Kinetics and Selectivity of the Rhodium Complex Catalysed Carbonylation of Isopropyl Alcohol

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The rhodium-complex catalysed carbonylation of secondary alcohols, exemplified by isopropyl alcohol, has been investigated. The dependence of rate on reaction parameters is in accord with the previous suggested mechanism for the carbonylation of primary alcohols. The thermodynamic activation parameters differ markedly from the corresponding values for primary alcohols.

The ratio between the two carbonylation products, n- and iso-butyric acid, is given as a function of reaction conditions.

THE synthesis of carboxylic acids and esters *via* the homogeneously catalysed carbonylation of alcohols has recently attracted much attention. In particular the carbonylation of methanol catalysed by rhodium complexes has been investigated in great detail. Reaction orders with respect to reactants, catalyst, and promotor (HI) were reported by Roth *et al.*,[1] and the suggested mechanism was confirmed by kinetic measurements.[2] The activation parameters supported the previous assumption, that the transition state is an adduct formed by oxidative addition of alkyl iodide to the catalytic complex. Spectroscopic studies reported by Forster[3] also supported the previously suggested mechanism and identified the active complex as $[Rh(CO)_2I_2]^-$. The liquid phase carbonylation of higher primary alcohols, including dihydric alcohols, seems to follow the same mechanism, with differences in observed activation parameters, being readily rationalized in terms of reactant structure.[4]

Attempts to carbonylate secondary alcohols have briefly been reported in the patent literature,[5] but only in the form of dihydric alcohols where the second hydroxy group is a primary one. However, the carbonylation of isopropyl alcohol in the gas phase, heterogeneously catalysed by rhodium on zeolite, has been investigated,[6] but only dehydration was observed. It should be noted that the successful carbonylation of primary alcohols in the gas phase, heterogeneously catalysed by supported rhodium, has been reported.[7,8]

Accordingly, the carbonylation of a monohydric, secondary alcohol has not so far been reported. However, considering the suggested mechanism for the carbonylation of methanol,[1,2] the reaction would be expected to occur readily with isopropyl alcohol although not necessarily with the same high degree of selectivity. Furthermore, formation of both n- and iso-butyric acid would be expected, since the initial reaction between the alcohol and hydrogen iodide may lead to two different substitutions.[9] In order to clarify the situation a kinetic investigation of the rhodium complex-catalysed carbonylation of isopropyl alcohol was undertaken.

EXPERIMENTAL

All experiments were run in an isothermal batch reactor (Hastelloy C) equipped with magnetic stirring (Magnedrive), and connected to a gas reservoir. The reaction was followed measuring the pressure drop in the reactor relative to the constant pressure in the reservoir (differential pressure transducer).

Rhodium trichloride hydrate (Engelhard Industries Ltd.), alcohol, and hydrogen iodide were dissolved in acetic acid in the required concentrations. This solution was transferred to the reactor, which after being heated to the desired temperature was pressurized with carbon monoxide. The reaction was initiated by stirring the mixture at a speed sufficiently high as to exclude transport restrictions between gas and liquid phase and the concomitant reaction rate limitations (700–1 000 rev. min^{-1}). Further experimental details are given in Tables 1 and 2.

The liquid phase was analysed using gas chromatographic

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[1] J. F. Roth, J. H. Graddock, A. Hershman, and F. E. Paulik, *Chem. Tech.*, 1971, 600.

[2] J. Hjortkjær and V. W. Jensen, *Ind. Eng. Chem., Prod. Res. Devel.*, 1976, **15**, 46.

[3] D. Forster, *J. Amer. Chem. Soc.*, 1976, **98**, 846.

[4] J. Hjortkjær and J. C. Jørgensen, *J. Mol. Catalysis*, 1978, **4**, 199.

[5] F. E. Paulik, A. Hershman, W. R. Knox, and J. F. Roth, German Patent 1,941,449/1969.

[6] B. Christensen and M. S. Scurrell, *J.C.S. Faraday I*, 1977, 2036.

[7] K. K. Robinson A. Hershman, J. H. Graddock, and J. F. Roth, *J. Catalysis* 1972, **27**, 389—396.

[8] B. K. Nefedov, N. S. Sergeeva, T. V. Zheva, E. M. Shutkina, and Ya. T. Eidus, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1976, 582.

