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Homogeneous Hydrogenations in Aqueous Solutions Catalyzed by Ruthenium–Phosphine Complexes

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By using m-*sulphophenyl-diphenylphosphine* ($mSP\phi_2$) *several ruthenium(II)–phosphine complexes were prepared and characterized. The complexes* $RuCl_2(mSP\phi_2)_2$, $HRuCl(mSP\phi_2)_3$, $HRu(OAc)(mSP\phi_2)_3$ *and* $HRuCl(CO)(mSP\phi_2)_3$ *are readily soluble in water, while the dicarbonyls,* cis- *and* trans-$RuCl_2(CO)_2(mSP\phi_2)_2$ *and* cis-$HRuCl(CO)_2(mSP\phi_2)_2$ *are water-insoluble.*

$RuCl_2(mSP\phi_2)_2$, $HRuCl(mSP\phi_2)_3$ *and* $HRu(OAc)(mSP\phi_2)_3$ *catalyze the hydrogenation of several C,O- and C,C-unsaturated compounds in aqueous solutions, at 20–70 °C and atmospheric hydrogen pressure.*

Detailed kinetic studies were made on the hydrogenation of crotonic and pyruvic acids. The results show an interesting selectivity, namely that the hydrogenation of pyruvic acid is catalyzed only by the trisphosphine species, $HRuX(mSP\phi_2)_3$ ($X^- = Cl^-$ *or* AcO^-), *while the hydrogenation of crotonic acid is catalyzed exclusively by the bisphosphine derivatives,* $HRuX(mSP\phi_2)_2$. $(HRuCl(mSP\phi_2)_2$ *may be prepared from* $RuCl_2(mSP\phi_2)_2$ *and* H_2, *while* $HRu(OAc)(mSP\phi_2)_2$ *arises from the dissociation of* $HRu(OAc)(mSP\phi_2)_3$. *This selectivity is a consequence of the different binding of the two types of substrates in the catalytically active intermediates.*

These complexes catalyze also the two-phase hydrogenation of hex-1-ene and styrene.

Introduction

In the past fifteen years several ruthenium–triphenylphosphine complexes have been prepared and investigated to explore their structure and catalytic properties [1]. The complexes $RuCl_2(PPh_2)_3$ [2], $HRuCl(PPh_3)_3$ [3], $HRu(OAc)(PPh_3)_3$ [4] and $HRuCl(CO)(PPh_3)_3$ [5] are primarily known as effective hydrogenation catalysts. As these compounds are insoluble in water, and the catalyzed reactions take place in non-aqueous media, up until the past few years no need had arisen for the investigation of reactions of phosphine complexes in aqueous systems.

Using *m*-sulphophenyl-diphenylphosphine ($mSP\phi_2$*, [6]) as ligand we have started a study of platinum metal–phosphine complexes catalyzed reactions. According to the initial observations [7–9], this phosphine stabilizes the lower oxidation states of several transition metal ions in aqueous solutions, and a ruthenium based catalyst – prepared *in situ* from $RuCl_3$ and $mSP\phi_2$ – is capable of hydrogenating pyruvic acid.

These compounds have gained more interest in the past three years, mainly because of their ability to act as catalysts in two-phase systems. Hydroformylation [11, 12], hydrocyanation [13], telomerization [14] and hydrogenation of olefines [12, 15, 16] are catalyzed by various transition metal–sulphonated triphenylphosphine complexes. Usually, the catalyst was applied as an aqueous solution, and could be recycled at the end of the reaction after simple phase separation. Some of the catalysts were prepared in crystalline form, examples are: $HRuCl(mSP\phi_2)_3$ [12, 17], and $RhCl(mSP\phi_2)_3$ [12, 18]. This latter Rh(I)-compound was found very suitable for the hydrogenation of phospholipids of cell membranes [19].

As a continuation of our early studies on the properties of water-soluble transition metal–phosphine complexes, we have prepared several ruthenium(II)–$mSP\phi_2$ compounds and investigated their catalytic properties in hydrogenation reactions. A short paper has already been published on these investigations [17] and now we report here the detailed results.

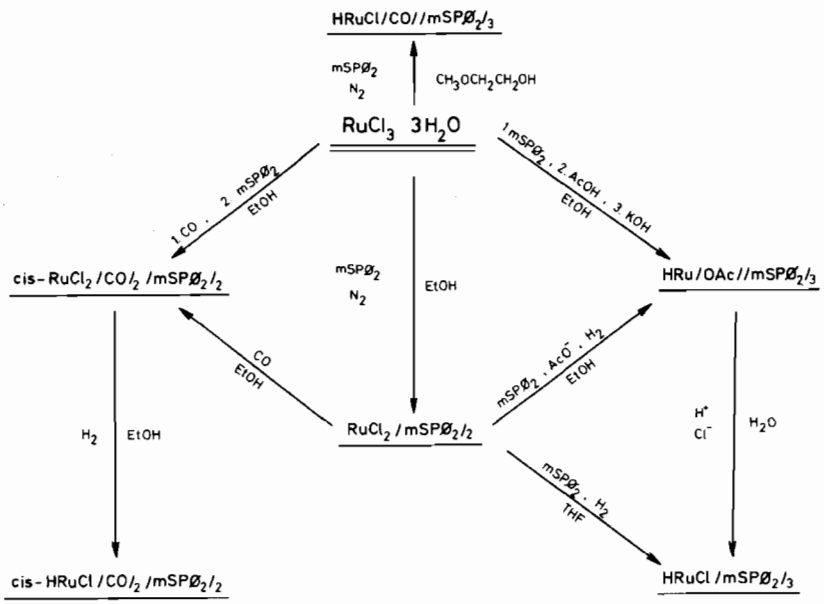
Results and Discussion

Preparation and Characterization of the Complexes

Complexes of *m*-sulphophenyl-diphenylphosphine can be prepared in two different ways:

1) from the corresponding PPh_3 complexes with ligand-exchange [12];

*Since several sulphonated triphenylphosphine derivates are known we suggest this abbreviation to replace the former dpm or TPM for *m*-sulphophenyl-diphenylphosphine Na-salt. For details of the abbreviation system see ref. [10].



