

Acetic Acid on Rh(110): The Stabilisation and Autocatalytic Decomposition of Acetate

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The decomposition of acetic acid on a Rh(110) single crystal has been studied using molecular beam reaction spectroscopy and temperature-programmed desorption (TPD). It was found that on all clean and coadsorbate predosed surfaces the first step of the reaction was the decomposition of the acid to hydrogen and acetate. On the clean surface the decomposition will go further to produce CO₂, carbon, and hydrogen. However, on carbon-, nitrogen-, or oxygen-predosed surfaces the acetate is stabilised to different extents. The reasons for the stabilisation effects are discussed, and a few structural sources are described. A "surface explosion" was observed with the acetate decomposed on the coadsorbate precovered surfaces. © 1993 Academic Press, Inc.

1. INTRODUCTION

As the most versatile transition metal to catalyse the hydrogenation of CO, rhodium has been the subject of considerable study. It is well known that depending on the exact state of the surface, the support and/or promoter used, and the reaction conditions, the product spread can include both hydrocarbons and alcohols (1, 2). Because of the obvious industrial interest, the synthesis of ethanol on rhodium catalysts has long drawn great attention (3); however, the mechanism of this reaction is still a controversial topic. Recently, one of us (4) reviewed this subject, giving a mechanism with acetate as an important intermediate. In our previous papers (5, 6), acetate formation was observed during ethanol oxidation on the Rh(110) surface, and an unusual mechanism of its decomposition, a "surface explosion" was found. Madix and co-workers (7, 8) were the first to report this kind of effect in TPD, when they observed the explosive decomposition of the adsorption phase of formic acid or acetic acid on a Ni(110) sample. However, there has been little further work in this area, and no other reports of such phenomena from organic adsorbates as far as we are aware. In this work, we found the formation of acetate

with the acetic acid/Rh(110) system, together with the "surface explosion" during TPD, but it was revealed that the stability of the acetate formed is very sensitive to the exact surface state of the sample, especially to the presence of a coadsorbate. Three coadsorbates have been used, namely, carbon, oxygen, and nitrogen; all of them can modify the stability of acetate when predosed onto the sample, so that the decomposition starts at different temperatures. Indeed, the presence of a coadsorbed atom appears to be an essential requirement for the observation of an autocatalytic "surface explosion."

2. EXPERIMENTAL

The techniques we have used are molecular beam reaction spectroscopy and temperature programmed desorption (TPD). The equipment and methodology were described in detail elsewhere (9, 10). The gas was first dosed into the gas line of the molecular beam system, and the beam impinged on the sample surface with a 0.29-cm-diameter circular spot as soon as a flag blocking it was lifted. The molecular beam system is an ideal means to study surface reactions *in situ*. It is a *single collision reactor*, since a molecule in the beam hits the

surface only once and is either reflected or desorbed again, or it sticks on the surface. The latter can lead to a reaction and release of products. A mass spectrometer (MS) is used to monitor the reaction. If there is no adsorption of the beamed gas, the corresponding MS signal would reach its maximum immediately and keep constant during beaming. However, if by any means the gas is consumed, the MS signal will appear on a lower level, and the difference between this level and the maximum rise (total reflection) reflects the sticking or reaction probability. Any reaction products can also be followed simultaneously. Subsequent TPD measurements can provide more information on the surface reaction, to explore any strongly held products not released during beaming.

The sample is a 1.1-cm-diameter circular rhodium single crystal disc oriented to within 0.4° of the (110) direction, which was cleaned by cycles of argon ion bombardment-annealing-oxidation and CO treatment until a sharp and clean (1X1) LEED pattern was achieved and an Auger spectroscopic measurement revealed only rhodium signals. Every time before beaming it was necessary to check the cleanliness of the surface by O_2 or CO adsorption, and if there was any doubt the initial checks by LEED and Auger were repeated, and the cycles of cleaning carried out again when necessary.

