Rhodium-catalysed Decomposition of Hydroxymercurated Ethylene to Ethanol and Acetate

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2-Hydroxyethylmercury complexes dissolved in aqueous sodium hydroxide are catalytically decomposed by $[\{Rh(C_5Me_5)\}_2(OH)_3]Cl$ and related complexes to ethanol (14—18%), acetate (82—86%), and metallic mercury. Some hydrogen is also formed showing that water acts as an oxidiser in this reaction sequence. It is proposed that two decomposition paths co-exist one (*ca.* 30%) giving acetaldehyde, which then disproportionates into equal amounts of ethanol and acetate by a known process, and the other (*ca.* 70%) leading directly to acetate and hydrogen. Mechanisms are suggested. Propylene gives acetone (82%) and propan-2-ol (2%) by a similar route *via* 2-hydroxypropylmercury complexes, but 2-ethoxy-ethyl or -propyl complexes do not react.

The hydration of ethylene to ethanol, $C_2H_4 + H_2O \longrightarrow C_2H_5OH$, is a very important commercial process. However, it suffers from the serious disadvantage that, as is normally practised, it requires rather stringent conditions, especially high temperature. Typically the reactions are carried out in the gas phase at 200—300 °C and 50—70 atm pressure (atm = 101 325 N m^{-2}) over acidic catalysts, often phosphoric acid over a porous inert support.[1] The stringent conditions are required, despite the more favourable thermodynamics of the process at low temperatures ($\Delta G^\circ = -8$ kJ mol^{-1} at 25 °C and +18 kJ mol^{-1} at 227 °C [2]), because the first step, protonation of the olefin, involves formation of the unstabilised primary carbonium ion, $CH_3CH_2^+$. A lower temperature route from ethylene to ethanol involving different chemistry would therefore be of considerable interest.

Our first thoughts centred around the possibility of constructing a cycle using the well known mercuration of ethylene to 2-hydroxyethylmercury [equation (i)],[3] followed by a more speculative transmetallation [equation (ii)] and a cleavage of the resultant m–C bond [equation (iii)]. A route such as this would be especially attractive for X = OH which was the reason for trying our pentamethylcyclopentadienyl-rhodium and -iridium hydroxy complexes[4] and their hexamethylbenzeneruthenium analogues.[5,6]

$$C_2H_4 + H_2O + HgX_2 \longrightarrow HOCH_2CH_2HgX + HX \quad \text{(i)}$$

$$HOCH_2CH_2HgX + mX \longrightarrow HOCH_2CH_2m + HgX_2 \quad \text{(ii)}$$

$$HOCH_2CH_2m + HX \longrightarrow HOCH_2CH_3 + mX \quad \text{(iii)}$$

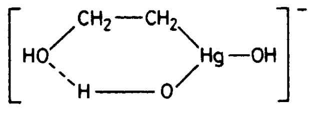
Our initial results showed that we had actually succeeded in accomplishing this reaction, although with rather low selectivity. However, further investigation has revealed that the ethanol and acetate obtained from reaction of 2-hydroxyethylmercury complexes with $[\{Rh(C_5Me_5)\}_2(OH)_3]^+$ [7] are the result of a very complex series of redox processes. This forms the subject of the present paper.

Results and Discussion

2-Hydroxyethylmercury chloride (1) was prepared by the well known reaction of mercury(II) chloride and ethylene in aqueous base.[8] The complex (1) is very insoluble except in aqueous sodium hydroxide solution in which it readily dissolves to give a clear solution presumably containing '$HOCH_2CH_2HgOH$'. The ^1H n.m.r. spectrum of this solution showed the CH_2 protons to be rather complex multiplets, as had already been observed.[8c] This is clearly due to inequivalence of all the four CH_2 hydrogens and must arise from restricted rotation about the C–C bond. We suggest that this is due to a cyclic structure such as (A) or (B). We note that the ^1H n.m.r. spectrum of the methoxyethyl compound $[HgCl(CH_2CH_2OMe)]$ in $CDCl_3$ is quite normal and shows the expected two triplets for the CH_2 groups; however, the spectrum in aqueous sodium hydroxide is again more complex suggesting that an analogous cyclic structure with restricted rotation is also formed there.