Scheme I. Reactions of $RuCl_3$ with *m*-sulphophenyl-diphenylphosphine ($mSP\phi_2$) in various conditions.

2) according to the syntheses of the corresponding PPh_3 complexes, using $mSP\phi_2$ instead of PPh_3 [8, 9]. With this latter strategy we have prepared six Ru(II)–$mSP\phi_2$ complexes (Scheme 1).

From boiling ethanolic solution of $RuCl_3$, on the action of a fivefold excess of $mSP\phi_2$, a light brown bisphosphine compound, $RuCl_2(mSP\phi_2)_2$, precipitates. Under similar conditions, a trisphosphine complex: $RuCl_2(PPh_3)_3$ can be obtained from $RuCl_3$ and PPh_3 [2]. The structure of $RuCl_2(mSP\phi_2)_2$ in solid form is not known. It cannot be excluded that the compound is a chloride-bridged dimer [20] but its chemical behaviour (aqueous solutions of the complex are not particularly sensitive to oxygen; there is no reaction with further $mSP\phi_2$) and the UV–VIS spectra do not seem to support such a view. The sulphonated phosphine itself also may act as a bridging ligand, as it was found in the case of a Rh-complex [12]. It is highly probable that in neutral aqueous solution the complex should be formulated as $(H_2O)_2RuCl_2(mSP\phi_2)_2$ and water may be coordinated to the metal ion also in the solid state (the complex contains *ca.* 4 moles of H_2O per metal). This problem needs further investigation.

The difference in the wavenumbers of symmetric and asymmetric OCO vibrations in the IR spectrum of $HRu(OAc)(mSP\phi_2)_3$ ($\Delta\nu$ = 93 cm^{-1}) suggests a bidentate acetate ligand, similarly to $HRu(OAc)(PPh_3)_3$ [4].

In the course of the reaction between $RuCl_2(mSP\phi_2)_2$ and carbon monoxide, first a greenish-yellow solid precipitates, which can be characterized as *trans*-$RuCl_2(CO)_2(mSP\phi_2)_2$ (ν_{CO} = 2005 cm^{-1}). On prolonged heating this complex transforms to *cis*-$RuCl_2(CO)_2(mSP\phi_2)_2$ (ν_{CO} = 2000 and 2060 cm^{-1}).

The complexes are practically insoluble in benzene, n-hexane and diethylether, poorly soluble in acetone, alcohols and THF, and readily soluble in 2-methoxyethanol and – with the exception of the dicarbonyls – in water. They can be salted out from aqueous solutions with NaCl.

Except $HRuCl(mSP\phi_2)_3$ and $HRu(OAc)(mSP\phi_2)_3$, the complexes are stable to air in the solid state. $HRu(OAc)(mSP\phi_2)_3$ can be stored approximately for one week without significant decomposition; $HRuCl(mSP\phi_2)_3$ only for hours. Except the carbonyls, they are very sensitive to oxygen in solution.

Although the water content of the compounds cannot be unambiguously determined from the data of elementary analysis it seems very probable that they contain two moles of H_2O per phosphine ligand. This is also supported by the observation of Salvesen and Bjerrum [21] who found that the two moles of water of crystallinity is so strongly bound in $mSP\phi_2$ that it cannot be eliminated with heating at 400 °C.

Reactions of the Complexes

Hydrolysis

Neutral aqueous solutions of $HRuCl(mSP\phi_2)_3$ do not show the characteristic colour and spectrum of the compound, which is very similar to the colour and spectrum of $HRuCl(PPh_3)_3$ [22]. Addition of NaCl or $HClO_4$ does not cause any change of the UV–VIS spectrum, however, on the joint action of H^+ and Cl^- (*i.e.* in aqueous hydrochloric acid solutions) an intense violet colour indicates the reappearance of

$HRuCl(MSP\phi_2)_3$ (Fig. 1). These observations suggest that – contrary to the findings of Wilkinson *et al.* [12] – this complex is present in neutral solutions as a hydrolyzed, hydroxo-compound. The substitution of OH^- by Cl^- is kinetically not favoured, and requires proton catalysis. (Similar phenomena were also observed in the transformation of $HRu(OAc)(mSP\phi_2)_3$ to $HRuCl(mSP\phi_2)_3$).

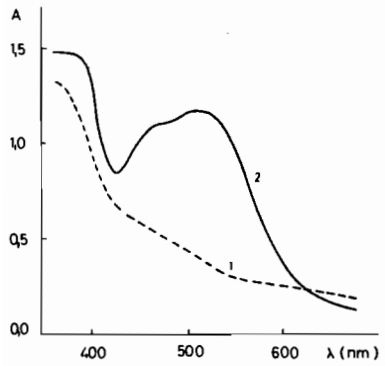


Fig. 1. Change of absorption spectra of $HRuCl(mSP\phi_2)_3$ in water (1), and in 0.1 *M* HCl (2). [Ru] = 10^{-3} *M*, d = 1 cm, T = 40 °C.

Reaction with dioxygen

In aqueous solution $HRuCl(mSP\phi_2)_3$ and $HRu(OAc)(mSP\phi_2)_3$ readily react with O_2, however, the oxidation of $RuCl_2(mSP\phi_2)_2$ is very slow. The colour of the solutions of the oxidized complexes is green (in the case of the first two compounds) and violet (in the case of the acetato-complex). The oxidation of the trisphosphine complexes requires 1.5 mole O_2 per mole Ru, which suggests the oxidation of $mSP\phi_2$ to the phosphineoxide.

Reaction with carbon monoxide

At room temperature and atmospheric pressure $RuCl_2(mSP\phi_2)_2$ takes up 2 moles of CO per complex molecule. Even in the case of dilute aqueous solutions, the product *cis*-$RuCl_2(CO)_2(mSP\phi_2)_2$ precipitates as white microcrystals.