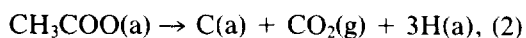
To achieve a precoverage of oxygen on the sample the oxygen was simply dosed through the molecular beam for a certain period. To achieve a precoverage of nitrogen the sample was first exposed to an NO beam at 393 K; at that temperature most NO decomposed to nitrogen and oxygen atoms (11). At the same temperature CO was beamed to remove adsorbed oxygen atoms by reaction to CO_2 , while nitrogen remained on the surface. Subsequently the sample was heated to 503 K and kept there for 1 min, which desorbed the unreacted CO and any molecular NO. A small portion of the nitrogen atoms recombined to N_2 and were released, but most remained. The ad-

sorption of oxygen and NO on Rh(110) have been described in detail elsewhere (11, 12). To deposit carbon, acetic acid was beamed at ca. 315 K and heated afterwards to ca. 573 K, during which the acid decomposed to carbon, hydrogen, and CO_2 ; the CO_2 and hydrogen were desorbed, leaving carbon alone on the surface. The behaviour of the carbon deposition will be discussed in detail elsewhere (13). All the adsorptions were carried out at ca. 315 K, unless otherwise stated.

3. RESULTS

3.1. On Clean Rh(110)

The adsorption of acetic acid onto Rh(110) is shown in Fig. 1A and resulted in CO_2 and hydrogen release. By analogy with the adsorption of the low-carbon acids on rhodium samples the acetic acid will decompose into acetate and hydrogen first (14–18). The acetate at 315 K was not stable on Rh(110) and decomposed to CO_2 , surface carbon, and hydrogen. After a short period of acetic acid beaming up to 1 min the subsequent TPD measurement detected only CO desorption, which is due to the contamination, as the ratio of the beamed area to that of the whole sample face is about 1 : 14. By comparing the peak area of the CO desorption and the CO adsorption area when CO was beamed to a clean surface, the CO contaminant was equivalent to ca. 7% of the saturation adsorption. Afterwards a LEED measurement showed a 2×2 pattern in the beam area, indicating a carbon-contaminated sample. The mechanism would be as follows:



After a certain coverage of carbon is formed (90 s beaming, that is, ca. 1.3×10^{14} acetic acid molecules/cm² being introduced) the stabilized acetate intermediate begins to form, as described below (Section 3.2).