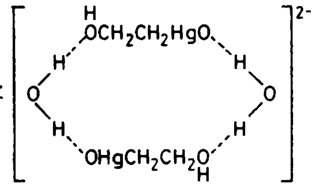
$$\underset{(1;\ X = Cl)}{HOCH_2CH_2HgX} + NaOH \longrightarrow HOCH_2CH_2HgOH + NaX$$

$HOCH_2CH_2HgOH + OH^- \rightleftharpoons$



(A)

$2\,HOCH_2CH_2HgOH + 2\,OH^- \rightleftharpoons$



(B)

The hydroxyethyl complex (1) was quite stable in 2 mol dm^{-3} NaOH solution at 80 °C over 6 h; however, when a sample was injected into a gas chromatography (g.c.) column at 175 °C it broke down rapidly to give largely acetaldehyde (72%) and ethylene. This behaviour parallels that reported to occur when aqueous solutions of 2-hydroxypropylmercury complexes are heated;[9] much lower temperatures (50 °C) were however sufficient to generate acetone in this case.

Addition of small quantities of $[\{Rh(C_5Me)_5\}_2(OH)_3]Cl$ (2) to alkaline solutions of (1) caused rapid decomposition with the formation of metallic mercury even at 25 °C. Proton n.m.r. spectroscopy showed that ethanol and acetate were formed simultaneously; the ethanol was confirmed by g.c.–mass spectrometry which also showed trace amounts of acetaldehyde, possibly again from thermal decomposition of (1). Quantitative analysis showed that approximately 0.16 mol of

Table 1. Rhodium-catalysed decomposition of $[HgCl(CH_2CH_2OH)]$ in aqueous sodium hydroxide

Catalyst [complex (2)/mmol]	$[HgCl(CH_2CH_2OH)]$/mmol	Products/mmol Ethanol	Products/mmol Acetate	$\frac{[EtOH]}{[catalyst]}$	$\frac{[O_2CMe^-]}{[catalyst]}$
0.05	0.05	0.01	0.04	0.2	0.8
0.05	0.10	0.02	0.07	0.4	1.4
0.05	0.48	0.08	0.38	1.6	7.6
0.05	1.05	0.17	0.87	3.4	17.4
0.05	1.80	0.27	1.44	5.4	28.8
0.05	2.29	0.42	1.89	8.4	37.8

Table 2. Rhodium-catalysed decomposition of the product of the reaction between C_2H_4 and HgX_2 in water

HgX_2 (mmol)	Products/mmol Ethanol	Products/mmol Acetate	$\frac{[EtOH]}{[HgX_2]}$	$\frac{[O_2CMe^-]}{[HgX_2]}$
$Hg(O_2CMe)_2$ (0.04)	0.004		0.10	
$Hg(O_2CMe)_2$ (0.50)	0.08		0.16	
$Hg(O_2CMe)_2$ (1.04)	0.13		0.13	
$Hg(O_2CMe)_2$ (2.03)	0.28		0.14	
$Hg(NO_3)_2$ (0.79)	0.12	0.62	0.15	0.78
$Hg(NO_3)_2$ (1.54)	0.25	1.19	0.16	0.77
$HgSO_4$ (1.12)	0.15	0.96	0.13	0.86

ethanol and 0.84 mol of acetate were formed per mol of (1) in a reaction that was catalytic in (2) but stoicheiometric in $[OH^-]$ (Table 1). No significant differences in product distribution were found at temperatures from 3 to 50 °C and the reaction was very fast over the whole range. Attempts to increase the turnover numbers based on catalyst (2) were frustrated by solubility problems. However, when a solution of (1) in 2 mol dm^{-3} NaOH was added to the red solution remaining from a previous reaction (after removal of mercury) the new complex (1) was again quickly converted into ethanol and acetate. The red solution therefore still contained active catalytic species but these could not be isolated pure or characterised. The presence of $Rh(C_5Me_5)$ complexes was shown by the conversion into $[\{Rh(C_5Me_5)\}_2Cl_4]$ on reaction with HCl.

