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Hydrocarboxylation of isoprene catalyzed by iodo-carbonylrhodium derivatives. Spectroscopic evidence for participation of $H^+ \cdots Rh(CO)_2I_2^-$ tight ion pairs and *cis*-$Rh(CO)_2(H_2O)I$ in catalysis

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Abstract

Hydrocarboxylation of isoprene catalyzed by iodocarbonylrhodium derivatives is described. Either 4-methyl-3-pentenoic (pyroterebic) acid or its lactone derivative (γ,γ-dimethyl-γ-butyrolactone) can be selectively produced in high yield depending on the experimental conditions. Spectroscopic evidence indicates the possible participation of $H^+ \cdots Rh(CO)_2I_2^-$ tight ion pairs and/or *cis*-$Rh(CO)_2(H_2O)I$ in the catalysis. The identification of these two new species is based on spectroscopic investigation of the interconversion reactions between solvent-separated $[H_3O]^+[Rh(CO)_2X_2]^-$ ions and $[Rh(CO)_2X]_2$ (X = Cl, I).

Introduction

Catalytic hydrocarboxylation and hydroesterification of alkynes, alkenes, and dienes have attracted much interest since their discovery by Reppe, and in a few cases they are of industrial application [1,2]. The commercial application of a butadiene route to adipic acid, via a two-step hydroesterification catalyzed by $Co_2(CO)_8$ and pyridine [3], has also been noted recently [4]. These reactions could be more important for the efficient and selective synthesis of fine chemicals rather than for production of bulk products [4–6].

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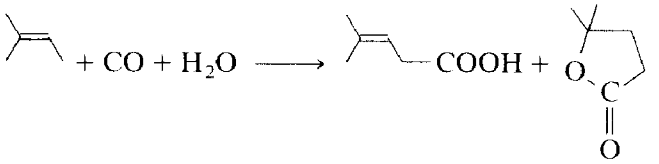
We report here some initial results on the hydrocarboxylation of isoprene catalyzed by iodocarbonylrhodium species, which point to the probable relevance of the presence of $H^+ \cdots Rh(CO)_2I_2^-$ tight ion pairs and/or *cis*-$Rh(CO)_2(H_2O)I$ on the activity and selectivity of the system. Depending on the experimental conditions either the 4-methyl-3-pentenoic (pyroterebic) acid or its lactone derivatives γ,γ-dimethyl-γ-butyrolactone, can be effectively and selectively obtained (eq. 1).



(1)

Pyroterebic acid is a valuable intermediate for the synthesis of chrysanthemic acid [7], or as a starting material for polymers and pharmaceuticals [8]. The lactone is a member of an important class of compound present as a component in several natural products and sesquiterpenes [9]. To our knowledge only the catalytic hydroesterification of isoprene has previously been investigated with palladium salts or complexes as catalysts, and it was shown to give mainly an isomeric mixture of ethyl pentenoates, with an excellent selectivity for the 4-ethyl-3-pentenoate, but with rather unsatisfactory yields and rates [10].

Results and discussion

1. Hydrocarboxylation of isoprene

Reaction 1 has been investigated at various temperatures (100–180 °C) and CO pressures (50–125 atm) by use of either $[PPN][Rh(CO)_2X_2]$ (PPN = bis(triphenylphosphine)iminium; X = Cl, I) or $Rh_4(CO)_{12}$ as catalyst precursor in the presence of variable amounts of aqueous HI as cocatalyst and THF (tetrahydrofuran) as solvent. Table 1 shows the results obtained with $[PPN][Rh(CO)_2I_2]$ as precursor under various experimental conditions. First of all, no significant difference was noticed when either $[PPN][Rh(CO)_2Cl_2]$ or $[PPN][Rh(CO)_2I_2]$ was used in the presence of HI as cocatalyst, probably owing to the ready transformation of the

Table 1

Hydrocarboxylation of isoprene with $[PPN][Rh(CO)_2I_2]$ promoted by HI

([Isoprene] = 1 *M*; $[H_2O]$ = 1.3 *M*; [Rh] = 0.01 *M*; aqueous HI (weight% = 57); THF (20 ml) as solvent; conversion and selectivities are given as molar percent; hydrogenated = 2-methylbutene, 3-methylbutene and (mainly) 2-methyl-2-butene; oxygenated = pyroterebic acid and γ,γ-dimethyl-γ-butyrolactone)