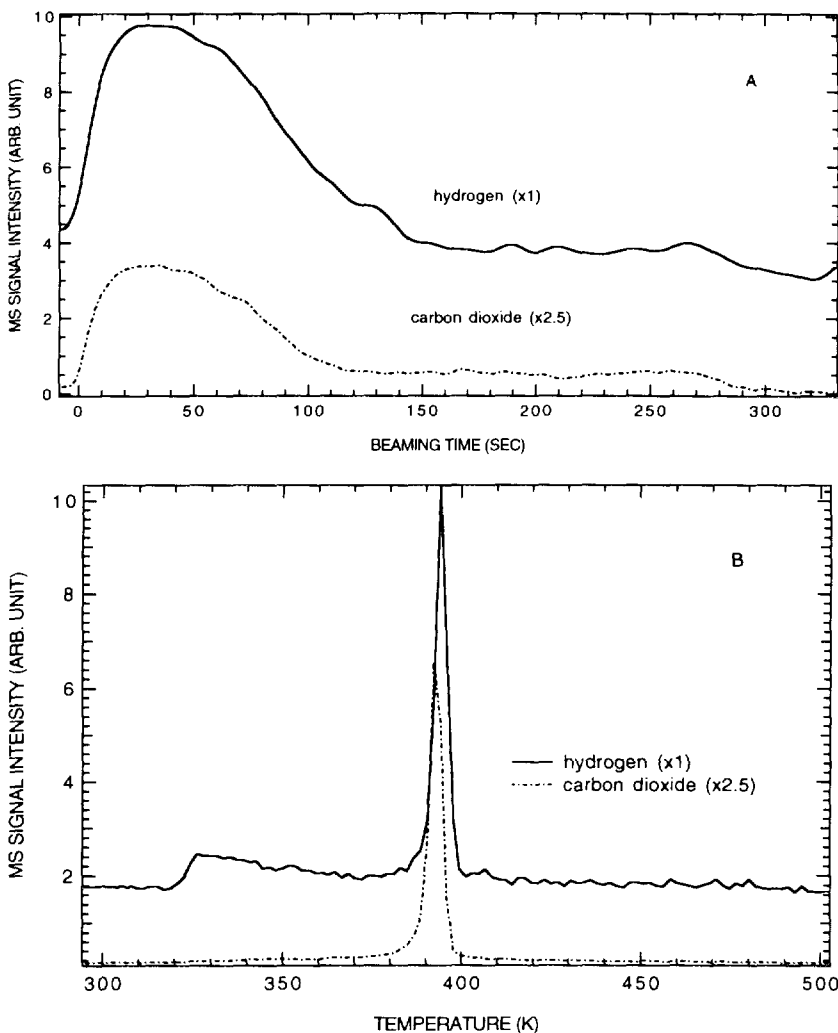


FIG. 1. (A) Acetic acid beaming onto clean Rh(110) at 315 K. (B) TPD after (A). Heating rate = 1.5 K/s.

3.2. On Carbon-Precovered Rh(110)

From Fig. 1A it can be seen that after about one minute of acetic acid beaming the signals of hydrogen and CO_2 start to decrease, and are constant after another 1.5 min. The hydrogen signal seems to decrease more slowly and end later than that of CO_2 , which indicates a stabilised acetate phase on the surface formed by dehydrogenation at the acid group. When the sample was heated after adsorption the TPD spectra showed the very sharp, coincident

peaks of CO_2 and hydrogen at 391 K (Fig. 1B), which we observed in the TPD spectra of the ethanol adsorption phase on the oxygen-precovered Rh(110) surface, and described as a "surface explosion" (5, 6), after Madix and co-workers (7, 8). It was suggested that the beamed ethanol reacted with surface oxygen and acetate was formed (5). The acetate was stabilised by the oxygen and remained on the surface until being heated to ca. 390 K, where it decomposed into hydrogen, carbon, and CO_2 .

In the case of acetic acid, no surface oxygen is needed to form acetate; it is formed straight away upon adsorption, and, if the surface is clean enough, decomposes rapidly. However, the carbon deposition accumulated during the reaction contaminates the surface gradually and poisons the decomposition, so that an acetate phase can be retained on the surface below 380 K. The question posed by this carbon-induced stability is: can other coadsorbates have a similar effect? Keeping this in mind we did other experiments of acetic acid adsorption onto nitrogen- and oxygen-precovered Rh(110), as detailed in the following sections.

3.3. On Nitrogen-Precovered Rh(110)

With the method mentioned in Section 2 an atomic nitrogen phase could be formed. We are not certain about the coverage values because of the somewhat complicated procedure and the possible loss during heating. Nevertheless, according to many authors (19–23), the saturation coverage of NO on Rh(111) and Rh(100) is rather high, ranging from 0.65 to 0.75 ML. Particularly, Bowker *et al.* (11) reported that the coverages of atomic nitrogen and oxygen after a saturated NO adsorption were both 0.75 at 380 K. Based on these findings we suggest that after saturation NO adsorption and the CO and heating treatments the coverage of the atomic nitrogen remains between 0.6 and 0.7 monolayers. By reducing the initial NO dosing, or repeating the process for another one or more cycles, the coverage of nitrogen can be changed, but the exact value is more difficult to determine. Estimates of the coverages are given in Table 1.

Figure 2 shows the TPD spectra of the

acetic acid phase on nitrogen-precovered surfaces. Apparently the ability of the Rh surface to decompose acetic acid/acetate is greatly reduced by the influence of the nitrogen atoms. With as little as 15 s of NO beaming, CO₂ and hydrogen signals evolved during adsorption are significantly reduced. Interestingly, the hydrogen signal lasted longer than CO₂, again, like that with initially clean surface, indicating that some acetate might be left behind. As a trend the atomic nitrogen layer decreased the peak height of the explosive products gradually, but at the same time the peak was broader, and therefore the uptake seemed little changed. In Table 2 the desorption peak areas of CO₂ after saturated acetic acid adsorption versus NO dosing period are listed. It should be mentioned that due to the sharpness of the desorption peaks this measurement is subject to a $\pm 10\%$ error. The acetate decomposed at lower temperature than it did when coadsorbed with C: the nitrogen layer after 5 s NO dosing moved the peak temperature to 386 K (Fig. 2B). This is because it is mostly coadsorbed with C. After 15 s dosing it moved to 374 K, which reflects the temperature for acetate adsorbed with N atoms alone (Fig. 2C). Higher nitrogen coverages shifted the peak position no more.

