Studies Towards the Homogeneously Catalysed Hydration of Ethylene to Ethanol

By John Cook and Peter M. Maitlis*
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary $HOCH_2CH_2HgX$ (**1**; X = Cl) in aqueous base is catalytically decomposed to ethanol and acetate by $[Rh_2(C_5Me_5)_2(OH)_3]Cl\cdot 4H_2O$ (**2**); direct reaction of ethylene with $Hg(OAc)_2$–complex (**2**) in the presence of base also yields comparable amounts of ethanol, some acetaldehyde also being formed.

The hydration of ethylene to ethanol is a commercially important reaction which is usually carried out heterogeneously (at 200—300 °C and 50—70 atm) over an acidic catalyst, typically a phosphoric acid supported on silica.[1] We have been interested in finding a homogeneously catalysed process for this reaction and now report our first results.

In the hydroxymetallation reaction, ethylene (and other olefins) are converted into β-hydroxyethylmetal complexes[2] and mercury(II) salts, for example, readily form stable complexes such as (**1**) [equation (1)].[3,4] The stoicheiometric reduction of (**1**) to ethanol (using, for example, sodium amalgam, borohydride, *etc.*) has long been known[3,5] but no catalytic decomposition of (**1**) to ethanol has so far been reported.

$$C_2H_4 + H_2O + HgX_2 \rightleftharpoons \underset{(\mathbf{1})}{HOCH_2CH_2HgX} + HX \qquad (1)$$

We find that a solution of (**1**, X = Cl) in 2 M NaOH reacts with catalytic amounts of, for example, $[Rh_2(C_5Me_5)_2(OH)_3]Cl\cdot 4H_2O$[6] (**2**), to give 0·12—0·15 equiv. of ethanol per equiv. of (**1**, X = Cl) (Table); the remaining organic material was largely acetate together with some acetaldehyde.† Metallic mercury was precipitated.

Exactly analogous results were obtained when ethylene was passed into aqueous solutions of mercury(II) acetate and catalytic amounts of complex (**2**) after addition of base; presumably (**1**, X = OAc) was formed *in situ*. Analysis again showed the production of *ca.* 0·12 equiv. of ethanol per equiv. of mercury salt. Both sets of reactions were catalytic in complex (**2**) (Table).

Table. Yields of Ethanol.

[HgXY]/mol (×10⁵)	[complex (**2**)] mol (× 10⁵)	[EtOH]/mol (× 10⁵)	$\frac{[EtOH]}{[HgXY]}$	$\frac{[EtOH]}{[complex\ (2)]}$
5[a]	5	0·7	0·14	0·1
10[a]	5	1·9	0·19	0·4
50[a]	5	8	0·16	1·6
180[a]	5	27	0·15	5·4
4[b]	4	0·4	0·10	0·1
50[b]	4	8	0·16	2·0
100[b]	4	13	0·13	2·8
203[b]	4	28	0·14	7·0

[a] Using $HOCH_2CH_2HgCl$ in 4 ml 2 M NaOH solution at 3—5 °C. [b] Using $Hg(OAc)_2$ in 2 ml water. Ethylene was bubbled through the solution for 1·5 h at 20 °C and 1 atm at a rate of *ca.* 1 l h^{-1}, and then 2 ml of 2 M NaOH solution added.

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† Ethanol and acetaldehyde were identified by g.l.c. retention times and peak enhancement, g.l.c.–mass spectrometry, and n.m.r. spectroscopy; acetate was shown to be present by n.m.r. spectroscopy.

Studies to determine the mechanism and the scope of the reaction are in hand but for the moment we note that it is not limited to the formation of ethanol from ethylene. Thus we have found that propylene reacts with $Hg(OAc)_2$—$[Rh_2(C_5Me_5)_2(OH)_3]Cl{\cdot}4H_2O$ in water to give some propan-2-ol as well as acetone and that the same catalyst system in ethanol gives diethyl ether when treated with ethylene.

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