

## Hydrogenation of olefinic substrates in aqueous and aqueous–organic biphase systems using rhodium complex of sulphonated triphenyl phosphine

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**Abstract.** Water-soluble meta sulphophenyldiphenylphosphine complex of rhodium prepared *in situ* catalyses the homogeneous hydrogenation of fumaric, maleic and crotonic acids in water and 1:1 water–methanol mixture as solvents. Fumaric acid gives a higher rate of hydrogenation than maleic acid. Rate of hydrogenation also increases on changing the solvent from pure water to 1:1 mixture of methanol and water. Rate law for the reaction has been proposed.

**Keywords.** Water soluble Rh(I) complex; homogeneous hydrogenation; rate law.

### 1. Introduction

The solubilisation of transition metal complexes in water permits reactions in aqueous media. Water-soluble complexes of rhodium and ruthenium with meta sulphophenyldiphenylphosphine ( $mSP\phi_2$ ), which are modified versions of Wilkinson's catalyst have been investigated for hydrogenation of water-soluble substrates (Joo *et al* 1978; Joo and Toth 1980; Toth *et al* 1980). These complexes are also anchored to strongly basic anion-exchange resins (Joo and Beck 1984). Further these complexes can be used in aqueous–organic biphase systems with the aid of a phase transfer catalyst (Alper 1981; Smith *et al* 1983).

### 2. Experimental

Triphenylphosphine was sulphonated by the literature method (Arhland *et al* 1958). A solution of  $RhCl_3 \cdot 3H_2O - mSP\phi_2$  was prepared in the molar ratio 1:3 and used *in situ* as catalyst. Reactions were carried out in a static reactor at 35°C and under hydrogen at 1 atm. The progress of the reaction was monitored by the uptake of hydrogen using a gas burette.

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### 3. Results and discussion

#### 3.1 Rate of reaction

Reactions were carried out in homogeneous medium in water and water-methanol (1:1 mixture by volume) and the results are summarised in table 1.

The observation of higher rate of reaction for fumaric acid (*trans* isomer) than for maleic acid (*cis* isomer) is somewhat unusual when compared to the studies with Wilkinson's catalyst, in the case of maleate and fumarate esters (James 1973). However a higher rate of reaction has been observed for *trans* isomer using  $[\text{Rh}(\text{cyclooctene})_2\text{Cl}]_2 + \text{Cl}^-$  or  $\text{Et}_2\text{S}$  as the catalyst in dimethylacetamide solution (James and Ng 1975). Similar observations were made for hydrogenation of maleic and fumaric acid (Joo *et al* 1984).

Rates of reaction increased on changing the solvent from water to a water-methanol mixture due probably to the increase in solubility of  $\text{H}_2$ . The increase in rate is more significant in the case of fumaric acid than for maleic and crotonic acids.

The UV-visible spectrum of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in water showed absorption bands at 382 and 482 nm (figure 1). The spectrum of the catalyst solution is similar to that of the Rh(I) complex,  $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ , with  $\lambda_{\text{max}}$  at  $\sim 340$  and  $\sim 390$  nm (figure 2) (Brady *et al* 1976). There is a shift in the  $\lambda_{\text{max}}$  values for the catalyst solution compared to that of  $\text{RhCl}_3$ .

This shift in  $\lambda_{\text{max}}$  suggests a change in oxidation state of rhodium from +3 to +1 in the presence of the ligand (Larpent *et al* 1987).

Hydrogenation did not occur with a 1:6 molar solution of  $\text{RhCl}_3 - m\text{SP}\phi_2$ . This suggests the initial dissociation of ligand prior to the coordination of  $\text{H}_2$  or substrate during the course of the reaction.

The rate of reaction was influenced by the order of addition of the catalyst and the substrate (figure 3). The reaction had a higher initial rate when the substrate was introduced to a well-stirred solution of the catalyst in hydrogen. When the substrate was added first, followed by the catalyst, the rate was less than the previous case with an induction period of 10 minutes. In this experiment crotonic acid was used as the substrate. This observation suggests that the coordination of hydrogen to the catalyst is an important step which is hindered if the substrate has access to the catalyst before the hydrogen.