The atomic nitrogen layer also decreased the beaming time needed to form stable acetate on the surface. If the surface was covered by N obtained by 30 s of NO beaming and the subsequent treatments, after 60 s of acetic acid beaming the explosive decomposition of acetate was detectable by TPD, instead of ca. 120 s for the initially clean surface.

TABLE 1

Estimated Coverages of Atomic Nitrogen

NO beaming period	5 s	15 s	30 s	3 min
Coverage	0.06–0.07	0.17–0.2	0.32–0.37	0.6–0.7

TABLE 2

The Desorption Peak Areas of CO₂ after Saturated Acetic Acid Adsorption versus the Beaming Period of NO (in Arbitrary Unit)

NO predose	0 s	5 s	15 s	180 s
CO ₂ area (a.u.)	384	381	338	326

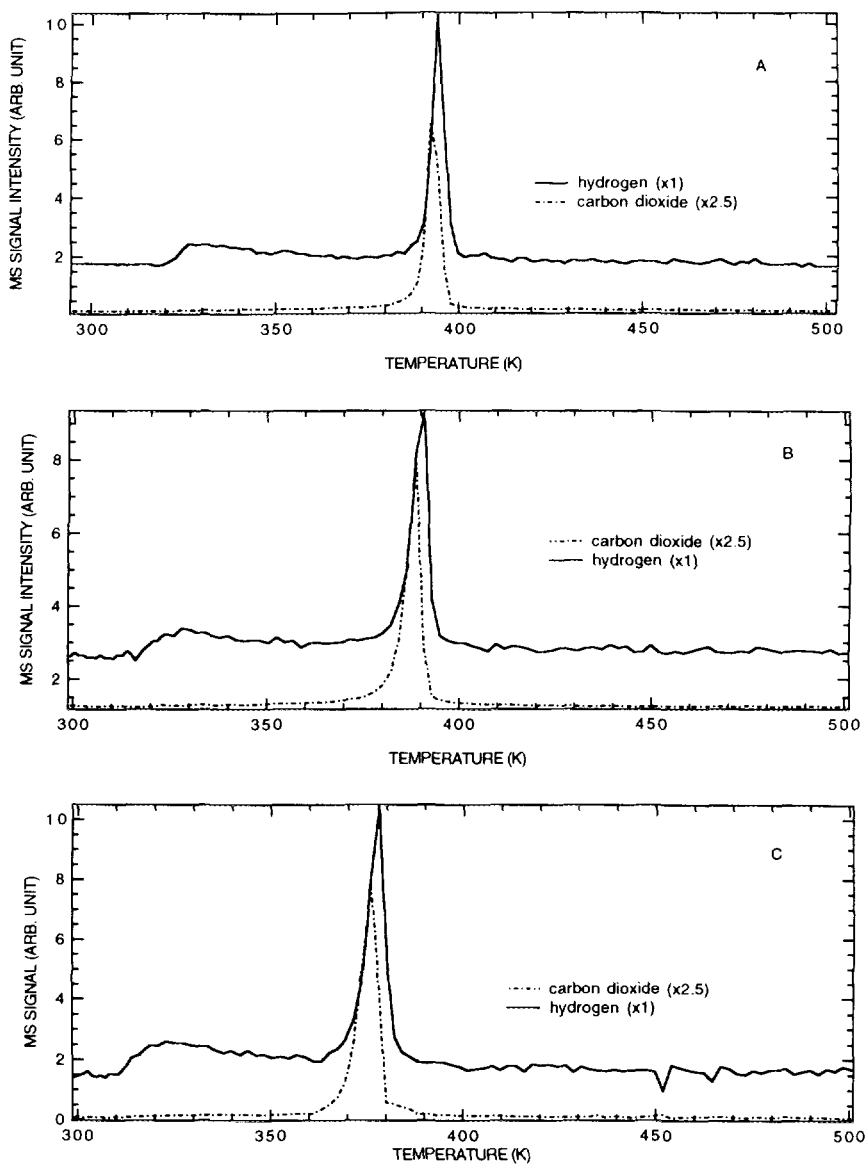


FIG. 2. TPD of the acetic acid phase after beaming onto (A) clean, (B) 5 s of NO-predosed, and (C) 15 s of NO-predosed Rh(110).

