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A Kinetic Investigation of the Hydrogenation of Acetone by $[Ru(2,2'\text{-bipyridyl})_2(CO)H]PF_6 \cdot 0.5$acetone

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Abstract

A kinetic investigation of the hydrogenation of acetone to propan-2-ol by $[Ru(2,2'\text{-bipyridyl})_2(CO)H]^+$ in buffered aqueous solutions has been carried out. The dependence of the pseudo-first order rate constant of the reaction, k_{obs}, on acetone, buffer and H^+ concentration, has been studied. No dependence of k_{obs} on temperature was observed. The kinetic data support a mechanism involving general acid catalysis.

Introduction

Recently the synthesis of a series of ruthenium and osmium (2,2'-bipyridyl) hydride complexes has been reported along with preliminary studies of their reactivity [1–4]. The hydride character of the metal–hydrogen bond in some of these complexes is evidenced by their reaction with H^+ in aqueous solution to give dihydrogen gas [1, 3]. Japanese workers have studied the water–gas shift reaction catalysed by $[Ru(bipy)_2(CO)Cl]^+$ (bipy = 2,2'-bipyridyl). In this system $[Ru(bipy)_2(CO)H]^+$ has been proposed as the hydrogen producing intermediate [5]. Insertion of H^- by $[Os(bipy)_2(CO)H]^+$ in the tropylium ion has been reported by Meyer and co-workers [3]. With this background the study of the reactivity of these complexes seems worthwhile. In an earlier paper we reported that acetone reacts in aqueous solution with rutheniumbis(bipy) hydrides [4]. In this paper we wish to report the results of a kinetic study of the hydrogenation of acetone to propan-2-ol by $[Ru(bipy)_2(CO)H]^+$. The reaction has been followed by UV–Vis spectroscopy and the reaction constants have been determined as a function of pH, buffer concentration, acetone concentration and temperature.

Experimental

$[Ru(bipy)_2(CO)H]PF_6 \cdot 0.5$acetone was prepared as described elsewhere [1]. The compound was dissolved in acetone or in acetone/acetonitrile mixtures. 0.5 cm^3 of such a solution was added to 2.5 cm^3 of the appropriate Britton–Robinson buffer (0.04 M acetic acid, 0.04 M phosphoric acid and 0.04 M boric acid). The pH of the buffers was adjusted using sodium hydroxide. The addition of acetone or acetonitrile to the buffer solutions changed the pH of these solutions slightly, the values given here are those obtained after addition of the organic solvent. The experiments were carried out at 303 K in aerated solutions unless stated otherwise. The reactions were followed using a Shimadzu UV-240 spectrophotometer. The spectra obtained were analysed and rate constants were calculated using the Guggenheim method [6] or using least-squares methods using a plot of $\log(OD_0 - OD_\infty)/(OD_t - OD_\infty)$ *versus* time, where OD_0 is the optical density at time 0, OD_t the optical density at time t and OD_∞ the optical density at time infinity. The rate constants reported are averages obtained from at least three experiments. The organic reaction product, propan-2-ol, was detected using a Pye-Unicam GCD gas chromatograph, with a Carbowax column operating at 80 °C.

Results

The homogeneous hydrogenation of acetone in buffered aqueous solution as in eqn. (1) has been studied

$$[Ru(bipy)_2(CO)H]^+ + (CH_3)_2CO \xrightarrow{H^+/H_2O} [Ru(bipy)_2(CO)H_2O]^{2+} + (CH_3)_2CHOH \qquad (1)$$

The ruthenium compound formed was shown to be spectroscopically identical with an authentic sample. The organic product, propan-2-ol, was identified using gas chromatography. The effect of a variation of the reaction parameters on the observed reaction

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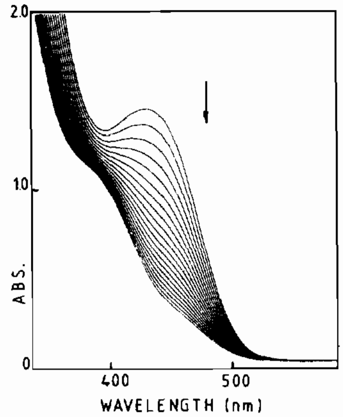