**Table 1.** Initial rates of hydrogenation for substrate in water and water-methanol (1:1 mixture).

Substrate (0.05)	Initial rate/moles of $\text{H}_2$ (moles of cat) $^{-1}\text{h}^{-1}$	
	In water	In water-methanol (1:1)
	Maleic acid	18
Fumaric acid	21	72
Crotonic acid	30	36

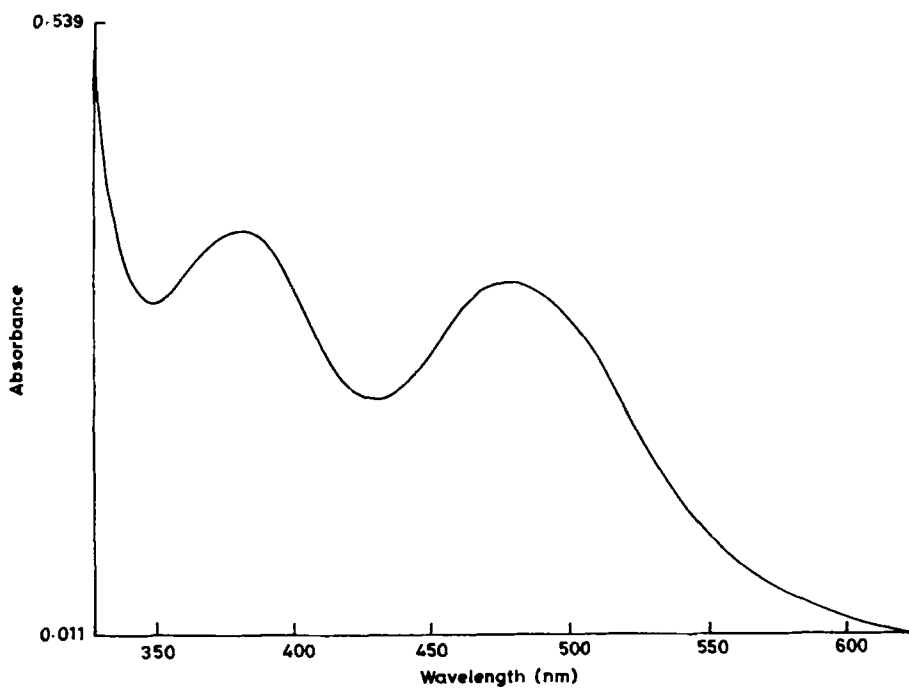


Figure 1. UV-visible spectra of RhCl<sub>3</sub> in water.

