

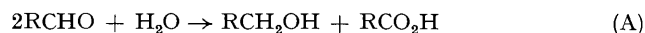
Formaldehyde as a Hydrogen-donor to Aldehydes and Ketones in Metal-catalysed Reactions in Water

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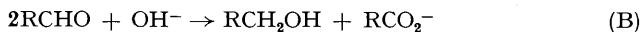
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Summary Formaldehyde reacts with other aldehydes (RCHO) (or ketones) in water in the presence of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$ to give mainly RCH_2OH ; the reaction is substantially accelerated by alkali.

We have previously reported that the complexes $[\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4]$,¹ $[\text{Ir}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$,¹ and particularly $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$,² are catalysts for the disproportionation of aldehydes to the corresponding alcohols and carboxylic acids in water in the pH range 4–7 (equation A).^{3,4}



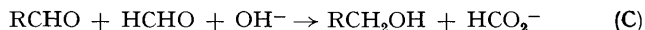
We now report (i) that all these reactions are considerably accelerated (by a factor of *ca.* 10^5 , Table, reactions 1 and 2) in aqueous alkali (pH > 12.5), and (ii) that hydrogen can be transferred between different aldehydes and that selectivity is manifested. Under basic conditions the reaction (A) becomes stoichiometric in added alkali and is now a metal-catalysed Cannizzaro reaction (equation B).



† HCO_2H decomposes under the reaction conditions.

In contrast with the normal Cannizzaro reaction, however, it also works for aldehydes such as acetaldehyde. The metal-catalysed reaction is so fast that the more usual base-induced aldol condensation can be entirely repressed. All catalysts gave a 1:1 ratio of alcohol to carboxylate.

Formaldehyde (and also acetaldehyde, but less effectively) can also readily transfer hydrogen to other aldehydes and ketones under the influence of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl}$ or the other catalysts mentioned. These reactions again proceed rather slowly under neutral aqueous conditions (Table, reactions 7–10) but are vastly accelerated in base (reactions 3–6). The reactions show selectivity towards formation of the alcohols [derived from RCHO (or R_2CO), equations (C) and (D)] and this will clearly be further improved when the optimisation studies, currently in progress, are complete.



Although metal-catalysed hydrogen-transfer reactions are well known^{5,6} these appear to be the first reported in

TABLE. Hydrogen-transfer reactions catalysed by $[\text{Rh}_2(\text{C}_6\text{Me}_6)_2(\text{OH})_3]\text{Cl}\cdot 4\text{H}_2\text{O}$.

Reaction	Conditions ^b	Time/min	Temp./°C	Reactants (mmol)	Products (mmol)
1	A	2760	22	MeCHO (10.7)	MeCH ₂ OH (0.6) + MeCO ₂ H (0.7)
2	B	<0.17	20	MeCHO (10.7)	MeCH ₂ OH (1.7) + MeCO ₂ ⁻ (1.7)
3	C	10	20	MeCHO (2.3) HCHO (2.3)	MeCH ₂ OH (2.0) + MeCO ₂ ⁻ (0.4) MeOH (0.3) + HCO ₂ ⁻ (2.0)
4	C	3	20	EtCHO (0.46) HCHO (0.46)	EtCH ₂ OH (0.42) + EtCO ₂ ⁻ (trace) MeOH (0.06) + HCO ₂ ⁻ (0.42)
5	C	10	20	Me ₂ CO (2.3) HCHO (2.3)	Me ₂ CHOH (0.5) MeOH (0.6) + HCO ₂ ⁻ (1.6)
6	C	10	20	Me ₂ CO (2.3) MeCHO (2.3)	Me ₂ CHOH (0.2) MeCH ₂ OH (1.0) + MeCO ₂ ⁻ (1.2)
7	A	1440	50	MeCHO (10.7) HCHO (10.7)	MeCH ₂ OH (5.6) + MeCO ₂ H (1.2) MeOH (trace) + HCO ₂ H (trace)
8	A	1440	50	EtCHO (2.5) HCHO (2.5)	EtCH ₂ OH (1.3) + EtCO ₂ H (0.3) MeOH (trace) + HCO ₂ H (trace)
9	A	1440	50	Me ₂ CO (10.7) HCHO (10.7)	Me ₂ CHOH (1.9) MeOH (trace) + HCO ₂ H (trace)
10	A	1440	50	Me ₂ CO (10.7) MeCHO (10.7)	Me ₂ CHOH (0.5) MeCH ₂ OH (2.5) + MeCO ₂ H (3.3)

^a All using 0.04 mmol catalyst; analysis by g.c. (Poropak Q) and ¹H n.m.r. spectroscopy.

^b A: In water (6 cm³); B: in water (2 cm³) and aqueous sodium hydroxide (0.5 M; 6 cm³). C: catalyst in aqueous sodium hydroxide (0.5 M; 5 cm³) was added to aldehydes in water (1 cm³).

which an aldehyde (formaldehyde) is used as source of hydrogen. The importance of such reactions lies in the fact that they can frequently be made to occur under milder conditions than conventional hydrogenations.

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