Run	HI/Rh	*T* (°C)	*P*(CO) (atm)	*t* (h)	Conversion	Hydrogenated (%)	Oxygenated (%)	Acid/lactone
1	5	150	110	4	46.5	38.5	61.5	4.4
2	10	150	110	4	65.6	41.2	58.8	1.8
3	25	150	110	4	89.9	82.2	17.8	0.2
4	5	120	110	8	49.9	15.9	84.1	3.4
5	10	120	110	8	73.8	22.8	77.2	2.9
6	25	120	110	8	89.3	47.9	52.1	0.4
7	5	120	50	8	32.8	13.8	86.2	15.0

former into the latter [11]. As shown by runs 1–6 in Table 1, the degree of conversion of isoprene steadily increases with increasing HI/Rh ratio and/or increasing temperature. However, increase of either one or both of these two parameters markedly lowers the selectivity toward oxygenated products, owing to a steeper increase in the rate of the hydrogenation of isoprene to give an isomeric mixture of methylbutenes. Spectroscopic analysis of the depressurized solutions reveals a progressive conversion of the starting $[Rh(CO)_2I_2]^-$ anion into $[Rh(CO)_2I_4]^-$ [12], which is known to catalyze the water gas shift reaction [13] but to be inactive for the hydrocarboxylation of olefins [14]. This may be responsible for the observed shift toward hydrogenation at the expense of hydrocarboxylation, of isoprene. Alternatively, a high HI/Rh ratio could favour hydrolysis of the alkylrhodium intermediate before carbonylation can occur. Oxygenated products are favoured by a decrease of the temperature and the HI/Rh molar ratio, which, however, causes a significant fall in the activity of the system. In addition to the activity and the selectivity for products, the composition of the oxygenated mixture is also greatly affected by change in the HI/Rh ratio. Thus, use of a low HI/Rh ratio (e.g. runs 1, 4 and 7) greatly depresses the formation of the lactone, and the pyroterebic acid can be obtained with an overall selectivity of ca. 85%. Conversely, the highest HI/Rh ratios greatly favour the formation of the γ,γ-dimethyl-γ-butyrolactone, which is almost exclusively obtained for HI/Rh = 25. We have so far been unable to establish unambiguously whether the lactone is a primary product of the reaction or a secondary product arising from acid [15] or transition metal [16] catalyzed isomerization of pyroterebic acids. The latter interpretation is more consistent with the observation that the acid/lactone molar ratios fall slightly with time.

It is known that the $[Rh(CO)_2X]_2$ dimer is readily split by aqueous HX (X = Cl, Br, I) and converted into solvent separated $[H_3O]^+[Rh(CO)_2X_2]^-$ ions [17]. Spectroscopic monitoring indicates that a similar mixture is also readily formed by reaction of $Rh_4(CO)_{12}$ in THF with aqueous HX ($HX/Rh_4(CO)_{12} \geqslant 10$) under nitrogen as a result of reaction 2, which affords the known $[Rh_6(CO)_{15}X]^-$ [18] and some $Rh_6(CO)_{16}$, followed by a slower reaction (eq. 3).

$$3Rh_4(CO)_{12} + 2HX + 2H_2O \xrightarrow{THF} 2[H_3O]^+[Rh_6(CO)_{15}X]^- + 6CO \quad (2)$$

$$2[H_3O]^+[Rh_6(CO)_{15}X]^- + 22HX + 10H_2O \longrightarrow 12[H_3O]^+[Rh(CO)_2X_2]^- + 6CO + 6H_2 \quad (3)$$

This prompted us to investigate the hydrocarboxylation of isoprene using either $Rh_4(CO)_{12}$ or $[Rh(CO)_2X]_2$ and aqueous HX to examine the effect on catalysis of the absence of any counterion other than the solvated proton. A few selected results are listed in Table 2. Both the $Rh_4(CO)_{12}$/HI and $[Rh(CO)_2Cl]_2$/HI systems show rather similar catalytic behaviour (see runs 14 and 17 in Table 2), and under comparable experimental conditions, they are catalytically superior to the $[PPN][Rh(CO)_2I_2]$/HI system. The higher activity of these systems is also shown by the observation that significant amounts of THF are hydrocarboxylated to give valeric acid and C_5-lactones, as previously reported [19]. A further difference is that only the lactone is obtained, and the pyroterebic acid is always a minor product. As shown by runs 12 and 13, variation of the CO pressure has only a minor effect, if

Table 2

Hydrocarboxylation of isoprene with $Rh_4(CO)_{12}$ and $[Rh(CO)_2X]_2$ promoted by HX (X = Cl, Br, I)

(Other parameters as in Table 1; in runs 12–18 [Rh] = 0.02 *M*)