The following complexes also catalysed the aqueous base-promoted decomposition of $[HgX(CH_2CH_2OH)]$ at rates broadly similar to (2) and giving again ethanol (14—18%) and acetate (82—86%): $[\{Rh(C_5Me_5)\}_2(OH)_3]OH$, $[\{Rh(C_5Me_5)\}_2Cl_4]$, and $[\{Rh(C_5Me_5)\}_2(NO_3)_3]NO_3$; the complex $[\{Ru(p\text{-cymene})\}_2Cl_4]$ reacted giving ethanol (12%) and acetate (61%) but required 30 min at 60 °C. The following were not found to be catalytically active: the chloride hydrates of Rh, Ru, and Ir, $NiCl_2$, $CuCl_2$, $CoCl_2$, and Na_2MoO_4.

The same reaction also occurred when (1) or derivatives thereof were formed *in situ*. Thus reaction of ethylene with aqueous mercury(II) acetate containing some (2) was shown to give $[Hg(O_2CMe)(CH_2CH_2OH)]$ by n.m.r. spectroscopy. This solution was quite stable and did not decompose even at 50 °C. However, on addition of 2 mol dm^{-3} NaOH solution and after a short induction period the yellow solution turned dark with precipitation of mercury, and ethanol was detected [0.14 mol per mol of $Hg(O_2CMe)_2$ used] (Table 2). Some hydrogen was also given off at this stage in the reaction. Mercury(II) nitrate and sulphate gave analogous results showing that the other (major) organic product was again acetate.

When the above solution of $[Hg(O_2CMe)(CH_2CH_2OH)]$ and catalyst (2) was titrated with aqueous NaOH two equivalence points were found. The first (at pH 6—7) corresponded to neutralisation of acetic acid formed in the reaction (iv),

$$C_2H_4 + Hg(O_2CMe)_2 + H_2O \longrightarrow HOCH_2CH_2HgO_2CMe + HO_2CMe \quad \text{(iv)}$$

while the second, when the pH quickly increased to 11.5, coincided with the precipitation of mercury and the formation of ethanol.

Propylene is hydroxymercurated analogously to ethylene to give $[HgX(CH_2CHMeOH)]$;[10] a solution of this complex in aqueous base was again catalytically decomposed by addition of complex (2). In this case the products were acetone (82% based on the complex) and a small amount of propan-2-ol (2%). This reaction showed a turnover of 26 based on (2) but it must be emphasised that this is a minimum, not an optimum value. The same result was obtained when propylene was passed into a solution of mercury(II) acetate containing some (2), and 2 mol dm^{-3} NaOH was then added. It is instructive to compare this catalytic decomposition with the thermal decomposition in which a 48% yield of acetone was obtained after heating (6 h, 100 °C) a solution of $[HgX(CH_2CHMeOH)]$ in very strong base (pH 13).[11]

By contrast, the β-ethoxyalkyl complexes $[HgX(CH_2CHROEt)]$ (R = H or Me)[12] were quite stable in aqueous base solutions containing catalyst (2); only on heating (2 mol dm^{-3} NaOH, 50 °C, 1 h) was even a small amount of decomposition, to EtOCHRMe, detected. From this result we draw the conclusion that the rhodium catalyst (2) must in some way be interacting with the hydroxyethyl group. Our studies on the (related) aldehyde disproportionation reaction, also catalysed by (2), indicated such a base-promoted interaction between a rhodium and a hydroxy group of an aldehyde hydrate to be the first step in the reaction scheme.[6] We presume therefore that a condensation takes place here between the hydroxyethyl and the hydroxy on rhodium; when this cannot occur, as with $[HgX(CH_2CH_2OR)]$, we suggest that either no reaction at all takes place or that the reaction will be very difficult.

In the acetaldehyde disproportionation reaction catalysed by (2), however, equal amounts of acetate and of ethanol were formed.[6] Therefore a reaction scheme based upon a catalysed decomposition of (1) into acetaldehyde followed by disproportionation can only at best explain 30—35% of the reaction (giving *ca.* 15—17% ethanol and the same amount of acetate). The remaining 70% acetate must derive from another path. One reaction, carried out under rigorously anaerobic conditions, gave precisely the same result and the same proportions of ethanol and acetate as those carried out in air. This result and the observation that hydrogen is formed in the reaction implies that water is acting as an oxidiser and is itself reduced to hydrogen. Mercury(II) is also of course reduced to mercury metal.

