Stoichiometric hydrogenation of ethene on Rh(111); mechanism, importance of weakly adsorbed ethene, and relationship to homogeneous catalysis

Michael Bowker[1], John L. Gland[2], Richard W. Joyner[3], Yongxue Li,
Marina M. Slin'ko[4] and Robin Whyman[5]

Leverhulme Centre for Innovative Catalysis and Surface Science Research Centre,
University of Liverpool, PO Box 147, Grove Street, Liverpool L69 3BX, UK

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The hydrogenation of ethene is an important reaction in heterogeneous catalysis and, despite its apparent simplicity, many aspects of the reaction mechanism remain unclear. By contrast, the mechanism using homogeneous catalysts such as Wilkinson's catalyst $[(RhCl(PPh_3)_3]$ is thought to be well understood. To allow a comparison between the homogeneous and heterogeneous reactions we have studied ethene/hydrogen interactions on the (111) plane of rhodium in the temperature range 160–500 K. Under UHV conditions no catalytic reaction was detected. However, we have been able to observe stoichiometric hydrogenation and exchange in the chemisorbed layer. A mixed adlayer of either ethene/deuterium (or perdeuteroethene and hydrogen) was formed at ca. 160 K, and allowed to warm up. From previous spectroscopic studies, ethene is adsorbed at 165 K as partially rehybridised, π bonded species with a C–C bond order of ca. 1.5, similar to ethene in Zeise's salt. At 190–210 K we observe coincident desorption of undeuterated ethene – the major species – together with much smaller quantities of deuterated ethane and partially deuterated ethenes. The influence of both hydrogen and ethene pre-coverage has been studied as has the relative extent of hydrogenation and exchange. The ethane formation results parallel those reported by other authors on Pd(110) and Pt(111) and Pt(110). We propose that on all three metals both hydrogenation and exchange follow the same pathway, with a common intermediate for exchange and hydrogenation. This is *a weakly held, π bonded species formed during the desorption process*, which can be converted *reversibly* into an adsorbed ethyl species. A detailed comparison indicates that the mechanism of heterogeneous hydrogenation closely parallels that in the homogeneous phase.

Keywords: hydrogenation; Rh single crystal; mechanism; heterogeneous/homogeneous catalysis

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[1] Now at the Chemistry Department, University of Reading, Reading, Berkshire, UK.

[2] Permanent address: Departments of Chemistry and Chemical Engineering, Unversity of Michigan, Ann Arbor, Michigan, USA.

[3] To whom correspondence should be addressed.

[4] Permanent address, Institute of Chemical Physics, Russian Academy of Sciences, Kosygina St. 4, Moscow 117334, Russia.

[5] Department of Chemistry, University of Liverpool, PO Box 147, Grove Street, Liverpool L69 3BX, UK.

1. Introduction

Hydrogenation of ethene (ethylene) is one of the simplest catalytic reactions that can be imagined. Despite many experimental studies over more than 50 years, there is still controversy over the mechanism of reaction. The heterogeneous reaction can be catalysed by a wide range of metals and oxides and there are apparent kinetic similarities with the homogeneously catalysed reaction [1]. Our aim in this paper is to present a proposal for the mechanism of the heterogeneous reaction that rationalises and reconciles a wide range of kinetic and spectroscopic observations and to draw attention to a marked parallel between the mechanism of reactions on homogeneous and heterogeneous catalysts. We start with a mechanistic review and then present results on the (111) plane of rhodium.

The earliest influential study of the hydrogenation of double bonds is due to Horiuti and Polanyi [2] who suggested in 1934 that the olefin could become chemisorbed by breaking of the double bond. Subsequent addition of a single hydrogen atom gave a species which could progress to the alkane by further hydrogen addition, or dehydrogenate resulting in exchange. In 1956 Kemball examined the low temperature (ca. 170 K) reaction between ethene and deuterium over a number of metals. He concluded that exchange and hydrogenation occurred simultaneously, probably through the common intermediacy of an adsorbed ethyl species [3].

The next important development took place in 1965, when Wilkinson et al. demonstrated rapid olefin hydrogenation in the homogeneous phase, with $RhCl(PPh_3)_3$ [4]. The mechanism of operation of this catalyst has been investigated in considerable detail and the steps thought to comprise the catalytic cycle are shown in fig. 1. While all of the other species shown in fig. 1 have been identified spectroscopically, those argued to comprise the catalytic cycle have not been detected.

The Horiuti–Polanyi–Kemball view of the mechanism of heterogeneous hydrogenation prevailed until 1975, when Thomson and Webb re-examined the evidence, concluding that hydrogen transfer from $M{-}CH_x$ species played an important role [5]. Subsequently, they also showed that ethene was present at the catalyst surface in both irreversibly and more weakly held forms, and that only the weakly held species were hydrogenated [6]. A further complication was introduced by the observation that, particularly on (111) surfaces, molecularly adsorbed ethene transforms irreversibly into adsorbed ethylidyne species, ($-C-CH_3$) [7]. The transformation temperature is in the range 250–350 K, varying with the metal. Somorjai suggested that ethylidyne was the key intermediate in ethene hydrogenation, although with colleagues he went on to demonstrate that its rate of hydrogenation was much too slow to explain the rate of hydrogenation of ethene by the single crystal catalysts [8].

