Journal of Organometallic Chemistry, 372 (1989) 61–66
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09745

EXAFS infrared and kinetic studies on a ruthenium carbonyl hydroformylation system

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(Received October 20th, 1988)

Abstract

Alkali metal halides and iodine are effective promoters for ethylene hydroformylation catalysis by ruthenium carbonyls in basic media; the major species is $[HRu_3(CO)_{11}]^-$ characterised by IR and Ru K-edge EXAFS, but kinetic studies indicate that mononuclear and possibly, dinuclear fragments are responsible for the catalytic activity.

Ruthenium carbonyls have been reported to catalyse a variety of CO transformations, including syngas conversion [1], the water gas shift reaction [2], and also alkene hydroformylation [3,4]. The latter reaction has been thought to involve the anion $[HRu_3(CO)_{11}]^-$ (**1**) [4], rather than $[H_3Ru_4(CO)_{12}]^-$ (**2**) which has been observed in some water gas shift systems [3]. Our interest was whether the promotion effects in, for example, syngas conversion were shared in the hydroformylation reaction.

Table 1 comprises the activity studies performed on differing precursors and possible promoters. The activity ratio using $[Ru_3(CO)_{12}]$ (**3**) and $[H_4Ru_4(CO)_{12}]$ (**4**) is 0.7, which approximates to the total ruthenium concentration and suggests a possibly common active species. As in other CO conversion reactions [1,2] alkali halides cause a significant rate enhancement; this effect increases with the ionic radius of the cation. Iodine is also an effective promoter. The optimum I_2/Ru_3 ratio was 3/1, consistent with an oxidation to a ruthenium(II) complex. The major metal carbonyl species recovered from the more efficient catalysis systems was $[HRu_3(CO)_{11}]^-$; increasing the hydrogen pressure to > 25 atm resulted in a higher proportion of anion **2** being recovered and a reduced reaction rate.

FTIR spectra in the C–O stretching region were obtained on samples from an autoclave at the temperature of the catalytic runs (150 °C) and at an elevated pressure using an arrangement similar to that of Noack [5]. From both $[Ru_3(CO)_{12}]$ (**3**)/KOH and $PPN[H_3Ru_4(CO)_{12}]$, under CO (5 bar at ambient temperature), the major species formed at 150 °C was $[HRu_3(CO)_{11}]^-$, with some residual precursor.

0022-328X/89/$03.50

Table 1

Average turnover frequencies (TF, h^{-1}) and product compositions (%) for ethylene hydroformylation using as standard conditions: C_2H_4, 15 atm; CO, 30 atm.; H_2, 30 atm; 150 °C, 2.5 h, 0.05 mmol ruthenium compound 10 cm^3 THF, 0.15 mmol of promoter and 1 cm^3 of 0.5 *M* base were used optionally.

Catalyst system	TF	Product composition			
		EtCHO	EtC(O)Et	PrOH	2-Me-pent-2-en-1-al
$RuCl_3 \cdot 3H_2O$	6	14.2	85.8	–	–
$RuCl_3 \cdot 3H_2O$/NaOH	12	75.7	24.3	–	–
$H_4Ru_4(CO)_{12}$/NaOH	171	84.5	3.1	1.5	10.9
$H_4Ru_4(CO)_{12}$/NaOH/KI	205	85.8	5.0	5.2	4.0
$Ru_3(CO)_{12}$ (3)/NaOH	119	88.9	3.1	1.1	6.9
3/NaOH/KCl	161	90.9	2.9	1.6	4.6
3/NaOH/KBr	190	85.4	1.5	0.7	12.4
3/NaOH/KI	149	92.3	3.7	1.8	3.7
3/KOH/KI	194	83.0	9.1	6.2	1.7
3/RbOH/RbI	226	93.4	3.0	–	3.6
3/CsOH/CsI	285	82.6	8.5	2.0	6.9
3/NaOH/I_2	227	86.9	5.7	2.4	5.0
PPN[$HRu_3(CO)_{11}$]	183	88.7	4.1	1.4	5.8
PPN[$HRu_3(CO)_{11}$]/KI	222	81.7	2.9	0.6	14.8

The addition of KI to the system accelerated the formation of the anions **1** and **2**. On mixing, the addition of iodine to [$Ru_3(CO)_{12}$] resulted in the observation of [$Ru(CO)_4I_2$] and [$Ru(CO)_3I_3$]$^-$, as well as a third, unidentified carbonyl complex. However, once heated to the reaction temperature under CO/H_2 with or without C_2H_4, there was again rapid formation of the two cluster ions **1** and **2**, with **3** and $Ru(CO)_4I_2$ being minor components.