[9] R. T. Morrison and R. N. Boyd, 'Organic Chemistry', Allyn and Bacon, Boston, 1966, 2nd edn., p. 529.

separation with a column of Chromosorb 101 (Perkin-Elmer Ltd.). The column length was 1.5—5.5 m, and the temperature in the range 398—473 K, depending upon the components present in the samples. Flame-ionization detection (Perkin-Elmer F 11) was utilized with nitrogen carrier gas.

RESULTS

TABLE 1

Expt. no.	[Rh]/mmol l^{-1}	[HI]/mol l^{-1}	$[C_3H_8O]$/mol l^{-1}	p_{CO}/atm	T/K	Rate × 10^6/mol l^{-1} s^{-1}
(1)	4.65	0.50	2.60	35	474	429
(2)					457	179
(3)					493	2 230
(4)					515	3 890
(5)					484	1 400
(6)			5.19		473	620
(7)			1.30			575
(8)			0.65			59
(9)			8.00			346
(10)	8.01		2.60			1 300
(11)	2.49					441
(12)	4.65	1.00				713
(13)		1.50				920
(14)		1.00				737
(15)		0.30				610
(16)		0.16				340
(17)		0.076				185

The carbonylation rate was measured as a function of the concentrations of isopropyl alcohol, catalyst (Rh), promotor (HI), and carbon monoxide. A survey of reaction conditions and rates is given in Table 1. All rates are initial rates, but in experiment (1) the reaction was allowed to run until almost all the CO was consumed. Over the total pressure range (*ca.* 35 atm) the rate was constant (*ca.* 430 × 10^{-6} mol l^{-1} s^{-1}) implying that the reaction rate is independent (zero-order) on both CO pressure and alcohol concentration (a pressure drop of 35 atm CO corresponds to a change in alcohol concentration of *ca.* 1 mol l^{-1}).

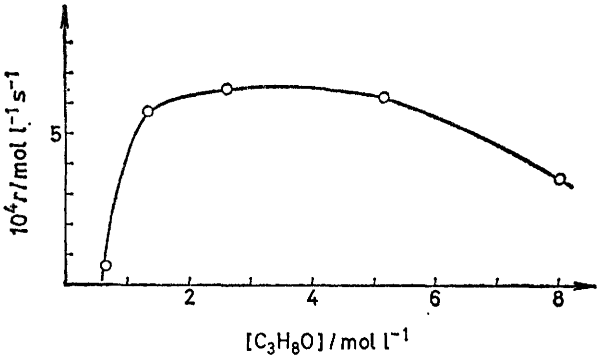

FIGURE 1 Carbonylation rate *versus* isopropyl alcohol concentration. Reaction conditions: [Rh] = 4.65 mmol l^{-1}, [HI] = 0.5 mol l^{-1}, p_{CO} = 35 atm, T = 473 K; solvent = acetic acid

Figure 1 gives the carbonylation rate as a function of isopropyl alcohol concentration over a wider range. The maximum in rate reported for methanol [2,10] and ethanol [4] was not observed. The decrease in rate at higher concentrations is probably due to a solvent effect as suggested for methanol.[10]

The dependence on hydrogen iodide concentration was investigated in the range 0.076—1.5 mol l^{-1}. At lower concentrations (up to *ca.* 0.3 mol l^{-1}) the dependence is first order with the slope 2 × 10^{-3} s^{-1}. The results are shown in Figure 2. These observations differ markedly from those found for methanol carbonylation,[1,2] where the rate was found to be first order over a wide concentration range.

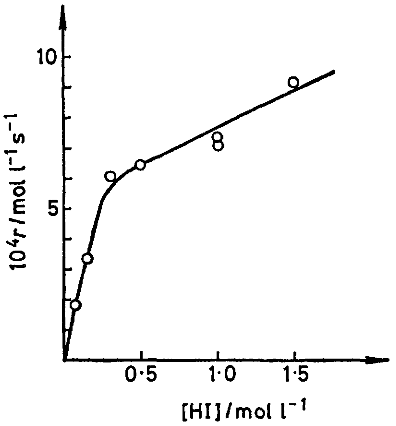

FIGURE 2 Carbonylation rate *versus* hydrogen iodide concentration. Reaction conditions: [Rh] = 4.65 mmol l^{-1}, p_{CO} = 35 atm, $[C_3H_8O]$ = 2.6 mol l^{-1}, T = 473 K; solvent = acetic acid

The rate dependence on temperature is given as an Arrhenius plot in Figure 3. From these data the thermodynamic activation parameters were calculated: E = 25.9 kcal mol^{-1}, $\Delta H^‡$ = 24.9 kcal mol^{-1}, and $\Delta S^‡$ = −9.8 e.u.