Reaction with dihydrogen

In aqueous solution, $RuCl_2(mSP\phi_2)_2$ takes up 1 mole H_2 per mole complex. The amount of the absorbed hydrogen depends only on the amount of complex present, and is independent of the amount of excess phosphine. The colour of hydrochloric acid solutions of the reduced complex changes from orange to violet, depending on the concentration of the excess phosphine, its UV–VIS spectra becoming more and more similar to that of $HRuCl(mSP\phi_2)_3$ (Fig. 1, curve 2). According to these observations the following reaction takes place under these circumstances:

$$RuCl_2(mSP\phi_2)_2 + H_2 + mSP\phi_2 \rightarrow HRuCl(mSP\phi_2)_3 + HCl \quad (1)$$

As this reaction gives a possibility for the *in situ* preparation of the unstable $HRuCl(mSP\phi_2)_3$ for catalytic hydrogenation purposes, we have examined its kinetics in some detail.

The initial rate of the hydrogen uptake is proportional to the initial concentration of $RuCl_2(mSP\phi_2)_2$ and to the partial pressure of H_2, but it is not influenced by the concentration of the free phosphine (Fig. 2). Based on these observations the mechanism of the reaction and the corresponding rate law can be given as follows:

$$RuCl_2(mSP\phi_2)_2 + H_2 \xrightarrow{k_I} HRuCl(mSP\phi_2)_2 + H^+ + Cl^- \quad (2)$$

$$HRuCl(mSP\phi_2)_2 + mSP\phi_2 \overset{K_{II}}{\rightleftharpoons} HRuCl(mSP\phi_2)_3 \quad (3)$$

$$-\frac{d[H_2]}{dt} = k_I[Ru]_0[H_2] \quad (4)$$

where $[Ru]_0$ = initial concentration of $RuCl_2(mSP\phi_2)_2$; $[H_2]$ = concentration of dihydrogen in the solution (at 60 °C and 1 atm total pressure: 5.9×10^{-4} *M* [23]); $k_I = 43\ M^{-1}\ s^{-1}$ (60 °C).

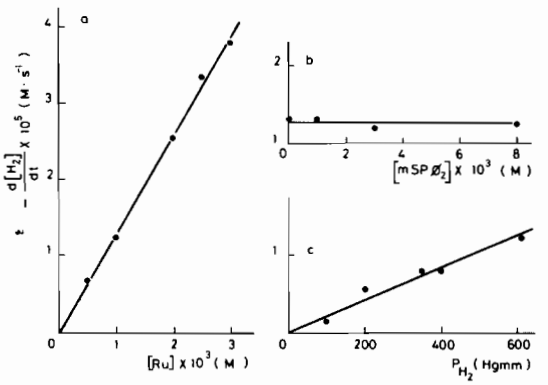


Fig. 2. Effect of the concentration of complex (a), of free phosphine (b), and of the partial pressure of dihydrogen (c) on the initial rate of reaction between $RuCl_2(mSP\phi_2)_2$ and H_2. (a) $[mSP\phi_2] = 10^{-2}$ *M*, P_{H_2} = 610 mmHg; (b) [Ru] = 10^{-3} *M*, P_{H_2} = 610 mmHg; (c) [Ru] = 10^{-3} *M*, $[mSP\phi_2] = 8 \times 10^{-3}$ *M*; 10 cm^3 0.1 *M* HCl, T = 60 °C.

We have investigated equilibrium (3) separately, by means of spectrophotometric measurements. As these reactions were carried out in 0.1 *M* HCl solutions, the protonation of the phosphine had to be accounted for in the calculations. Wright and Bjerrum [24] found that the protonation of $mSP\phi_2$ in perchloric acid solutions can be described by the fol-

lowing equation

$$-\lg K_{PH^+} = 0\ 13 + 0.50[HClO_4] \quad (5)$$

In the case of the acid concentrations studied, there is no significant difference between the Hammett-acidities [25] of HCl and $HClO_4$, therefore we have used the same equation in the calculations

Molar ratio measurements indicated the formation of a 1 1 complex by $HRuCl(mSP\phi_2)_2$ and $mSP\phi_2$ The equilibrium constant of reaction (3) was determined graphically using the equation of Olerup [26]

$$\frac{\Delta A_{510}}{[mSP\phi_2]_0} = [Ru]_0 \Delta\epsilon K_{II} - K_{II}\Delta A_{510} \quad (6)$$

where ΔA_{510} = difference in the absorption of the equilibrated solution and the sum of the absorption of the initial ones at 510 nm, $\Delta\epsilon$ = difference in the molar absorbances of the product $HRuCl(mSP\phi_2)_3$ and the reactants At 40 °C the stability constant proved to be $K_{II} = 860\,M^{-1}$

Catalytic Hydrogenations

At 20–70 °C and atmospheric pressure $RuCl_2(mSP\phi_2)_2$, $HRuCl(mSP\phi_2)_3$ and $HRu(OAc)(mSP\phi_2)_3$ catalyze the hydrogenation of different C,C-unsaturated acids (crotonic, maleic, fumaric, cinnamic, itaconic acids and butadiene-1-carboxylic acid), dihydroxyacetone and fructose in aqueous solutions or in aqueous HCl Moreover, $HRuCl(mSP\phi_2)_3$ and $HRu(OAc)(mSP\phi_2)_3$ are also able to catalyze the hydrogenation of 2-oxo-carboxylic acids (pyruvic, phenyl-pyruvic, 2-oxo-petanoic, 2-oxo-glutaric and 2-oxo-caprylic acids), [17] (Under similar conditions 3-oxo-acids decarboxylate, and the hydrogenation of 4-oxo-acids is hindered by lacton-formation)

In order to establish the mechanism of the catalytic hydrogenations, we have investigated in detail the kinetics of hydrogenation of crotonic acid (*trans*-CH_3–CH=CH–COOH) and pyruvic acid (CH_3–CO–COOH)

Kinetics of the hydrogenation of crotonic acid

The rate of crotonic acid hydrogenation, catalyzed by $RuCl_2(mSP\phi_2)_2$, is a linear function of catalyst concentration, and partial pressure of dihydrogen, varies according to a saturation curve with varying substrate concentration, and decreases exponentially on increasing concentration of excess phosphine (Fig 3)