3.4. On Oxygen-Precovered Rh(110)

Figures 3 and 4 show the adsorption and TPD spectra of acetic acid adsorbed on oxygen-precovered surfaces. After 60 s oxygen predose there was little if any CO_2 and hydrogen released during acetic acid beaming; instead, water was the only product detected (Fig. 3). Longer oxygen beaming did

not result in much difference during subsequent acetic acid admittances. Much like nitrogen, oxygen precovering reduced the acetic acid beaming time needed to stabilise acetate on the surface: onto the oxygen fully covered surface, after 40 s of acetic acid beaming the TPD showed the explosive desorption but, this time, produced

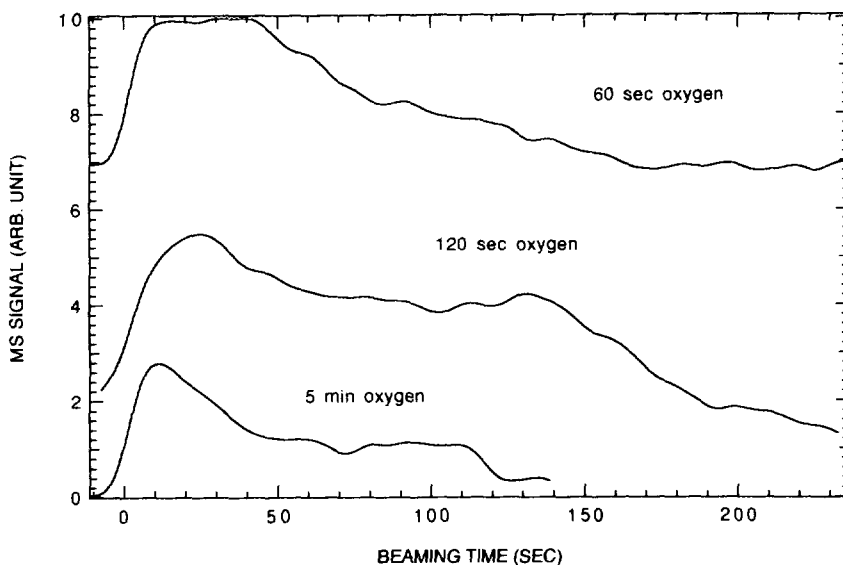


FIG. 3. Water desorption during acetic acid beaming onto Rh(110) with various amounts of oxygen pre-dose. Water was the only product detectable during adsorption after such doses.

CO₂ and water. This is due to the reaction of the hydrogen released with the excess surface oxygen. Actually the more concentrated the surface oxygen was, the higher the ratio between water and hydrogen in the products. If oxygen was dosed for 60 s or less, the main products were hydrogen and CO₂, with water as a *minor* one (Figs. 4A and 4B). Higher oxygen doses of 120 s depressed all the peak heights of the three, but the water signal was stronger than that of hydrogen (Fig. 4C). With saturated oxygen pre-dosing there was no hydrogen signal during TPD at all (Fig. 4D). In Table 3 the coverages of oxygen versus the dosing period are listed.

With increased surface oxygen the explosion temperature increased. With 30 and 60 s of oxygen pre-dosed the explosion temperature was 406 K (Figs. 4A and 4B), in com-

parison to the 391 K of the carbon-contaminated surface. With 120 s pre-dosing, this was increased to 417 K (Fig. 4C), and with full oxygen pre-coverage (5 min) it was 465 K (Fig. 4D).

Like nitrogen, high oxygen pre-coverage made the explosive desorption peaks less sharp. The full width at half maximum of CO₂ peak was broadened from ca. 5 K for the carbon-contaminated surface (Fig. 1B) to ca. 16 K for the saturated oxygen-pre-covered surface (Fig. 4D).