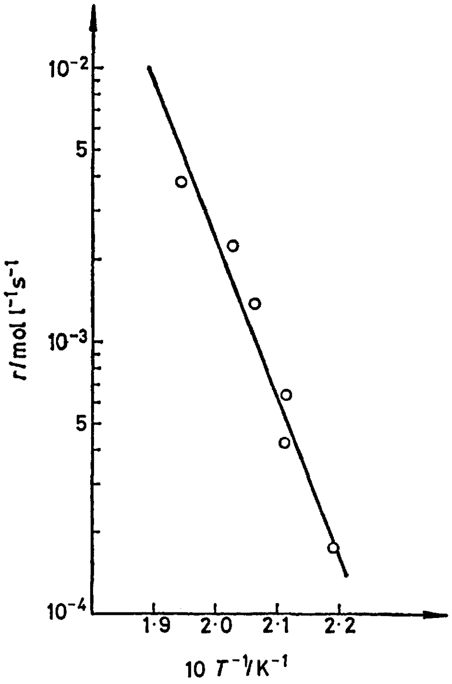

FIGURE 3 Arrhenius plot. Reaction conditions: [Rh] = 4.65 mmol l^{-1}, [HI] = 0.5 mol l^{-1}, p_{CO} = 35 atm, $[C_3H_8O]$ = 2.6 mol l^{-1}; solvent = acetic acid

As mentioned earlier the initial reaction between isopropyl alcohol and HI will give rise to the formation of n- and iso-propyl iodide. This was confirmed by gas chromatographic analysis of the reaction products. Besides

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[10] J. Hjorkjær and O. R. Jensen, *Ind. Eng. Chem. Prod. Res. Devel.*, 1977, **16**, 281.

propyl acetate, the two expected n- and iso-butyric acids are found together with smaller amounts of propene, n-propanol, and the four possible esters of propanol and butyric acid. Analytical data are given in Table 2.

TABLE 2

Product distribution (mol %)

Expt. no.	2	3	4	5	6	9	10	13	14	17
Propene	3.15	8.65	5.24	7.57		21.48	1.05	1.49	1.61	10.34
n-Propyl alcohol	1.12	3.38	10.46	3.98	5.33	34.48				13.36
Isopropyl n-butyrate	1.36	3.01	2.42	1.20	9.00	7.39	0.52	10.07	4.84	
Isopropyl isobutyrate	40.62	17.67	12.90	14.74	13.00	7.49	8.38	30.60	27.82	9.05
n-Propyl n-butyrate	3.39	1.31	1.61	2.39	14.00	11.33			0.81	
n-Propyl isobutyrate	0.67	2.26	1.21	0.80						
Isobutyric acid	27.10	26.32	25.81	29.48	25.33	7.98	37.70	20.52	24.60	24.14
n-Butyric acid	22.58	37.59	40.32	39.84	33.33	9.85	52.36	37.31	40.32	43.10
n-/iso- ratio *	0.40	0.89	1.11	0.97	1.41	1.84	1.15	0.93	0.83	1.30

* Defined as the molar ratio between n- and iso-butyric acid, including the acid bound in esters.

The relative amounts of n- and iso-butyric acid, given as the n-/iso- molar ratio and including acid bound as ester, is shown in Figure 4 as a function of the reaction parameters.