From these considerations we may therefore define two reaction sequences, (*a*) plus (*b*), and (*c*), both of which appear to be catalysed by complex (2). Path (*c*) would then be *ca.* twice as common as (*a*) + (*b*).

$$HOCH_2CH_2HgOH \xrightarrow{(2)} CH_3CHO + H_2O + Hg^0 \quad (a)$$

$$2\,CH_3CHO + OH^- \xrightarrow{(2)} CH_3CH_2OH + CH_3CO_2^- \quad (b)$$

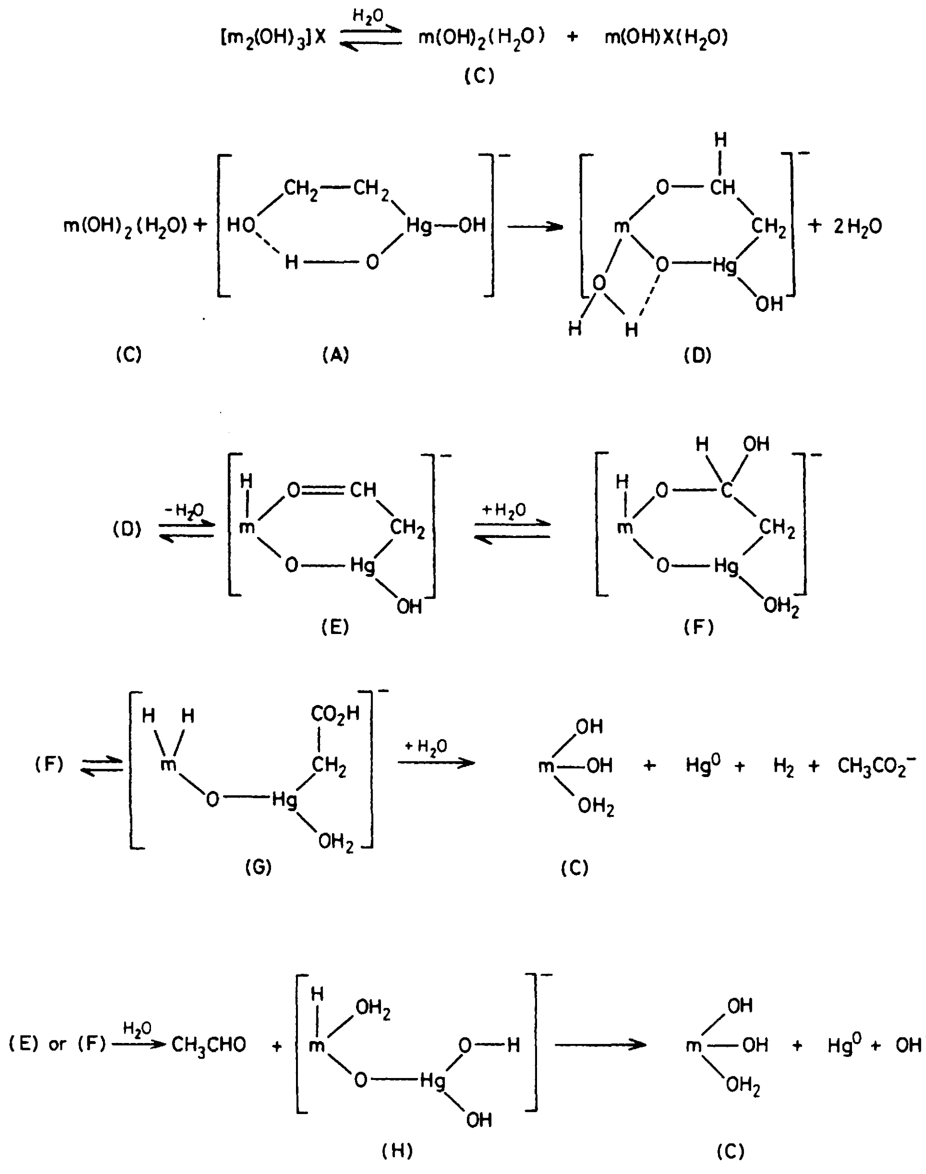
$$HOCH_2CH_2HgOH + OH^- \xrightarrow{(2)} CH_3CO_2^- + H_2O + H_2 + Hg^0 \quad (c)$$

Path (*b*) is of course the aldehyde disproportionation [6] and need concern us no further here, but (*a*) and (*c*) are novel. The fact that the reactions only proceed in very strong base (pH > 11) suggests that the rhodium complex (2) is attacked by a highly nucleophilic mercury species such as (A) or (B) or possibly even a dianionic species $OCH_2CH_2HgO^{2-}$ in equilibrium with them.