4. DISCUSSION

From the results above, it is likely that during acetic acid adsorption on the clean Rh(110) surface the O–H bond breaks and the acetate so produced is adsorbed with both O atoms attached to a pair of adjacent Rh atoms in a bidentate structure with coincident hydrogen evolution. This is by analogy with simple carboxylic acids adsorbed on other transition metals (14–18). With a clean surface there are free Rh sites available around the adsorbed acetate. It is generally accepted that both formate and acetate adsorb on (110) faces of transition

TABLE 3

O Coverage versus O₂ Dosing Period

Period (s)	30	60	120	300
Coverage (ML)	0.56	0.62	0.67	0.70

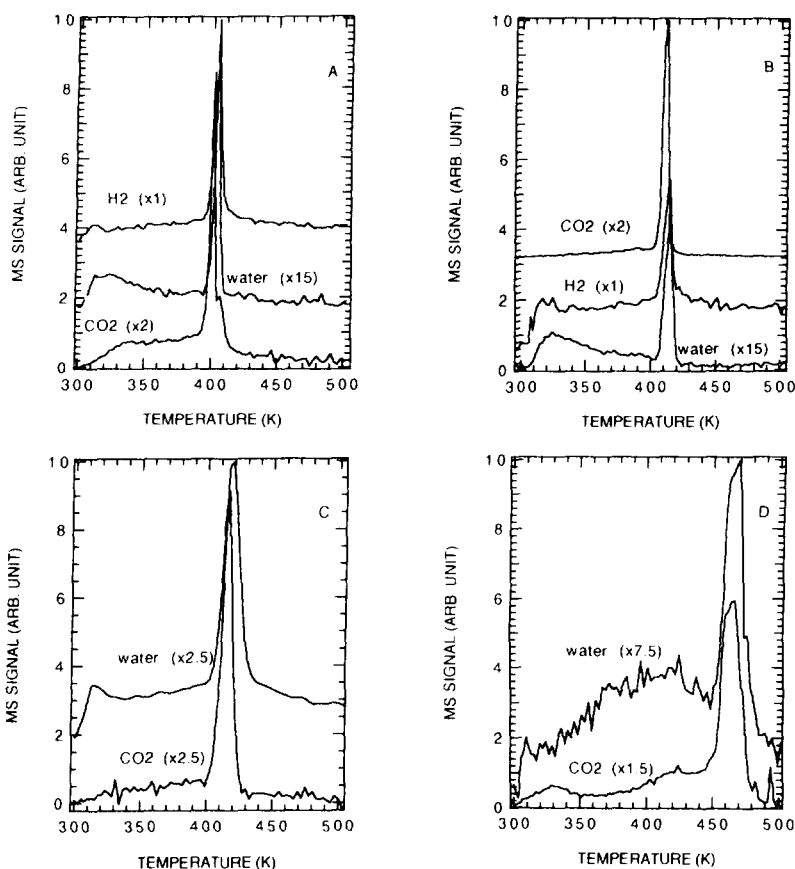


FIG. 4. TPD of the acetic acid phase after beaming onto (A) 30 s, (B) 60 s, (C) 120 s, and (D) 600 s of oxygen-predosed Rh(110).

metals symmetrically, so that both oxygen atoms in the intermediate are equivalent (14–18). There are many possible reasons for the stabilisation of the acetate and for its autocatalytic decomposition, but for simplicity here we make the assumption that the acetate is adsorbed with the O–C–O plane in the [110] azimuth (illustrated in Fig. 5). This is supported by work on other metals, for instance HREELS of formate on Ni(110) (24, 25), NEXAFS and EXAFS of formate on Cu(110) (26–28), HREELS of formate on Pt(110) (29), photoelectron diffraction of formate and acetate on Cu(110) (30–32), and angle resolved photoemission studies of acetate on Cu(110) (32, 33). In order to confirm/disprove this view we

shall shortly begin studies using “forward focussing” measurements of core level XPS emission in an attempt to establish the detailed structure of acetate on this surface. We shall combine this with a study of the acetate on Rh(111), for which preliminary results indicate a much more stable acetate on the clean surface (34). We shall continue on the assumption of (110) oriented intermediate, with the C–C bond near normal to the surface plane.

How then can we explain the significantly increased stability (by > 100 K in temperature) of the acetate which is induced by the presence of a coadsorbed atom? There appear to be three major possibilities, as follows.

