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Preliminary communication

METHANOL AS HYDROGEN-DONOR IN HOMOGENEOUSLY CATALYSED REACTIONS

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Summary

Methanol in the presence of a number of soluble complexes of Rh, Ru, Ir or Os will hydrogenate organic functional groups, especially ketones and activated olefins. Methyl formate is also formed.

Although hydrogen (H_2) is the obvious reagent for catalytic hydrogenations, it suffers from a number of disadvantages. It is not very easily handled, is quite expensive and has only low solubility in organic solvents. Thus there has been wide interest in organic molecules which can act as hydrogen donors; two of the most popular have been formic acid and isopropanol [1].

Another in situ source of hydrogen which has enormous potential and which has so far been little exploited is methanol. Not only is methanol very cheap today and likely to remain so [2], since it can be made from a variety of feedstocks, but each mole of methanol can, at least in principle, give rise to two of hydrogen by a reversal of its formation reaction,

$$CH_3OH \rightarrow 2H_2 + CO$$

Thus one litre of methanol could have a hydrogenating ability equivalent to 49.4 mol of H_2. With a suitable hydrogen acceptor the rather unfavourable thermodynamics (ΔH^{298} + 92 kJ mol^{-1}) [3] could be overcome; alternatively, only a part of the available hydrogen could be used in a thermodynamically more favourable process.

We have begun an examination of the potential of methanol to act as a hydrogen donor towards a variety of organic substrates when catalysed by soluble transition metal complexes. There have only been scattered reports of such reactions in the literature [4—6] and it may be inferred that a further difficulty in using methanol is a high kinetic barrier to reaction [6].

Our preliminary results are summarised in Table 1 from which it may be seen

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TABLE 1

HYDROGEN DONOR ACTIVITY OF METHANOL CATALYSED BY TRANSITION METAL COMPLEXES

Catalyst [a] (mmol)	Time temperature (h/°C)	Substrate (mmol)	Product (mmol (T/N)) [b]	Methyl formate (mmol (T/N)) [b]
A (0.08)	19/150	Cyclohexanone (8)	Cyclohexanol 1.1 (14)	1.3 (16)
B (0.5)	5/150	Cyclohexanone (48)	Cyclohexanol 4.1 (8)	2.1 (4)
B (0.5)	5/150	Buten-3-one (48)	Butan-2-one 25 (52)	12 (25)
C (0.08)	18/145	Cyclohexanone (8)	Cyclohexanol 5.4 (67)	2 (25)
C (0.08)	18/145	4-Methylpent-3-en-2-one (8)	4-Methylpentan-2-one 7.2 (90)	2.8 (35)
C (0.08)	18/145	4-t-Butylcyclohexanone (8)	4-t-Butylcyclohexanol 6.2 (77) (*trans*/*cis* 4/1)	0.7 (9)
C (0.08)	18/155	Butan-2-one (8)	Butan-2-ol 2.1 (27)	2.9 (36)
D (0.08)	18/150	Cyclohexanone (8)	Cyclohexanol 6.5 (81)	2.5 (30)
E (0.08)	18/141	Cyclohexanone (8)	Cyclohexanol 2.0 (25)	[c]
F (0.08)	18/150	Cyclohexanone (8)	Cyclohexanol 1.2 (15)	[c]

[a] Catalysts: A, $[(C_5Me_5Rh)_2Cl_4]$; B, $[(C_5Me_5Rh)_2(OH)_3]Cl$; C, $[Ru(PPh_3)_3Cl_2]$; D, ruthenium trichloride hydrate + 3 equivalents PPh_3; E, $OsH(Br)(CO)(PPh_3)_3$; F, $[(C_5Me_5Ir)_2Cl_4]$. [b] T/N, turnover number: moles of product per mol of catalyst; estimated by quantitative GC on Carbowax 20. [c] Trace.

for cyclohexanone as hydrogen acceptor, the complexes showing significant catalytic activity at 150°C for the formation of cyclohexanol included $[(C_5Me_5Rh)_2Cl_4]$, $[(C_5Me_5Rh)_2(OH)_3]^+$, $[(C_5Me_5Ir)_2Cl_4]$, $[OsH(Br)CO(PPh_3)_3]$, and $[Ru(PPh_3)_3Cl_2]$ (I)*, or its equivalent, ruthenium trichloride hydrate plus three equivalents of triphenylphosphine. Other ketones were also reduced by methanol plus I, as were benzaldehyde and activated olefins (e.g., mesityl oxide which gave 4-methylbutan-2-one). Cyclohexene was only reduced in trace amount under these conditions.

The other product from these reactions was methyl formate**, and the reduction of ketones by methanol may thus be described by the equation,

$$2R_2C{=}O + 2CH_3OH \rightarrow 2R_2CHOH + CH_3O_2CH$$

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*Complex I has been widely used for catalysing hydrogen transfer from higher alcohols [1].

**A related series of reactions was carried out using similar substrates and catalysts but with ethanol as hydrogen donor. These required milder conditions and gave higher turnovers; acetaldehyde was the dehydrogenation product.

References

1 I.S. Kolomnikov, V.P. Kukolev, and M.E. Volpin, Russ. Chem. Rev. (Engl. Trans.), 43 (1974) 399; G. Brieger and T.J. Nestrick, Chem. Rev., 74 (1974) 567. See also: Y. Sasson and J. Blum, J. Org. Chem., 40 (1975) 1887 and G. Speier and L. Markó, J. Organomet. Chem., 210 (1984) 253.
2 See, for example, Chem. Eng. News, June 20, 1983, p. 20.
3 D.F. Stull, E.K. Westrum, and G.C. Sinke, Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
4 J.C. Bailar, and H. Itatani, J. Am. Chem. Soc., 89 (1967) 1592 and 1600; J. Am. Oil Chem. Soc., 43 (1966) 337, 44 (1967) 147.
5 J.M. Landesberg, L. Katz, and C. Olsen, J. Org. Chem., 37 (1972) 930.
6 H. Iamai, T. Nishiguchi, and K. Fukuzumi, J. Org. Chem., 39 (1974) 1622.