A proposed reaction path is set out in the Scheme. We assume that the dinuclear catalyst (2) dissociates to give the reactive monomers such as (C) in a pre-equilibrium. This has been shown to occur in other reactions catalysed by (2) and closely related molecules.[6,13] For simplicity, to avoid complications caused by the presence of other anions, we follow the course of a reaction based on (C) and the putative cyclic mercury complex (A).

Reaction of (A) and (C) gives a six-membered *cyclic* intermediate (D) also containing a rhodium–oxygen–mercury unit. This conclusion arises from the requirement noted above that if the oxygen on the β-carbon of the ethylmercury is protected the reaction does not proceed. Although no completely comparable species are known we have prepared complexes of the type $[Rh(C_5Me_5)(PMe_3)X_2HgX_2]$ (X = Cl, Br, or O_2CMe) and have shown that the metal atoms are linked by bridging X ligands.[14] Unfortunately, owing to solubility problems, we were not able to prepare complexes of this or related types with hydroxy- or oxy-bridges.

The following steps are simple β-migrations of hydride from the β-carbon onto rhodium giving (E), which contains an internally co-ordinated aldehyde which can undergo attack by hydroxide on carbon giving (F). Intermediate (F) may then again move the remaining hydride onto rhodium giving (G), a



Scheme. m = $Rh^{III}(C_5Me_5)$

Table 3. Rhodium-catalysed oxidation of acetaldehyde in the presence of $HgCl_2$ and base

$HgCl_2$/mmol	CH_3CHO/mmol	Products/mmol		S */%
		Ethanol	Acetate	
0.32	1.2	0.43	0.76	64
0.61	1.2	0.35	0.83	70
1.24	1.2	0.27	0.95	78
1.83	1.2	0.16	1.01	86
2.38	1.2	0.11	1.06	91

* Selectivity towards acetate.

rhodium dihydride bonded through an oxide to a mercury carboxylic acid, which breaks down with generation of (C), H_2, mercury metal, and acetate. Alternatively (E) or (F) can themselves break down similarly giving acetaldehyde and (H) which regenerates (C) and mercury. The acetaldehyde can then undergo the disproportionation reaction [6] to give equal amounts of acetate and ethanol. The path *via* (H) then represents *ca.* 30—35% of the reaction.

Some evidence in favour of this proposal is provided by the behaviour of the grey solid which arises from reaction of acetaldehyde and mercury(II) chloride in aqueous base. This has been suggested to be a polymer based on $(HOHgCH_2CHO)_n$,[15] but owing to the intractability of the material (it is quite insoluble and could not be purified) confirmation of the structure has not yet been possible. Nevertheless, the fact that it reacts, albeit slowly, in 2 mol dm^{-3} NaOH to give acetate and mercury metal but only in the presence of complex (2) gives support to our postulate of intermediates such as (E) in the reaction of (1). A faster reaction occurred if a solution containing equimolar amounts of acetaldehyde and mercury(II) chloride was added to a solution of catalyst (2) in aqueous base. Acetate was again the major product (together with mercury), but ethanol, the amount depending on the amount of mercury(II) used, was also formed (Table 3). Turnovers of 25—40 based on (2) could be obtained within 3 min. Better solubility was certainly the reason why this experiment proceeded faster than that in which the grey polymeric solid was used.

Overall then, these results show that acetaldehyde can undergo fast oxidation reactions catalysed by the rhodium complex (2) and some others in the presence of base and mercury(II) to give acetate. Since the metal-promoted formation of acetaldehyde from ethylene occurs readily this therefore represents a path from ethylene to acetate.

The reaction in which propylene is converted, *via* a 2-hydroxypropylmercury complex into acetone must be completely analogous. In this case, however, the reaction path yielding the alcohol (propan-2-ol) [corresponding to (F) $\longrightarrow$ (G)] is of less importance than in the ethylene reaction.

