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Probing elementary steps under reaction conditions using infrared spectroscopy

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Abstract

The reaction pathway for the palladium-catalyzed synthesis of vinyl acetate from acetic acid, ethylene and oxygen is investigated using reflection-absorption infrared spectroscopy by monitoring the rate of acetate titration by gas-phase ethylene. This reveals that acetate species are removed by reaction with gas-phase ethylene resulting in vinyl acetate formation. Reaction with C_2D_4 reveals a large (~6) isotope effect indicating that hydrogen is involved in the rate-limiting step. This also results in the appearance of an infrared feature that is assigned to an acetoxyethyl-palladium intermediate. Acetate reaction rates are different for the isotopomers, CH_2CD_2 and CHDCHD. These observations are consistent with a reaction pathway first proposed by Samanos in which ethylene reacts with an acetate species to form an acetoxyethyl-palladium intermediate, which then reacts to form vinyl acetate by a β-hydride elimination reaction.

Key words: Infrared spectroscopy; Pd(111); vinyl acetate synthesis.

Estudio de las etapas elementales bajo condiciones de reacción de la síntesis de acetato de vinilo usando espectroscopía infrarroja

Resumen

En este trabajo se estudia el mecanismo de reacción de la síntesis catalizada por paladio de acetato de vinilo a partir de ácido acético, etileno y oxígeno usando espectroscopia infrarroja de reflexión-absorción, evaluando la velocidad de titulación de acetato con etileno de la fase gaseosa. Los resultados revelaron que las especies de acetato son promovidas por la reacción con etileno de la fase gaseosa resultando en la formación de acetato de vinilo. La reacción con C_2D_4 reveló el efecto de un isótopo grande (~6) que indicó que el hidrógeno está involucrado en la etapa limitante de la reacción. También se observó la aparición una banda en el infrarrojo que fue asignada a un intermediario acetoxietil-paladio. Las velocidades de la reacción de acetato fueron diferentes para los isotopomeros, CH_2CD_2 y CHDCHD. Estas observaciones son consistentes con el mecanismo de reacción inicialmente propuesto por Samanos en el cual el etileno reacciona con las especies de acetato para formar el intermediario acetoxietil-paladio, el cual reacciona posteriormente para formar el acetato de vinilo por una reacción de eliminación β-hidruro.

Palabras clave: Espectroscopia infrarroja; síntesis de acetato de vinilo; Pd (111).

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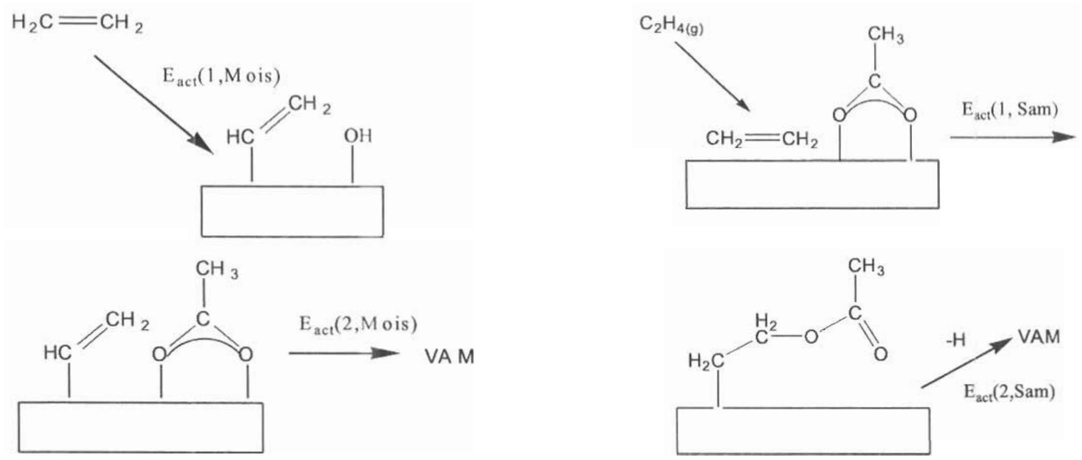
Introduction

