

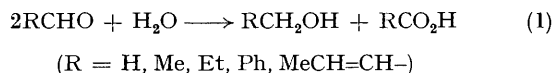
Homogeneously Catalysed Disproportionation of Acetaldehyde into Ethanol and Acetic Acid

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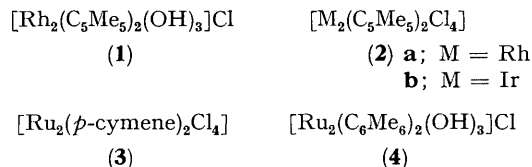
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Summary The complexes $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{OH})_3]^+$ (**1**), $[\text{M}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$, $\text{M} = \text{Rh}$ or Ir , $[\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4]$, and $[\text{Ru}_2(\text{C}_6\text{Me}_6)_2(\text{OH})_3]^+$ all catalyse the disproportionation of acetaldehyde to acetic acid and ethanol in water in the absence of base, and other aldehydes react similarly; rhodium hydride complexes can be isolated from the reactions involving (**1**).

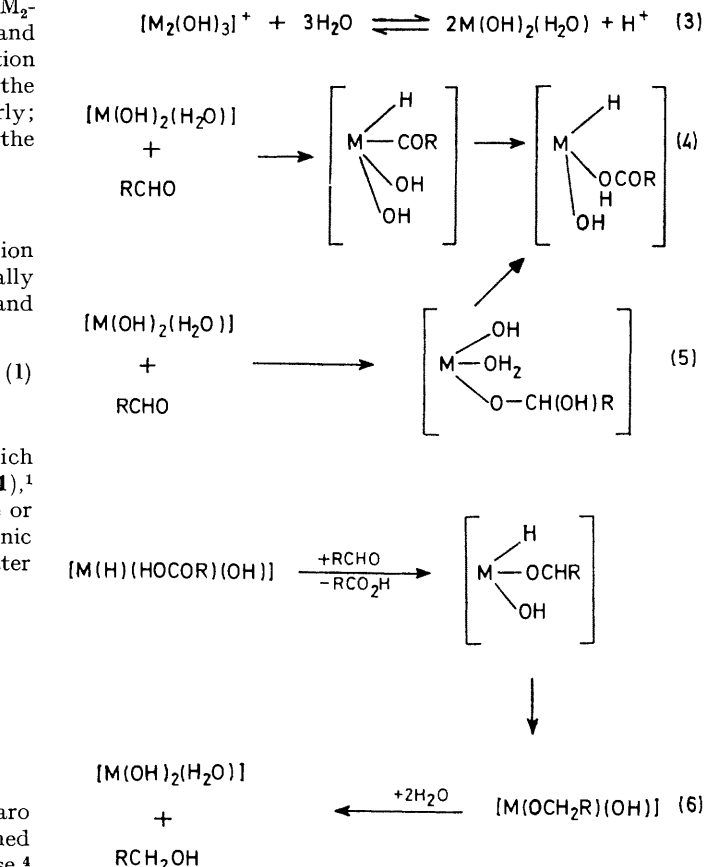
We report a new type of homogeneously catalysed reaction in which aldehydes are converted, in water under essentially neutral conditions, into the corresponding alcohols and carboxylic acids (equation 1).



The reaction is catalysed by a variety of half-sandwich complexes of Rh, Ir, and Ru including the complexes (**1**),¹ (**2**),¹ (**3**),² and (**4**).³ It proceeds at ambient temperature or above and can also be carried out in mixed aqueous-organic solvents for aldehydes or catalysts which are poorly water soluble.



The reaction is reminiscent of the well known Cannizzaro reaction (equation 2) in which aldehydes are transformed into alcohols and carboxylic acid *salts* in aqueous base.⁴ However the Cannizzaro reaction does not usually occur in the absence of base or for aldehydes bearing a hydrogen α to the $-\text{CHO}$ group since the competing aldol condensation is very much faster.



SCHEME. M = Rh, C₅Me₅, etc.†

In contrast, the metal catalysed reactions readily give, for example, ethanol and acetic acid from acetaldehyde (Table).