Run	HX	HX/Rh	*T* (°C)	*P*(CO) (atm)	*t* (h)	Conversion	Hydrogenated (%)	Oxygenated (%)	Acid/lactone
$Rh_4(CO)_{12}$									
8	HI	25	150	110	4	94.3	54.2	45.8	0.03
9	HI	10	180	50	8	94.9	48.8	51.2	0.11
10	HI	10	150	50	8	96.2	40.2	59.8	0.04
11	HI	10	120	50	8	99.7	28.3	71.7	0.04
12	HI	5	120	50	2	87.2	22.8	77.2	0.12
13	HI	5	120	125	2	89.9	16.5	83.5	0.08
14	HI	5	120	50	4	98.2	13.9	86.1	0.05
15	HBr	5	120	50	4	46.4	64.4	35.6	0.32
16	HCl	5	120	50	4	25.9	89.3	10.7	0.66
$[Rh(CO)_2Cl]_2$									
17	HI	4	120	50	4	91.0	8.6	90.4	0.05
18	HCl	4	120	50	4	10.8	83.9	16.1	1.07

Table 3

Effect of the isoprene/H_2O molar ratio on the hydrocarboxylation of isoprene with $Rh_4(CO)_{12}$ and HI ([Rh] = 0.04 *M*; HI/Rh = 4.5; aqueous HI (weight% = 57); THF (20 ml) as solvent; *P*(CO) 50 atm; *T* 120 °C; *t* 1 h; other parameters as in Table 1)

Run	[Isoprene] (*M*)	Isoprene/H_2O	Conversion	Hydrogenated (%)	Oxygenated (%)	Acid/lactone
19	0.5	0.55	98.4	12.5	87.5	0.03
20	0.75	0.83	99.0	8.4	91.6	0.03
21	0.8	1.00	98.8	9.0	91.0	0.03
22 [a]	1.0	1.11	89.5	9.2	90.8	0.03
23 [a]	1.5	1.67	59.6	8.3	91.7	1.92
24 [a]	2.0	2.22	44.7	5.9	94.1	2.85
25 [a]	3.0	3.33	29.6	7.8	92.2	8.49

[a] Conversion with respect to H_2O, which represents the limiting reagent, is almost complete.

any, on both activity and selectivity, whereas increase in the temperature and/or HI/Rh ratio lowers the selectivity. Optimization of these parameters and doubling of the rhodium concentration afforded two active and selective catalytic systems. In contrast, as shown in Table 2, replacement of HI by HBr or HCl in the $Rh_4(CO)_{12}$ and $[Rh(CO)_2Cl]_2$ system caused a sharp decrease of both activity and selectivity.

Some features which help in interpreting the differenting catalytic performances of these systems appear in the results of runs shown in Table 3. In the experiments carried out with $Rh_4(CO)_{12}/HI$ the water required by reaction 1 is only provided by the aqueous HI (weight% = 57) which is kept at a constant HI/Rh ratio of 4.5 and the initial isoprene concentration is varied in the 0.5–3 *M* range so that water progressively becomes the stoichiometrically limiting reagent. To facilitate direct IR spectroscopic analysis of the depressurized catalytic solutions a rather high Rh concentration of 4×10^{-2} *M* was also employed. As shown in Table 3, under these conditions the conversion of the limiting reagent (isoprene or water) is always nearly complete after 1 h, and a high selectivity towards oxygenated products is always observed. With a sub-stoichiometric isoprene/water ratio (entries 19 and 20 in Table 3) the system essentially catalyzes the complete conversion of isoprene into γ,γ-dimethyl-γ-butyrolactone. In contrast, when the isoprene/H_2O molar ratio increased so that water becomes the sub-stoichiometric reagent (entries 22–25), the relative amount of pyroterebic acid present progressively increases at the expenses of the lactone, and the former can also be almost exclusively obtained with this much more active catalytic system. It is noteworthy that the switch in selectivity from lactone to pyroterebic acid in runs 24 and 25 is in keeping with fall in the rate of the HI-promoted iodo-lactonization [15] owing to competitive removal of HI by unreacted isoprene (trace amounts of a iodoalkene derived from isoprene were detected by linked GC–MS). At the same time the amount of by-products arising from the hydrocarboxylation of THF becomes progressively negligible. Concomitant infrared analysis of depressurized solutions reveals a significant change in the infrared spectra arising from a progressive transformation of the initially present solvent-separated $[H_3O]^+[Rh(CO)_2I_2]^-$ ions into the $[Rh(CO)_2I]_2$ dimer, through the intermediate formation of new species having their strongest absorptions in the 2075–2065 and 2000–1990 cm^{-1} range. Although the $[Rh(CO)_2I]_2$ dimer and the

$[Rh(CO)_2I_2]^-$ anion are among the most thoroughly investigated compounds owing to their involvement in several catalytic processes [1,4], to our knowledge no mention of the above species has been made in the literature. In the attempt to gain a better insight into their nature and into the reasons for the observed drop in catalytic activity on replacing iodine by chlorine, we re-investigated the behaviour of $[Rh(CO)_2X]_2$, as well as $Rh_4(CO)_{12}$, in the presence of water and/or aqueous or dry HX (X = Cl, I).

