 10^{-6} \text{ M min}^{-1}$ (calculated based on the reported second-order rate constant $k = 2.0 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$). The maximum rate observed in our study at 80 °C is *ca.* $3.0 \times 10^{-5} \text{ M min}^{-1}$, which is about the same order of magnitude if we consider the temperature difference between the two reaction systems. The advantage of our study is that complex **1** catalyst system is stable, reproducible and free from HCl in the reaction mixture. Therefore, the present system offers advantages with respect to the non-corrosive nature of the reaction.

Using the activation energy evaluated from Arrhenius plot (Fig. 3), the thermodynamic activation parameters for complex **1**-catalyzed acetylene hydration to give acetaldehyde at 80 °C and 1 atm calculated as $\Delta H^\ddagger = 32.5 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 75 \text{ e.u.}$ The high positive enthalpy of the reaction

TABLE 1

Thermodynamic activation and kinetic parameters of $K[Ru^{III}(EDTA-H)Cl]2H_2O$ catalyzed hydration of acetylene and carbon monoxide reactions

Hydration of	Equilibrium constant (M^{-1})	Rate constant (min^{-1})	E_a (kcal mol $^{-1}$)	ΔH^\ddagger (kcal mol $^{-1}$)	ΔS^\ddagger (e.u.)
acetylene (80 °C, 1 atm C_2H_2)	14.1	9.3×10^{-4}	33.4	32.5	+75
carbon monoxide (50 °C, 15 atm CO)	11.0	80	1.5	0.83	+2.5

indicates that the activation of acetylene $-C\equiv C-$ and its insertion in the $M-OH$ bond is a fairly endothermic process. The reaction is, however, favoured by a fairly positive entropy for the reaction.

It is of interest to compare the hydration of carbon monoxide (water-gas shift reaction) in the liquid phase catalyzed by the complex **1** at 50 °C and 15 atm CO [14]. The activation parameters involved in the two reactions are presented in Table 1.

The equilibrium constant (Table 1) obtained for the formation of carbonyl $LRu^{II}CO$ complex ($L = EDTA-H$) in the water-gas shift reaction is $K_1 = 11.0 M^{-1}$, and for the π -acetylinic $Ru(III)$ complex **3** (Scheme 1) it is ($K = 14.1 M^{-1}$). The π -acetylene complex of $Ru(III)$ is slightly more stable than the $Ru(II)$ carbonyl complex. This may be attributed to the differences in the π -acidic nature of the adducts. However, the rates of hydration, *i.e.* insertion of $C\equiv O$ and $-C\equiv C-$ into the $M-OH$ bond, are for acetylene $k = 9.3 \times 10^{-4} min^{-1}$ and for CO $k = 80 min^{-1}$. The rate of hydration of carbon monoxide is thus at least several orders of magnitude higher ($\sim 8 \times 10^4$) than that of acetylene. The activation energy for the insertion of CO in the $M-OH$ bond is about 32 kcal mol $^{-1}$ more exothermic than the acetylene insertion. The lower values of E_a and ΔH^\ddagger obtained for CO hydration indicate that insertion of CO in $M-OH$ bond is much easier than $-C\equiv C-$ insertion in the $M-OH$ bond. The difference may be interpreted in terms of a higher polarity of the $C\equiv O$ bond as compared to the $-C\equiv C-$ bond which makes the nucleophilic attack of coordinated OH on the carbonium ion from $C\equiv O$ more facile than in acetylene.

References

- 1 P. H. Emmett, *Catalysis*, Vol. 7, Reinhold, New York, 1960, pp. 163–169 and references therein.
- 2 J. A. Nieuwand and R. R. Vogt, *The Chemistry of Acetylene*, Reinhold, New York, 1945, p. 118.
- 3 R. B. Randall, *Inst. Petroleum Rev.*, 2 (1948) 107.
- 4 M. C. Boswell and H. M. Dilworth, *J. Phys. Chem.*, 29 (1925) 1487.
- 5 A. S. Brown, O. S. Kuratova, D. V. Muschenko and R. P. Urinson, *J. Chem. Ind. (U.S.S.R.)*, 18 (1941) 24.

- 6 A. W. Dyck, *Can. Chem. Proc. Ind.*, **30** (1946) 195.
- 7 P. P. Jones, *Ind. Chem.* **22** (1946) 195.
- 8 W. L. Budde and R. E. Dessy, *J. Am. Chem. Soc.*, **85** (1963) 3964.
- 9 J. Halpern, B. R. James and A. L. W. Kemp, *J. Am. Chem. Soc.*, **83** (1961) 4097.
- 10 M. M. Taqui Khan, S. B. Halligudi and S. H. R. Abdi, *J. Mol. Catal.*, **44** (1988) 179.
- 11 M. M. Taqui Khan, S. B. Halligudi and S. H. R. Abdi, *J. Mol. Catal.*, **48** (1988) 325.
- 12 M. M. Taqui Khan, S. B. Halligudi and S. H. R. Abdi, *J. Mol. Catal.*, **45** (1988) 215.
- 13 M. M. Taqui Khan, S. B. Halligudi and S. H. R. Abdi, *J. Mol. Catal.*, **48** (1988) 313.
- 14 M. M. Taqui Khan, S. B. Halligudi and Sumita Shukla, *Angew. Chem. Int. Ed. Engl.*, **27** (1988) 1735.
- 15 M. M. Taqui Khan, Kumar and Z. Shirin, *J. Chem. Res.*, **5** (1986) 130.
- 16 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1981, p. 83.
- 17 S. Siggia, *Quantitative Organic Analysis via Functional Groups*, Wiley, New York, 1966, pp. 124–127.
- 18 A. Seidell, *Solubilities of Organic Compounds*, Vol. 2, Van Nostrand, New York, 1941, p. 74.
- 19 A. A. Diamantis and J. V. Dubrawaski, *Inorg. Chem.*, **20** (1981) 1142.