From the IR studies, experiments were devised to test the application of X-ray absorption spectroscopy to carbonylation catalysts. Ideally the same concentration and pressure conditions should be employed as for the catalytic runs or the IR spectroscopy. The concentration of the cluster employed (4.5 m*M*) is in the range generally investigated using fluorescence detection. However, organic solvents and polymers are relatively transparent at the wavelength of the Ru K-edge and so the IR cell was modified to allow a 1 cm sample path length using 0.5 cm Perspex windows faced with Mylar to prevent etching by the THF solvent. It was then possible to obtain high quality X-ray absorption spectra in transmission mode which showed EXAFS features 1000 eV to high energy of the Ru K-absorption edge for the required sample concentration.

The analysis of one of these spectra is shown in Fig. 1. This was obtained using PPN[$H_3Ru_4(CO)_{12}$] as the precursor, with the solution being sampled from an autoclave charged with CO and at 150 °C and at 225 psig. IR studies had shown the [$HRu_3(CO)_{11}$]$^-$ was formed under these conditions, and the data and its Fourier transform could be satisfactorily fitted to this model. The following metric parameters were obtained by this analysis: Ru–C_{term} 1.94(1) Å, Ru–C_{br} 2.17(1) Å, Ru–Ru 2.84(1) Å, Ru...O_{br} 2.88(3) Å, and Ru...O_{term} 3.08(1) Å.

The data analysis was performed using a full spherical wave multiple scattering formalism, of the type applied to metal carbonyls in previous reports [6]. Ru–C–O