These experimental findings can be explained by the following simple mechanism As in reaction (2), $RuCl_2(mSP\phi_2)_2$ gives a catalytically active hydride, $HRuCl(mSP\phi_2)_2$ This hydride reacts with crotonic acid (CA) forming an alkyl-derivative

$$HRuCl(mSP\phi_2)_2 + CA \underset{}{\overset{K_V}{\rightleftharpoons}} (HCA)RuCl(mSP\phi_2)_2 \quad (7)$$

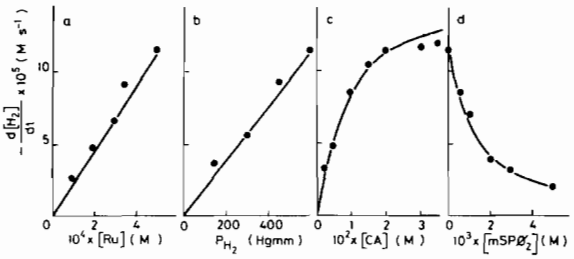


Fig 3 Effect of the concentration of $RuCl_2(mSP\phi_2)_2$ (a), of H_2 (b), of crotonic acid (c), and of free $mSP\phi_2$ (d) on the initial rate of crotonic acid hydrogenation (a) $[CA]_0 = 2 \times 10^{-2}\,M$, P_{H_2} = 610 mmHg, (b) $[Ru]_0 = 5 \times 10^{-4}\,M$, $[CA]_0 = 2 \times 10^{-2}\,M$, (c) $[Ru]_0 = 5 \times 10^{-4}\,M$, P_{H_2} = 610 mmHg, (d) $[Ru]_0 = 5 \times 10^{-4}\,M$, P_{H_2} = 610 mmHg, $[CA]_0 = 2 \times 10^{-2}\,M$, T = 60 °C, 10 cm^3 water

The rate determining step is the reaction of the alkyl intermediate with dihydrogen, in which butyric acid (BA) is formed and the catalyst becomes regenerated

$$(HCA)RuCl(mSP\phi_2)_2 + H_2 \xrightarrow{k_V} HRuCl(mSP\phi_2)_2 + BA \quad (8)$$

In the presence of excess phosphine a competitive equilibrium should be taken into consideration

$$HRuCl(mSP\phi_2)_2 + mSP\phi_2 \underset{}{\overset{K_{II}}{\rightleftharpoons}} HRuCl(mSP\phi_2)_3 \quad (9)$$

The fact that chloride does not affect the rate of hydrogenation indicates that, either there is no formation of crotonato- or butyrato-complexes in this system, or their catalytic activity does not differ significantly from the activity of chloro-compounds

A rate law, corresponding to this mechanism, can be derived, taking into account that the rate of hydrogen consumption is as follows

$$-\frac{d[H_2]}{dt} = k_V[(HCA)RuCl(mSP\phi_2)_2][H_2] \quad (10)$$

Considering equilibria (7) and (9)

$$K_V = \frac{[(HCA)RuCl(mSP\phi_2)_2]}{[HRuCl(mSP\phi_2)_2][CA]} \quad (11)$$

and

$$K_{II} = \frac{[HRuCl(mSP\phi_2)_3]}{[HRuCl(mSP\phi_2)_2][mSP\phi_2]} \quad (12)$$

and the mass-balance for ruthenium

$$[Ru]_0 = [HRuCl(mSP\phi_2)_2] + [HRuCl(mSP\phi_2)_3] + [(HCA)RuCl(mSP\phi_2)_2] \quad (13)$$

the concentration of $(HCA)RuCl(mSP\phi_2)_2$ can be given by eqn (14) ($[mSP\phi_2]_f$ denotes the concen-

tration of the uncomplexed phosphine)

$$[(HCA)RuCl(mSP\phi_2)_2] = \frac{K_V[Ru]_0[CA]_0}{1 + K_V[CA]_0 + K_{II}[mSP\phi_2]_f} \quad (14)$$

(Under our experimental conditions $[CA]_0 \gg [Ru]_0$, therefore $[CA]_f \approx [CA]_0$, at the start of the reaction.) Now, eqn. (10) can be rewritten as follows:

$$-\frac{d[H_2]}{dt} = \frac{k_V K_V[Ru]_0[H_2][CA]_0}{1 + K_V[CA]_0 + K_{II}[mSP\phi_2]_f} \quad (15)$$

In order to determine the values of constants in eqn. (15), one should know $[mSP\phi_2]_f$. Though K_{II} proved to 860 M^{-1} under slightly different conditions (40 °C, solvent: 0.1 *M* HCl), it seems reasonable to assume that at $[Ru]_0 \geq 5 \times 10^{-4}$ *M* and $[CA]_0 = 2 \times 10^{-2}$ *M* the following approximation holds:

$$[mSP\phi_2]_f \approx [mSP\phi_2]_t - 2[Ru]_0 \quad (16)$$

When the free $mSP\phi_2$ in the solution originates exclusively from dissociation of $HRuCl(mSP\phi_2)_3$, then the great excess of crotonic acid completely reverses equilibrium (9) through equilibrium (7), therefore eqn. (16) is a good approximation for $[mSP\phi_2]_f$. On increasing $[mSP\phi_2]$ eqn. (16) becomes more and more valid since the concentration of complexed $mSP\phi_2$ varies only between $2[Ru]_0$ and $3[Ru]_0$.

Using eqn. (16), the rate equation can be expressed in known parameters:

$$-\frac{d[H_2]}{dt} = \frac{k_V K_V[Ru]_0[H_2][CA]_0}{1 + K_V[CA]_0 + K_{II}([mSP\phi_2]_t - 2[Ru]_0)} \quad (17)$$

The rate and equilibrium constants were determined by linearization of this equation; data are shown in Table I. (Curves, calculated with the use of these constants, are drawn in bold in Fig. 3.)

TABLE I. Rate and Equilibrium Constants of Scheme 2.