2. Chemical behaviour of $[Rh(CO)_2X]_2$ and $Rh_4(CO)_{12}$ in the presence of HX (X = Cl, I) and H_2O

The results of our investigation of the chemical behaviour of $[Rh(CO)_2X]_2$ and $Rh_4(CO)_{12}$ in the presence of H_2O and/or aqueous or dry HX (X = Cl, I) are summarized in Scheme 1. One difference between $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2I]_2$ is immediately apparent from their IR patterns in donor and non-donor solvents, which cannot be simply interpreted on the basis of solvent effects. Thus, a comparison of the IR spectra of the $[Rh(CO)_2Cl]_2$ dimer in n-hexane (ν(CO) at 2108w, 2094s, 2077w, 2037s, 2003w cm^{-1}) and in THF (ν(CO) at 2108w, 2092s, 2083sh, 2035s, 2009s cm^{-1}) suggests the presence of a chloride-bridge splitting equilibrium, arising from the donor ability of THF, which gives rise to *cis*-$Rh(CO)_2(THF)Cl$ (vide infra). This conclusion is based on the presence in the infrared spectrum in this solvent of an additional shoulder at ca. 2083 and a strong absorption at 2009 cm^{-1} (see Fig. 1a), which are absent for solutions in non-donor solvents such as n-hexane, toluene and dichloromethane. If identical absorption coefficients are assumed for the carbonyl groups in the dimer and monomer, the amount of $Rh(CO)_2(THF)Cl$ present at the equilibrium in pure THF is ca. 50–60 molar%. In contrast, the corresponding iodine-bridge splitting equilibrium of the $[Rh(CO)_2I]_2$ dimer is almost completely shifted toward the dimer, and the IR absorptions due to *cis*-$Rh(CO)_2(THF)I$ are barely noticeable.

Progressive addition of water (up to a three-fold stoichiometric excess) to a THF solution of $[Rh(CO)_2X]_2$ (X = Cl, I) leads to quantitative formation of a new species showing infrared carbonyl absorptions at 2100w(sh), 2081s, 2005s for X = Cl and 2076s, 2000s cm^{-1} for X = I. Related species with almost identical carbonyl absorptions also appear on addition of stoichiometrical amounts of methanol to $[Rh(CO)_2X]_2$ solutions in hexane. So far all the attempts to isolate these species in the solid crystalline state have been unsuccessful, and have resulted in isolation of the starting material or decomposition products. Monitoring of the reaction of $[Rh(CO)_2Cl]_2$ with water by ^1H NMR at room temperature shows the growth of a sharp singlet at δ 7.39 ppm, which broadens as the amount of added water approaches the stoichiometric amount, and shifts to δ 4.5 ppm on subsequent addition of D_2O in excess. The room temperature ^{13}C NMR spectrum of the solution obtained by treatment of an isotopically-enriched sample of $[Rh(CO)_2Cl]_2$ with a three-fold molar excess of water consists of a doublet at δ 182.1 ppm (J(Rh–C) 71.5 Hz); this is split in two equally intense doublets at δ 184.5 (J 72.6 Hz) and 180.1 ppm (J 72.5) Hz) at −90 °C, indicating the presence of two inequivalent CO groups. In principle, there are several possible species consistent with this spectroscopic behaviour, e.g.: (a) water (as well as other oxygen donors) adducts of $[Rh(CO)_2X]_2$ with unsplit or partially-split halide-bridges; (b) a tetra-coordinated halide-bridge split *cis*-$Rh(CO)_2(H_2O)X$ aquo complex; and, (c) a

