

Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 33.¹ The Metal-catalysed Disproportionation of Acetaldehyde into Acetic Acid and Ethanol

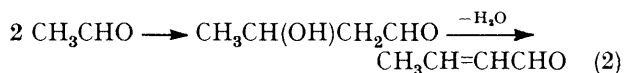
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Acetaldehyde is converted into ethanol and acetic acid (1 : 1) by dilute neutral aqueous solutions of pentamethylcyclopentadienyl-rhodium or -iridium complexes, *e.g.* $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]^+$. Areneruthenium complexes catalyse a similar reaction but more acetic acid than ethanol is formed; the ratios change with added ligand. The reaction is first-order in aldehyde and half-order in the binuclear catalysts $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{Cl}$ or $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}]\text{Cl}$. When the reactions using $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{OH}$ were quenched with PF_6^- or when aqueous solutions of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}][\text{PF}_6]$ were reacted with acetaldehyde, μ -hydrido-complexes $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{O}_2\text{CMe})_2\}][\text{PF}_6]$ and $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}_2(\text{O}_2\text{CMe})\}][\text{PF}_6]$ were isolated. Addition of acetaldehyde to $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}][\text{PF}_6]$ gave $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{O}_2\text{CMe})_3\}][\text{PF}_6]$. In base ($\text{pH} \geq 12.8$) the disproportionation of acetaldehyde was very much ($> 10^4$ fold) accelerated in the presence of catalyst and gave alcohol and acetate in a 1 : 1 ratio for *all* catalysts. The rhodium-catalysed reaction competed successfully with the aldol condensation even at high base strength ($1.5 \text{ mol dm}^{-3} \text{ NaOH}$) but the ruthenium- and iridium-catalysed reactions were slower. Other aldehydes (EtCHO , PhCHO , $\text{MeCH}=\text{CHCHO}$) reacted similarly. Hydride complexes $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{O}_2\text{CR})_2\}][\text{PF}_6]$ could again be isolated from the neutral regime reactions and addition of alkali caused significant accelerations in rate. The mechanism is suggested to be related to that of the Cannizzaro reaction, except that the attack by the aldehyde hydrate anion is at the metal to which hydride transfer initially occurs. Formation of the carboxylate (or carboxylic acid) and of the alcohol (or alkoxide) thus occur in the co-ordination sphere of the complex. A variety of non-half-sandwich complexes of Rh and Ru as well as the metals themselves were essentially inactive.

In the course of our systematic study of the reactions of simple organic molecules with pentamethylcyclopentadienyl-rhodium and -iridium complexes,² and in particular with the tri- μ -hydroxo-complexes $[\{\text{M}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]^+$ ($\text{M} = \text{Rh}$ or Ir),^{3,4} we have also studied the reactions of aldehydes. A part of this work has already been communicated;⁵ the present paper gives a full account of that work and of new results obtained since.

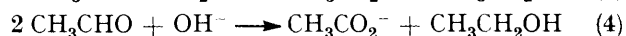
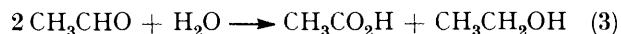
The most interesting aspect of this work was the discovery that in water, acetaldehyde underwent a catalysed redox disproportionation to give ethanol and acetic acid (or acetate), usually but not invariably, in a 1 : 1 ratio. The reaction also applied to other aldehydes which gave the corresponding alcohols and the carboxylic acids (or their salts).

The reaction therefore is reminiscent of the classical Cannizzaro reaction [equation (1)] in which aldehydes are transformed into the corresponding alcohols and the carboxylate salts by the action of aqueous base.⁶ However, the Cannizzaro reaction is normally rather slow and, at the levels of base required, it competes unfavourably with other reactions such as the aldol condensation [equation (2)], when the aldehyde has a hydrogen on the carbon α to the CHO function. For this reason acetaldehyde (and structurally similar aldehydes) do not undergo the Cannizzaro reaction.



We find that the metal-catalysed reaction operates in two regimes, a slower reaction in the region of pH 5–7

and a very fast reaction in alkaline solution at $\text{pH} > 10$. The former gives the acid [equation (3)] and the latter the carboxylate salt [equation (4)]. Although the pH of the second corresponds to that used for the Cannizzaro reaction, which does normally not work for acetaldehyde, when the conditions are suitably controlled it can be made so effective that the aldol condensation is essentially non-competing. The two reactions are described separately although we propose them to have very similar mechanisms.



RESULTS AND DISCUSSION

Reactions under Neutral/Acidic Conditions.—This reaction is catalysed by a wide variety of half-sandwich complexes of Rh, Ru, and Ir. Other complexes investigated showed zero or very low activity. For example, none of the following compounds, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$, $[\text{Rh}(\text{acac})_3]$ (acac = acetylacetonate), $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$, $[\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$, or $[\text{RuHCl}(\text{PPh}_3)_3]$, showed total 'turnovers' of more than 6 in 20 h at 50 °C. The metals themselves (2.5% Rh/alumina, 1% Pt/alumina, and 3% Pd/carbon) were also inactive. By contrast, typical turnover numbers (mol of ethanol plus acetic acid produced per mol of catalyst) were in the region of 38–185 for the $\text{Rh}(\text{C}_5\text{Me}_5)$, $\text{Ir}(\text{C}_5\text{Me}_5)$, or $\text{Ru}(\text{C}_6\text{Me}_6)$ complexes under these conditions (Table 1).

Since the reactions were carried out in water, those complexes which were more soluble were in general the better catalysts. The iridium complexes were excep-

TABLE 1

Catalysis for the disproportionation of acetaldehyde to ethanol and acetic acid under neutral conditions ^a

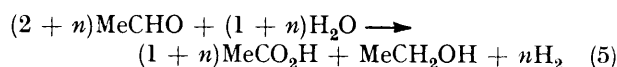
Catalyst	Time/h	Temp./°C	Ethanol		Acetic acid		Acetic acid Ethanol
			mmol	T/N	mmol	T/N	
{Rh(C ₅ Me ₅) ₂ Cl ₄ }	24	45	0.77	19	0.89	19	1.1
{Rh(C ₅ Me ₅) ₂ (OH) ₃ }Cl·4H ₂ O	24	45	1.37	34	1.79	41	1.2
{Rh(C ₅ Me ₅) ₂ (OH) ₃ }Cl·4H ₂ O ^b	216	45	72.8	1 160	103.3	1 291	1.1
{Rh(C ₅ Me ₅) ₂ (OH) ₃ }OH·11H ₂ O	40	53	4.00	100	4.00	100	1.0
Rh(C ₅ Me ₅)(O ₂ CMe) ₂ ·xH ₂ O	40	53	2.27	57	3.34 ^c	84	1.5
{Ir(C ₅ Me ₅) ₂ Cl ₄ }	20	50	1.44	35	1.66	38	1.1
{Ir(C ₅ Me ₅) ₂ (OH) ₃ }OH·xH ₂ O	20	45	0.13	3	0	0	
{Ir(C ₅ Me ₅) ₂ (OH) ₃ }O ₂ CMe·14H ₂ O	20	45	0.16	4	0.04 ^c	1	
[Ru ₂ (<i>p</i> -cymene) ₂ Cl ₄]	20	50	1.71	43	3.89	97	2.3
{Ru(C ₆ Me ₆) ₂ (OH) ₃ }Cl·4H ₂ O	20	50	1.60	40	5.75	144	3.6
{Ru(C ₆ Me ₆) ₂ (OH) ₃ }Cl·4H ₂ O ^b	216	45	37.3	462	191.6	2 395	5.2
{Ru(C ₆ Me ₆) ₂ (OH) ₃ }[PF ₆] ₂ ·2H ₂ O	20	45	1.56	40	4.96	124	3.2
[Ru(C ₆ Me ₆)(O ₂ CMe) ₂]	20	45	1.22	30	2.19	55	1.8
RhCl ₃ ·xH ₂ O	20	50	0.13	3	0.10	2	
RuCl ₃ ·xH ₂ O	20	50	0.17	4	0.06	2	
[Ru(acac) ₃]	20	50	0.03	<1	0.08	2	

^a Conditions: aqueous acetaldehyde (6 cm³, 10% v/v, 10.7 mmol CH₃CHO) plus catalyst (0.04 mmol). ^b Conditions: aqueous acetaldehyde (110 cm³, 19% v/v, 370 mmol CH₃CHO) plus catalyst (0.08 mmol). ^c Amounts of acetate corrected to allow for that present in catalyst.

tions to this; [{Ir(C₅Me₅)₂Cl₄}] although insoluble was reasonably active, whereas the soluble complexes [{Ir(C₅Me₅)₂(OH)₃}OH·xH₂O and [Ir(C₅Me₅)(O₂CMe)₂·xH₂O] showed zero and a low turnover number respectively.