In 1987 understanding of the homogeneous hydrogenation was much advanced by Morokuma et al., who published high level quantum mechanical calculations

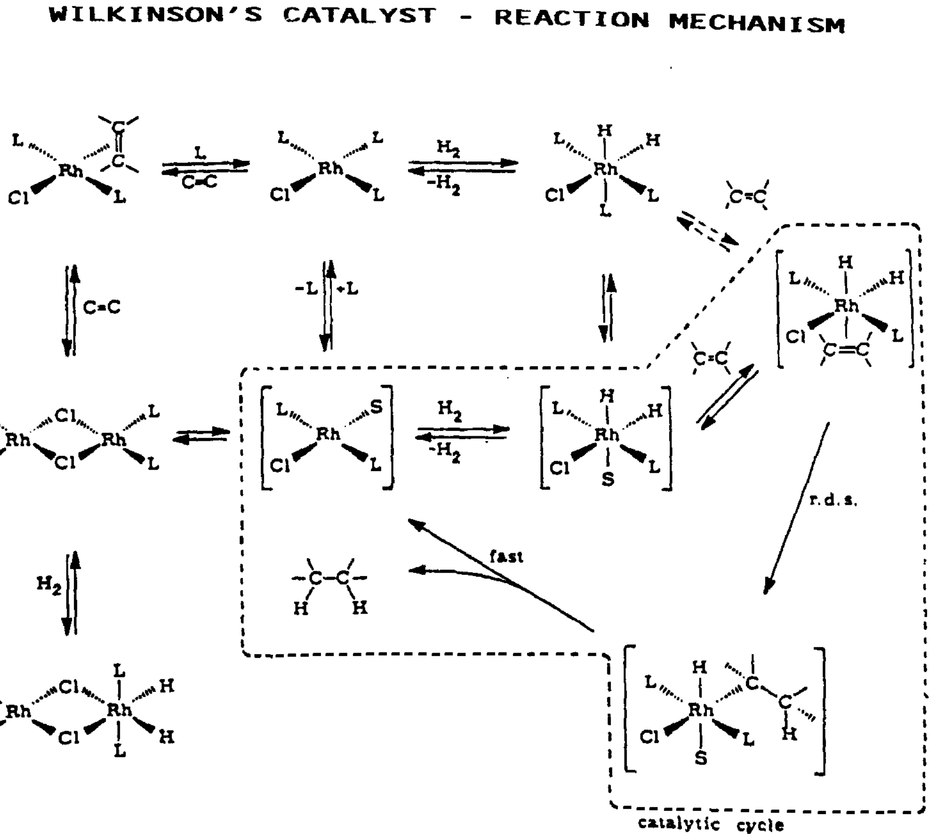

Fig. 1. Catalytic cycles and other species generated during hydrogenation using Wilkinson's catalyst, Rh(I)Cl(PPh$_3$)$_3$; from ref. [30]. Note that none of the species invoked in the catalytic cycle has been observed spectroscopically.

charting the energetics and structure of intermediates and transition states in hydrogenation by Wilkinson's catalyst [9].

The early 1980s saw the start of useful spectroscopic characterisation of adsorbed molecular ethene on single crystal surfaces, using HREELS. It soon became clear that there was a considerable range of bonding configurations on different metals, ranging from those where the adsorbed ethene molecule is only weakly perturbed, e.g. Cu(111), to Pt(111) where complete rehybridisation of the electronic configuration around carbon occurs and the ethene is 1,2 di-σ bonded to the surface [10]. It is common to characterise the bonding of ethene adsorbed species simply as either π or di-σ, although the spectroscopic evidence suggests that it is more accurate to describe the π bond as partially rehybridised. A paradigm is provided by Zeise's salt, $KPt{\cdot}Cl_3{\cdot}(C_2H_4){\cdot}H_2O$, which is shown in fig. 2. Structural studies show that the C=C bond is elongated to 1.375 Å from the free molecule value of 1.337 Å. The four hydrogen atoms are no longer coplanar with the two carbon atoms [11], showing that they have substantial sp^3 character.

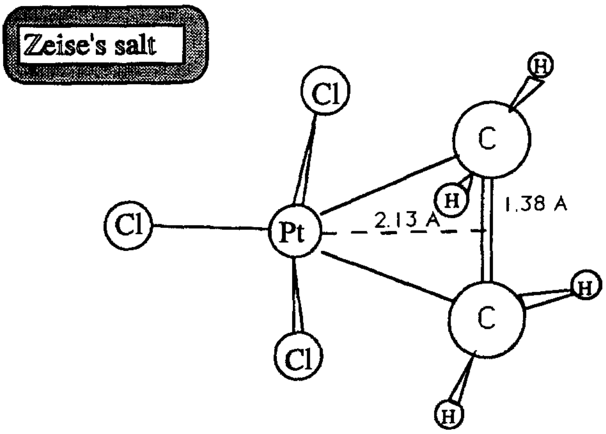

Fig. 2. Platinum–ethene bonding in Zeise's salt, from ref. [16].

Bent et al. have analysed the carbon–carbon stretching frequencies for ethene adsorbed on a many metals and have concluded that the position of this stretch can be used to determine the carbon–carbon bond order in adsorbed ethene [12]. We follow their analysis here, using vibrational frequencies for adsorbed perdeuteroethene where these are available. The resulting values of carbon–carbon bond order for molecularly adsorbed ethene on the surfaces of interest here are shown in table 1.