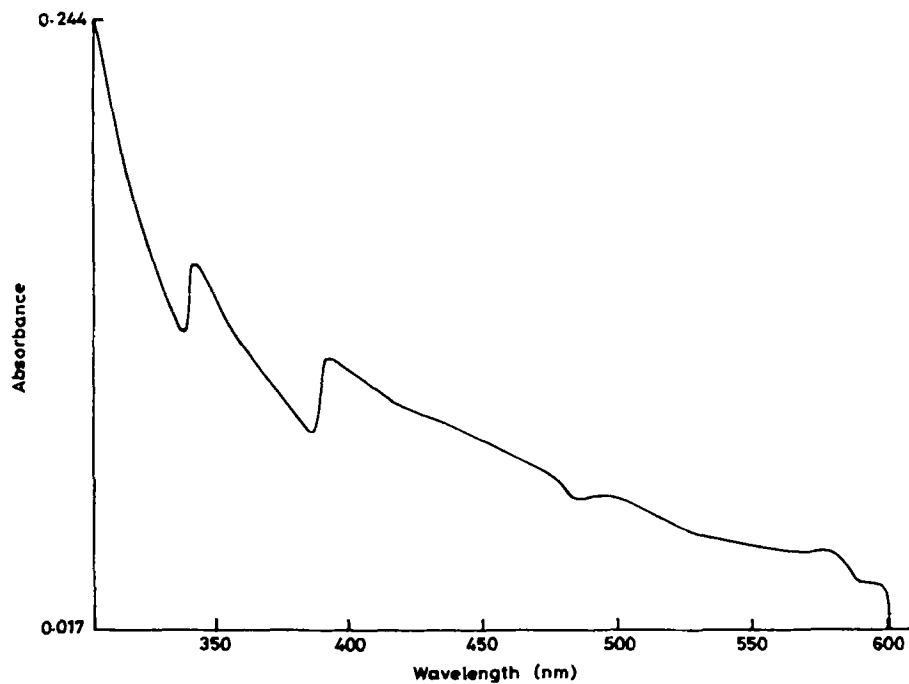


Figure 2. UV-visible spectra of RhCl<sub>3</sub> - mSP $\phi$ <sub>2</sub> (1:3) in water.

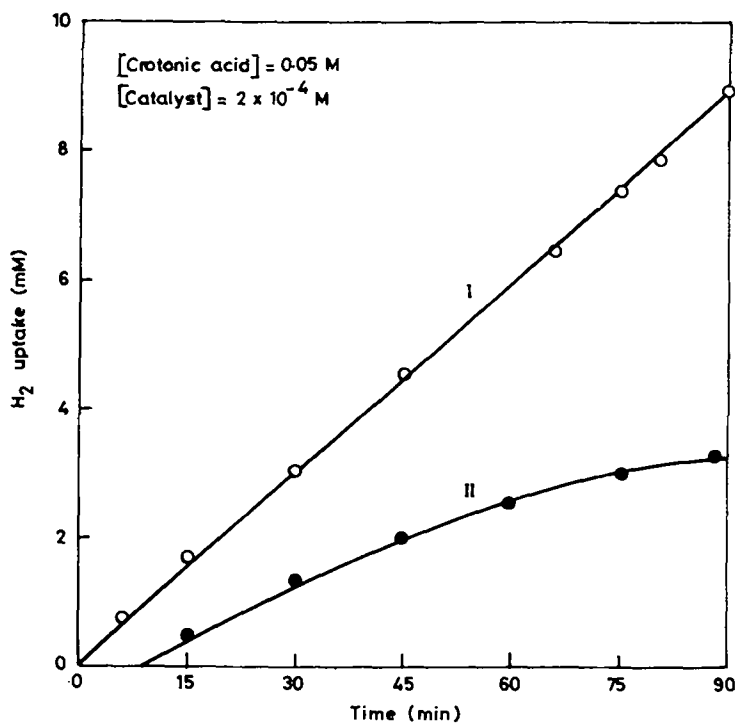
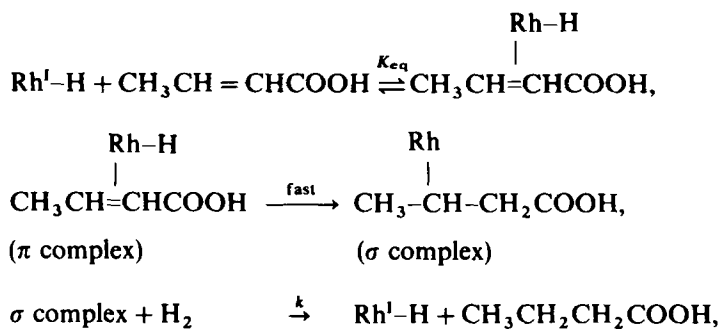


Figure 3. Influence of order of addition of catalyst and substrate on the rate of reaction. I – substrate was added after stirring the catalyst with H<sub>2</sub>. II – substrate was added prior to catalyst.