The ability to understand catalytic reaction pathways in detail requires kinetic measurements to be made on the elementary reaction steps. When the heats of adsorption of the reactants are larger than, or of the same magnitude as, the activation energy of the surface reaction step, ultrahigh vacuum techniques such as temperature-programmed desorption can be used to probe elementary step reaction kinetics. If this is not the case, the reactants merely desorb without reacting. In such cases, elementary reaction steps can only be explored when the surface is pressurized by the reactant and requires the nature of the surface to be probed in the presence of high pressures of one or more of the reactants, therefore requiring surface-sensitive techniques that can operate under high-pressure conditions. Photon-based methods such as infrared spectroscopy are ideally suited to such experiments and its utility is illustrated in the following using the example of the palladium-catalyzed synthesis of vinyl acetate monomer (VAM) from acetic acid, ethylene and oxygen:

$$CH_3COOH + C_2H_4 + \tfrac{1}{2}O_2 \rightarrow CH_3COOC_2H_3 + H_2O \quad [1]$$

a reaction that was first discovered some thirty years ago (1). Two alternative mechanisms have been proposed to describe the palladium-catalyzed formation of VAM. The first, suggested by Samanos, involves the coupling of ethylene directly with chemisorbed acetate on Pd (2). The resulting acetoxyethyl-palladium intermediate then undergoes a β-hydride elimination reaction to form vinyl acetate. Alternatively, ethylene could first dehydrogenate to form a vinyl-palladium intermediate, which then couples with a surface acetate species to form VAM directly. This is known as the Moiseev mechanism (3) and these pathways are illustrated in Scheme 1.

The structures of adsorbed η^2-acetate (4) and ethylene (5) have been determined separately on Pd(111) using low-energy electron diffraction (LEED) and reflection absorption infrared spectroscopy (RAIRS) (4-7). These experiments reveal that the acetate adsorbs with the molecular plane oriented perpendicular to the palladium surface with the oxygen atoms located almost above atop palladium sites such that the carbon atom in the carboxylate is positioned directly above a bridge site. The saturation coverage is ~1/3 of a monolayer (where coverages are referenced to the palladium atom site density on the surface) (4). Ethylene is



Scheme 1. Illustrations of the proposed Moiseev and Samanos reaction pathways.

substantially rehybridized on clean Pd(111) and also adsorbs at the bridge site on the clean surface so that the adsorption of di-σ-bonded ethylene should therefore be blocked by the acetate species (5).

The work outlined in the following addresses the question of the nature of the reaction pathway primarily using isotopically labeled reactants.

Experimental

The apparatus that was used to collect the infrared spectra has been described in detail elsewhere (7). Briefly the sample cell used for these experiments is constructed from a six-way cross, which was modified by moving one flange by ~20° to allow infrared radiation to impinge on the sample with the optimal 80° infrared incidence angle. The cell is attached to the main chamber *via* a gate valve, which, when closed, completely isolates the infrared cell from the ultrahigh vacuum chamber and, when open, allows sample transfer into it. Spectra are collected with a Bruker Equinox spectrometer using a liquid-nitrogen-cooled mercury cadmium telluride detector. Kinetic measurements were generally carried out by collecting spectra for 100 scans. The large intensity of the asymmetric OCO vibrational mode allowed relatively low signal-to-noise ratio spectra to be collected with such short collection times. Some experiments were carried out using a larger number of scans to yield better signal-to-noise ratio spectra to allow additional surface species to be identified.

The surface was pressurized by ethylene, which effused from a capillary placed close to the Pd(111) single crystal sample. The source enhancement factor was estimated to be ~200 by comparing the uptake of CO onto the surface with the known adsorption kinetics of CO on Pd(111). The adsorption kinetics of acetate species on Pd(111) was measured both from the variation in intensity of the acetate vibrational mode at 1414 cm^{-1} (assigned to the asymmetric OCO vibrational mode) (8) and using the King and Wells method in a separate chamber. The latter method measured the adsorbate coverage directly and, since both methods yielded identical acetate uptake curves, this indicates that, within experimental error, the acetate coverage varies linearly with the intensity of the 1414 cm^{-1} mode.

The Pd(111) single crystal was cleaned using a standard protocol and its cleanliness monitored using Auger spectroscopy and temperature-programmed desorption collected following oxygen adsorption. The ethylene (Matheson, Research Grade), acetic acid (Aldrich, 99.99+ %), C_2D_4 (CIL. 98% D), CD_2CH_2 (CDN, 99% D), CHDCHD (CDN, cis/trans mixture, 99% D) and $^{18}O_2$ (CIL, 95% $^{18}O_2$) were transferred to glass bottles, which were attached to the gas-handling line for introduction into the vacuum chambers.