Our experiments involve coadsorption first of hydrogen and then of ethene at a relatively low temperature, followed by warming under temperature programmed conditions. This experiment has previously been carried out on Pt(110) by Yagasaki and Masel [13], on Pt(111) by Zaera [14] and on Pd(110) by Sekitani et al. [15]. Yagasaki and Masel reported that coadsorption of ethene and hydrogen substan-

Table 1
C=C stretching frequencies and estimated bond orders for adsorbed perdeuteroethene and some reference compounds

Surface	C=C stretching frequency [a] (cm^{-1})	C–C bond order [b]
(gas phase	1515	2.0)
Cu(100)	1420	1.66
Pd(110)	1400	1.64
(Zeise's salt	1353	1.57)
Rh(111)	1300	1.52
Pt(110)	1290	1.51
Ni(111)	1200	1.33
Pt(111)	1150	1.13
($C_2D_4Br_2$(g)	1141	1.00)

[a] Data from the summary in ref. [17], except for Pt(110), ref. [19], and Pd(110), ref. [21].
[b] From the correlation in Bent et al., ref. [17] (fig. 5 and table III).

tially changed the nature of the metal/ethene bond. In the absence of adsorbed hydrogen, HREELS spectra suggested the formation of di-σ bonded species. In the presence of hydrogen an additional form of adsorbed ethene was noted, referred to as "weakly π bonded ethene". The observed frequencies imply a C–C bond order of about 1.5, the species desorbing at 160 K. A small amount of ethane was formed, which desorbed in a broad peak centred at about 190 K.

Zaera has carried out extensive studies on the Pt(111) plane (ref. [20] and references therein). In the absence of adsorbed hydrogen some self hydrogenation is noted, resulting in a relatively narrow ethane desorption peak, centred at 311 K. The presence of adsorbed hydrogen again weakens ethene binding to the surface. The molecular desorption peak broadens to lower temperature by ca. 70 K and desorption of *ethene*, *ethane* and *exchanged ethene* (in isotopically labelled experiments), occurred in the same temperature range, 220–300 K.

Sekitani et al. adsorbed hydrogen and ethene on Pd(110) at ca. 100 K; on warming a very small quantity of *ethane* desorbed in a broad peak centred at 250 K [15]. About one sixth of the *ethene* desorbed, forming a sharp peak centred at 150 K. The low temperature desorption peak is not observed in the absence of hydrogen. Ethene was molecularly adsorbed up to 350 K, when transformation to ethylidyne occurred.

Key questions

The profusion of results and widely differing mechanistic ideas has left the subject in some confusion. The key questions which we consider in this paper are:

(1) Which ethene species undergoes hydrogenation and is it likely to be the same on different metal surfaces?

(2) Is hydrogen transfer in the adlayer important?

(3) Are there mechanistic parallels between the heterogeneous and homogeneous reactions?

2. Experimental

Experiments were carried out in UHV apparatus which has been described previously [16]. Preparation of the clean rhodium crystal has also been described. Most gases were obtained from Argo International and had the following purities: ethene, 99.7%; hydrogen, 99.975% and deuterium, 99.7%. Perdeuteroethene was supplied by MSD Isotope and was 99.8% pure. The crystal was cleaned by a combination of ion bombardment and annealing and monitored by LEED and Auger electron spectroscopy. Exposures were measured with an ionisation gauge and desorption spectra recorded with a quadrupole mass spectrometer (VG Micromass PC). Desorption spectra were obtained at a heating rate of 1.5 K s^{-1}. Mass spectral cracking patterns were either measured in situ or taken from the literature, [17].