### 3.2 Mechanism

Considering Rh<sup>I</sup>-H, the hydrido complex as the catalytically active species, the following rate law has been proposed:



$$\text{Rate} = k[\sigma \text{ complex}][\text{H}_2], \quad (1)$$

$$K_{\text{eq}} = \frac{[\sigma \text{ complex}]}{[\text{Rh-H}]_f[\text{CH}_3\text{CH}=\text{CHCOOH}]}, \quad (2)$$

$$[\text{Rh} - \text{H}]_t = [\text{Rh} - \text{H}]_f + [\sigma \text{ complex}], \quad (3)$$

$$[\text{Rh} - \text{H}]_t = [\text{Rh} - \text{H}]_f \{1 + K_{eq}[\text{CH}_3\text{CH}=\text{CHCOOH}]\}, \quad (4)$$

$$\text{Rate} = k K_{eq} [\text{Rh} - \text{H}]_f [\text{CH}_3\text{CH}=\text{CHCOOH}], \quad (5)$$

Substituting for  $[\text{Rh} - \text{H}]_f$

$$\text{Rate} = \frac{k K_{eq} [\text{Rh} - \text{H}]_t [\text{CH}_3\text{CH}=\text{CHCOOH}]}{1 + K_{eq} [\text{CH}_3\text{CH}=\text{CHCOOH}]} \quad (6)$$

$[\text{Rh} - \text{H}]_t$  and  $[\text{Rh} - \text{H}]_f$  refer to the total amount of active catalyst and that in the free (uncomplexed) state respectively.

This rate expression agrees well with the experimental observation of the first-order dependence of rate on catalyst (figure 4) and  $\text{H}_2$ . On increasing the substrate concentration the rate reaches a limiting value becoming independent of substrate concentration. The plot of  $[\text{rate}]^{-1}$  is presented in figure 5 and the plot is linear.

### 3.3 Experiment in biphasic medium

The biphasic system consisting of water and a non-miscible organic solvent offers an interesting modification of homogeneous catalysis since the catalytically active species remain in aqueous phase and can be recycled (Kuntz 1987).

1-Octene was hydrogenated in a benzene-water system using tetrabutylammonium bromide as the phase-transfer catalyst. The reaction proceeded after an induction time of 60 min. Figure 6 shows a plot of hydrogen uptake vs time. Subsequent

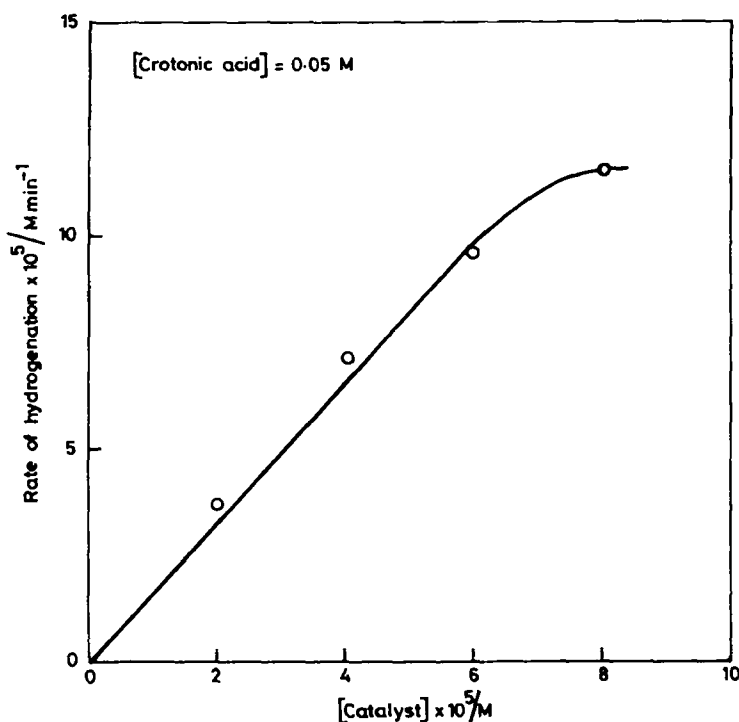


Figure 4. Effect of catalyst concentration on the rate of reaction.