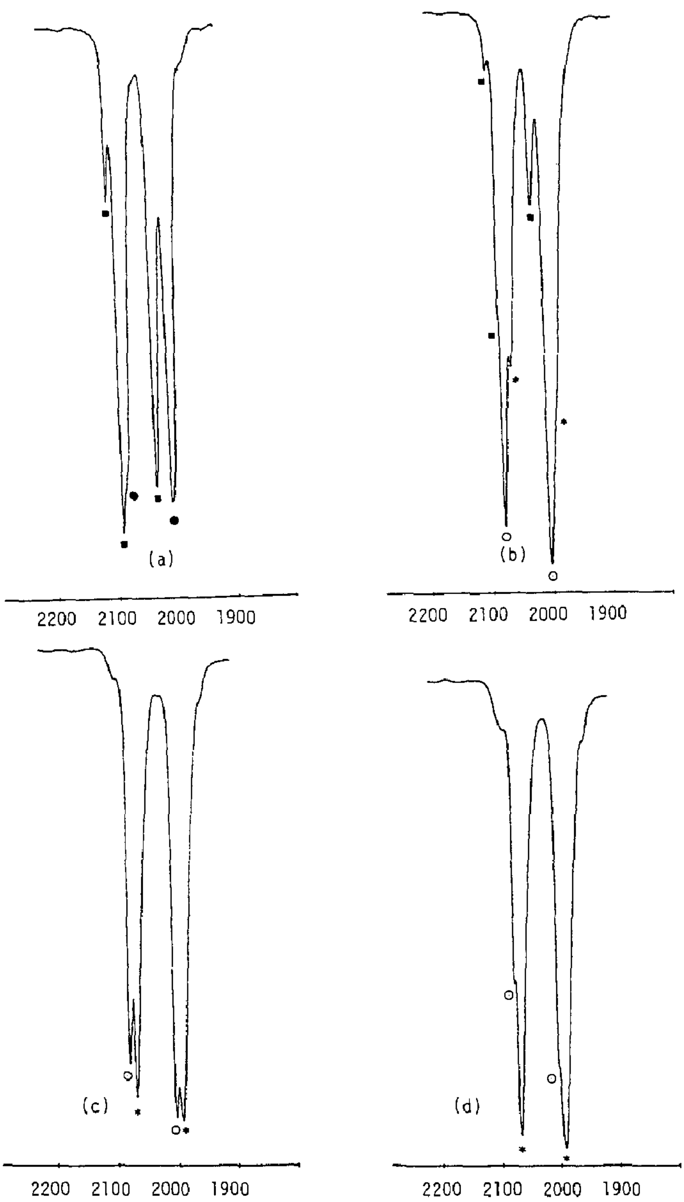
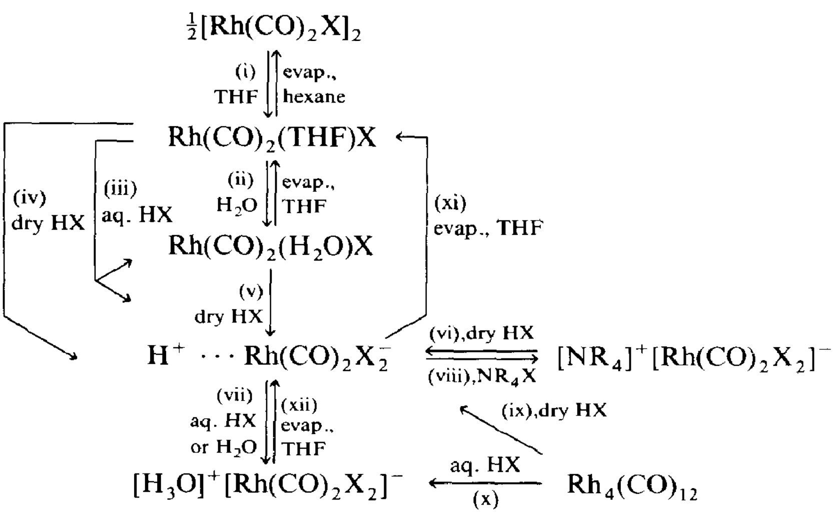


Fig. 1. The reaction of $[Rh(CO)_2Cl]_2$ (■) with aqueous (37%) HCl in THF showing the progressive formation of $Rh(CO)_2(THF)Cl$ (●), $Rh(CO)_2(H_2O)Cl$ (○) and $H^+ \ldots Rh(CO)_2Cl_2^-$ (*) tight ion pairs. (a) $[Rh(CO)_2Cl]_2$ (0.114 g) in THF (5 ml); (b) after addition of 30 μl of aqueous HCl (37%); (c) after further addition of 30μl of HCl; (d) after further addition of 20 μl of HCl.