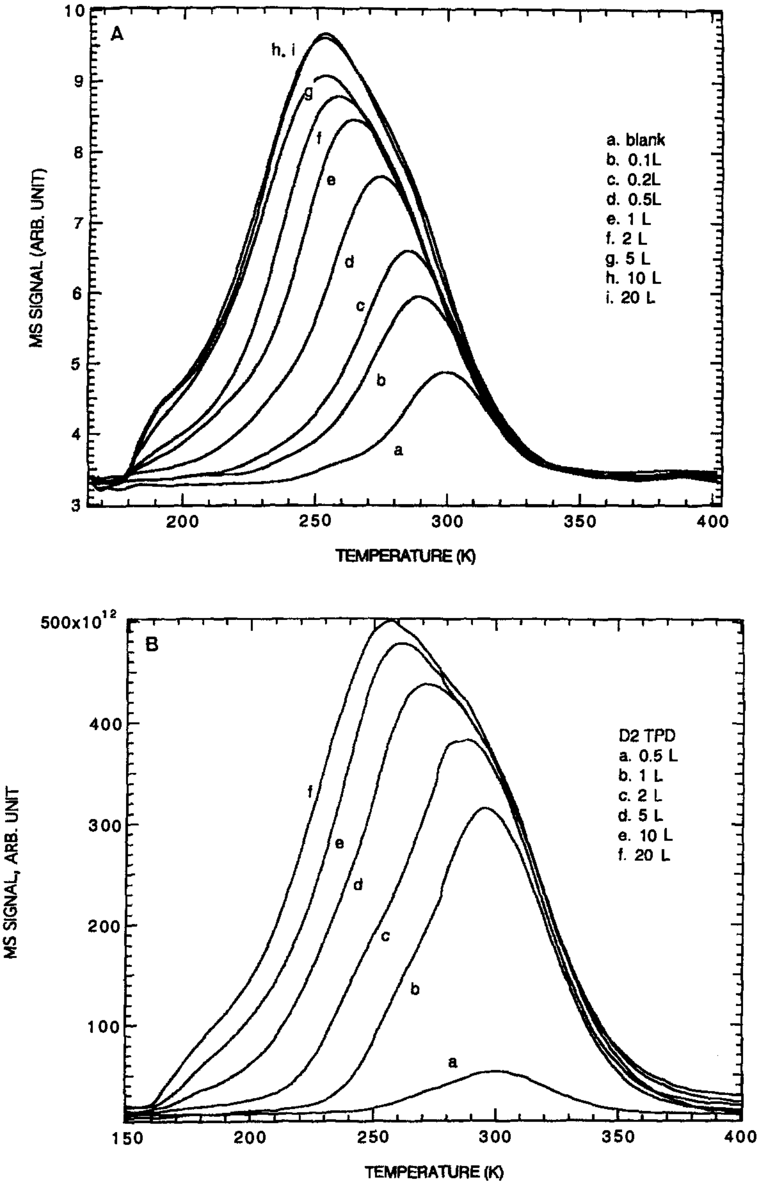

Fig. 3. Temperature programmed desorption results after adsorption on Rh(111) at 160 K. (A) Hydrogen, exposures: (a) blank; (b) 0.1 L; (c) 0.2 L; (d) 0.5 L; (e) 1 L; (f) 2 L; (g) 5 L; (h) 10 L; (i) 20 L. (B) Deuterium, exposures: (a) 0.5 L; (b) 1 L; (c) 2 L; (d) 5 L; (e) 10 L and (f) 20 L.

3. Results

Temperature programmed desorption measurements for hydrogen, deuterium ethene and perdeuteroethene from the clean Rh(111) surface are shown in figs. 3 and 4. Fig. 5 shows the result of desorption following exposure of the crystal first to

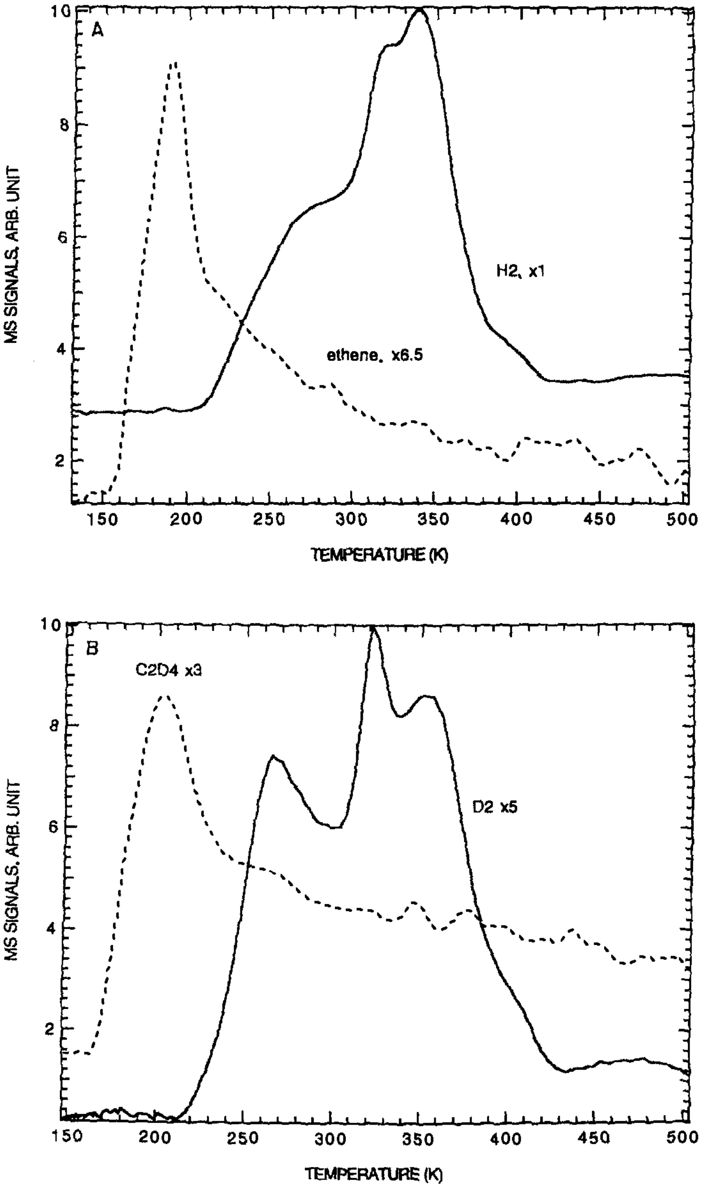

Fig. 4. Temperature programmed desorption results after adsorption of (A) 5 L ethene; and (B) 5 L perdeuteroethene on Rh(111) at ca. 168 K; the main peaks observed are ethene at low temperature and hydrogen at higher temperature.

5 L (langmuir) of hydrogen and then 5 L of perdeuteroethene. Several desorption peaks are observed at low temperatures, the peak at 34 amu results form hydrogenation to give $C_2D_4H_2$, and is not seen when only perdeuteroethene is adsorbed. The peak at 31 amu predominantly represents C_2D_3H formed by hydrogen–deuterium exchange, and is vanishingly small when only C_2D_4 is adsorbed. Parallel