	$X^- = Cl^-$	$X^- = AcO^-$
k_I	43	–
K_{II}	2.6×10^3 8.6×10^{2} [b]	9.1×10^3
k_{IV}	85	44
K_{IV}	2×10^3	2×10^3 3.0×10^{3} [a]
k_V	553	1330
K_V	1.0×10^2	2.0×10^2
K_{III}	8.5×10^{2} [b]	

Conditions: T = 60 °C, P_{tot} = 1 atm, solvent = water; [a]obtained spectrophotometrically; [b]obtained spectrophotometrically, T = 40 °C, solvent: 0.1 *M* HCl. Unit of equilibrium constants: M^{-1}. Unit of rate constants: M^{-1} s^{-1}.

Contrary to the case of $RuCl_2(mSP\phi_2)_2$, in the case of $HRu(OAc)(mSP\phi_2)_3$ the rate of hydrogen consumption is a saturation-type function of the catalyst concentration. According to the previously described mechanism, this deviation from the first order in catalyst concentration is due to the effect of free phosphine arising from dissociation of the initial catalyst molecule. The rate and equilibrium constants, calculated with use of eqn. (17), are summarized also in Table I. In case of higher crotonic acid concentrations the kinetic curves defined by eqn. (17) deviate significantly from the experimental ones (see for example Fig. 3(c)). This can be accounted for as an effect of pH. In separate experiments it was shown that increasing acidity decreases the rate of hydrogenation (*i.e.* a rate of 2.7×10^{-5} *M* s^{-1} was found instead of 11.0×10^{-5} *M* s^{-1} when 0.1 *M* aqueous methane-sulphonic acid was used as solvent instead of water). Changes in the pH may influence the rate (*i*) by changing the concentration of the catalytically active hydride-complexes (see later in connection with pyruvic acid hydrogenations), and (*ii*) through the protonation of the substrate, which may affect the latter's reactivity.

The rate law and mechanism of hydrogenation of crotonic acid in aqueous solutions are identical with those of olefin hydrogenations catalyzed by $HRuCl(PPh_3)_3$ [1]. This indicates a similar behaviour of $mSP\phi_2$ and PPh_3 complexes of ruthenium in the activation of molecular hydrogen.

Kinetics of pyruvic acid hydrogenation.

On the addition of pyruvic acid (PA), the colour of $HRuCl(mSP\phi_2)_3$ and $HRu(OAc)(mSP\phi_2)_3$ solutions suddenly changes, and simultaneously hydrogen consumption begins. The rate of hydrogenation is constant throughout reaction. After complete reduction of PA, hydrogen consumption ceases and the solution regains its initial colour (violet or yellow, respectively).

In both cases, the rate of hydrogenation is proportional to the concentration of the catalyst (Fig. 4(a)), to the partial pressure of dihydrogen (Fig. 4 (b)), independent of the excess of phosphine (Fig. 4(c)), and also independent – in the concentration range of our investigations – of initial concentration of pyruvic acid (Fig. 4(d)).

According to these findings the empirical rate law is:

$$-\frac{d[H_2]}{dt} = a[Ru]_0[H_2] \quad (18)$$

where $[Ru]_0$ denotes the concentration of the catalyst Ru-complex ($HRuCl(mSP\phi_2)_3$ or $HRu(OAc)(mSP\phi_2)_3$), and $[H_2]$ stands for dihydrogen concentration in the solution.

The mechanism of the reaction seems to be similar to that of crotonic acid hydrogenation, except that

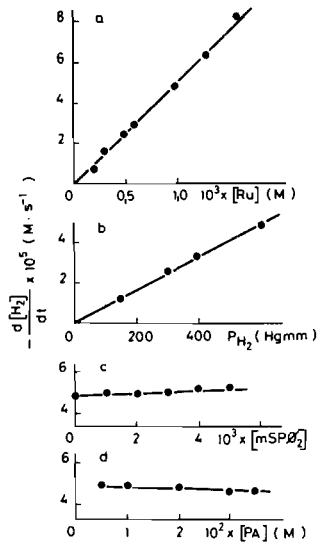
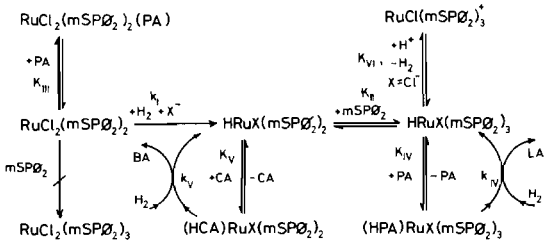


Fig. 4. Effect of the concentration of $HRuCl(mSP\phi_2)_3$ (a), of H_2 (b), of free $mSP\phi_2$ (c), and of pyruvic acid (d) on the rate of pyruvic acid hydrogenation. (a) $[PA]_0 = 2 \times 10^{-2}$ *M*, P_{H_2} = 610 mmHg; (b) $[PA]_0 = 2 \times 10^{-2}$ *M*, $[Ru]_0 = 10^{-3}$ *M*; (c) $[PA]_0 = 2 \times 10^{-2}$ *M*, P_{H_2} = 610 mmHg, $[Ru]_0 = 10^{-3}$ *M*; (d) $[Ru]_0 = 10^{-3}$ *M*, P_{H_2} = 610 mmHg; T = 60 °C, 10 cm^3 water.



Scheme II. Mechanism of hydrogenation of pyruvic acid (PA), and crotonic acid (CA) catalyzed by ruthenium(II)–*m*-sulphophenyl-diphenylphosphine complexes. (The values of equilibrium and rate constants are shown in Table 1.)

the catalytically active intermediates contain three phosphine ligands per catalyst molecule. The following main steps can be suggested: the ruthenium hydrides of eqn. (9) react with pyruvic acid which is followed by reaction with dihydrogen, in which lactic acid (LA) is produced and the catalyst is regenerated (Scheme II).

By analogy to the case of crotonic acid hydrogenation the following rate law can be derived:

$$-\frac{d[H_2]}{dt} = \frac{k_{IV}K_{IV}[Ru]_0[PA]_0[H_2]}{1 + K_{IV}[PA]_0 + \dfrac{1}{K_{II}[mSP\phi_2]_f}} \qquad (19)$$

where $[Ru]_0$ and $[PA]_0$ denote initial concentrations of the catalyst complex and pyruvic acid respectively, and $[mSP\phi_2]_f$ stands for the concentration of free phosphine.