$Rh_2(CO)_4(\mu\text{-}OH)(\mu\text{-}X)$ hydroxo-bridged species. To our knowledge there are no reported examples of unsplit adducts of the rhodium-halocarbonyl dimers. In contrast, bridge-splitting reactions or $[Rh(CO)_2X]_2$ ($X = Cl$, Br, I) to give *cis*-$Rh(CO)_2(L)X$ have been suggested or shown to be brought about by a wide variety of ligands, including amines, phosphines, arsines, stibines, and nitriles, [17,20–22], whereas alcoholates and thioalcohols give rise to $[Rh(CO)_2(\mu\text{-}ER)]_2$ ($E = O$, S; $R =$ alkyl, aryl) dimer [23–25]. It has also been previously suggested that the reduction of $[Rh(CO)_2Cl]_2$ to $Rh_4(CO)_{12}$ with water could proceed through an initial rate-determining step involving the formation of a $Rh_2(CO)_4(\mu\text{-}OH)(\mu\text{-}Cl)$ dimer [26]. The close similarity between the IR carbonyl absorptions of this new species and those of both *cis*-$Rh(CO)_2(NR_3)X$ [17,20] and $[Rh(CO)_2(\mu\text{-}OMe)]_2$ [23,24] and the inequivalence of the carbonyl groups in the ^{13}C NMR suggest both *cis*-$Rh(CO)_2(H_2O)X$ and $Rh_2(CO)_4(\mu\text{-}OH)(\mu\text{-}X)$ as possible formulations. However, observation of related species with other oxygen-donor ligands such as THF and the complete reversibility of step (ii) of the SCHEME clearly point to *cis*-$Rh(CO)_2(H_2O)X$ as the most probable formulation. Both of the equilibria (i) and (ii) are completely reversed upon evaporation in vacuum, followed by dissolution in dry THF and re-evaporation in vacuum in the case of equilibrium (ii), as shown by the fact that the residue of the evaporation is completely soluble in n-hexane, to give a solution showing the typical infrared pattern of the $[Rh(CO)_2X]_2$ dimer. It is noteworthy that on standing in solution the aquo-complex slowly undergoes further transformations, in keeping with previous findings [26].

The reactions of the $[Rh(CO)_2X]_2$ dimer with aqueous HX acids have been reported to result in halide-bridge splitting to give $[Rh(CO)_2X_2]^-$ [17]. This is substantially true, but as shown in Fig. 1b–1d, the progressive addition of stoichiometric amounts of aqueous HCl (37% in weight) to the $[Rh(CO)_2Cl]_2$ dimer causes complete disappearance of the starting material and formation of an approximately 1/1 mixture of *cis*-$Rh(CO)_2(H_2O)X$ and a new species showing infrared absorptions at 2071s and 1995s cm^{-1}, values slightly higher than those for the $[Rh(CO)_2Cl_2]^-$ anion. In contrast, addition of azeotropic aqueous HI (57% in weight) to a THF solution of $[Rh(CO)_2I]_2$ mainly produces mixtures of $Rh(CO)_2(H_2O)I$ and $[Rh(CO)_2I_2]^-$; intermediate absorptions at 2065s and 1988s cm^{-1} became unambiguously detectable only when more concentrated aqueous HI (ca. 87% in weight) was used. Almost pure solutions of these last intermediate species were obtained by the action of dry HX on THF solution of either $[Rh(CO)_2X]_2$ or *cis*-$Rh(CO)_2(H_2O)X$, as shown in steps iv and v of the Scheme 1. Their presence was also been detected in THF solutions of $[PPN][Rh(CO)_2X_2]$ after treatment with dry HX (step vi of Scheme 1). In the light of this information the species showing IR absorptions at 2071s and 1995s for X = Cl and 2065s and 1988s cm^{-1} for X = I seem probably to be $H^+ \cdots Rh(CO)_2X_2^-$ tight ion pairs. Thus, repeated evaporation in vacuum of solutions containing the $H^+ \cdots Rh(CO)_2X_2^-$ tight ion pairs, eventually alternated with dissolution of the residue in anhydrous THF, regenerates the starting rhodium carbonyl halide dimers through steps xi and i of Scheme 1. In contrast, the solutions undergo a progressive lowering of their absorption frequencies on addition of either water or aqueous HX in excess (HCl 37%; HI 57% in weight), down to the typical values for solvent separated $[Rh(CO)_2X_2]^-$ salts step vii). Attempts to precipitate these intermediate species by addition of anhydrous tetrasubstituted ammonium salts on the basis of the alternative assumption of their possible formulation as $[HRh(CO)_2X_3]^-$, likewise resulted in a shift of the absorptions down to the positions for solvent separated $[Rh(CO)_2X_2]^-$ salts (step viii; X = Cl, ν(CO) at 2061s, 1984s; X = I, ν(CO) at 2056s, 1978s cm^{-1}), probably as a consequence of the increased ionic strength of the solution. The alternative formulation as a Rh^{III} hydride is also inconsistent with the ^1H NMR spectra which show signals in the δ 6–9 ppm range, depending on the sample and experimental conditions, rather than in the expected hydride region.