While the rhodium and iridium half-sandwich complexes generally gave a ratio of acetic acid to ethanol of unity (within experimental error) at temperatures from 22 to 115 °C (Tables 1 and 2), the ruthenium complexes gave significantly larger amounts of acetic acid. For example, in a long run (45 °C, 216 h) where 2 857 equivalents of acetaldehyde were turned over the ratio of acetic acid to ethanol was 5.2 : 1 using [{Ru(C₆Me₆)₂-

ruthenium complex), bubbles of gas were formed and the solution 'fizzed' gently. This gas was identified as hydrogen and therefore the overall balance of the ruthenium reaction is given by equation (5) (*n* ≈ 1).



The ruthenium complexes could also be tuned to give differing ratios of acid to alcohol. Examples using [{Ru(C₆Me₆)₂(OH)₃}Cl·4H₂O] as catalyst are given in Table 3; they show a change in the ratio from 3.6 : 1 for the complex by itself to 1.7 : 1 in the presence of one

TABLE 2

Effects of temperature on the disproportionation of acetaldehyde to ethanol and acetic acid under neutral conditions ^a

Catalyst	Time/h	Temp./°C	Ethanol		Acetic acid		Acetic acid Ethanol
			mmol	T/N	mmol	T/N	
{Rh(C ₅ Me ₅) ₂ Cl ₄ }	46	22	0.23	6	0.31	6	1.0
	24	50	0.77	19	0.89	22	1.2
^b	1	115	3.23	162	3.45	170	1.0
{Rh(C ₅ Me ₅) ₂ (OH) ₃ }Cl·4H ₂ O	46	22	0.60	15	0.66	15	1.0
	24	50	1.37	34	1.79	41	1.2
^b	1	115	3.41	171	3.63	179	1.1
[Ru ₂ (<i>p</i> -cymene) ₂ Cl ₄]	46	22	0.39	10	1.24	31	3.2
	20	50	1.71	43	3.89	97	2.3
^b	1	115	1.70	85	4.00	200	2.4
{Ru(C ₆ Me ₆) ₂ (OH) ₃ }Cl·4H ₂ O	46	22	0.11	30	2.12	53	1.9
	20	50	1.60	40	5.75	144	3.6
^b	1	115	1.94	97	6.03	302	3.1

^a Conditions: aqueous acetaldehyde (6 cm³, 10% v/v, 10.7 mmol CH₃CHO), plus catalyst (0.04 mmol). ^b Conditions: as above but catalyst (0.02 mmol); the catalyst decomposed during the reaction which was run in a sealed tube.

(OH)₃]Cl as catalyst. A similar experiment with [{Rh(C₅Me₅)₂(OH)₃}Cl] as catalyst turned over 2 451 equivalents of aldehyde and the ratio of acetic acid to ethanol was 1.1 : 1.

Over longer times, the activity of the two catalysts was comparable but the ruthenium complexes were more active at lower temperatures and shorter times than the rhodium complexes.

When aqueous acetaldehyde was added to a neutral aqueous solution of [{Ru(C₆Me₆)₂(OH)₃}Cl] (or other

equivalent of triphenylphosphine. This is accompanied by a small decrease in turnover from 188 to 163 (50 °C, 20 h). More triphenylphosphine causes only a small further change while other phosphines, dimethyl sulphoxide, or pyridine have similar although rather less marked effects. 2,2'-Bipyridyl completely deactivated the catalyst, presumably by blocking all the reaction sites.

Kinetic runs at 53 °C using either [{Rh(C₅Me₅)₂(OH)₃}Cl·4H₂O] or [{Ru(C₆Me₆)₂(OH)₃}Cl·4H₂O] as cata-

lyst showed similar behaviour. In both cases there was a fast initial rate (pH *ca.* 7) which slowed down within an hour to give a steady rate (pH *ca.* 4) (Figure 1). In this

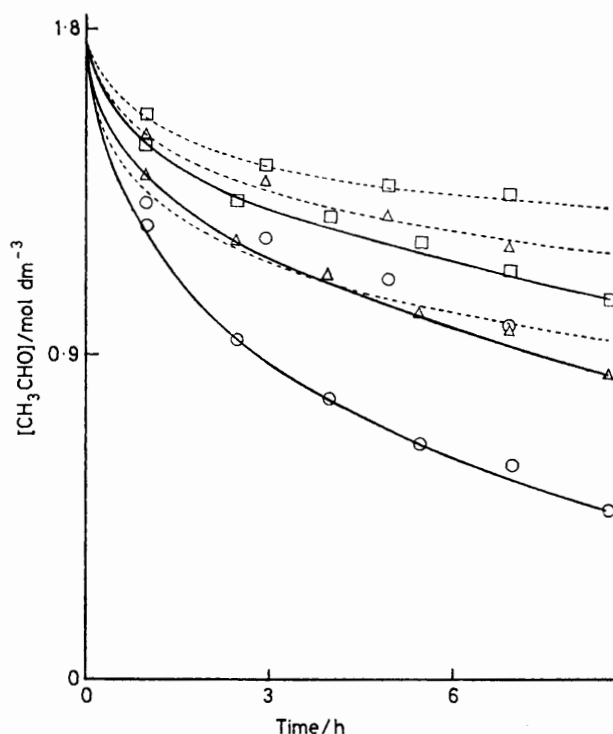


FIGURE 1 Typical reaction profiles of the acetaldehyde disproportionation reaction in the neutral catalysed regimes (conditions given in Experimental section) using catalyst $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}\cdot 4\text{H}_2\text{O}]$: 3.33 (---□---), 6.67 (---△---), 16.67 mol dm⁻³ (---○---); or $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}\text{Cl}\cdot 4\text{H}_2\text{O}]$: 6.67 (—□—), 10 (—△—), and 16.67 mol dm⁻³ (—○—)

steady period the rates in both cases were found to be first-order in aldehyde and half-order in catalyst (Figures 2 and 3).

The reacting solutions also underwent some remarkable colour changes during the course of the reaction. This was especially so for the rhodium complexes which were initially yellow but rapidly turned red, purple, and finally orange. Attempts to isolate pure single substances from reactions using $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}]$ as catalyst were unsuccessful. Addition of a precipitating agent (PF_6^-) gave solids; however, they proved on examination to be mixtures with compositions corresponding to $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{Cl}_x\text{H}_y(\text{O}_2\text{CMe})_z\}]^+$ ($x + y + z = 3$), as shown by their microanalyses, $\nu(\text{CO}_2)$ at 1375 and 1550 cm⁻¹, and the presence of a hydride resonance in the n.m.r. spectrum at $\delta -8.83$ [t, $J(\text{Rh}-\text{H})$ 27 Hz].