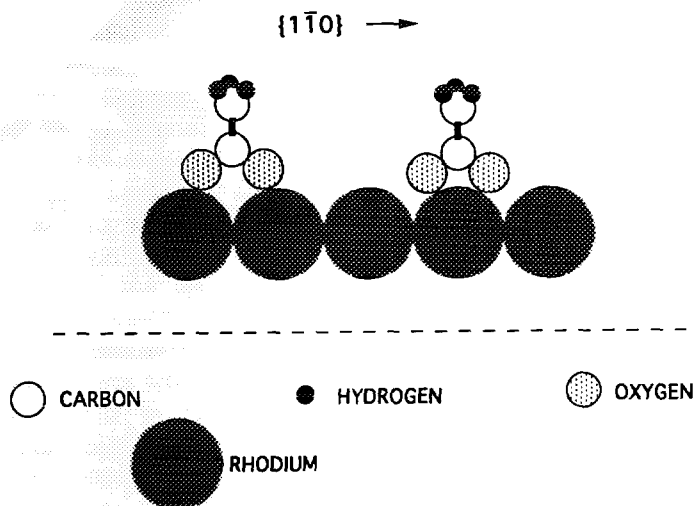


FIG. 5. Possible acetate adsorption sites on Rh(110).

(1) *Site blocking*. It could be that the adatom simply acts as a poison, blocking the sites adjacent to the acetate which are active for decomposition. This can be visualised as shown in Fig. 6 with the atom sterically hindering the frustrated rotation mode of the acetate which would occur in the [001] direction and is likely to be the mode of importance in the decomposition reaction pathway. It is likely that the pres-

ence of the atoms would cause an increase in the energy required in this mode to enable surface attack at the active centre in the molecule (either C-H or C-C bond breakage, discussed further below).

(2) *Surface reconstruction*. It is possible that surface reconstruction occurring upon preadsorption of the atomic species (known to occur for oxygen (12, 35)) creates different sites from those on the clean surface

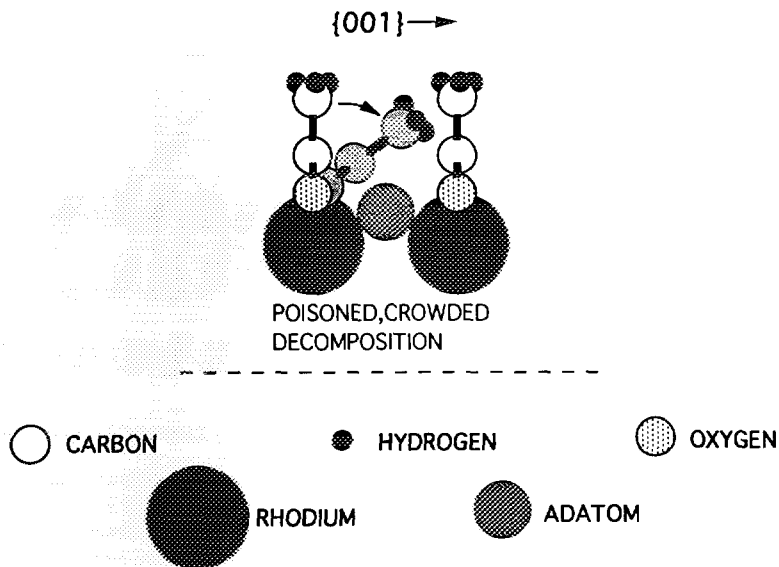


FIG. 6. Site blocking model of the acetate stabilisation.

described above. It is proposed, for instance, that oxygen induces row pairing on Rh(110) (12) which may induce the acetate to bridge across adjacent rows in the [001] direction.

(3) *Adsorbate-induced ordering.* Illustrated in Fig. 7 this is perhaps the most useful of the possibilities to explain our observations. It can explain the "poisoning" effect on acetate decomposition, because the blocking of sites is actually done largely by the acetates themselves, for which ordering is induced by the presence of the ordered atomic layer. On the clean surface the acetate is unstable at room temperature and the adatoms confer stability by (i) being adjacent to the acetate with which there is an attractive interaction and (ii) the ordering, which puts acetate onto the active sites for decomposition, further blocking the reaction. The big advantage of this is that, in our previous paper, it was proposed that there were vacancies in the *acetate* adlayer which induced the autocatalytic "explosion," the full equation for the evolution being of the following form:

$$R_d = k \cdot B \cdot \theta_N^{1/2} (1 - \theta)^{1/2}. \quad (4)$$

Here the model was of a self-accelerating reaction beginning at certain "special" sites (e.g., steps, defects) whose coverage is θ_N , and then a circular patch of acetate-free surface *expands* until all the acetate is lost. The "explosion" is related to the negative dependence on acetate coverage θ , the opposite of normal desorption processes. In Eq. (4), k is the "normal" rate constant and B is a constant containing the density of active sites at the circumference of an island, the area of the beam, and the total number of sites. Thus, within this model, acetates block decomposition and the cause of the explosion is the adsorbate-induced ordering of the acetate layer. The detailed mathematical treatments of such systems will be described in more detail in the near future (36).