Results

A Pd(111) surface saturated with acetate species was pressurized with ethylene (P(ethylene) = 2×10^{-7} Torr) and the integrated intensity of the acetate feature at 1414 cm^{-1} (proportional to the acetate coverage) followed as a function of time, where the data for reaction with C_2H_4 (■) are displayed in Figure 1. This clearly shows that surface acetate species react with gas-phase ethylene and temperature-programmed desorption experiments performed in the presence of gas-phase ethylene confirm that these react to form vinyl acetate [9]. In order to investigate whether the rate-limiting step involves hydrogen, the acetate species on Pd(111) was also reacted with C_2D_4 (●) CD_2CH_2 (▲) and CHDCHD (■) and the resulting plots of acetate coverage *versus* time are also displayed in Figure 1. Shown as lines on this Figure are fits to a kinetic model that will be discussed in greater detail below. Clearly there are substantial differences in the reaction rates between C_2H_4 and C_2D_4 indicating that hydrogen is involved in the rate-limiting step. Interestingly, the reaction rates for

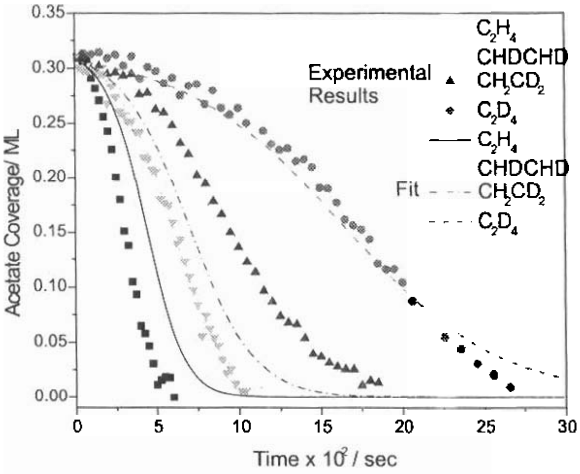


Figure 1. Plot of the time dependence of the coverage of the acetate species measured from the intensity of the 1414 cm^{-1} acetate mode for the reaction of C_2H_4 (■), CH_2CD_2 (▲), CHDCHD (▼) and C_2D_4 (●) with acetate species on Pd(111) with an ethylene pressure of 2×10^{-7} Torr at a reaction temperature of 327 K.

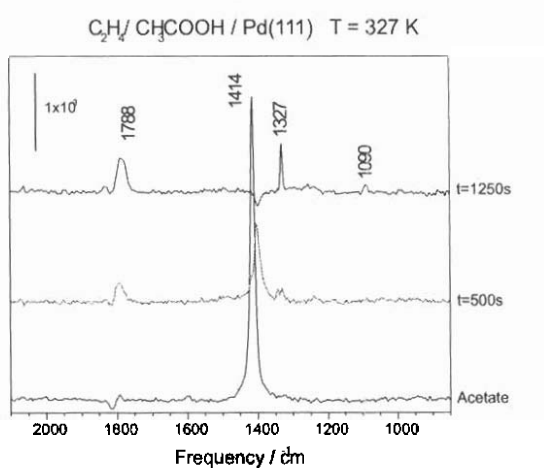


Figure 2. Infrared spectra of acetate species on Pd(111) reacted with ethylene at a pressure of ~2×10^{-7} Torr at 327 K for various times collected for 1000 scans to improve the signal-to-noise ratio. The reaction times are indicated adjacent to the corresponding spectrum.

d_2-ethylene isotopomers depend on the deuterium position: reaction is slower for the 1,1-dideuterated reactant than for 1,2 dideuteroethylene. The implication of this result will be discussed in greater detail below.

Experimental data shown in Figure 1 were collected for 100 scans to allow a large number of data points to be collected for the kinetic measurements. Similar experiments were carried out as a function of time, but now by collecting spectra for 1000 scans to yield better signal to noise. The resulting spectra are displayed in Figure 2 for reaction at 327 K on clean Pd(111) and show a decrease in the intensity of the 1414 cm^{-1} feature due to the removal of acetate species noted in Figure 1, along with the formation of ethylidyne (from the peak at 1327 cm^{-1}) [9]. An additional feature is observed to grow at ~1778 cm^{-1}, in the C=O stretching region. Heating an acetate-covered surface to this temperature in the absence of ethylene does not result in the appearance of this peak. Shown in Figure 3 are a series of infrared spectra collected at identical temperatures and ethylene pressures until the acetate species had been removed using: (b) C_2H_4 (reproducing the spectrum in Figure 2, (c) C_2H_4 on an ^{18}O-covered surface and (d) using C_2D_4. Shown for comparison is the spectrum of CO on Pd(111) (Figure 3a), where the CO exposure was selected to yield a similar intensity to the features produced by reaction between ethylene and adsorbed acetate species. This confirms that these features are not due to CO adsorbed from the background. The peaks at 1330 and 1090 cm^{-1} in spectra 3(b) and (c) are due to ethylidyne species (9). These data also show that surface oxygen does not appear to be involved in the surface reaction, but the 1778 cm^{-1} feature shifts to ~1718 cm^{-1} when the reaction is carried out using C_2D_4.