Eqn. (19) and the empirical rate law, eqn. (18), are identical only when $K_{IV}[PA]_0 \gg (1 + 1/K_{II}[mSP\phi_2]_f)$. In this case eqn. (19) reduces to:

$$-\frac{d[H_2]}{dt} = k_{IV}[Ru]_0[H_2] \qquad (20)$$

According to our experimental data the values of k_{IV} are: 85 M^{-1} s^{-1} (in the case of $HRuCl(mSP\phi_2)_3$) and 44 M^{-1} s^{-1} (in the case of $HRu(OAc)(mSP\phi_2)_3$). Since in the concentration range studied the rate of hydrogenation is described by eqn. (20), it is not possible to derive the stability constants of eqn. (19) from kinetic parameters. Approximate values, however, can be estimated as follows.

The rate of hydrogenation is independent of the concentration of pyruvic acid (Fig. 4(c)), therefore it is $K_{IV}[PA]_0$ which controls the denominator of eqn. (19) even in case of $[PA]_0 = 5 \times 10^{-3}$ *M*. Taking $K_{IV}[PA]_0 \geqslant 10$ leads to $K_{IV} \geqslant 2 \times 10^3$ M^{-1}.

To obtain K_{IV} from independent experiments, the following equilibrium was studied spectrophotometrically:

$$HRu(OAc)(mSP\phi_2)_3 + PA \overset{K_{IV}}{\rightleftharpoons} (HPA)Ru(OAc)(mSP\phi_2)_3 \qquad (21)$$

The formation of a 1:1 complex was confirmed by the molar ratio method. By linearization, K_{IV} proved to be 3.0×10^3 M^{-1}, in fair agreement with the value estimated from kinetic data.

Taking into account that the rate of hydrogenation is independent of phosphine concentration, $1/K_{II}[mSP\phi_2]_f$ should be $\leqslant 1$, when $[mSP\phi_2]_f \geqslant 10^{-3}$ *M*, therefore $K_{II} \geqslant 10^3$ M^{-1} holds. This limiting value agrees fairly well with K_{II}, derived from kinetic parameters of crotonic acid hydrogenation.

On the effect of HCl, the rate of pyruvic acid hydrogenation (cat.: $HRuCl(mSP\phi_2)_3$) decreases exponentially (Fig. 5). Separate experiments have shown that Cl^- has no influence, consequently the changes in the rate of hydrogenation are caused by increasing $[H^+]$. These phenomena could be accounted for by considering an H_2-elimination leading to a catalytically inactive complex:

$$HRuCl(mSP\phi_2)_3 + H^+ \overset{K_{VI}}{\rightleftharpoons} RuCl(mSP\phi_2)_3^+ + H_2 \qquad (22)$$

By virtue of eqn. (22), eqn. (19) transforms to:

$$-\frac{d[H_2]}{dt} = \frac{k_{IV}K_{IV}[Ru]_0[PA]_0[H_2]}{1 + K_{IV}[PA]_0 + \dfrac{1}{K_{II}[mSP\phi_2]_f} + \dfrac{[H^+]}{K_{VI}}} \qquad (23)$$

Taking $K_{IV}K_{VI} = 6.65$ M^{-1} (*i.e.* $K_{VI} \leqslant 3.3 \times 10^{-3}$), the calculated rates (Fig. 5, full line) fit well the

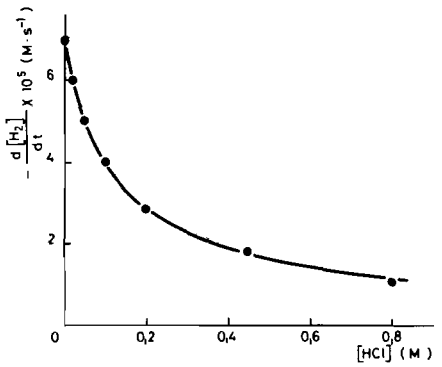


Fig. 5. Effect of the proton concentration on the rate of pyruvic acid hydrogenation, catalyzed by $HRuCl(mSP\phi_2)_3$. $[Ru]_0 = 1.4 \times 10^{-3}$ *M*, $[PA]_0 = 2 \times 10^{-2}$ *M*, $P_{H_2} = 610$ mmHg, 10 cm^3 solution, T = 60 °C.

experimental values. However, when the hydride elimination equilibrium was directly studied by measuring the quantity of dihydrogen liberated by strong acids a much smaller value of K_{VI} (*ca.* 10^{-5} M^{-1}) could be estimated. Therefore equilibrium (22) is not primarily responsible for the decrease in the rate of hydrogenation and the protonation of pyruvic acid should also be taken into consideration.

Kinetic investigation with catalysts prepared in situ *from $RuCl_3$ and $mSP\phi_2$, in the presence of pyruvic acid*

It is known from our earlier studies [8, 9], that in hydrochloric acid solutions of $RuCl_3$ containing $mSP\phi_2$ in excess and saturated with dihydrogen, $HRuCl(mSP\phi_2)_3$ is formed. If this catalyst is prepared in presence of pyruvic acid, a characteristic induction period appears on the hydrogenation curve.** Moreover, the intense violet colour of $HRuCl(mSP\phi_2)_3$ is seen only after complete reduction of the substrate. The duration of the induction period decreases on increasing ruthenium (Fig. 6(a)) and phosphine concentration (Fig. 6(b)), but increases on increasing the pyruvic acid concentration (Fig. 6(c)).

These phenomena indicate that the intermediates of the catalyst-forming reaction (bisphosphine species) give relatively stable complexes with pyruvic acid, which are catalytically inactive. As the hydrogenation proceeds, the concentration of these bisphosphine complexes continuously decreases while the rate of hydrogenation increases to the value determined by the concentration of free $mSP\phi_2$, and then it remains constant throughout the rest of the reaction.

**Kinetic curves of this kind, shown in some of our previous papers [7–9], arrived at saturation well before 100% conversion. This inactivation of the catalyst was caused by traces of oxygen and not by "self-hydrogenation" of the ligand, as was supposed.

