Dimeric Metal Acetates for the Homogeneous Hydrogenation of Olefins

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Summary Certain transition-metal acetates function as homogeneous catalysts for the hydrogenation of olefins in a wide variety of solvent media.

THE protonation of dimeric transition-metal carboxylates such as the tetra-bridged dimeric rhodium(II) acetate $Rh_2(OCOMe)_4$, has led to the formation of binuclear cationic species which in the presence of a stabilizing ligand are active for the homogeneous hydrogenation of C:C and C⋮C bonds.[1]

The spectrochemical behaviour of $Rh_2(OCOMe)_4$ in a wide variety of solvents indicates rapid adduct formation with the solvent occupying the terminal positions of the bridged complex,[2,3] and these co-ordinated solvent molecules appear to be quite labile to substitution, being readily displaced upon the addition of ligands having a somewhat higher donor strength[4] (*e.g.* dimethyl sulphoxide displaces dimethylformamide or dimethylacetamide). Thus, the metal carboxylates themselves have the potential to provide suitable sites at their terminal positions for the activation of olefins and hydrogen. Such catalytic activity is observed for $Rh_2(OCOMe)_4$ and the recently synthesized $Ru_2(OCOMe)_4$[5] for the hydrogenation of a number of olefins in polar solvents such as dimethylformamide, tetrahydrofuran, and ethanol at ambient conditions of temperature (25—80°) and pressure ($H_2 < 1$ atm). Some representative rates under stated conditions are given in the Table. The catalysts appear to be active for the hydrogenation of ethylene, certain substituted ethylenes, and straight chain terminal and cyclic monoenes. *trans*-Internal olefins and dienes appear to be hydrogenated only by the $Ru_2(OCOMe)_4$ catalytic system.

G.l.c. analysis of the organic reaction products arising from hex-1-ene indicated that n-hexane was the major product. A small amount of isomerization of hex-1-ene to *cis*- and *trans*-hex-2-ene did also occur. In the case of pent-1-ene or oct-1-ene as substrate, the major product was again the alkane with small amounts of isomerized olefins being produced. Under the reaction conditions used, the isomerization reactions appear to require the presence of molecular hydrogen.

Although the metal carboxylates are not as active as the dimeric cations resulting on protonation of the metal carboxylates,[1] they do have a number of important advantages over the protonated species. The metal carboxylates do not require the presence of an activating ligand such as an aryl- or alkyl-phosphine ligand. The $Rh_2(OCOMe)_4$ catalyst has a distinct advantage over other Group VIII metal—phosphine catalysts in that the presence of oxygen does not cause any marked decrease in catalytic activity. Molecular oxygen is reduced to water by H_2 in the presence of $Rh_2(OCOMe)_4$, thus rendering the system extremely easy to handle. The presence of small amounts of impurities in the olefin does not hamper the activity of the $Rh_2(OCOMe)_4$ catalyst. At the completion of hydrogenation of the substrate the $Rh_2(OCOMe)_4$ complex can be easily recovered in solution or as the crystalline solid, and re-used without any appreciable loss in activity.

Initial studies have been carried out on the nature of the $Rh_2(OCOMe)_4$ system. $Rh_2(OCOMe)_4$ readily forms adducts of the type $L{\cdot}Rh(OCOMe)_4Rh{\cdot}L$.[2,6] Hence, the displacement of the terminally co-ordinated solvent by the olefin or hydrogen would seem to be required before activation of the reactants could occur. Solvents with a strong donor strength[4] may be expected to inhibit catalytic activity. In general, the $Rh_2(OCOMe)_4$ complex functioned best in alcohols, cyclic ethers, and substituted amides. The $Rh_2(OCOMe)_4$ complex also showed activity in stronger donor solvents such as Me_2SO, but a long induction period was observed before hydrogenation began.