In order to establish whether the 1718 cm^{-1} feature is due to an isotope shift of the 1778 cm^{-1} mode, and to aid in establishing the nature of the species giving rise to the

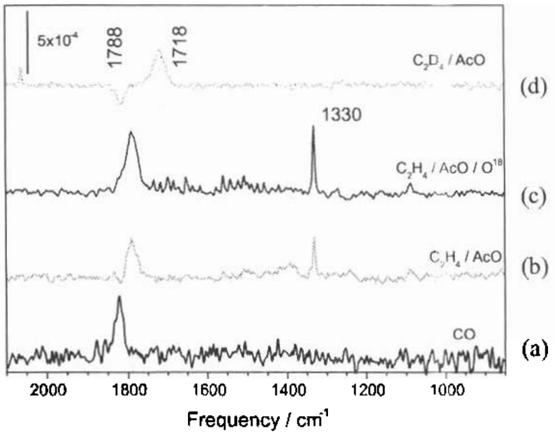


Figure 3. Infrared spectra of acetate species reacted with ethylene at 327 K until the acetate had been removed, for reaction with (b) C_2H_4 with acetate-covered Pd(111), (c) C_2H_4 with acetate-covered ^{18}O-(2×2)/Pd(111) (d) C_2D_4 with acetate-covered Pd(111). Shown for comparison in the infrared spectrum of CO on Pd(111) (a)

~1778 cm^{-1} feature, both d_6- and normal vinyl acetate were adsorbed on ethylidyne-covered Pd(111) at 300 K for ethylidyne coverages of 0.25 (saturation) and ~0.1 monolayers. The resulting spectra are shown in Figure 4 for normal (Figure 4(A)) and perdeuterated (Figure 4(B)) VAM. The spectra reveal that VAM exhibits a single feature at ~1778 cm^{-1} for both normal and perdeuterated vinyl acetate on an ethylidyne-saturated Pd(111) surface. This observation provides confirmation that the reaction between ethylene and adsorbed acetate species yields vinyl acetate, in accord with previous temperature-programmed desorption results where gas-phase vinyl acetate was detected (9). It should be emphasized that this spectrum is considerably different from that of vinyl acetate on clean Pd(111) (11), which exhibits a large number of features, one of which is a C=O stretching mode at ~1760 cm^{-1} (10). Furthermore, heating this surface to ~300 K results in substantial vinyl acetate

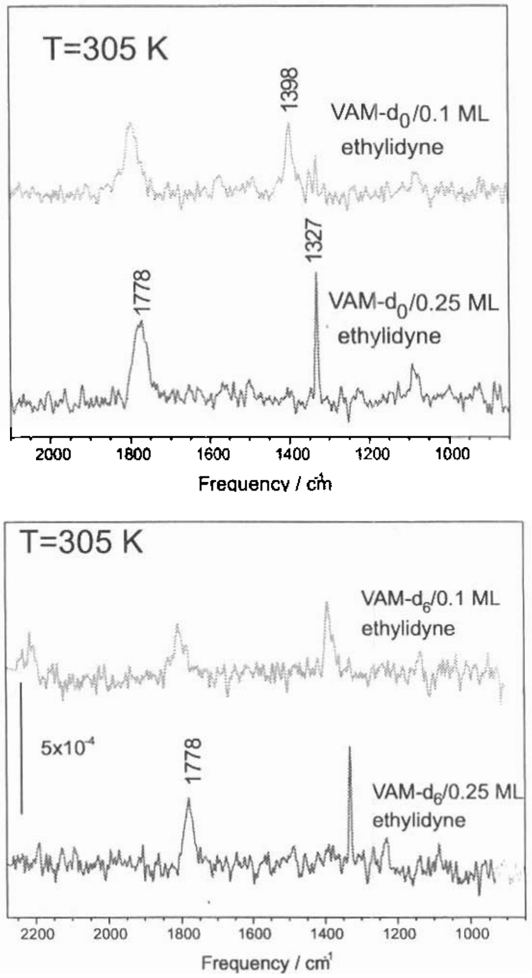


Figure 4. Infrared spectrum of (A) d_0-vinyl acetate adsorbed on 0.25 and 0.1 ML of ethylidyne and (B) d_6-vinyl acetate on 0.25 and 0.1 ML of ethylidyne at 305 K.