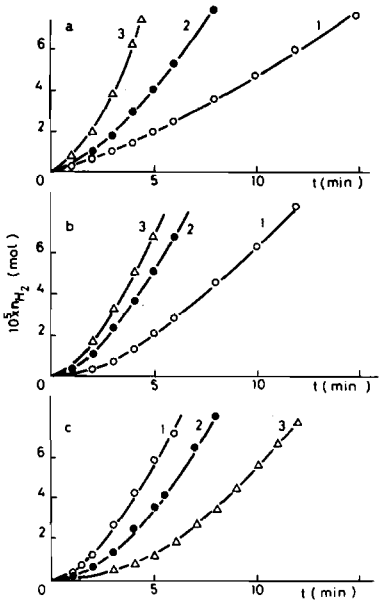


Fig. 6. Effect of the concentration of ruthenium(III) (a), of $mSP\phi_2$ (b), and of pyruvic acid (c) on the induction period of the hydrogen absorption curves measured in the $RuCl_3$–PA–$mSP\phi_2$–H_2 system. (a) $[mSP\phi_2]_0 = 10^{-2}$ *M*, $[PA]_0 = 2 \times 10^{-2}$ *M*, $[Ru]_0 = 10^{-4}$ *M* (1), 5×10^{-4} *M* (2), 2×10^{-3} *M* (3). (b) $[Ru]_0 = 10^{-3}$ *M*, $[PA]_0 = 2 \times 10^{-2}$ *M*, $[mSP\phi_2]_0 = 2.5 \times 10^{-3}$ *M* (1), 5×10^{-3} *M* (2), 10^{-2} *M*. (c) $[Ru]_0 = 10^{-3}$ *M*, $[mSP\phi_2]_0 = 5 \times 10^{-3}$ *M*, $[PA]_0 = 10^{-2}$ *M* (1), 3×10^{-2} *M* (2), 5×10^{-2} *M* (3). $P_{H_2} = 610$ mmHg, 10 cm^3 0.1 *M* HCl, T = 60 °C.

There are three basic observations supporting the idea of formation of catalytically inactive pyruvato-complexes: (*i*) pyruvic acid causes a change of colour of $HRuCl(mSP\phi_2)_2$ solutions, however no hydrogen consumption takes place; (*ii*) pyruvic acid inhibits the hydrogenation of crotonic acid, catalyzed by $HRuCl(mSP\phi_2)_2$ [17]; (*iii*) pyruvic acid and $RuCl_2(mSP\phi_2)_2$ form a stable 1:1 complex.

This latter reaction was studied spectrophotometrically, and the stability constant of the product was found to be 850 M^{-1} (at 40 °C).

Comparison of the hydrogenation of unsaturated and oxo-acids

There is much similarity in the reaction mechanisms of hydrogenation of crotonic and pyruvic acids, catalyzed by water-soluble phosphine complexes. However, there is also an obvious difference: only the complexes containing three phosphine ligands per molecule are able to catalyze the hydrogenation of pyruvic acid; the bisphosphine species form catalytically inactive complexes with this substrate. It seems plausible that in the case of the $HRuX(mSP\phi_2)_3$ ($X = Cl^-$ or AcO^-) catalysts, pyruvic acid coordinates as a monodentate ligand (presumably by its carbonyl oxygen atom to favour the reduction). On the other

hand, there are two free coordination sites in the bisphosphine compounds, allowing a bidentate coordination [27] of PA, through its carbonyl and carboxyl oxygens, and leading to the formation of stable, unreactive products.

Two-phase hydrogenations

$RuCl_2(mSP\phi_2)_2$, $HRuCl(mSP\phi_2)_3$ and $HRu(OAc)(mSP\phi_2)_3$ catalyze the two-phase hydrogenation of olefins. As can be seen from data of Table II, in every case the reactions are very slow. (Under similar conditions $RhCl(mSP\phi_2)_3$ proved to be more active for the hydrogenation of hex-1-ene and styrene by *ca.* an order of magnitude [10, 16].)

TABLE II. Initial Rates of Two-phase Hydrogenations.

Catalyst[a]	Substrate	T (°C)	Initial rate ($M\ s^{-1}$)
$RuCl_2(mSP\phi_2)_2$	hex-1-ene[b]	30	5×10^{-6}
		50	20×10^{-6}
	styrene[c]	60	3×10^{-6}
$HRuCl(mSP\phi_2)_3$	styrene[c]	60	3×10^{-6}
$HRu(OAc)(mSP\phi_2)_3$	styrene[c]	60	7×10^{-6}

[a] 10^{-5} mole catalyst in 10 cm^3 water. [b] 1 cm^3 hex-1-ene. [c] 5 cm^3 styrene. P_{tot} = 1 atm.

Experimental

m-Sulphophenyl-diphenylphosphine ($mSP\phi_2 \cdot 2H_2O$) was prepared by sulphonation of PPh_3 [6]. The crude product was several times recrystallized from ethanol and water. *Analysis* (calculated values in parentheses): C, 55.6% (54.0%); H, 4.2% (4.5%); P, 7.8% (7.7%); S, 8.4% (8.0%).

Ruthenium complexes were synthesized starting from Fluka purum or Pierce $RuCl_3 \cdot 3H_2O$. All the manipulations were carried out in an oxygen-free atmosphere using standard vacuum-line techniques. Degassed, oxygen-free solvents were applied throughout.

Spectrophotometric measurements were done on a Perkin Elmer 402 or a Beckman Acta II registrating UV–VIS spectrophotometer, using cells closed by silicon rubber septa.

For the measurements of gas absorption conventional gas-burettes of constant pressure were used filled with Na_2SO_4/H_2SO_4 solution. Solubility of dihydrogen in water at 60 °C and 1 atm total pressure was taken as 5.9×10^{-4} *M* [23].

Phosphorus content of the complexes was determined spectrophotometrically, after digestion in $H_2SO_4/HClO_4$ mixture in the form of molybdenum- and vanadium-containing mixed complexes. The volatile RuO_4 does not disturb the determination. The pronounced disturbing effect of sulphonated phosphine on the AAS determination of ruthenium was eliminated by the addition of cyanide [28].