TABLE^a

Catalyst (0.04 mmol)	Aldehyde (mmol)	Reaction time/h	Temp./°C	EtOH formed		HOAc formed	
				(mmol)	T/N ^b	(mmol)	T/N ^b
(1)	MeCHO (3.6)	23	22	0.35	9	0.35	9
(1)	MeCHO (17.8)	16	50	2.5	63	2.5	63
(1) ^c	MeCHO (372)	216	45	93	1160	103	1291
(2a)	MeCHO (17.8)	16	50	1.7	43	1.6	40
(2b)	MeCHO (10.7)	20	50	1.4	35	1.5	38
(3)	MeCHO (10.7)	20	50	1.7	43	3.9	97
(4)	MeCHO (10.7)	20	50	1.6	40	5.8	144
(4) ^c	MeCHO (372)	216	45	37	462	192	2395
				PrOH		EtCO ₂ H	
(1)	EtCHO (1.7)	72	50	0.6	15	0.6	14
(3)	EtCHO (1.7)	72	50	0.3	8	0.8	20

^a A 10% v/v aqueous solution of acetaldehyde (or 2% v/v of propionaldehyde) was allowed to react with the metal complex; products were analysed by v.p.c. and n.m.r. spectroscopy. ^b T/N = turnover number = number of moles of product formed per mole of catalyst. ^c 0.08 mmol of catalyst.

† This is an idealised Scheme; in practice O₂CR and Cl can act as ligands in place of OH.

When the reaction of acetaldehyde is carried out with an aqueous solution of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{OH})_3][\text{PF}_6]$ a red crystalline complex, which we have identified as the known⁵ $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{H}(\text{OAc})_2][\text{PF}_6]$, is rapidly precipitated. Similar complexes are obtained from other aldehydes. We therefore propose that the hydrogen transfer that occurs in reaction (1) takes place *via* a metal hydride. We also find that the reaction of acetaldehyde catalysed by complex (1) [and by complex (4)] is first order in aldehyde and half-order in catalyst. This suggests that the dinuclear complex dissociates prior to reaction (equation 3) and that the reaction with the aldehyde occurs at a single metal atom.

Two reaction paths may be proposed for the interaction of the aldehyde with the metal, one involving an oxidative addition of RCO-H (equation 4), and the other a hydroxy-metallation followed by a β -hydride elimination (equation 5).

In either case the resultant metal hydride can then reduce the aldehyde (equation 6).

Although the reactions (4/5) and (6) are equally coupled for the rhodium and iridium catalysts they need not be so. Thus, for example, in the reactions of acetaldehyde with the ruthenium complexes (3) and (4) more acetic acid than ethanol is formed and hydrogen is evolved. No metal hydrides were detected in these reactions and $[\text{Ru}_2(\text{C}_6\text{Me}_6)(\text{OH})_3][\text{PF}_6]$ gave $[\text{Ru}_2(\text{C}_6\text{Me}_6)_2(\text{OAc})_3][\text{PF}_6]$.

Under these conditions a variety of other types of metal complexes {including MCl_3 hydrate ($\text{M} = \text{Rh}, \text{Ru}$), $[\text{Rh}_2(\text{OAc})_4]$, $[\text{Ru}(\text{acac})_3]$ ($\text{Hacac} = \text{acetylacetonone}$), and $[\text{Ru}_2(\text{Me}_2\text{SO})_6\text{Cl}_3]\text{Cl}$ } showed only very low activity or were totally inactive.

We thank the S R C for support and B P Chemicals Ltd and Johnson Matthey Co Ltd for CASE awards (to J C and A N).

(Received, 19th October 1979, Com 1115)

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² M A Bennett and A K Smith *J C S Dalton*, 1974, 233

³ Prepared from $[\text{Ru}_2(\text{C}_6\text{Me}_6)_2\text{Cl}_4]$ M A Bennett, T N Huang, A K Smith, and T W Turney, *J C S Chem Comm*, 1978, 582

⁴ T A Geissman, *Org Reactions*, 1944, **2**, 94, see also C G Swain, A L Powell, W A Sheppard and C R Morgan, *J Amer Chem Soc*, 1979, **101**, 3576

⁵ C White, A J Olver, and P M Marthls, *J C S Dalton*, 1973, 1901