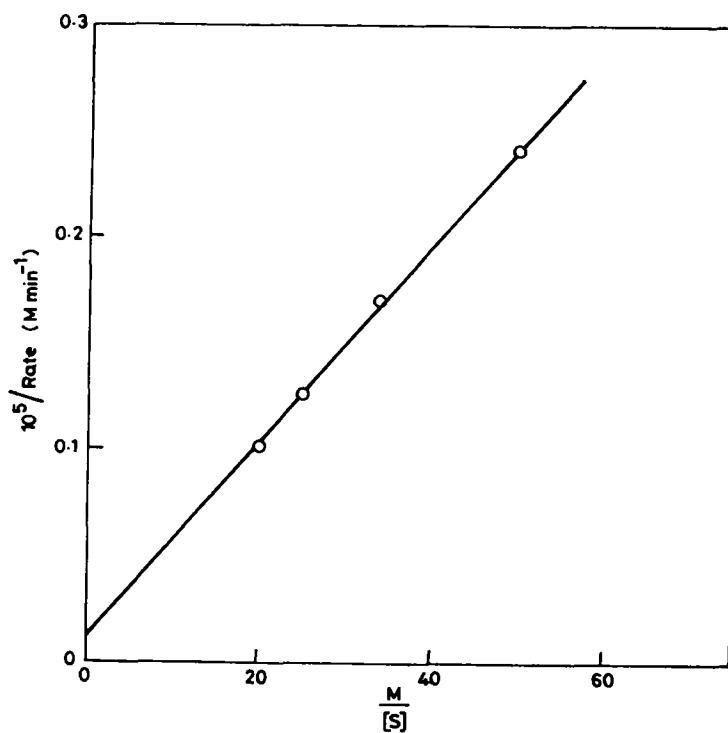


Figure 5. Plot of reciprocal of the rate of hydrogenation vs reciprocal of substrate concentration.

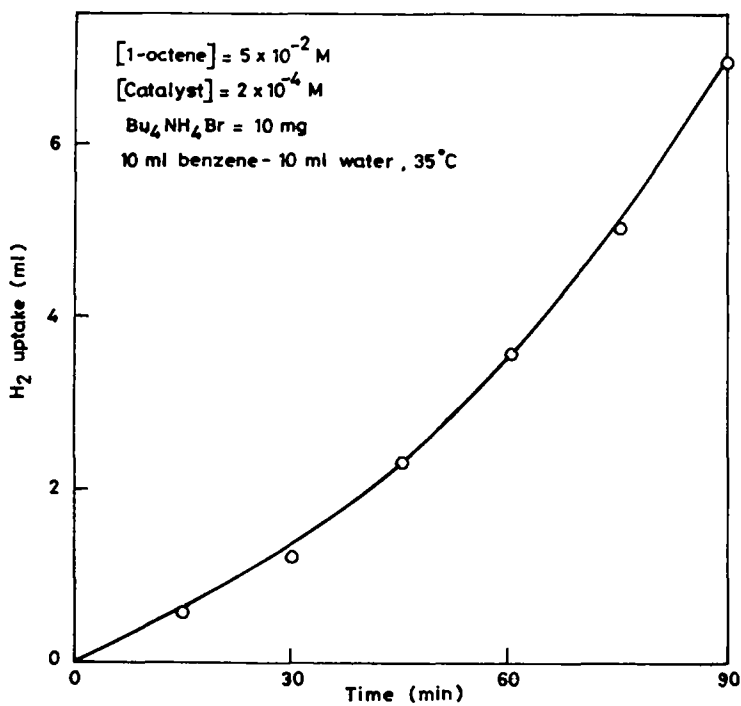


Figure 6. Reaction under phase transfer conditions.

reactions with fresh substrate proceeded at the same rate of reaction suggesting no loss of catalytic activity.

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