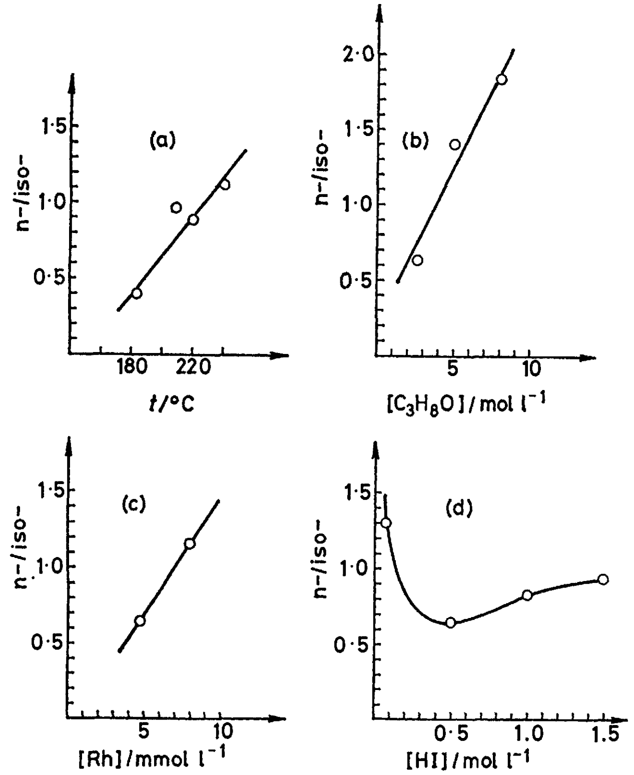

FIGURE 4 Ratio between n- and iso-butyric acid as a function of (a) temperature, (b) isopropyl alcohol concentration, (c) rhodium concentration, and (d) hydrogen iodide concentration. The constant reaction parameters had the values: $T = 473$ K, [Rh] = 4.65 mmol l^{-1}, [HI] = 0.5 mol l^{-1}, $p_{CO} =$ 35 atm, $[C_3H_8O] = 2.6$ mol l^{-1}; solvent = acetic acid.

Surprisingly enough this ratio not only increases with temperature, but also with isopropyl alcohol and rhodium concentration. The dependence on hydrogen iodide concentration is more complex, with the ratio passing through a minimum at a hydrogen iodide concentration of *ca.* 0.3 mol l^{-1}.

DISCUSSION

The kinetic measurements at HI concentrations below *ca.* 0.3 mol l^{-1} give the same reaction orders with respect to reactants, catalyst, and promotor as previously reported for methanol.[1,2] It may, thus, be assumed that the isopropyl alcohol carbonylation follows the same mechanism, involving the oxidative addition of alkyl iodide to the active rhodium complex as the rate determining step. This assumption is supported by the observed thermodynamic activation parameters.[11]

The HI concentration (*ca.* 0.3 mol l^{-1}) at which a break is observed in the rate curve (Figure 2), is virtually identical to that at which the n-/iso- ratio shows a minimum value (Figure 4d).

This non-linear dependence of the carbonylation rate on HI concentration might be caused by a more intensive dehydration of isopropyl alcohol at higher H^+ concentrations. However, in that case the dehydration rate would have to increase very rapidly in order to explain the observed deviation from first-order dependence for the carbonylation rate.

A more reasonable explanation may be found by considering the observed change in the n-/iso- ratio. The measured pressure drop is the result of the carbonylation of two different iodides, namely n- and iso-propyl iodide, and it may be expected that the carbonylation rate for isopropyliodide is higher. However, the observed change in the n-/iso- ratio seems too small to account entirely for the decline in slope at HI concentrations above 0.3 mol l^{-1}.

Assuming that the n-/iso- ratio is determined only by the formation of propyl iodide, the carbonylation rate may be expressed as follows:

$$r = a \cdot k_n \cdot \exp\left(\frac{E_m}{-RT}\right) + b \cdot k_{iso} \cdot \exp\left(-\frac{E_{iso}}{RT}\right)$$

With this equation one would expect the n-/iso- ratio to be independent of the rhodium and alcohol concentrations, which is not the case (Figure 4). Furthermore, the observed activation energy of 25.9 kcal mol^{-1} for the isopropyl alcohol carbonylation should then be the result of a ' mixing ' of the activation energies for the carbonylation of the primary and the secondary propyl iodide. The previously reported values for the activation energies for the carbonylation of the primary alcohols methanol[2]

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[11] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136.

and ethanol[4] justify the assumption that the activation energy for the carbonylation of n-propyl iodide is of the same order of magnitude, namely *ca.* 15 kcal mol^{-1}. This then leads to the conclusion that the activation energy for the carbonylation of isopropyl iodide is very high, again leading to the expectation that the n-/iso-ratio should decrease with increasing temperature. The opposite effect was, in fact, observed.

The observed total reaction rate for the carbonylation of isopropyl alcohol is thus in accord with the previous suggested mechanism for the carbonylation of primary alcohols.[1-4] However, the influence of the reaction parameters on the ratio between the formation of n- and iso-butyric acid is not explicable by this mechanism alone.

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