A pure single complex was obtained directly from reaction of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}[\text{PF}_6]]$ with acetaldehyde and was shown to be the di- μ -acetato-mono- μ -hydrido-complex $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{O}_2\text{CMe})_2\}[\text{PF}_6]]$.⁷ Since this hexafluorophosphate complex was insoluble and pre-

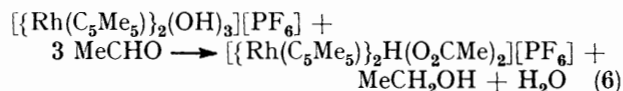
TABLE 3

Effect of ligands on the disproportionation of acetaldehyde to ethanol and acetic acid catalysed by $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}\text{Cl}\cdot 4\text{H}_2\text{O}]$ under neutral conditions *

Added ligand	Ethanol		Acetic acid		Acetic acid Ethanol
	mmol	T/N	mmol	T/N	
None	1.60	40	5.75	144	3.6
PPh_3	2.37	58	4.26	105	1.7
2 PPh_3	2.35	57	4.12	101	1.7
3 PPh_3	2.56	63	3.99	98	1.5
PPh_2Me	1.97	49	4.42	111	2.3
PMe_2Ph	1.62	41	4.19	105	2.6
PEt_3	1.77	44	3.29	82	1.9
Me_2SO	1.65	41	4.89	122	2.7
Pyridine	1.48	37	3.84	96	2.6
2,2'-Bipyridyl	0	0	0	0	

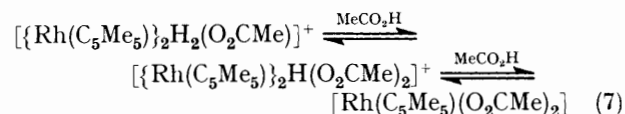
* All reactions were run at 50 °C for 20 h; aqueous acetaldehyde (6 cm³, 10% v/v, 10.7 mmol CH₃CHO) and catalyst (0.04 mmol).

cipitated, this reaction was stoichiometric and not catalytic [equation (6)].



A very effective catalyst was the hydroxo-hydroxide complex $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{OH}\cdot 11\text{H}_2\text{O}]$. The reaction could be quenched by addition of KPF_6 to the aqueous solution. This gave a precipitate that could be analysed by ¹H n.m.r. spectroscopy which showed the presence of both the red complex $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{O}_2\text{CMe})_2\}[\text{PF}_6]]$ and purple $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}_2(\text{O}_2\text{CMe})_2\}[\text{PF}_6]]$.^{7,8} The ratios of these two complexes depended on the precise conditions and especially on the time over which reaction had occurred. When the solution had reacted for several days before addition of KPF_6 no precipitate was formed; evaporation of the solution gave a sticky solid which had similar properties to the acetate complex $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{O}_2\text{CMe})_2]$.³

If the complexes isolated from this reaction accurately reflect the species in solution then it is probable that the differences arise from the effects of differing acetic acid levels. It is known that acids will react with μ -hydrido-dirhodium complexes to generate hydrogen and the appropriate salt and presumably this occurs here in the sense of equation (7).



The ruthenium complexes behaved a little differently and attempts to intercept the catalytically active hydrides were unsuccessful. Addition of acetaldehyde to $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}[\text{PF}_6]]$ in water gave, after evaporation of solvent, $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{O}_2\text{CMe})_3\}[\text{PF}_6]]$. We suggest that this reflects the greater sensitivity of hydrides such as $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2\text{H}(\text{O}_2\text{CMe})_2\}]^+$ and $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2\text{H}_2(\text{O}_2\text{CMe})\}]^+$ to acid.

The iridium complexes $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{O}_2\text{CMe}]$ and $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{OH}]$ ⁴ were very poor catalysts but

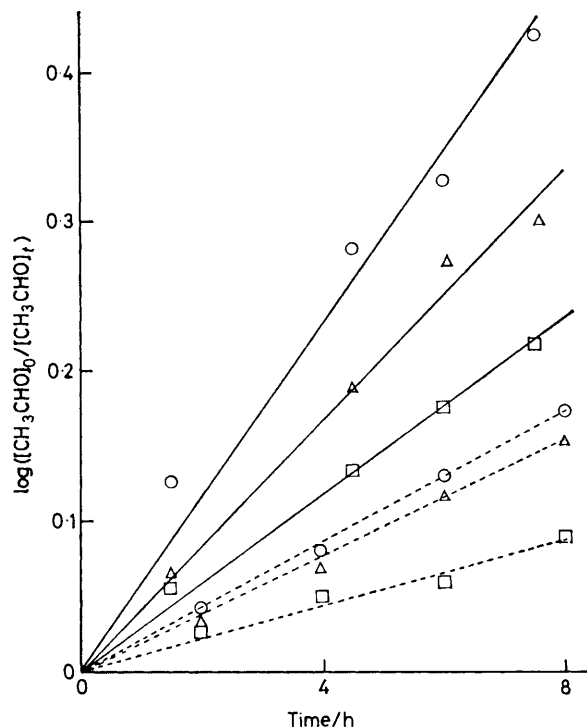


FIGURE 2 Graph showing first-order aldehyde dependence (see Figure 1 and Experimental section)

did show stoichiometric reactions. When KPF_6 was added to a solution of the first complex and acetaldehyde, the product was the known complex $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2\text{-H}_2(\text{O}_2\text{CMe})\}][\text{PF}_6]$, while similar treatment of the second gave the tri- μ -hydrido-complex $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2\text{H}_3\}][\text{PF}_6]$. We have shown that di- μ -hydrido-iridium complexes are poor catalysts for the homogeneous hydrogenation of olefins and that the tri- μ -hydrido-analogue is quite inactive.^{9,10} The observed efficiencies of these complexes in the aldehyde disproportionation (Table 1) exactly mirror this behaviour. The iridium chloride complex $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2\text{Cl}_4\}]$ has useful activity and this probably arises from the effectiveness of chloride as a ligand; it seems to compete very well with either μ -hydride or μ -acetate and hence these are displaced and catalytic cycles promoted. Again, in olefin hydrogenation $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2\text{Cl}_4\}]$ has good activity.^{9,10}

Reactions under Alkaline Conditions.—We also found that the rhodium and ruthenium complexes catalysed reaction under alkaline conditions (pH 12.8, initially) much better than under neutral to acid conditions. These reactions compete very effectively with the aldol condensation and are essentially stoichiometric in added base (sodium hydroxide) in the same way as the Cannizzaro reaction, and are in fact simply metal-catalysed Cannizzaro reactions. The reaction in alkaline solution is very fast indeed and we have not been able to measure the rate. The turnover numbers given in Table 4 are those found in the minimum time (3 min) needed to carry out the measurements. However, by quenching with excess hydrochloric acid we have shown that the

reaction is complete within 15 s (at 20 °C). If more alkali is added then more aldehyde is immediately converted (Figure 5); in this way it was shown that the reaction is stoichiometric in added alkali. Using $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{Cl}$ as catalyst (and under comparable conditions) the turnover number after 15 s was 36 in 0.5 mol dm^{-3} sodium hydroxide at 22 °C. Under mildly acid (pH 4–5) equilibrium conditions (Table 1) it takes 24 h

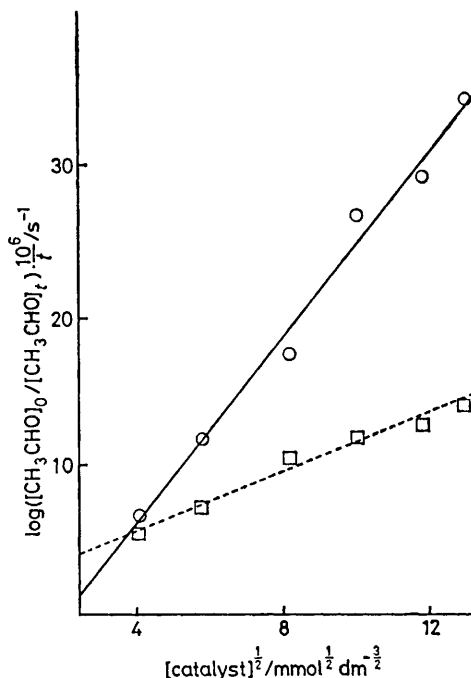


FIGURE 3 Graph showing half-order catalyst dependence for $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{Cl}\cdot 4\text{H}_2\text{O}$ (---□---) and $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}]\text{Cl}\cdot 4\text{H}_2\text{O}$ (—○—) (see also Figures 1 and 2)

at 45 °C to achieve the same turnover. This implies that the reaction under basic conditions is at least 5×10^4 times as fast as under neutral/acidic ones.