Rates of hydrogenation of substrates by $Rh_2(OCOMe)_4$ *and* $Ru_2(OCOMe)_4$. *Metal complex concentration* 5·0 mM; *substrate concentration* 1·0 M; *temp.* 30°; H_2 *pressure* = (76 *cm* — *vapour pressure of solvent media*)

Complex	Solvent	Substrate	Initial rate × 10^2 (ml/min)
$Rh_2(OCOMe)_4$	$HCONMe_2$	Pent-1-ene	6·8[a]
		Hex-1-ene	17·0
		Hex-1-en-3-ol	8·1
		Hexa-1,5-diene	[b]
		trans-Hex-2-ene	[b]
		Oct-1-ene	9·6
		Cyclo-octene	1·3
		Dec-1-ene	11·5[c]
		Ethylene	3·2[d,e]
		Diethyl maleate	5·9
		Diethyl fumarate	[b]
		Styrene	6·6
	$MeCONMe_2$	Hex-1-ene	4·4[c]
	Tetrahydrofuran	Hex-1-ene	15·8
	EtOH	Hex-1-ene	3·8[b]
	Dioxan	Dec-1-ene	3·8[c]
	Me_2SO	Dec-1-ene	5·3[c,e]
$Ru_2(OCOMe)_4$	$HCONMe_2$	Oct-1-ene	15·3[g,e]
		Dec-1-ene	18·0[g,e]
		Diethyl maleate	7·0[g,e]
		Cyclo-octa-1,3-diene	16·8[g,e]

[a] Temp. 26°.
[b] No hydrogenation observed.
[c] Temp. 50°; substrate concentration 0·1 M.
[d] Temp. 50°; rate is volume of $C_2H_4 + H_2$ consumed [$p'(C_2H_4) = 36{\cdot}5$ cm, $p'(H_2) = 37{\cdot}0$ cm]
[e] Reported rate is maximum rate measured.
[f] Metal complex concentration 3·8 mM.
[g] Temp. 80°.

In the $Rh_2(OCOMe)_4$ catalytic system, no evidence for the presence of a paramagnetic species has been obtained,[5,7] thus suggesting that a dimeric Rh^{II} species is the active catalyst. The initial visible absorption spectrum of the $Rh_2(OCOMe)_4$ in $HCONMe_2$ λ_{max} (ϵ) 591 nm (137·6), 442·5 (51·6) does not change on the addition of olefin and/or molecular hydrogen to the solution and remains unchanged throughout the course of the reaction. Although ethylene is reduced to ethane by hydrogen in the presence of $Rh(OCOMe)_4$ there does not appear to be any measurable uptake of ethylene in the absence of hydrogen or *vice versa*. The catalytic solutions do not appear to decrease in spectral intensity or catalytic activity after treatment with ionic exchange resins, thus suggesting that the catalytic species is not ionic.

Preliminary kinetic results, using dec-1-ene as substrate and $Rh_2(OCOMe)_4$ as catalyst (50°, 1 atm H_2, solvent $HCONMe_2$) suggest that the dimer $[Rh_2(OCOMe)_4]$ is the active species. The reaction is first order in dimer and in hydrogen. The dependence on olefin changes from first order to zero order as the olefin concentration is increased.

The following sequence of steps for the observed hydrogenation reaction are consistent with the present kinetic data and experimental observations:

$$Rh_2(OCOMe)_4 + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh_2(OCOMe)_4H_2$$

$$Rh_2(OCOMe)_4H_2 + \text{olefin} \xrightarrow{k_2} Rh_2(OCOMe)_4 + \text{saturated product.}$$

(solvent molecules omitted)

The induced hydridic character of the hydrogen atoms upon co-ordination to *one* of the Rh atoms of the dimer could result in a deactivating effect on the second Rh due to a shift of electron density towards the first Rh atom. Thus the hydrogenation reaction may be expected to proceed only at one of the Rh atoms in the dimeric species, as suggested by the observed reaction kinetics.

We thank the National Research Council of Canada for financial support.

(*Received, July 27th,* 1970; *Com.* 1231.)

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