Experimental

The complexes $[\{Rh(C_5Me_5)\}_2(OH)_3]Cl\cdot 4H_2O$ (2), $[HgCl(CH_2CH_2OH)]$ (1), $[HgCl(CH_2CHROEt)]$ *etc.* were all prepared by standard methods described in the literature and cited in the text. Gas chromatographic analyses were carried out on reaction solutions by injecting measured aliquots into the preheater of a Pye Unicam 104 gas chromatograph fitted with FiD detector and a Poropak Q column. Since the mercury complexes themselves decomposed under these conditions very careful blank experiments were run to ensure that only free ethanol in solution was being analysed. Hydrogen analysis was carried out using a 5A molecular sieve column. Acetate and ethanol were quantitatively analysed by ^1H n.m.r. spectroscopy (60 MHz, Perkin-Elmer R-12B) in aqueous base solution by integrating the resonances at δ 1.15 (t, CH_3CH_2OH) and 1.9 (s, CH_3CO_2Na). Typical experiments are described.

Rhodium-catalysed Decomposition of the Adduct formed between Mercury(II) *Chloride and Acetaldehyde in Aqueous Base.*—The adduct formed by the reaction of $HgCl_2$ with acetaldehyde in aqueous base was isolated as a grey powder as described.[15] Portions of this (0.1—0.3 g) were suspended in NaOH (2 mol dm^{-3}, 4 cm^3) containing a catalytic amount of complex (2) (0.04 mmol) and a known weight of $(CH_3)_3Si(CH_2)_3SO_3Na$ as a standard for integration. The suspension was vigorously stirred for 14 h at room temperature and the resulting solution was filtered and analysed by ^1H n.m.r. spectroscopy.

Rhodium-catalysed Oxidation of Acetaldehyde by Hg^{2+} *in Aqueous Base.*—Mercury(II) chloride was dissolved in dilute aqueous acetaldehyde (1.2 mmol in 5 cm^3) containing a known weight of $(CH_3)_3Si(CH_2)_3SO_3Na$. A solution of complex (2) (0.04 mmol) in NaOH (2 mol dm^{-3}, 3 cm^3) was then added with vigorous stirring. A black precipitate of metallic mercury immediately came down, leaving a yellow solution. Analysis by ^1H n.m.r. spectroscopy showed that the acetaldehyde had been converted to ethanol and acetate. Results are presented in Table 3.

The catalyst appeared to be unchanged at the end of the reaction.

The Decomposition of $[HgCl(CH_2CH_2OH)]$ *in Aqueous Base catalysed by* (2).—The complex $[HgCl(CH_2CH_2OH)]$ (1) was weighed directly into a 10-cm^3 sample tube and dissolved in NaOH (2 mol dm^{-3}, 2 cm^3). A solution of the catalyst (2) (0.05 mmol) in NaOH (2 mol dm^{-3}, 2 cm^3) was added, and the tube then made air-tight with a rubber Subaseal and allowed to stand at room temperature until reaction occurred (marked by the appearance of a black precipitate). The variable induction period could be shortened by placing the stoppered tube into a thermostatted water-bath at 50—60 °C. Analysis was by g.c., g.c.–mass spectrometry, and ^1H n.m.r. spectroscopy; results are presented in Table 1.

The reaction with $[HgCl(CH_2CHMeOH)]$ was carried out similarly. For the less active catalysts or the less reactive organomercury species $[HgCl(CH_2CHROEt)]$ (R = H or Me), the reaction solution was heated to 50—60 °C in a water-bath and monitored with time.

Rhodium-catalysed Decomposition of the Product of the Reaction between Olefins and HgX_2 *in Water.*—Ethylene (*ca.* 1 l h^{-1}) was passed through an aqueous solution (2 cm^3) containing the mercury(II) salt and catalyst (2) (0.04 mmol) for 1.5 h at 20 °C and 1 atm.

The *in situ* formation of $[HgX(CH_2CH_2OH)]$ was shown by n.m.r. spectroscopy which also indicated that no reaction with the catalyst occurred until the solution was made basic (pH > 11) by addition of NaOH (2 mol dm^{-3}, 2 cm^3). Metallic mercury then precipitated after 1—20 min. Analysis was by g.c., g.c.–mass spectrometry, and ^1H n.m.r. spectroscopy; results are presented in Table 2.

The reaction with propylene was performed in the same way.

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