TABLE 4

Metal-catalysed disproportionation of acetaldehyde to ethanol and acetate in alkaline solution^a

Catalyst	Ethanol		Acetate		Acetate Ethanol
	mmol	T/N	mmol	T/N	
$[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{Cl}$	1.67	42	1.65	41	1.0
$[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}]\text{Cl}^{\text{b},\text{c}}$	0.07	2	0.07	2	1.0
$[\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4]^{\text{c}}$	0.31	8	0.34	8	1.1
$[\{\text{Ir}(\text{C}_5\text{Me}_5)_2\text{Cl}_4\}]^{\text{c}}$	0.32	8	0.30	7	0.9

^a Conditions: acetaldehyde (10.7 mmol) in water (2 cm^3), aqueous sodium hydroxide (0.5 mol dm^{-3} , 6 cm^3), and catalyst (0.04 mmol) at 20 °C. The reactions were immediately monitored by gas chromatography and ^1H n.m.r. spectroscopy; traces were recorded *ca.* 3 min after mixing (see text). ^b Catalyst only partially soluble. ^c Aldol products also observed.

The competition between this metal-catalysed Cannizzaro reaction and the aldol condensation will depend on many factors. A qualitative idea of the effect of initial concentration of base used can be obtained from the following experiment. In an aqueous solution of

acetaldehyde (94 mmol in 12 cm³) and catalyst (0.08 mmol) the metal-catalysed Cannizzaro reaction is faster than the aldol condensation up to a base concentration of 1.5 mol dm⁻³ (Figure 4). Above this the rate of the disproportionation starts to decrease quite sharply and large quantities of aldol products are formed.

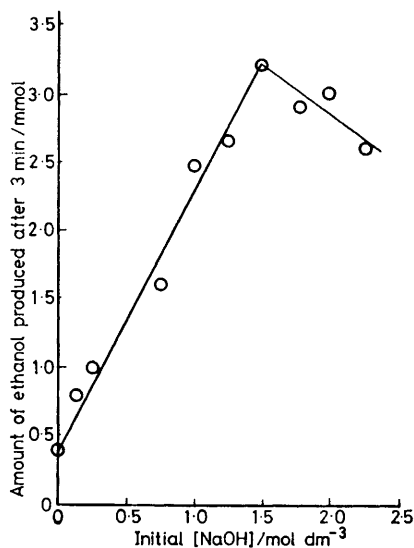


FIGURE 4 Effect of initial base concentration on the reaction $2 \text{MeCHO} + \text{OH}^- \rightarrow \text{MeCH}_2\text{OH} + \text{MeCO}_2^-$; acetaldehyde (94 mmol) and $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$ (0.08 mmol) plus aqueous sodium hydroxide (4 cm³ of $x \text{ mol dm}^{-3}$)

A similar increase in activity under alkaline conditions also occurs for the ruthenium-catalysed reactions. However, the reaction also changes its course quite dramatically and instead of the preponderance of acetic acid which is formed under neutral/acidic conditions, the ratio of acetate to ethanol is now equal to one. No hydrogen is evolved. This reaction is substantially slower than the rhodium-catalysed one since the turnover number is lower and some aldol formation was also observed.

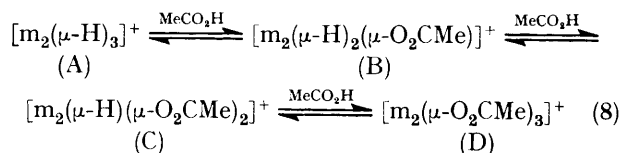
The reason for the fast initial rate in the neutral regime reactions is now also clear. At the beginning the solution is neutral (pH 7) and the rate-determining step, which we postulate to be the attack of nucleophile on the metal, occurs relatively easily. Once appreciable amounts of acetic acid are formed, this creates an acidic buffer solution (pH < 5) and the amount of OH⁻ available is much lower.

The difference between the rhodium and the ruthenium reactions may then simply be due to the relative ease with which the intermediate hydride species either use their hydrides to form the alcohol or react with H⁺ to give hydrogen gas.

The hydroxoiridium complexes easily form μ -hydrido-complexes which are also very inert. Comparison of Tables 1 and 4 shows the activity of $\{[\text{Ir}(\text{C}_5\text{Me}_5)_2\text{Cl}_4]\}$ is enhanced by base but here again the reaction is still relatively slow and aldol products are also formed; the ethanol to acetate ratio is again equal to one.

The reactions therefore appear to be controlled by a

series of equilibria which may in part be represented by equation (8) [$m = \text{Rh}(\text{C}_5\text{Me}_5)$, $\text{Ir}(\text{C}_5\text{Me}_5)$, or $\text{Ru}(\text{arene})$].



For rhodium, the di- and mono- μ -hydrido-complexes (B) and (C) are stable but can easily give rise to reactive species even under mildly acid conditions. The same situation holds for ruthenium in alkaline solution, but in dilute acetic acid hydrogen is given off and the only intermediate isolable is the tri- μ -acetato-complex (D). Again, hydrido-species are invoked to explain the reactivity of the iridium complexes but here deactivation occurs very easily by formation of the very stable tri- μ -hydrido-complex (A).

Reactions with Other Aldehydes.—A number of other aldehydes were also examined briefly to establish that similar reactions occurred there too. This was indeed the case as shown in Table 5 for the reaction of propionaldehyde to give propionic acid and propanol under neutral conditions. The pattern is similar to that for the acetaldehyde reactions except that turnover numbers are lower, largely because of the lower solubility of propionaldehyde in water. Base again caused an

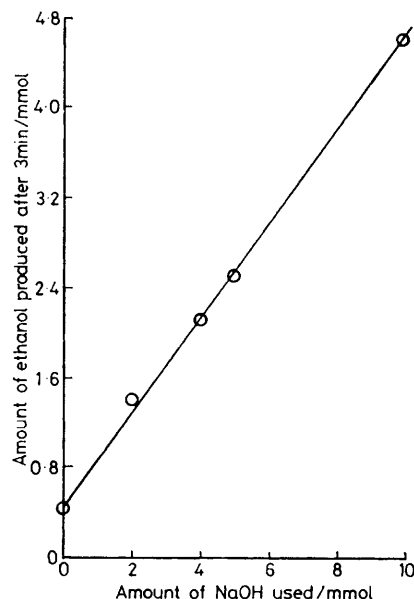


FIGURE 5 Illustration of the stoichiometric consumption of base for $2 \text{MeCHO} + \text{OH}^- \rightarrow \text{MeCH}_2\text{OH} + \text{MeCO}_2^-$; acetaldehyde (94 mmol) and $\{[\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$ (0.08 mmol) in water (8 cm³) plus aqueous sodium hydroxide ($x \text{ cm}^3$ of 1 mol dm⁻³)

enhancement in rate. This was not, however, as great as for acetaldehyde since the competing aldol condensation is much faster for propionaldehyde and is the predominant reaction, even in 0.13 mol dm⁻³ NaOH, whereas the acetaldehyde could tolerate NaOH solutions up to 1.5 mol dm⁻³.

TABLE 5
Metal-catalysed disproportionation of propionaldehyde to n-propanol and propionic acid^a

Catalyst	n-Propanol		Propionic acid		Propionic acid Propanol
	mmol	T/N	mmol	T/N	
$\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{Cl}_4\}$	0.42	10	0.37	9	0.9
$\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}\cdot 4\text{H}_2\text{O}$	0.59	15	0.56	14	0.9
$\{\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4\}$	0.34	8	0.89	22	2.6
$\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}\text{Cl}\cdot 4\text{H}_2\text{O}$	0.33	8	0.81	20	2.4
$\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}\cdot 4\text{H}_2\text{O}^b$		no products detectable			
$\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}\cdot 4\text{H}_2\text{O}^c$	0.21	5	not estimated		
$\{\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4\}^b$		no products detectable			
$\{\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4\}^c$	0.13	3	not estimated		

^a Conditions: propionaldehyde (1.7 mmol) in water (6 cm³) plus catalyst (0.04 mmol), at 50 °C after 72 h. Analysis by g.c.