Crotonic acid (Fluka purum) and sodium pyruvate (Reanal p.a.) were used as received.

Preparation of the Complexes

$RuCl_2(mSP\phi_2)_2 \cdot 4H_2O$

4 g (10 mmol) $mSP\phi_2 \cdot 2H_2O$ was dissolved in 50 cm^3 of hot 96% ethanol. To this solution 0.50 g (*ca.* 20 mmol) $RuCl_3 \cdot 3H_2O$ in 20 cm^3 hot ethanol was added. After 90 min the mixture was cooled to r.t., the brown precipitate was filtered, washed with small amounts of acetone and diethyl ether, dried at 50 °C. Yield: approx. 80% (based on Ru). *Analysis*: C, 43.7% (44.4%); H, 3.8% (3.7%); P, 6.2% (6.3%); Cl, 7.3% (7.3%); Ru, 10.6% (10.4%).

cis-$RuCl_2(CO)_2(mSP\phi_2)_2 \cdot 4H_2O$.

(*a*) An ethanolic solution (10 cm^3) of 0.10 g (*ca.* 0.4 mmol) $RuCl_3 \cdot 3H_2O$ was refluxed under CO for 5 hours. To the red solution 0.64 g (1.6 mmol) $mSP\phi_2 \cdot 2H_2O$ in 10 cm^3 ethanol was added. After 15 min of reflux the solution was cooled, the yellowish white precipitate was filtered, washed with diethyl ether. Yield: approx. 60%.

(*b*) 0.2 g (0.2 mmol) $RuCl_2(mSP\phi_2)_2 \cdot 4H_2O$ in 10 cm^3 ethanol was refluxed under CO. After 5 min the originally brown solid became first greenish yellow, then gradually turned to yellowish white. After 3 hours the cooled solution was filtered, the solid was washed with diethyl ether. Yield: 70%. *Analysis*: C, 43.4% (44.3%); H, 3.5% (3.5%); P, 5.9% (6.0%); IR: ν_{CO} = 2000 and 2060 cm^{-1} (KBr).

$HRuCl(mSP\phi_2)_3 \cdot 6H_2O$

0.50 g (0.5 mmol) $RuCl_2(mSP\phi_2)_2 \cdot 4H_2O$ and 0.40 g (1 mmol) $mSP\phi_2 \cdot 2H_2O$ were suspended in 10 cm^3 THF, containing 5 v/v % water. This mixture was boiled under H_2 for 8 hours. The cooled solution was filtered, the red precipitate was washed with small amounts of THF and diethyl ether. Yield: 90%. *Analysis*: C, 43.8% (48.4%); H, 4.2% (4.1%); P, 6.8% (6.9%); Ru, 7.6% (7.5%). IR: ν_{Ru-H} = 2070 cm^{-1} (in aq. HCl solution).

$HRu(OAc)(mSP\phi_2)_3 \cdot 6H_2O$

(*a*) To the hot ethanolic solution (5 cm^3) of 0.50 g (1.25 mmol) $mSP\phi_2 \cdot 2H_2O$ were rapidly added in the following order: 0.050 g (*ca.* 0.2 mmol) $RuCl_3 \cdot 3H_2O$ in 3 cm^3 ethanol, 0.5 cm^3 (*ca.* 10 mmol) glacial acetic acid and 0.1 g KOH in 2 cm^3 hot ethanol. After 5 min of reflux a yellow solid precipitated from the violet solution. After filtration the precipitate was washed with a small amount of acetone. The product obtained by this method contains inorganic contaminations (*Analysis* for P: 5.5% instead of 6.8%).

(*b*) 1.0 g (1 mmol) $RuCl_2(mSP\phi_2)_2 \cdot 4H_2O$, 0.40 g (1 mmol) $mSP\phi_2 \cdot 2H_2O$ and 0.26 g (2 mmol) NaOAc·

$3H_2O$ were suspended in 20 cm^3 of 96% ethanol. The suspension was refluxed under H_2 for 16 hours. From the cooled solution a yellow solid precipitated which was filtered and washed with acetone. Yield: 90%. *Analysis*: C, 44.6% (49.3%), H, 4.0% (4.3%), P, 6.6% (6.8%); Ru, 7.1 (7.4%). IR: ν_{Ru-H} = 1996 cm^{-1} (nujol), $\nu_{OCO,s}$ = 1435 cm^{-1} (KBr), $\nu_{OCO,as}$ = 1528 cm^{-1} (nujol).

$HRuCl(CO)(mSP\phi_2)_3 \cdot 6H_2O$

0.10 g (*ca.* 0.4 mmol) $RuCl_3 \cdot 3H_2O$ and 0.48 g (1.2 mmol) $mSP\phi_2 \cdot 2H_2O$ were dissolved in 10 cm^3 2-methoxy-ethanol. The solution was refluxed for 8 hours under N_2. The orange solution was cooled, and poured with intense stirring into 100 cm^3 of cold diethyl ether. The pale yellow precipitate was collected, washed with diethyl ether and acetone. After drying a cream-white crystalline solid was obtained. Yield: 80%. *Analysis*: C, 47.1% (48.3%), H, 4.4% (4.0%), P, 6.8% (6.8%); Ru, 7.3% (7.4%). IR: ν_{Ru-H} = 2060 cm^{-1}, ν_{CO} = 1900 and 1970 cm^{-1} (all in nujol).

cis-$HRuCl(CO)_2(mSP\phi_2)_2 \cdot 4H_2O$

0.10 g (0.1 mmol) *cis*-$RuCl_2(CO_2)_2(mSP\phi_2)_2 \cdot 4H_2O$ was suspended in 5 cm^3 of ethanol and refluxed under H_2 for 8 hours. After filtration the white precipitate was washed with diethyl ether. Yield. 70%. *Analysis*: C, 41.8% (45.9%), H, 3.9% (3.7%); P, 6.2% (6.2%). IR: ν_{Ru-H} = 1940 cm^{-1}, ν_{CO} = 1997 and 2060 cm^{-1} (all in KBr).

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