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Homogeneous Hydrogenations in Aqueous Solutions Catalyzed by Transition Metal Phosphine Complexes

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As was already shown [1], sulphonated triphenylphosphine (Dpm) can be efficiently used for the preparation of water soluble transition metal phosphine complexes. This permits the study of reactions in aqueous solutions catalyzed by water soluble analogs of triphenylphosphine complexes. Furthermore, recently a new method of heterogenization of homogeneous catalysts has been reported, based on this type of complexes [2]. In the course of our systematic study of this class of compounds, $HRu(OOCCH_3)(Dpm)_3$ (I), $RuCl_2(Dpm)_2$ (II) and a red ruthenium hydride, most likely $HRuCl(Dpm)_3$, (III) were prepared and used as catalysts of the hydrogenation of several oxo- and $>C=C<$ unsaturated acids.

Catalysts (I) and (II) were prepared following published procedures [3, 4] but using Dpm instead of PPh_3. IR data of $HRu(CH_3COO)(Dpm)_3$: ν_{Ru-H} 1996 cm^{-1}, $\nu_{OCO,sym.}$ 1435 cm^{-1}, $\nu_{OCO,asym.}$ 1528 cm^{-1}. Integrated NMR intensities show $Dpm/CH_3COO = 3$. The crude product is contaminated by KCl, therefore it analyses for P = 5.5% (calc. 7.12%). There is no characteristic band in the IR spectrum of $RuCl_2(Dpm)_2$; of the several weak bands in the 230–330 cm^{-1} region none can be safely assigned to ν_{Ru-Cl}. Again, due to NaCl contamination, the product contains a somewhat lower percentage of phosphorus than required by the formula (6.16%; calc. 6.87%). Catalyst (III) can easily be obtained by the action of molecular hydrogen on aqueous HCl solutions of $RuCl_3 \cdot aq$ and Dpm, as well as by the reaction of H_2 and $RuCl_2(Dpm)_2$ in the presence of excess Dpm. Its composition is supported by kinetic data of hydrogenation reactions (dependence of catalytic activity on Dpm/Ru ratio), and the close resemblance of its electronic spectrum ($\lambda_{max} = 510$ nm) to that of $HRuCl(PPh_3)_3$.

When 0.1 *M* acetate buffer was used as solvent (pH = 4.8), (I) proved to be a very effective catalyst of the hydrogenation of unsaturated acids, compared to its moderate activity in the case of oxo-acids (Figure 1, curves 1 and 2). At pH = 1 (adjusted using methanesulphonic acid) the hydrogenation rates of both types of acid are almost equal and somewhat lower than that of the oxo-acids at higher pH.

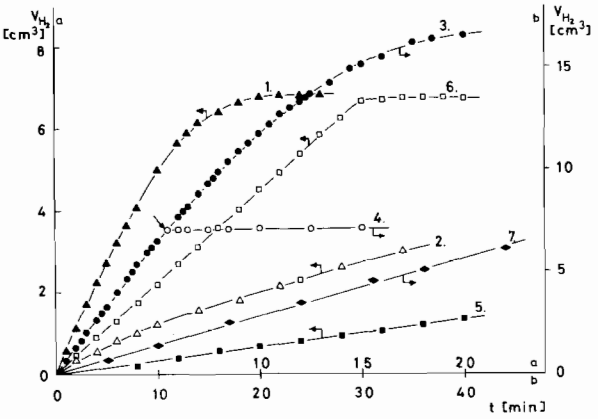

Fig. 1. Kinetic curves of the hydrogenation of a) crotonic acid, catalysed by (I), (1), (II) (3), (III) (5); b) pyruvic acid, catalysed by (I) (2), (II) (4), (III) (6); c) fructose, catalysed by (III) (7). Conditions are given in the legend of the Table.