^b Propionaldehyde (0.9 mmol) in water (6 cm³) plus catalyst (0.04 mmol), 20 °C after 3 min. ^c Propionaldehyde (0.9 mmol) in water (3 cm³), aqueous sodium hydroxide (0.5 mol dm⁻³, 3 cm³), and catalyst (0.04 mmol), 20 °C after 3 min. Aldol condensation products detected after 2 min.

Addition of other aldehydes, RCHO (R = H, Ph, or MeCH=CH), to aqueous solutions of $\{\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}[\text{PF}_6]\cdot 3\text{H}_2\text{O}\}$ gave precipitates of $\{\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{O}_2\text{CR})_2\}[\text{PF}_6]\}$ in the first two cases and of $\{\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{OH})(\text{O}_2\text{CCH}=\text{CHMe})\}[\text{PF}_6]\}$ with crotonaldehyde (*trans*-CH₃CH=CHCHO) [Table 6, and equations (9) and (10) respectively]. In addition, g.c. monitoring of the aqueous solutions from reactions catalysed by $\{\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}\}$ under neutral conditions showed the presence of both the alcohol and the appropriate carboxylic acid.* These results therefore indicate that the neutral disproportionation reaction is quite general.

Although benzaldehyde also undergoes the Cannizzaro reaction in base alone, we find a substantial acceleration in the presence of our catalysts. Thus under conditions where 8% of the benzaldehyde was converted into benzyl alcohol and sodium benzoate in the absence of

catalyst, with a benzaldehyde : $\{\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{Cl}\}$ ratio of 130 : 1 the conversion was 35% corresponding to a turnover number of 43.

This establishes that a hydrogen on the α -carbon of the aldehyde is not necessary for the metal-catalysed reaction to proceed.

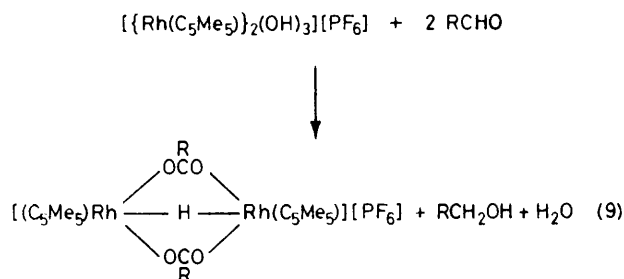
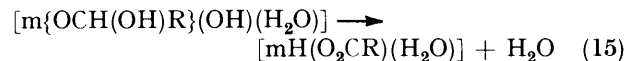
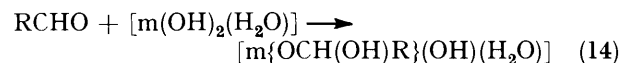
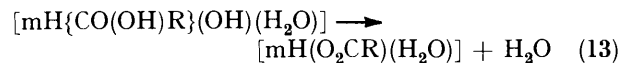
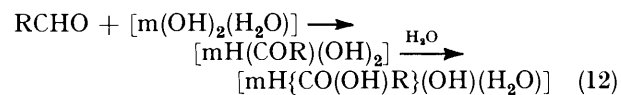
Mechanism of the aldehyde disproportionation reaction. The kinetic data we have observed for the reaction under steady-state neutral conditions indicate that the reaction is half-order both in the rhodium and in the ruthenium catalysts and first order in aldehyde. Since the starting materials are dinuclear and since all the other complexes isolated from the reaction are dinuclear we propose that the rate-determining step is the reaction of the aldehyde with a mononuclear species formed in a pre-equilibrium from the isolable dinuclear complexes.

Many different types of ligand are present so an actual 'working catalyst' will be of the type $\text{M}(\text{C}_n\text{Me}_n)\text{XY}\cdot\text{H}_2\text{O}$, where X and Y = OH, O₂CMe, H, or Cl, and may be the same or different. For simplicity of representation, we consider the case of $\{\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{OH}\cdot 11\text{H}_2\text{O}\}$

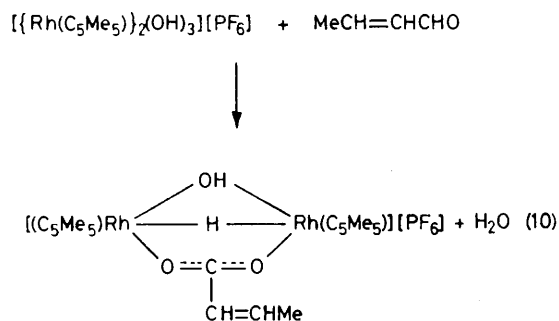


where the active mononuclear species would then be as shown in equation (11).

In our Communication⁵ on the mechanism, we proposed as the next step the co-ordination of the aldehyde to the metal. This was followed by *either* oxidative addition of RCO-H to the metal and attack by co-ordinated OH at the acyl carbon [equations (12) and (13)] *or* by a β -hydride migration from carbon to metal in a hydroxymetallated intermediate such as $[\text{M}\{\text{OCH}(\text{OH})\text{R}\}(\text{OH})(\text{H}_2\text{O})]$ [equations (14) and (15)]. In either



(R = H, Me, Et, or Ph)



* Note added at proof: However, we find that formic acid is itself unstable under these conditions.

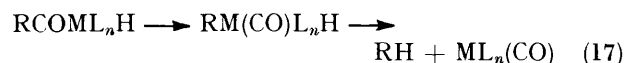
TABLE 6
Microanalytical and spectroscopic data for new complexes

Complex	Microanalysis ^a /%		¹ H N.m.r. spectrum ^b			I.r. spectrum ^c /cm ⁻¹
	C	H	Assignment	δ/p.p.m.	Signal (<i>J</i> /Hz)	
[{Rh(C ₆ Me ₆) ₂ H(O ₂ CH) ₂][PF ₆]	36.9 (37.1)	4.7 (4.7)	C ₆ Me ₆ hydride	1.77 -8.55	s t, <i>J</i> (Rh-H) 25	ν(CO) 1 580s, 1 353s ν(PF) 840vs
[{Rh(C ₆ Me ₆) ₂ H(O ₂ CET) ₂][PF ₆]	40.5 (40.6)	5.6 (5.4)	HCO ₂ C ₆ Me ₆ hydride	7.70 1.72 -9.03	t, <i>J</i> (Rh-H) 3 s t, <i>J</i> (Rh-H) 25	ν(CO) 1 567s, 1 420s ν(PF) 840vs
[{Rh(C ₆ Me ₆) ₂ H(O ₂ CPh) ₂][PF ₆]	47.5 (47.2)	4.6 (4.8)	CH ₂ CH ₃ C ₆ Me ₆ hydride	2.30 1.07 1.92 -8.37	q, <i>J</i> (H-H) 7 t, <i>J</i> (H-H) 7 s t, <i>J</i> (Rh-H) 25	ν(CO) 1 560s, 1 400s ν(PF) 840vs
[{Rh(C ₆ Me ₆) ₂ H(OH)(O ₂ CR)][PF ₆] ^d	40.0 (39.8)	5.1 (5.2)	Ph C ₆ Me ₆ hydride	7.70 1.93 -8.75	m s t, <i>J</i> (Rh-H) 25	ν(CO) 1 535s, 1 415s ν(CO) 3 580s ν(PF) 840vs
[{Ru(C ₆ Me ₆) ₂ (OH) ₃]Cl·4H ₂ O ^e	41.8 (42.1)	6.7 (6.9)	C ₆ Me ₆	1.52 ^f	s	
[{Ru(C ₆ Me ₆) ₂ (OH) ₃][PF ₆]·2H ₂ O	40.9 (40.7)	5.7 (5.6)	C ₆ Me ₆ OH, H ₂ O	2.02 2.94	s s	
[{Ru(C ₆ Me ₆) ₂ (O ₂ CMe) ₃][PF ₆]·H ₂ O	41.4 (41.6)	5.5 (5.5)	C ₆ Me ₆ O ₂ CMe	2.07	s	
[Ru(C ₆ Me ₆)(O ₂ CMe) ₂]·H ₂ O	48.1 (48.1)	6.6 (6.6)	H ₂ O C ₆ Me ₆ O ₂ CMe H ₂ O	2.90 2.14 1.97 2.70	s s s s	

^a Calculated values in parentheses. ^b In [2H₆]acetone. ^c Nujol mulls. ^d R = CH²=CH²-CH¹₃. ^e Found (calc.): Cl, 5.2 (5.2)%. ^f In CDCl₃.

case the product was a hydrido-carboxylate, which could either form the complexes isolated by dimerisation, or where the carboxylate could be displaced by another molecule of aldehyde. The latter is then reduced to alcohol or alkoxide by a hydrogen migration.