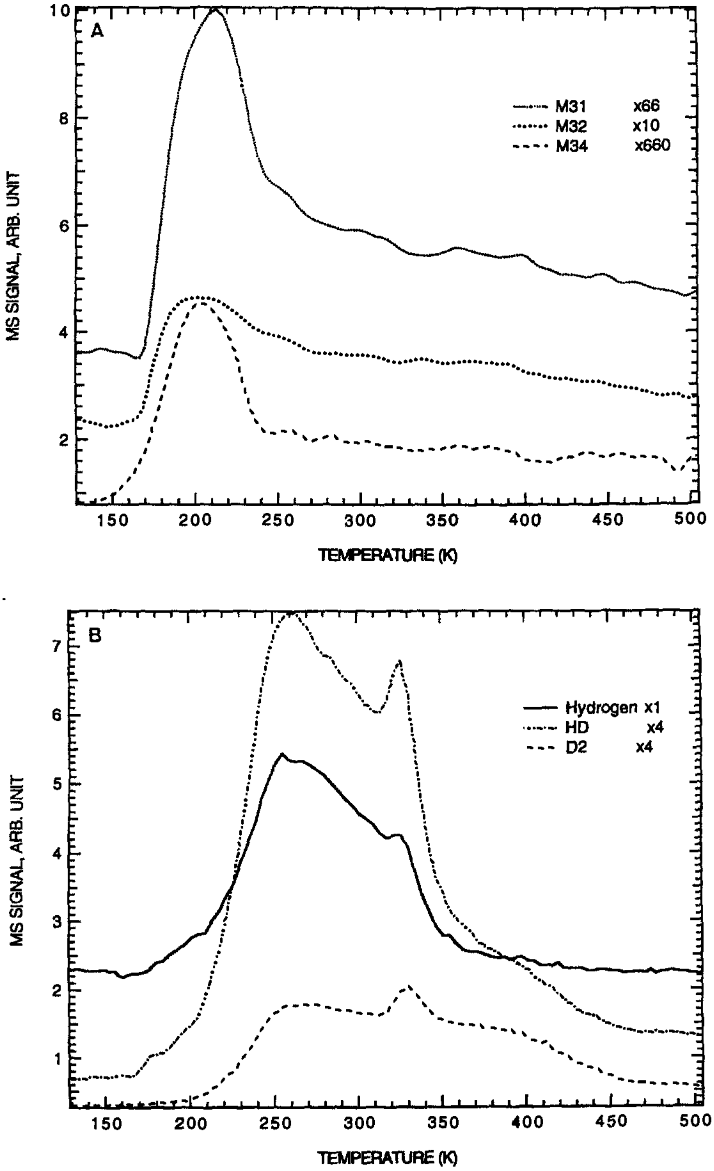

Fig. 5. Temperature programmed desorption results from Rh(111). The surface at ca. 165 K was exposed to 5 L of hydrogen followed by 5 L of perdeuteroethene, and then heated at ca. 1.5 K s^{-1}. (A) Mass 31 (C_2D_3H); mass 32 (C_2D_4); mass 34 ($C_2D_4H_2$), showing coincident desorption, exchange and hydrogenation. Note that peaks at the lower masses ($M < 34$) include contributions from the fragmentation of heavier species in the mass spectrometer. (B) Mass 2 (H_2); mass 3 (HD) and mass 4 (D_2).

experiments have been performed by coadsorbing first 5 L of deuterium and then 5 L of ethene, and the results are shown in fig. 6. Coincident low temperature peaks are again observed, due to ethene and $C_2H_4D_2$. Analysis of the mass spectral data

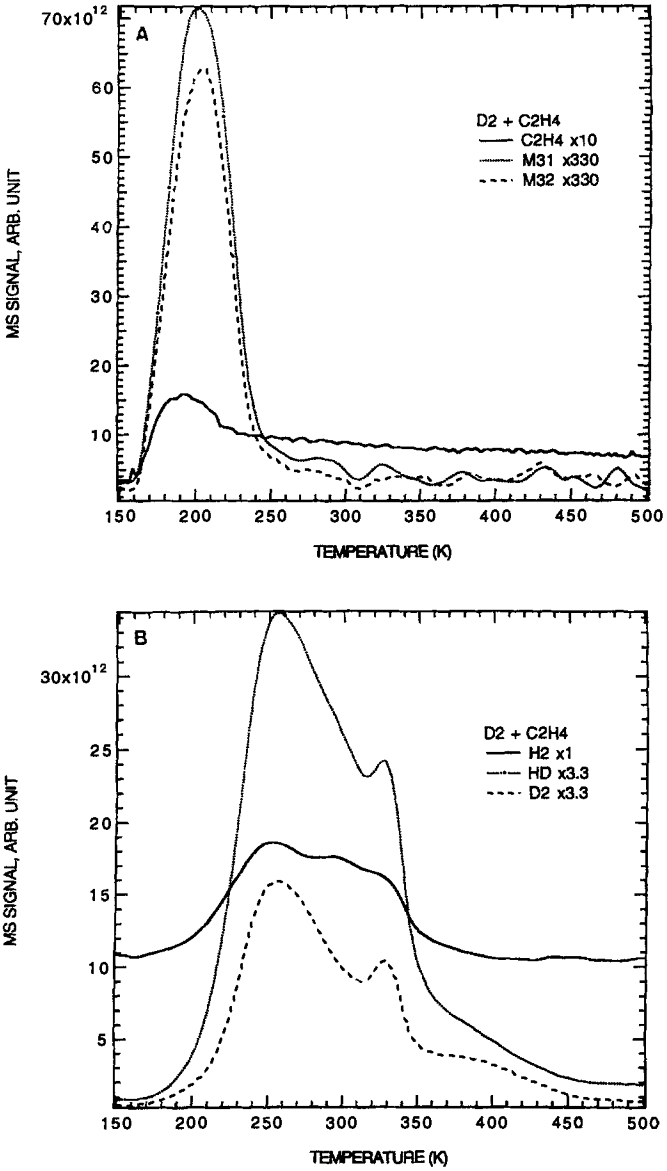

Fig. 6. As fig. 5, but first adsorbing deuterium and then ethene. (A) Mass 28 (C_2H_4); mass 31 (C_2H_5D); mass 32 ($C_2H_4D_2$), again showing coincident desorption and hydrogenation. Note that peaks at the lower masses ($M < 32$) include contributions from the fragmentation of heavier species in the mass spectrometer. (B) Mass 2 (H_2); mass 3 (HD) and mass 4 (D_2).

taking cracking into account indicates that only a single hydrogen atom in the ethene molecule is exchanged. Because of cracking it is difficult to say how much of the mass 29 peak is due to CH_3D.