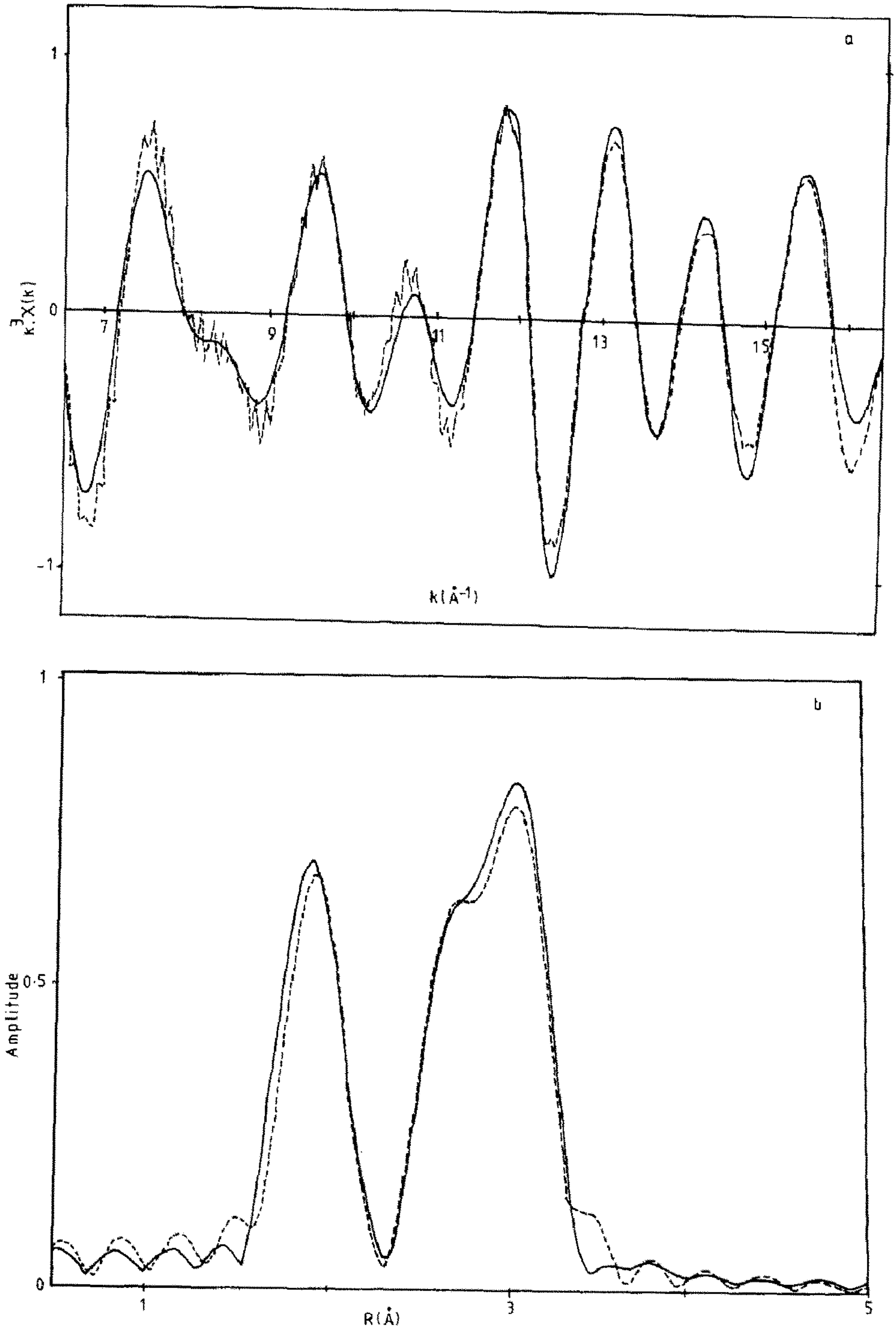

Fig. 1. Ruthenium K-edge absorption data recorded in transmission on a solution sampled from an autoclave charged with PPN[$H_3Ru_4(CO)_{12}$] and under CO; Conditions: 150 °C and 225 psig; (a) k^3 weighted EXAFS and (b) Fourier transforms. Experimental (———) and theoretical (- - - - -) curves.

bond angles of 180° and 137° were utilised for the terminal and bridging carbonyl groups respectively. The agreement with the mean of the crystallographic values [7] is generally within 0.02 Å, the exception being for the solitary bridging group (mean

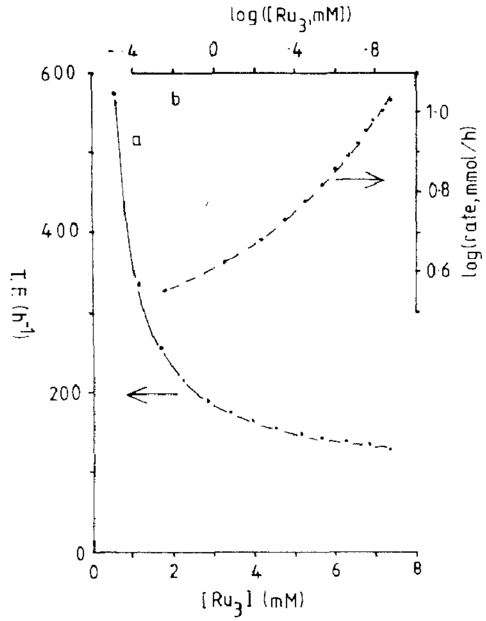

Fig. 2. Plots showing the dependence of the catalysis rate on concentration of [$Ru_3(CO)_{12}$]; (a) turnover frequency (TF) against [$Ru_3(CO)_{12}$] concentration and (b) a log–log plot of the rate of product formation against [$Ru_3(CO)_{12}$] concentration.

Ru–C and Ru...O 2.07 and 3.04 Å respectively). Since its contribution interferes strongly with that of the more populous terminal groups strongly enhanced by multiple scattering pathways, it is poorly defined.

The kinetics of the total hydroformylation product formation display non-integer orders in the initial gas pressures of the three reagent gases. The apparent order in ethylene varied markedly with pressure; this increased from ca. 0.3 at a lower pressure range (10–15 atm) to ca. 1.5 at higher pressure (16–20 atm). Sigmoid curves were obtained for log–log plots of the rate dependence on $P(H_2)$ (10 atm < $P(H_2)$ < 26 atm) and $P(CO)$ (10 atm < $P(CO)$ < 27 atm); the mean reaction order was found to be 0.64(2) and 0.44(3) for hydrogen and CO, respectively. The turnover frequency decreased with increasing cluster concentration (Fig. 2a). The log–log plot of catalysis rate against concentration in Fig. 2b shows a varying and low order in [$Ru_3(CO)_{12}$] concentration which ranged from ca. 0.3 and ca. 0.5 m*M* to ca. 0.65 at ca. 5 m*M*. This behaviour indicates competing reaction mechanisms, and although the trinuclear anion predominates under elevated gas pressures, there must be an equilibrium with a more reactive cluster fragment [8]. The dependence on ruthenium concentration bears a much closer similarity to that reported for the water gas shift reaction [2] than syngas conversion [1c,9]; the former process was described in terms of active mono- and di-nuclear fragments; this fits the order change from ca. 1/3 to ca. 2/3. It seems that reaction pathways previously ascribed to the anion **1** are possibly more complex [4] and are more closely related to the water gas process than syngas conversion.