These steps have now become clearer in the light of further results. Although oxidative addition of aldehyde C-H bonds to electron-rich metal centres is well-established¹¹ and leads initially to acyl hydrides [equation (16)] these species in turn undergo carbonyl migration very easily and reductively eliminate to give the alkane [equation (17)].¹² Indeed, in some cases, the

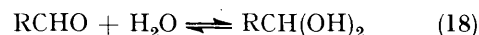


decarbonylation of aldehydes to alkanes can be made catalytic.¹³

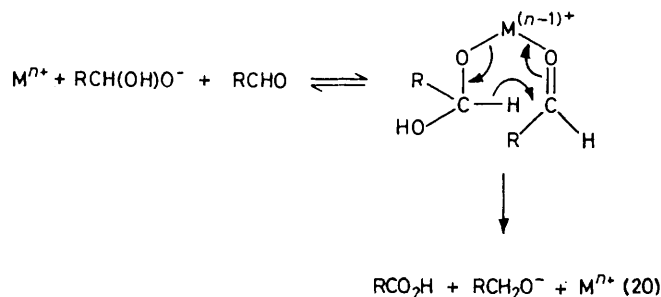
We may therefore expect any reaction in which an acyl metal hydride is formed by oxidative addition of an aldehyde to be very likely to yield some hydrocarbon. Despite numerous attempts, we have completely failed to find any in such reactions. For example, reactions of benzaldehyde gave no detectable (by g.c.) amounts of benzene. Further, quinoline-8-carboxaldehyde, which oxidatively adds easily to other rhodium complexes to give stable chelate complexes,^{11a} did not react at all under our conditions. Thus we conclude that an oxidative addition of aldehyde is *not* likely to be significant in these metal-catalysed reactions.

In water, aldehydes form the hydrates [equation (18)]. The extent of this reaction depends on R; thus

for acetaldehyde it is 58%, for propionaldehyde 41%, but butyraldehyde 33% in the form of the hydrate.¹⁴ Formaldehyde is essentially completely hydrated.



The classical Cannizzaro reaction is usually presumed to proceed *via* the anion of the hydrate [equation (19)] and to involve an intermolecular transfer of hydride from this anion (or the corresponding dianion) to a neutral aldehyde molecule.^{6,15} The existence of a 'cation effect' in the Cannizzaro reaction is well established, but it is generally accepted that the cation acts by binding both RCHO and RCH(OH)O⁻ to give a transition state where direct hydride transfer is facilitated [equation (20)].^{16,17}

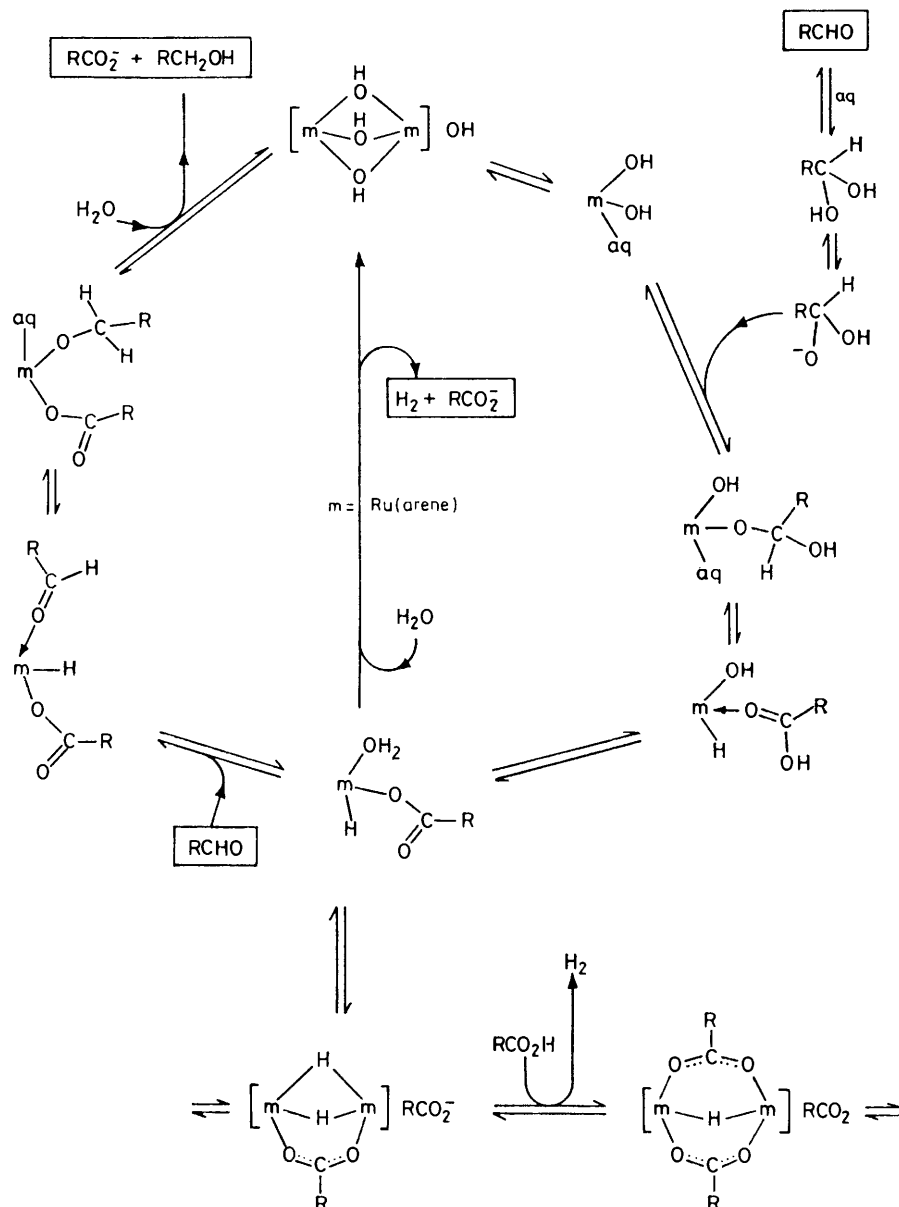


We propose that a similar process occurs in our transition-metal-catalysed reactions. The main difference is that the hydride transfer occurs in a stepwise manner *via* a metal hydride and that this is substantially faster than the 'direct' transfer in the non-catalysed Cannizzaro reaction.

The large acceleration that base causes is then again due to the need to form the hydrate anion.* However, in this case the anion is needed to facilitate a nucleophilic displacement of a ligand present on the metal. In a typical catalytic cycle the ligand displaced is most likely

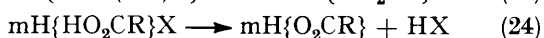
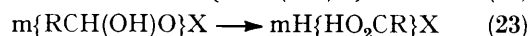
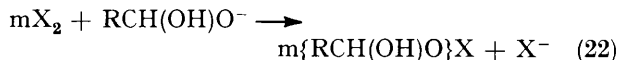
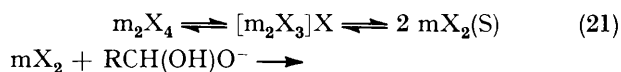
(23), a (fast) hydride transfer to the metal, is followed by loss of HX, equation (24).