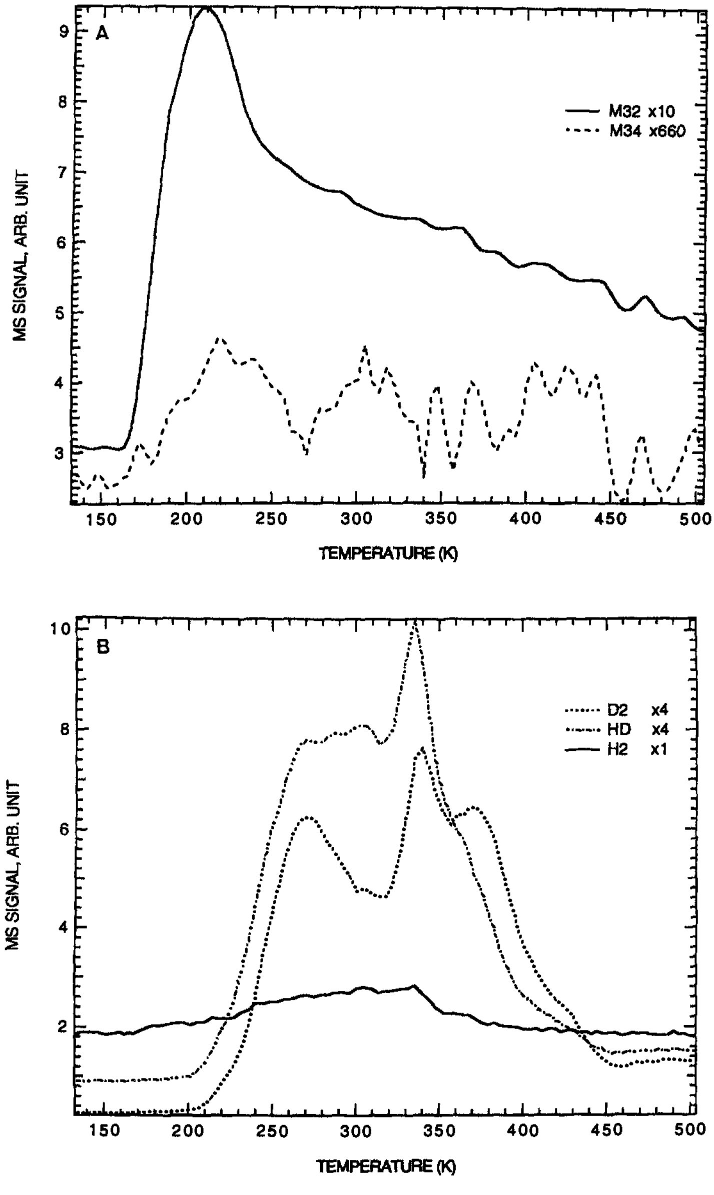

Fig. 7. As fig. 5, but first exposing the rhodium surface to 5 L C_2D_4 and then 5 L of hydrogen. (A) Mass 32 (C_2D_4); mass 34 ($C_2D_4H_2$). (B) Mass 2 (H_2); mass 3 (HD) and mass 4 (D_2).

In both sets of experiments LEED observations indicated the presence of a $(\sqrt{3} \times \sqrt{3})R30°$ structure at low temperature, which became a (2×2) mesh at ca. 210 K, after the first burst of ethene desorption. Preadsorption of ethene rather than hydrogen suppresses hydrogen adsorption and reaction, as shown in fig. 7.

4. Discussion

4.1. Rh(111)-TEMPERATURE PROGRAMMED DESORPTION

The temperature programmed desorption measurements for hydrogen on rhodium are in agreement with those seen previously [18]. The movement of the desorption maximum to lower temperature as the coverage increases indicates second order recombination kinetics. For similar exposures, the peak maximum for deuterium is observed at a slightly higher temperature than for hydrogen.

The TPD results from ethene are also in general agreement with previous reports, [19]. The first species to desorb is molecular ethene, which reaches a maximum at 195 K for C_2H_4 and 207 K for C_2D_4. The changes in LEED pattern suggest that the ethene coverage falls from 33 to 25% of an adsorbed monolayer, so that about one quarter of the ethene desorbs. The activation energy for desorption is about 40 kJ mol^{-1}. The only other species to desorb is hydrogen, which has a characteristically complex shape. There is a very broad desorption feature, which commences at ca. 220 K, and superimposed on this are maxima at 309 and 333 K. The desorption curves for D_2 after C_2D_4 adsorption are similar, with the peak maxima now at 324 and 350 K. The hydrogen desorption results from the transformation of adsorbed ethene to ethylidyne and possibly other intermediates.