Scheme 1

Equilibria in solution between metal carbonyl hydrides, contact $SH^+ \cdots M(CO)_n^-$ (S = solvent or base) ion pairs and solvent-separated S_xH^+ and $M(CO)_n^-$ ion pairs, are well documented [27], and the presence of contact ion pairs in the solid state between a coordinated proton and a metal carbonyl anion has been unequivocally shown by X ray diffraction studies on $NR_3H^+ \cdots Co(CO)_4^-$ [28]. It is to mention that $[Ru(CO)_3I_3]^-$ salts in the presence of acid show spectroscopic behaviour similar to those described above, and this was similarly interpreted in terms of tight ion pairing [29–31]. A preliminary report of similar behaviour of $[Rh(CO)_2I_2]^-$ appeared while this paper was in preparation [32].

The solutions exclusively containing H^+ and $[Rh(CO)_2X_2]^-$ as solvent separated ions, generated by addition and aqueous HX in excess to either $[Rh(CO)_2X]_2$ or $Rh_4(CO)_{12}$ (steps iii + vii or step x of Scheme 1) can, by repeated cycles of evaporation in vacuum and dissolution in anhydrous THF, be taken back to stage i through the intermediate formation of $H^+ \cdots Rh(CO)_2X_2^-$ tight ion pairs. The most obvious difference between the chloro and iodo system was noticed when azeotropic HX acids (37% HCl and 57% HI) were employed; apparently these acid compositions relatively favour formation of tight $H^+ \cdots Rh(CO)_2X_2^-$ ion pairs with HCl and $Rh(CO)_2(H_2O)X$ with the more dilute HI.

This investigation allows us to conclude that the infrared carbonyl absorptions shown by several depressurized catalytic solutions can be ascribed either to the *cis*-$Rh(CO)_2(H_2O)I$ complex or to $H^+ \cdots Rh(CO)_2I_2^-$ tight ion pairs, or to mixtures of both.

Concluding remarks

There are several possible mechanisms for the hydrocarboxylation and hydroesterification of olefins. For instance, the palladium-catalyzed hydrocarboxylation and hydroesterification have been shown to proceed by two mechanisms, involving addition of either Pd–H or Pd–COOR moieties to the C–C double bond, with the latter particularly predominating under basic conditions [33]. A similar conclusion has also been reached on the basis of model reactions [34,35] for the hydroesterification of butadiene catalyzed by the $Co_2(CO)_8$ pyridine system [3]. These models indicate that the more effective route involving addition of a Co–COOR moiety to butadiene to give a carboxylated allyl complex of cobalt, which eliminates alcoxypentenoates by subsequent reaction with either $HCo(CO)_4$ or $PyH^+Co(CO)_4^-$ tight ion pairs [34]. Mechanistic studies of the hydrocarboxylation of ethylene with $[Rh(CO)_2I_2]^-$ promoted either by ethyl iodide or HI indicated the occurrence of ethylene insertion into Rh–H bond, rather than oxidative addition of ethyl iodide to Rh^I, to be most effective route to propionic acid [14].

The identification of the carbonyl species detected in our depressurized solutions is not very helpful in deciding between the above possibilities. Furthermore, more than one mechanism could operate at the same time. Thus, the $Rh(CO)_2(H_2O)I$ and $H^+ \cdots Rh(CO)_2I_2^-$ species, often co-existing at low $HI/Rh_4(CO)_{12}$ ratios, could behave as the rhodium counterparts of the $[Co(CO)_4Py]^+/PyH^+$ $Co(CO)_4^-$ pair involved in the hydroesterification of butadiene. Alternately, as previously suggested [32], the $H^+ \cdots Rh(CO)_2I_2^-$ tight ion pair could be in equilibrium with undetectable amounts of $HRh(CO)_2I_2$, which could initiate the catalytic cycle by isoprene coordination. Finally, d^8 rhodium species with a negative charge varying smoothly from 0 to −1, which may undergo oxidative addition of an alkyl iodide derived from isoprene, are always present. From the presently available information it appears reasonable only to interpret the enhanced carbonylating behaviour of the $Rh_4(CO)_{12}/HI$ system, with respect to $[PPN][Rh(CO)_2I_2]/HI$, as arising from the absence in the former system of a counter-cation, other than solvated H^+, and to the consequently more favorable conditions for the generation of more active $H^+ \cdots Rh(CO)_2I_2^-$ tight ion pairs and $Rh(CO)_2(H_2O)I$. The relevance of the probable presence of $H^+ \cdots Rh(CO)_2I_2^-$ tight ion pairs in the rhodium catalyzed hydrocarbonylation of ethyl orthoformate has recently been discussed [36].