Two things can happen at this point. The complex formed in reaction (24) may dimerise to give a di- μ -hydrido- μ -carboxylate complex [equation (25)]; such



SCHEME m = Rh(C₅Me₅), Ir(C₅Me₅), or Ru(arene); aq = x H₂O

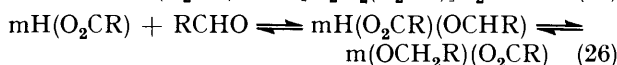
to be carboxylate. The rate-determining step of the reaction, which is first-order in aldehyde and half-order in the dinuclear catalyst, may therefore be represented by equations (21) (S = solvent) and (22). The next step



complexes are readily obtained from reaction mixtures when $m = Rh(C_5Me_5)$. Alternatively, the reaction sequence may proceed onwards by co-ordination of an aldehyde to the mononuclear metal species formed in reaction (24) which then undergoes a rapid hydride shift from metal to carbon [equation (26)]. This gives an

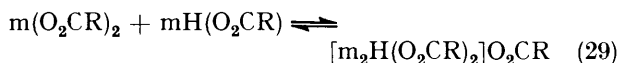
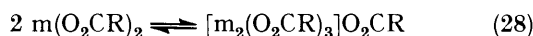
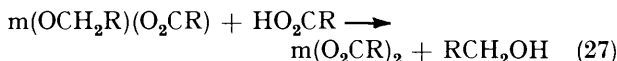
* The fact that the Cannizzaro reaction of benzaldehyde under alkaline conditions is also accelerated by catalyst shows that the reactive entity is not an enolate ion. On the contrary, such species react to give the aldol products by the normal base-induced reaction of aldehydes with α -CH groups.

alkoxide-carboxylate, which would be displaced by a suitable nucleophile $[\text{OH}^-, \text{H}_2\text{O}, \text{or RCH}(\text{OH})\text{O}^-]$ thus returning to the starting point of the cycle.



The whole postulated cycle is presented diagrammatically in the Scheme. In addition this also emphasises the relationship of the di- μ -hydrido-mono- μ -carboxylate and the mono- μ -hydrido-di- μ -carboxylate complexes. As mentioned above this depends on the metal and on the pH, the more acid pH favouring the more hydride-poor complexes. In the case of ruthenium, these hydrides are indeed so labile that they are not detectable under neutral or acid conditions and hydrogen gas is evolved. They appear to be more stable in basic solution, since the two halves of the cycle (carboxylate and alcohol production) are equally coupled there, and the competition between hydrogen production and alcohol formation is heavily weighted in favour of the latter.

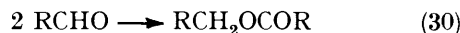
For rhodium the reaction probably does not go at all at pH low enough to generate significant amounts of hydrogen from a di- μ -hydrido-intermediate. In this case, therefore, there is presumably a different path by which the mono- μ -hydrido- (and hydride-free) complexes are generated. One such reaction may be represented by equations (27)–(29).



There is still a further complication in that we have shown⁸ that ethanol undergoes an essentially stoichiometric reaction with $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]^+$ to give a mixture of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{O}_2\text{CMe})_2\}]^+$ and $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}_2(\text{O}_2\text{CMe})\}]^+$. Other primary alcohols reacted similarly.⁸

The reason for the change of product with added ligand for the ruthenium reactions is not clear but possibly the intermediate hydrides may be more stabilised (towards acid attack) in species such as $[\text{Ru}(\text{arene})\text{H}(\text{O}_2\text{CR})(\text{PPh}_3)]$.

It is interesting to note that Yamamoto and co-workers¹⁸ found that under rigorously anhydrous conditions $[\text{RuH}_2(\text{PPh}_3)_4]$ and other ruthenium complexes converted aldehydes into the esters [equation (30)] in a Tishchenko type reaction. The mechanism of this re-



action is not known but an oxidative addition of RCO-H to a low-valent ruthenium complex, followed by transfer of the Ru-bound hydride to another co-ordinated aldehyde, has been proposed. Support for this came from the isolation of the acyl ruthenium complex $[\text{Ru}(\text{COEt})_2(\text{CO})_2(\text{PPh}_3)_2]$ from reactions with propionaldehyde.

EXPERIMENTAL

The compounds $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{Ru}(\text{acac})_3]$, $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$, and the supported metals Rh/alumina, Pt/alumina, and Pd/carbon were supplied by Johnson Matthey Ltd. The following complexes were prepared by standard literature methods: $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{Cl}_4\}]$,¹⁹ $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}\text{X}]$ ($\text{X} = \text{Cl}, \text{OH}, \text{and PF}_6$),^{3,4} $[\{\text{Ir}(\text{C}_6\text{Me}_6)_2\text{Cl}_4\}]$,¹⁸ $[\{\text{Ir}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}\text{X}]$ ($\text{X} = \text{O}_2\text{CMe}, \text{OH}, \text{and PF}_6$),^{3,4} $[\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4]$,²⁰ and $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2\text{Cl}_4\}]$.²⁰ New complexes were prepared as described below; microanalytical and spectroscopic data were collected in Table 6. Microanalyses were carried out by the University of Sheffield Microanalytical Service; ¹H n.m.r. spectra were determined on Perkin-Elmer R-12B (60 MHz) and R-34 (220 MHz) spectrometers. All reactions were carried out under an atmosphere of nitrogen. Analyses of the catalytic reactions were carried out by g.c. using a Pye-Unicam 104 chromatograph (FID detector, N₂ carrier gas) usually on a 6-ft Poropak Q column, or by ¹H n.m.r. spectroscopy (R-12B).

Tri- μ -hydroxo-bis(hexamethylbenzeneruthenium) Chloride Tetrahydrate.—Sodium hydroxide (1.5 g) in water (20 cm³) was added to a suspension of $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2\text{Cl}_4\}]$ (1.0 g, 1.5 mmol) in water (80 cm³) and the reaction mixture was stirred (20 °C, 2 h). The yellow solid which had formed was filtered off and dried *in vacuo*. Yield, 778 mg (85%).

Tri- μ -hydroxo-bis(hexamethylbenzeneruthenium) Hexafluorophosphate Dihydrate.—Silver hexafluorophosphate (100 mg, 0.4 mmol) was added to a suspension of $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}\text{Cl}]$ (200 mg, 0.35 mmol) in acetone-water (2 : 1, 60 cm³) and the mixture was stirred (20 °C, 15 h). It was then filtered through 'Hyflosupercel' filter-aid. The filtrate was reduced in volume and the bright yellow precipitate was filtered off and dried *in vacuo*. Yield, 195 mg (77%).

$[\{\text{Ru}(\text{C}_6\text{Me}_6)(\text{O}_2\text{CMe})_2 \cdot \text{H}_2\text{O}\}_n]$.—A suspension of $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2\text{Cl}_4\}]$ (100 mg, 0.15 mmol) and silver acetate (1.08 g, 6.47 mmol) in benzene (20 cm³) was heated under reflux with stirring for 3 h. The mixture was allowed to cool to 20 °C, filtered, and the residue was washed with benzene. The combined filtrates were evaporated to dryness and crystallised from benzene-hexane to yield yellow crystals of $[\{\text{Ru}(\text{C}_6\text{Me}_6)(\text{O}_2\text{CMe})_2 \cdot \text{H}_2\text{O}\}_n]$. Yield, 70 mg (61%).

Tri- μ -acetato-bis(hexamethylbenzeneruthenium) Hexafluorophosphate Hydrate.—Silver hexafluorophosphate (20 mg, 0.08 mmol) was added to a suspension of $[\{\text{Ru}(\text{C}_6\text{Me}_6)(\text{O}_2\text{CMe})_2 \cdot \text{H}_2\text{O}\}_n]$ in water (10 cm³). The reaction mixture was stirred (20 °C, 3 h), filtered through 'Hyflosupercel' filter-aid and the filtrate was evaporated to dryness to give a residue which was crystallised from acetone-diethyl ether to give yellow crystals of $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{O}_2\text{CMe})_3\}[\text{PF}_6] \cdot \text{H}_2\text{O}]$. Yield 40 mg (72%).