Contrary to (I), (II) is much more effective in the hydrogenation of $>C=O$ than in the case of $>C=C<$ bonds both at low and high pH values (*cf.* Figure 1, curves 5 and 6). The hydrogenation rate of pyruvic acid increased exponentially with increasing pH, while that of crotonic acid was almost unaffected by similar changes of pH.

In neutral aqueous solutions (II) is an active catalyst of the hydrogenation of $>C=C<$ bonds, and inactive in the case of $>C=O$ bonds. Keto-acids coordinate strongly to the catalyst, indicated by the immediate colour change (brownish-green to reddish-brown), and the resulting complexes are inactive for hydrogenation. This conclusion is supported by the fact that the rather fast hydrogenation of crotonic acid is completely inhibited by the addition of pyruvic acid (Figure 1, curves 3 and 4). Using 0.1 *M* HCl solutions as solvent, very slow hydrogenation of pyruvic acid can be observed, while the rate of hydrogenation of crotonic acid drops to about one third of that measured at pH ≃ 7.

The kinetics of hydrogenation follow the usual pattern [5], the rate determining step being the regeneration of the catalyst during the hydrogenation of the intermediate alkyl complex. Figure 1 demonstrates that there are significant differences in the stability of the different catalyst–substrate complexes (*e.g.* curves 1, 3 and 6). Usually one can observe product inhibition with decreasing number of catalytic cycles. However, in the hydrogenation of pyruvic acid catalysed by (III), the latter was found as high as 1300 mol H_2/mol catalyst. Some of the kinetic data are presented in Table I.

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TABLE I. Comparison of the Catalytic Activity of $HRu(CH_3COO)(Dpm)_3$, $RuCl_2(Dpm)_2$ and $HRuCl(Dpm)_3$, as Expressed in mol H_2/mol Catalyst·hr.

Substrate	Catalyst:	$HRu(CH_3COO)(Dpm)_3$	$RuCl_2(Dpm)_2$	$HRuCl(Dpm)_3$
	Solvent:	0.1 *M* acetate buffer, pH = 4.8	H_2O, pH = 6–7	0.1 *M* Cl pH = 1
$CH_3-CO-COOH$		46	–	157
$C_6H_5-CO-COOH$		46[a]		115
$CH_3-(CH_2)_2-CO-COOH$		74[a]		70
$CH_3-CO-(CH_2)_2-COOH$		25[a]		13
$CH_3-(CH_2)_5-CO-COOH$		74[a]		
$CH_3-(CH_2)_7-CO-COOH$		48[a]		
$HOOC-(CH_2)_2-CO-COOH$		67[a]		95
trans-$CH_3-CH=CH-COOH$		198	164	23
trans-$C_6H_5-CH=CH-COOH$		92		30
cis-$HOOC-CH=CH-COOH$		92		23
trans-$HOOC-CH=CH-COOH$		92		49
$CH_2=C(COOH)-CH_2-COOH$				84
$CH_2=CH-CH=CH-COOH$[c]		175		
$HO-CH_2-CO-CH_2-OH$				60
Fructose				5[b]

Unless otherwise stated: 2×10^{-4} mol substrate, 1×10^{-5} mol (I) or (II) or 5×10^{-6} mol (III) in 10 cm^3 solvent (Dpm/Ru = 5:1). p_{H_2} = 610 mmHg, at 1 atm total pressure. t = 60.0 ± 0.1 °C.
[a]As before, but 5×10^{-4} mol substrate. [b]As before, but 2×10^{-3} mol substrate and 5×10^{-5} mol catalyst. [c]Both double bonds are hydrogenated.

Kruse and Wright [6] have reported the homogeneous catalytic hydrogenation of carbohydrates under the catalytic action of $RuHCl(PPh_3)_3$ in DMA solutions at 75 °C and 3 atm hydrogen pressure. We have found that the hydrogenation of fructose is catalysed with moderate activity by (III) in 0.1 *M* aqueous HCl solutions (Figure 1, curve 7 and Table I). Under similar conditions 1,3-dihydroxy-acetone is rapidly hydrogenated.

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