Experimental

All the reactions were carried out under anaerobic conditions with freshly distilled and dried solvents. $Rh_4(CO)_{12}$ [37], $[Rh(CO)_2X]_2$ (X = Cl, I) [38,39], $[Rh(CO)_2X_2]^-$ salts [40], and dry HI [41] have been prepared by published methods.

Infrared spectra were recorded on a Perkin–Elmer 781 grating spectrophotometer using CaF_2 cells. Mass spectra were recorded on a VG 7070 EQ spectrometer and NMR spectra were run on a Brucker AC 200 instrument. GC analyses were performed on a Carlo Erba HRGC 4000 instrument (equipped with F.I.D. and a VG Micromass SX 200 quadrupole and using an OV17 25 m capillary column) or a Perkin–Elmer Sigma 115 instrument (Chromosorb 101 2m column).

In a typical catalytic experiment, 20 cm^3 of anhydrous THF, $Rh_4(CO)_{12}$, aqueous HI (57%), water, and isoprene were placed under nitrogen in a 50 cm^3 glass reactor equipped with a magnetic stirring bar. The reactor was placed in a 75 cm^3 stainless steel autoclave and pressurized with CO. The reaction was started by plunging the autoclave into a thermostatted oil bath and magnetically stirring the solution. The reactions were periodically tested by removing samples from the autoclave for GC or infrared analyses. As the gas uptake proceeded, additional amounts were introduced to maintain the pressure within about ±2 atm of the specified value.

The identities of the organic products were confirmed by mass spectrometry and ^1H NMR spectroscopy.

1. Synthesis of cis-Rh(CO)$_2$(H$_2$O)X (X = Cl, I)

A solution of $[Rh(CO)_2Cl]_2$ (0.483 g, 1.24 mmol) in anhydrous THF (25 ml) was treated with H_2O (0.11 g, 6.1 mmol) in three portions to give spectroscopically pure $Rh(CO)_2(H_2O)Cl$. Evaporation of the solution afforded orange needles of the starting material. The corresponding iodide $Rh(CO)_2(H_2O)I$ was similarly obtained from $[Rh(CO)_2I]_2$.

2. Reaction of [Rh(CO)$_2$Cl]$_2$ with aqueous (37%) HCl

A solution of $[Rh(CO)_2Cl]_2$ (0.114 g, 0.29 mmol) in anhydrous THF (5 ml) was progressively treated with 8 portions of 10 μl of aqueous HCl (37%), with monitoring by IR spectroscopy. After addition of 60 μl of HCl a ca. 1/1 mixture of $Rh(CO)_2(H_2O)Cl$ and $H^+ \cdots Rh(CO)_2Cl_2^-$ was present (Fig. 1c). The former was almost completely converted into the latter by addition of a further 20 μl of HCl (Fig. 1d).

3. Reaction of [Rh(CO)$_2$I]$_2$ with aqueous (57%) HI

A solution of $[Rh(CO)_2I]_2$ (0.172 g, 0.3 mmol) in anhydrous THF (5 ml) was progressively treated with 4 portions of 10 μl of aqueous (57%) HI. Monitoring of the solution by IR spectroscopy showed that only *cis*-$Rh(CO)_2(H_2O)I$ and $[Rh(CO)_2I_2]^-$ were formed. Addition of a large excess of aqueous HI resulted in formation of solvent-separated $[H_3O]^+$ and $[Rh(CO)_2I_2]^-$ ions.

4. Reaction of cis-Rh(CO)$_2$(H$_2$O)X (X = Cl, I) with anhydrous HX

A solution of $[Rh(CO)_2Cl]_2$ (0.167 g, 0.43 mmol) in anhydrous THF (5 ml) in a 50 ml flask and treated with 30 μl of water to give a solution mainly containing *cis*-$Rh(CO)_2(H_2O)Cl$. After evacuation of the nitrogen, dry HCl was admitted and the solution was stirred until IR monitoring showed the presence only of $H^+ \cdots Rh(CO)_2Cl_2^-$ ion pairs. Evaporation to dryness, followed by dissolution of the residue in THF and re-evaporation in vacuum gave an orange microcrystalline precipitate of the starting material.

The corresponding $H^+ \cdots Rh(CO)_2I_2^-$ ion pairs were similarly generated in solution from $[Rh(CO)_2I]_2$ (0.23 g, 0.4 mmol) and dry HI.

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