Fig. 1. UV–Vis spectra taken during the reaction of $[\mathrm{Ru(bipy)_2(CO)H}]^+$ with acetone at pH = 6.24. Temperature 298 K. Time between scans 1 min, acetone concentration 2.26 mol dm^{-3}, buffer concentration 0.10 mol dm^{-3}.

rate of the hydrogenation reaction was investigated by monitoring the disappearance of $[\mathrm{Ru(bipy)_2(CO)H}]^+$ using UV–Vis spectroscopy. Figure 1 shows the change with time in the adsorption spectrum in the 300–600 nm region, for a buffered water/acetone mixture containing $[\mathrm{Ru(bipy)_2(CO)H}]^+$. The spectrum observed in this region is solely due to the metal compound and consists of metal-to-ligand charge-transfer bands and inter ligand transitions [4, 7]. The disappearance of the band at 430 nm indicates the decomposition of the hydride complex, while the product band at *ca.* 380 nm is indicative of $[\mathrm{Ru(bipy)_2(CO)H_2O}]^{2+}$ [7].

Analysis of the spectra shows that, in the concentration range studied, the reaction proceeds in a pseudo-first order fashion with respect to ruthenium. The reaction rate was found to be dependent on the pH. The rate constants observed, k_{obs}, for pH values between 5.0 and 8.0 have been listed in Table I. An analysis of the data in this Table clearly suggest that the reaction is acid catalysed. A plot of log k_{obs} *versus* pH gives a straight line with a slope of −0.7.

TABLE I. Dependence of k_{obs} on the pH^a

pH	$k_{\mathrm{obs}} \times 10^4$ (s^{-1})
5.24	88 ± 8
5.73	40 ± 4
6.24	20 ± 2
6.76	6.7 ± 0.6
7.27	2.9 ± 0.3
7.85	1.6 ± 0.1

^{a}[Acetone] = 2.26 mol dm^{-3}; [RuH] = 4.0 × 10^{-4} mol dm^{-3}; [buffer] = 0.10 mol dm^{-3}; temperature 303 K.

TABLE II. Dependence of k_{obs} on the Concentration of the Britton–Robinson Buffer^a

[Buffer] (mol dm^{-3})	$k_{\mathrm{obs}} \times 10^4$ (s^{-1})
0.010	2.3 ± 0.2
0.020	3.8 ± 0.3
0.030	4.7 ± 0.4
0.048	6.9 ± 0.6
0.050	8.7 ± 0.8
0.060	10.8 ± 0.8
0.076	14 ± 1
0.10	16 ± 1

^{a}[RuH] = 4 × 10^{-4} mol dm^{-3}; [acetone] = 2.26 mol dm^{-3}; pH = 6.37; temperature 303 K.

In order to investigate whether it is a case of specific or general acid catalysis experiments were carried out at different buffer concentrations. At this point it is worthwhile pointing out that in non-buffered water/acetone mixtures with an initial pH of about 6 only a small amount of the ruthenium complex is used up. After this initial reaction the solution is stable. This behaviour is reflected in the fact that the title compound can be recrystallised from acetone/water mixtures in good yield [4]. The values for k_{obs} obtained at different buffer concentrations have been listed in Table II. The reaction rates are strongly dependent on the buffer concentration and therefore suggest general acid catalysis [8]. A plot of the reaction rate *versus* buffer concentration yields a straight line with a positive intercept.

A series of experiments was carried out to investigate the influence of the acetone concentration on the reaction rate. To keep the reaction conditions as similar as possible it was decided to keep the amount of organic solvent in the reaction mixture constant. This was thought to minimise variations in pH and also facilitate the dissolution of the ruthenium hydride complex used, as this compound is not soluble in the buffer solution. The ruthenium complex was therefore dissolved in appropriate acetonitrile acetone mixture and 0.5 cm^3 added to the buffer solution.