Di- μ -formato- μ -hydrido-bis(pentamethylcyclopentadienyl-rhodium) Hexafluorophosphate.—Aqueous formaldehyde (40%, 0.1 cm³, 1.33 mmol) was added to $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}[\text{PF}_6]]$ (150 mg, 0.20 mmol) in water (20 cm³) and the resulting solution was stirred (20 °C, 5 h). The precipitate was filtered off, dried *in vacuo*, and recrystallised from acetone-diethyl ether to give the product as red crystals. Yield, 100 mg (63%). *Di- μ -acetato- μ -hydrido-bis(pentamethylcyclopentadienylrhodium) hexafluorophosphate* (68% yield) and *μ -hydrido-di- μ -propionato-bis(pentamethylcyclopentadienylrhodium) hexafluorophosphate* (79% yield) were prepared similarly.

Di- μ -benzoato- μ -hydrido-bis(pentamethylcyclopentadienyl-

rhodium) Hexafluorophosphate.—Benzaldehyde (142 mg, 1.34 mmol) was added to $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}][\text{PF}_6]$ (150 mg, 0.21 mmol) in acetone–water (1 : 1, 20 cm³) and the resulting solution was stirred (20 °C, 5 h). The red precipitate was filtered off, dried *in vacuo*, and recrystallised from acetone–diethyl ether. Yield, 110 mg (57%).

μ-Crotonato-μ-hydrido-μ-hydroxo-bis(pentamethylcyclopentadienylrhodium) Hexafluorophosphate.—Crotonaldehyde (135 mg, 1.92 mmol) was added to $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}][\text{PF}_6]$ (350 mg, 0.48 mmol) in water (20 cm³) and stirred (20 °C, 20 h). The orange precipitate was filtered off, dried *in vacuo*, and recrystallised from acetone–diethyl ether. Yield, 255 mg (73%).

μ-Acetato-di-μ-hydrido-bis(pentamethylcyclopentadienylrhodium) Hexafluorophosphate.—A solution of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}][\text{PF}_6]$ (100 mg, 0.14 mmol) in aqueous acetaldehyde (0.5% v/v, 200 cm³) was allowed to stand (50 °C, 5 d). The solution was cooled and the violet crystals which had precipitated were filtered off and dried *in vacuo*. Yield, 30 mg (31%).

μ-Acetato-di-μ-hydrido-bis(pentamethylcyclopentadienyliridium) Hexafluorophosphate.—A solution of the complex $[\{\text{Ir}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}(\text{O}_2\text{CMe})\cdot 14\text{H}_2\text{O}$ (137 mg, 0.16 mol) in aqueous acetaldehyde (10% v/v, 5 cm³) was allowed to stand (45 °C, 16 h). The solution was cooled and stirred as potassium hexafluorophosphate (60 mg, 0.32 mmol) in water (1 cm³) was added. The brown precipitate formed was filtered off, washed with water (5 cm³), and dried *in vacuo*. Yield, 80 mg (38%). An analytical sample was crystallised from acetone–diethyl ether.

Reaction of $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}][\text{PF}_6]$ with Acetaldehyde.—Acetaldehyde (0.5 cm³, 9.0 mmol) was added to a suspension of $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}][\text{PF}_6]$ (100 mg, 0.14 mmol) in water (10 cm³). The reaction mixture was stirred (20 °C, 2 h), filtered, and evaporated to dryness to give a yellow solid. Yield, 74 mg. The ¹H n.m.r. spectrum showed this to contain at least 90% of $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{O}_2\text{CMe})_3\}][\text{PF}_6]$.

Reaction of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{OH}$ with Acetaldehyde.—A solution of $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{OH}$ (700 mg, 1.17 mmol) in water (25 cm³) was added to a solution of acetaldehyde (16.8 cm³, 13.2 g, 0.30 mol) in water (143 cm³) and the reaction solution was kept at 53 ± 0.5 °C in a thermostatted bath. Aliquots (17 cm³) were removed at intervals, evaporated under reduced pressure to 5 cm³, and potassium hexafluorophosphate (50 mg, 0.27 mmol) in water (0.5 cm³) was added. The hexafluorophosphate salts thus obtained were filtered off, analysed by ¹H n.m.r. spectroscopy, and found to be a mixture of the two complexes $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}_2(\text{O}_2\text{CMe})\}][\text{PF}_6]$ and $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2\text{H}(\text{O}_2\text{CMe})_2\}][\text{PF}_6]$. The ratios formed were 0.3 (5 min), 0.6 (1 h), 1.1 (3 h), 1.2 (7 h), and 0.3 : 1 (19 h). The yield of product decreased slowly from 49 mg (1 h) to 30 mg (19 h). After 6 days the reaction solution was evaporated to dryness and the major product of the mixture was shown to be $[\{\text{Rh}(\text{C}_5\text{Me}_5)(\text{O}_2\text{CMe})_2\cdot\text{H}_2\text{O}\}_n]$.

Catalytic Conversion of Aldehydes to their Corresponding Alcohols and Carboxylic Acids.—Most reactions were carried out in 10-cm³ sample tubes. The appropriate amount of catalyst was weighed directly into the sample tube, a solution of aldehyde in water was added, the tubes were made air-tight with a silicone Subaseal and then placed in a thermostatted bath. The reaction product was analysed by extracting 2 μl of reaction solution through the Subaseal with a syringe and injecting the solution directly onto a g.l.c. column (Poropak Q, 190 °C).

The reactions at the higher temperatures and those for kinetic analysis were carried out in sealed ¹H n.m.r. tubes and the progress of the reaction was monitored by ¹H n.m.r. spectroscopy.

The gas evolved from the reaction of acetaldehyde with ruthenium complexes was identified as hydrogen by comparison with the g.c. retention time of a genuine sample using a 6-ft molecular-sieve 5A column at 30 °C.

The reactions under basic conditions were carried out similarly to those under neutral conditions. For example, $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{Cl}$ (0.08 mmol) dissolved in aqueous sodium hydroxide (0.5 mol dm⁻³, 4 cm³, pH 12.8) was added to acetaldehyde (94 mmol) in water (8 cm³), at 20 °C. The solution turned red almost immediately and the pH dropped to 6 within 10 s and then continued to drop further, but only very slowly. Analysis of the solution by g.c. and ¹H n.m.r. spectroscopy was carried out as soon as practicable (3 min). An aliquot of the reaction was quenched after 15 s by addition of hydrochloric acid; analysis showed that the conversion had proceeded to ca. 90% of that determined after 3 min in base.

Reaction Kinetics.—The rates (under neutral conditions) of the acetaldehyde disproportionation were measured using varying amounts of catalyst, $[\{\text{Rh}(\text{C}_5\text{Me}_5)_2(\text{OH})_3\}]\text{Cl}\cdot 4\text{H}_2\text{O}$ or $[\{\text{Ru}(\text{C}_6\text{Me}_6)_2(\text{OH})_3\}]\text{Cl}\cdot 4\text{H}_2\text{O}$, and acetaldehyde (10.7 mmol) in water (6 cm³) at 53 °C. From the results presented in Figure 1 it will be evident that the rate becomes constant once the initial fast process is over and the system has reached an equilibrium pH. Plots of time against $(\log [\text{acetaldehyde}_0] - \log [\text{acetaldehyde}_t])$, where the subscripts 0 and *t* refer to time zero and time *t* respectively, gave straight lines (Figure 2) showing the reaction to be first-order in aldehyde. A plot of the rates against $[\text{catalyst}]^1$ gave a curve but a plot against $[\text{catalyst}]^{\frac{1}{2}}$ gave a straight line (Figure 3).

We thank the S.R.C., BP Chemicals Limited, and Johnson Matthey for support and for the award of CASE Studentships (to J. C. and A. N.) and Dr. W. Schäfer (Chemische Werke Hüls) for a gift of compounds.

[1/621 Received, 16th April, 1981]

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