A Reppe hydroformylation of ethylene ($C_2H_4/CO/H_2O$) under the similar conditions of temperature and pressure provided negligible activity. However increasing the base concentration (to 0.83 *M*) and utilising an aqueous methanol

Table 2

Average turnover frequency (TF, h^{-1}) for Reppe hydroformylation using the standard conditions: C_2H_4, 20 atm; CO 35 atm; 150 °C; 4 h; 0.05 mmol of $Ru_3(CO)_{12}$ (3) 10 cm^3 of MeOH 0.20 mmol of $M(CO)_6$, M = Cr, Mo or W, 0.15 mmol of KI or CsI, 2 cm^3 of 3.0 *M* KOH or 3 cm^3 of 50% CsOH were used optionally

Catalyst system	TF	Product composition				
		EtCHO	$EtCH(OMe)_2$	EtC(O)Et	PrOH	2-Me-pent-2-en-1-al
3/KOH	100	16.0	18.9	–	4.9	60.2
$3/Cr(CO)_6/KOH$	128	23.0	24.3	–	7.5	45.2
$3/Mo(CO)_6/KOH$	136	40.6	8.8	–	4.0	46.6
$2/W(CO)_6/KOH$	228	18.3	11.1	5.8	5.1	59.7
$3/W(CO)_6/KOH/KI$	320	20.5	4.8	3.7	3.7	67.3
$3/W(CO)_6/CsOH/CsI$	368	17.6	7.8	8.8	6.3	59.5
3/CsOH/CsI	204	23.7	9.0	16.8	16.8	40.2

medium provided significant activity. The results of these studies are presented in Table 2. The major organic product was 2-methylpent-2-en-1-al, emanating from an aldol condensation of propanal. Enhancement of this type of reaction [5,10] by promoters was also studied. In addition to the promotors employed in the former system, the Group VI hexacarbonyls were investigated because of their reported activity for the water gas shift reaction [2b,11,12]. CsI and tungsten carbonyls provided significant rate enhancements; the optimum W/Ru_3 ratio was 4. IR studies under elevated pressures showed $[HRu_3(CO)_{11}]^-$ as the only ruthenium carbonyl species with $W(CO)_6$ prevalent for tungsten. In the absence of ruthenium (when there was then no hydroformylation activity), a significant proportion of the tungsten was in the form of $[HW_2(CO)_{10}]^-$. With ruthenium present, this anion is converted to an unidentified carbonyl anion exhibiting CO absorptions at 1914s and 1860m cm^{-1}, at the early stages of the elevated pressure runs. This may possibly be $[W(CO)_5(O_2CH)]^-$, previously observed in a formate decomposition system [12].

These results confirm the view that the anion $[HRu_3(CO)_{11}]^-$ is predominant in active hydroformylation systems, and indicate that iodine and iodine promoters accelerate its formation. The low and varying order in cluster concentration indicates that, as for the water gas shift reaction, mononuclear complexes are responsible for the flux of the reaction when the metal is dilute with, possibly, di-nuclear species important at higher concentrations. This work also shows that X-ray absorption spectroscopy can potentially be used to establish structural information about the predominant species present under catalytic conditions, and can be applied in a similar concentration regime to F.T.I.R. spectroscopy of the intense metal carbonyl C-O absorptions.

Acknowledgements

We wish to thank the following for assistance: SERC for access to the facilities of the Daresbury Laboratory and for research studentships (A.C.S. and H.L.), BP Research International for supporting the CASE studentship (to H.L.) and providing high pressure equipment, the Fujian Institute for Research on the Structure of

Matter for study leave for G.J., and Johnson–Matthey for the loan of ruthenium salts.

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