The dependence of k_{obs} on the acetone concentration has been given in Table III. A plot of these data shows that k_{obs} depends on the acetone concentration in a first order manner over the whole concentration range studied. This is as expected as acetone is always in large excess.

The concentration of the ruthenium compound was varied between 0.5–4.0 × 10^4 mol dm^{-3} and in all cases a pseudo-first order behaviour was obtained. The temperature dependence of the reaction was investigated over the 300–313 K range. No significant change with temperature was observed for the reaction rate.

TABLE III. Dependence of k_{obs} on the Acetone Concentration[a]

[Acetone] (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})
0.30	2.7 ± 0.2
0.60	4.7 ± 0.4
0.90	7.3 ± 0.7
1.18	10.3 ± 1.0
1.45	12.5 ± 1.2
1.72	13.0 ± 1.3
1.99	16.3 ± 1.6
2.26	17.4 ± 1.7

[a] [RuH] = 3.3×10^{-4} mol dm^{-3}; [buffer] = 0.10 mol dm^{-3}; pH = 6.37; temperature 303 K.

Discussion

The kinetic data agree with a reaction mechanism that involves a fast pre-equilibrium as in eqn. (2)

$$\underset{[Ac]}{(CH_3)_2CO + HA} \overset{K_{eq}}{\rightleftharpoons} \underset{[Ac..HA]}{[(CH_3)_2CO.....HA]} \qquad (2)$$

where HA stands for H_3O^+ and/or undissociated acids, followed by a slow step, eqn. (3)

$$[(CH_3)_2CO...HA] + \underset{[RuH]}{[Ru(bipy)_2(CO)H]^+} \xrightarrow[k]{H_2O}$$

$$(CH_3)_2CHOH + [Ru(bipy)_2(CO)H_2O]^{2+} \qquad (3)$$

As we clearly are dealing with a case of general acid catalysis (see Table II) we assume a hydrogen bridged species such as Ac...HA to be the reactive acetone species rather than a completely protonated species AcH^+ [8].

The reaction mechanism yields the following rate equation

$$\begin{aligned} \text{rate} &= k[Ac...HA][RuH] \\ &= kK_{eq}[Ac][HA][RuH] \\ &= k_{obs}[RuH] \qquad (4) \end{aligned}$$

As more than one source of protons is available in the buffer solution one should however write

$$\text{rate} = K_{eq}[Ac][RuH][k_1[H^+] + \sum_i k_i[HA_i]] \qquad (5)$$

The results obtained were further analysed using the above model. For such an analysis the exact amount of active undissociated acids that takes part in the reaction [HA] has to be determined. At the pH at which the data in Tables II and III have been obtained (pH = 6.37), the main undissociated acids [HA] in a Britton–Robinson buffer are boric acid, $H_2PO_4^-$ and HPO_4. By using literature methods it can be calculated that their combined concentration is about 0.071 ± 0.002 mol dm^{-3}. ([Boric acid] = 0.033 mol dm^{-3}; [$H_2PO_4^-$] = 0.033 mol dm^{-3} and [HPO_4^-] = 0.005 mol dm^{-3}.)