In the coadsorption experiments where hydrogen (or deuterium) is preadsorbed, the ethene desorption spectra are little changed by the presence of hydrogen. For ethene the main molecular peak is still observed at 195 K, while for C_2D_4 the peak is at 201 K. The main differences are that now both *hydrogenation* and hydrogen/deuterium *exchange* occur. A small quantity of *ethane* is formed and desorbs with a peak maximum which is slightly higher than that of ethene, by ca. 6 K for C_2H_4 and ca. 3 K for C_2D_4. The activation energy for ethane formation is thus very similar to that for ethene desorption, 40 kJ mol^{-1}. We estimate that the ethane produced represents 7–10% of the ethene which desorbs, or ca. 2% of the ethene adsorbed initially. From the size of the peaks at $m/e = 29$ (C_2H_4 adsorbed after D_2) and 31 (C_2D_4 adsorbed after H_2), similar amounts of exchange and hydrogenation occur. Note that no further ethene or ethane desorption is observed at higher temperatures.

4.2. THE KEY INTERMEDIATE IN ETHENE HYDROGENATION

The studies of hydrogen and ethene coadsorption on platinum (111) and (110), rhodium (111) and palladium (110) have a common feature: *three reactions occur almost simultaneously at sub-ambient temperatures, namely ethene desorption, ethane formation and hydrogen/deuterium exchange.* The significance of hydrogenation and exchange occurring at the same time was recognised by Kemball [3], who concluded that these processes have a common intermediate. By contrast, the significance of ethane formation occurring at the same time as desorption of some weakly held ethene has not been fully recognised. To appreciate the significance of this result it is important to recall that no ethane formation is observed at higher temperatures, even though HREELS data indicate that both adsorbed hydrogen atoms and molecularly adsorbed ethene are still present on the surface. Taken together with the coincidence of desorption and hydrogenation, this shows that *the important intermediate state of adsorbed ethene must be located somewhere in the desorption trajectory of the ethene molecule*. The alternative explanation, that creation of vacant sites by ethene desorption is a prerequisite for the formation of the adsorbed ethyl species, seems unlikely. The carbon–carbon bond order in the intermediate on Rh(111) must be greater than 1.5, the value for the adsorbed ethene which remains on the surface, but is not hydrogenated (table 1 and ref. [17]).

Simultaneous desorption, hydrogenation and exchange is observed on three different metals, with the desorption temperatures in the range 200–300 K. Ethane does not undergo *molecular* chemisorption on metal surfaces, so its appearance cannot be desorption limited. On Rh(111) HREELS studies show that significant quantities of both molecularly adsorbed ethene and hydrogen remain on the surface, yet no further hydrogenation occurs. On platinum and palladium some ethene desorption occurs at temperatures lower than ethane formation, which however is always accompanied by desorption of ethene and exchange [13–15]. Thus it appears that on these metals weakly held ethene is again the important intermediate, although it is not clear why no hydrogenation accompanies ethene desorption at the lowest temperatures.

Why is only weakly held ethene hydrogenated? A possible reason is steric hindrance, where the more strongly held ethene blocks the approach of hydrogen atoms in a suitable trajectory for reaction. When the bonding becomes weaker and the ethene moves away from the surface, space for the hydrogen to approach becomes available.

4.3. PARALLELS BETWEEN HOMOGENEOUS AND HETEROGENEOUS HYDROGENATION

We have emphasised the need for heterogeneous catalysis to take advantage of the knowledge that has been developed in other areas of chemistry, particularly about bond forming reactions [20]. Also, there are intriguing and possibly important parallels between the kinetics of the homogeneous and heterogeneous hydrogenation reactions [1] so it seems important to look for mechanistic parallels.

The mechanism of hydrogenation of alkenes by Wilkinson's catalyst is shown in fig. 1. Reaction is thought to proceed by the oxidative addition of dihydrogen to the Rh(I) species *followed* by addition of the alkene. A key intermediate is the rhodium(I) hydrido–ethene complex shown in fig. 8, which reacts by migratory addition of hydride to give an ethyl species. There are no spectroscopic observations of these species, so the structural parameters are taken form the calculations of Koga et al. [9] where the ligand is PH_3, rather than triphenylphosphine in the catalyst.

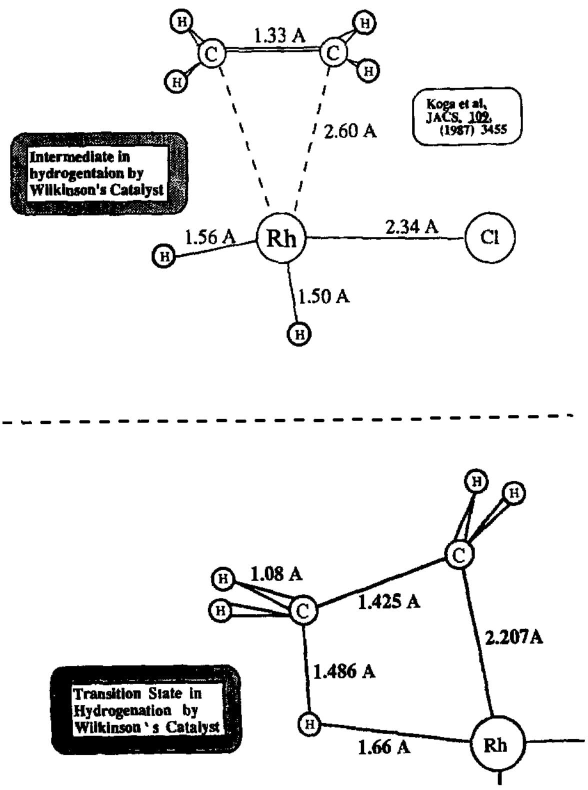

Fig. 8. Calculated structure of the rhodium hydrido–ethene intermediate and the subsequent transition state in ethene hydrogenation by Wilkinson's catalyst (from ref. [13]).