Thus we favour the latter model as the best description of our experiments, but all three possibilities must be left on the table. It is only through further experiments that we shall be able to eliminate some of these and define the detailed mechanism of this reaction at the atomic level. As described above, these studies will include structural methods (angle-resolved XPS, forward fo-

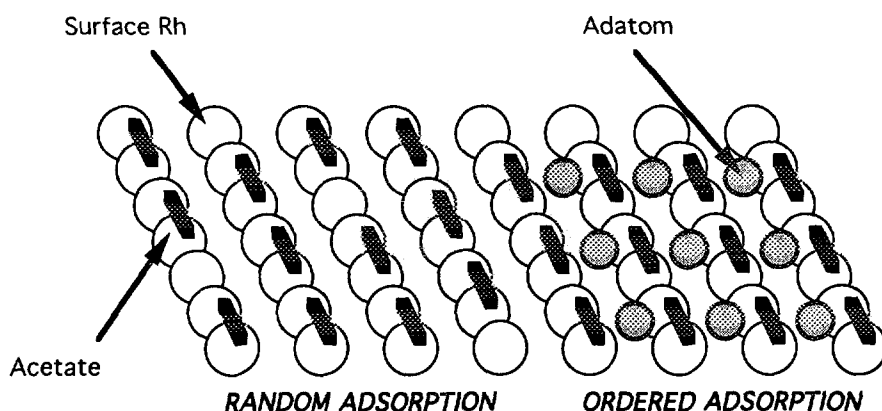


FIG. 7. Schematic diagram illustrating the effect of adsorbed atoms on ordering the acetate. The acetate is shown as a bar occupying two surface atoms, though it is possible that it is in an atop, rather than bridged configuration. Without an ordered adsorbate the acetate adsorbs randomly, leaving many vacancies in the adlayer which are active for decomposition. With the ordered atomic adlayer, due to interactions with the adatoms the acetates are ordered with respect to each other and mutually block their decomposition.

cussing), studies on other planes (work on Rh(111) has just begun and has recently been reported (34)), and we shall also carry out reflection infrared studies.

The general effects of different coadsorbed atoms are very similar, the only major difference being the peak temperature at which the "explosion" is seen. It is likely that, in terms of the model outlined above, this is due to a different number of initiation sites (θ_N in Eq. (4)) for each atomic adsorbate which in turn implies, as might be expected, a different degree of order in each of these adlayers. Thus it would appear that the N adlayer has the most defects (lowest temperature peak, Fig. 2) and oxygen the least (Fig. 4, highest temperature peak). However, it is also possible that different electronic effects of these adatoms on the intermediate environment could affect the acetate stability.

Returning to the mechanism of bond breaking itself, it is not completely clear how step 2 shown above occurs. Does C-C bond breaking or dehydrogenation occur first? One piece of evidence which could support the former is the observation of methane formation in the case of ethanol oxidation, described in earlier publications (5, 6). However, no methane is formed in acetate decomposition and it is probably a secondary step of reaction. Thus we favour the proposal of decomposition occurring through methyl group dehydrogenation initially followed by total rearrangement and multiple bond breaking. It is also hard to imagine the surface interacting with the carboxylate carbon atom when the methyl group is so bulky and to some degree protects the α -carbon from attack by the surface. This is illustrated in Fig. 6. Nevertheless, this is not proved and remains open to further experimentation.

5. CONCLUSION

On the clean Rh(110) surface acetic acid adsorbs to form acetate and hydrogen. Acetate will decompose further to carbon, CO₂, and hydrogen at room temperature. The

coadsorption of atomic carbon, nitrogen, and oxygen stabilises the surface acetate. The cause of the stabilisation is still an open question, but we propose that it is likely to be caused by adsorbate-induced ordering. A "surface explosion" is observed during the TPD experiments when the stabilised acetate decomposes autocatalytically.

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