These calculations were carried out at the pH value obtained for the buffer in the presence of the organic solvent. It was assumed that the presence of the organic solvent would have no further influence on the composition of the buffer. It was also assumed that the relative composition of the buffer did not change with dilution. Upon dilution of the buffer the pH of the solutions did not change. These results show that the active [HA] concentration is lower than the actual buffer concentration and this concentration obviously varies with the pH. This explains the slope of –0.7 obtained for the log k_{obs} *versus* pH plot. For the calculations of slopes and intercepts from the data in the Tables II and III, the active [HA] concentration has been used rather than the total buffer concentration. A linear regression analysis of the data in Table II yielded an intercept of 0.56×10^{-4} s^{-1} and a slope of 2.33×10^{-2} mol^{-1} dm^3 s^{-1}. The values obtained for intercept and slope can be used to calculate k_1 and as more than one undissociated acids is present, an average k_{iav}. According to eqn. (5) the slope is equal to $k_{iav}K_{eq}[Ac]$ and the intercept is equal to $k_1K_{eq}[Ac][H^+]$. From the intercept a value of 58.0 dm^6 mol^{-2} s^{-1} is obtained for k_1K_{eq} and a value of 1.09×10^{-2} s^{-1} for $k_{iav}K_{eq}$ from the slope. A similar analysis of the data in Table III yields a slope of 7.7×10^{-4} mol^{-1} dm^3 s^{-1}; this slope is equal to $K_{eq}(k_1(H^+) + k_{iav}[HA])$. This value of the slope agrees well with the value obtained when k_1K_{eq} and $k_{iav}[HA]$, as obtained from Table II, are inserted in this equation of the slope (7.55×10^{-4} mol^{-1} dm^3 s^{-1}).

To obtain a value for the second order rate constants k_1 and k_{iav} one has to know K_{eq}. However the value of K_{eq} for eqn. (2) has to our knowledge not been reported in the literature. One can attempt to estimate the second order rate constants by assuming that

$$K_{eq} = 1/K_a = \frac{[AcH^+]}{[Ac][H^+]} \qquad (6)$$

using the pK_a value for protonated acetone, AcH^+. The pK_a values reported range from –7 to –0.5. This variation has been explained by the different media and techniques used. Recently a value of –1.50 has been reported [9]. We have used this value to estimate our rate constants. In this manner we obtain a value for K_{eq} of 3.16×10^{-2}.

A linear regression of the data in Table II yielded a value of 58.0 mol^{-2} dm^6 s^{-1} for k_1K_{eq}. Using the value of K_{eq} calculated above one obtains a value of 1.83 X 10^2 mol^{-1} dm^3 s^{-1} for k_1. The slope similarly yields a value of 0.33 mol^{-1} dm^3 s^{-1} for k_{iav}. These rate constants point to rather fast reactions. It should however be pointed out that they are most likely overestimated because of our choice of K_{eq}. No appreciable temperature dependence of k_{obs} was observed. For a typical set of experiments in a pH 6.0 buffer k_{obs} varied from 1.6 to 1.7 X 10^{-3} s^{-1} in the temperature range 300–313 K. This points to a low activation energy and is compatible with general acid catalysis. If we assume no temperature dependence for reaction 2 then we can take $\log k_{obs} = A$, the preexponential factor. We can then from the formulae

$$A = e^{\Delta n}(kT/h)e^{\Delta S^{\neq}/R} \quad (7)$$

where the symbols have their usual meaning and Δn is taken as 2 (assuming an activated complex of the form RuH...Ac...HA) obtain a value of −312 J mol^{-1} deg^{-1} (25 °C) for $\Delta S^{\neq}$. Because of the expected complexity of the reaction involving the small reaction site on the ruthenium complex with at the same time interaction between acetone and acid, such a negative value for $\Delta S^{\neq}$ is not altogether surprising. For the reaction of the title compound with H$^+$ to produce dihydrogen gas an activation energy of 56 kJ/mol^{-1} deg^{-1} and a value of −100 J mol^{-1} deg^{-1} for the entropy of activation were obtained [10].

Conclusion

For the reaction of the title compound with H$^+$ at 303 K, a second order rate constant of 0.105 ± 0.01 mol^{-1} dm^3 s^{-1} has been obtained [10]. The value for k_1 estimated in this work (1.83 X 10^3 mol^{-1} dm^3 s^{-1}) is several orders of magnitude larger. This shows that the acid catalysed reaction of the hydride with acetone is much faster than the direct reaction of the compound with H$^+$. This opens the possibility for the hydrogenation by ruthenium hydride complexes of a whole range of ketones, aldehydes etc. Preliminary results suggest that in organic solvents hydrogenation of aldehydes by $[Ru(bpy)_2(CO)H]^+$ is fast in the presence of acetic acid. At present this system is under further investigation.

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