The important features of the intermediate are the short C=C distance, which indicates that the bond order remains very close to 2, and the very long Rh–ethene distance. The structure of this intermediate may be compared with that of platinum complex Zeise's salt, where the C=C bond order is close to that of ethene adsorbed on Rh(111). The platinum–ethene distance in the salt is considerably shorter than in the Wilkinson catalyst case and the C–C bond distance is longer. This suggests that in the homogeneous case ethene is only weakly rehybridised from the π bonded state. The long metal–olefin distance is ascribed to the strong influence of the hydride *trans* to the ethene. When ethene is trans to chloride the Rh–C distance is calculated to be much shorter, at ca. 2.1 Å. Ethene bonding to the active complex of the Wilkinson catalyst therefore resembles the weakly adsorbed state which is important on single crystal metal surfaces.

In heterogeneous studies the parallel occurrence of exchange and hydrogenation is well recognised. Exchange into the olefin is not normally considered in the homogeneous case. It should be noted, however, that the decomposition of the ethyl intermediate, which is the major route to exchange on the heterogeneous catalysts, takes place by β-hydride elimination, normally regarded as facile in homogeneous chemistry. Exchange in alkene containing organometallic complexes has been well demonstrated [21], so again there is a parallel between the homogeneous and heterogeneous reactions.

Another interesting similarity can be pointed out. Ethane is only observed in our studies when hydrogen (or deuterium) is adsorbed first. If ethene is preadsorbed the subsequent hydrogen uptake is decreased and no hydrogenation is observed, so hydrogen preadsorption may be necessary to allow ethene and hydrogen to bind at the same surface site. In homogeneous hydrogenation the order of addition of reactants to the complex is also important. Addition of the alkene first is considered to generate spectator species such as the $[L_2RhCl]_2$ dimer, which does not participate in the catalytic cycle (fig. 1). It is tempting to speculate that ethene becomes too strongly bound to the rhodium complex.

We can therefore give a positive answer to one of our key questions: there are indeed very close mechanistic parallels between homogeneous and heterogeneous hydrogenation.

4.4. THE RELATIONSHIP BETWEEN STOICHIOMETRIC AND CATALYTIC HETEROGENEOUS HYDROGENATION AND MECHANISTIC SUMMARY

Our mechanistic conclusions about the stoichiometric hydrogenation of ethene on Rh(111) are summarised in the scheme which forms fig. 1. About 2% of the ethene initially adsorbed on the surface undergoes hydrogenation and a similar amount undergoes exchange of one hydrogen atom with deuterium, appearing in the gas phase as C_2H_3D when C_2H_4 is adsorbed initially. Considering the statistics but neglecting isotope effects in the exchange process we estimate that about one half of all ethyl species formed are further hydrogenated and give ethane. The remainder revert to adsorbed ethene. In the experiments with C_2D_4, loss of deuterium leads to a mono-exchanged species.

We believe that our mechanism is of relevance to hydrogenation of ethene under catalytic as well as stoichiometric conditions. The most direct comparison of our stoichiometric studies is with the catalytic studies of Kemball on evaporated rhodium films at 169 K [3]. He observed that the hydrogenation and exchange reactions occurred at almost identical rates with an activation energy for both reactions of ca. 30 kJ mol^{-1}, close to our figure of 40 kJ mol^{-1}. He calculated the ratio in which adsorbed ethyl species converted to adsorbed ethylene or hydrogenated to ethane, reporting values of 12 for nickel and 0.4 for tungsten. No figure for rhodium was given, however his results suggest that the ratio is between these limits, and for rhodium we find a value of 1. Most importantly, Kemball determined the ratio of probabilities that an adsorbed ethene molecule would *desorb* or become an adsorbed ethyl species, reporting a value of 3 for both nickel and tungsten: again rhodium was not calculated, but it should be very similar. This high value at the low temperature of 169 K shows clearly that weakly adsorbed species are being hydrogenated, supporting our central postulate. In our stoichiometric experiments, the ratio of ethene desorbing to that hydrogenating is about 10.

The involvement of a very weakly held species is also in agreement with the results of Thomson and Webb [7], although they suggest that hydrogen transfer occurs above a strongly bound layer at the metal surface. The activation energy which we observe for ethane formation in the stoichiometric experiment is in good agreement with that found for the catalytic hydrogenation, again ca. 40 kJ mol^{-1} [1]. This again indicates that ethylidyne, which is present only in higher temperature hydrogenations, is not of catalytic relevance.

The case for the importance of a weakly bound ethene intermediate is reinforced by evidence that more strongly held ethene derived species are not rapidly hydrogenated. Ethylidyne has already been discussed, but the present results and other single crystal studies show that it is common for ethene and hydrogen to coexist on a catalyst surface at temperatures above where *ethane* formation can be observed, and yet for no reaction to occur. In these situations ethene is too strongly adsorbed for reaction.

We can therefore confidently answer another of the original key questions: the ethene species being hydrogenated is only weakly adsorbed, with comparatively little perturbation of the sp^2 hybridisation of the carbon atoms in the molecule.

We can only speculate about the importance of hydrogen transfer between adsorbed species. Under our conditions hydrogen transfer seems unlikely to be important. It must involve breaking a strong C–H bond, while hydrogen *addition* only requires the breaking of the much weaker M–H bond. In summary, we conclude that the important intermediate in ethene hydrogenation is a weakly held, π bonded species formed in the desorption trajectory of the ethene molecule. The pathway proposed suggests that there are very strong similarities between heterogeneous hydrogenation and the homogeneous reaction.

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