decomposition. Evidently, the presence of ethylidyne on the surface inhibits vinyl acetate decomposition. Indeed, lowering the ethylidyne coverage to ~0.1 ML (Figure 4) results in some decomposition as evidenced by the feature appearing at ~1398 cm^{-1}. However, the feature at ~1718 cm^{-1} is clearly not due to vinyl acetate adsorbed on the surface. The presence of this feature does, however, provide a clue to the reaction pathway. In the Moiseev pathway, the only species expected to be present on the surface are ethylene, vinyl and acetate species, and vinyl acetate, and the ~1718 cm^{-1} mode is due to none of these. The species participating in the Samanos pathway are ethylene, acetate, vinyl acetate and the acetoxyethyl-palladium intermediate resulting from insertion of ethylene into the acetate-Pd bond (see Scheme 1). Such an acetoxyethyl-palladium intermediate will have a C=O stretching frequency lower than that of vinyl acetate (11, 12) implying that the 1718 cm^{-1} mode could be due to the presence of the reaction intermediate. Density functional theory calculations for the acetoxyethyl-palladium intermediate confirm this. The enhanced intensity of this feature can be rationalized on the basis of the Samanos pathway (2). Since the acetoxyethyl-palladium intermediate decomposes to form vinyl acetate *via* a β-hydride elimination reaction, the rate of this reaction will be slowed substantially by deuteration at the β position accounting for its appearance when C_2D_4 reacts with surface acetate species. Indeed, further reaction with C_2D_4 results in a loss in intensity of the 1718 cm^{-1} mode and the growth of a mode at ~1788 cm^{-1} in accord with this proposal.

Discussion

Ethylene reacts with acetate species on Pd(111) to yield vinyl acetate (10), consistent with the detection of vinyl acetate adsorbed on ethylidyne-covered Pd(111) (Figure 4), detected by infrared spectroscopy following reaction between ethylene and acetate species. The feature appearing at ~1718 cm^{-1} after reaction between C_2D_4 and acetate species is assigned to the presence of an acetoxyethyl-palladium intermediate arising from a reaction between gas-phase ethylene and adsorbed acetate. This assignment is based on the observation that the C=O stretching frequency of alkyl acetate is ~60 cm^{-1} lower in frequency than for vinyl acetate (11, 12). This has been further tested by using DFT to calculate the vibrational frequencies of both vinyl acetate and the acetoxyethyl-palladium intermediate on a palladium surface where a similar shift of ~60 cm^{-1} is found theoretically. These data strongly suggest that vinyl acetate is formed by the insertion of ethylene into the O-Pd bond of the acetate species followed by β-hydride elimination to yiled vinyl acetate; the Samanos pathway (2).

Additional evidence for the Samanos pathway comes from the isotope data of Figure 1. Clearly, as noted above, hydrogen is involved in the rate-limiting step since the acetate removal rate when using C_2D_4 is substantially lower than when using C_2H_4. Of greater interest, however, are the different acetate removal rates for d_2-ethylene, where CD_2CH_2 reacts more slowly than does CHDCHD. This observatiçon allows us to immediately exclude the Moiseev model since, in this case, the rate-limiting step, which involves hydrogen, must be hydrogen abstraction from the ethylene to form the vinyl species. A fit to the experimental data (Figure 1) yields value of $k_i(H)/k_i(D) \sim 6$. This is a reasonable value for a primary isotope effect. In the case of reaction with d_2-ethylene, the rate constant should be $(k_i(H)+k_i(D))/2$ yielding an isotope effect of $2/(1+(k_i(D)/k_i(H)) \sim 1.7$. This will be the same irrespective of the location of deuterium, in contrast to what is observed experimentally.

At first sight, a similar effect should occur with the Samanos model. In the case of reaction with CD_2CH_2, there is an equal probability of CH_2 or CD_2 being in the β-position in the acetoxyethyl-palladium intermediate yielding an isotope effect of ~ 1.7, while for CHDCHD there will always be a CHD group at the β-position, similarly yielding an isotope effect of ~1.7. However, if the acetoxyethyl-palladium intermediate blocks the adsorption of ethylene, any acetoxyethyl-palladium intermediates formed from CH_2D_2 with two deuteriums in the β-position will decompose more slowly than those with hydrogens at that position, and block ethylene adsorption to a larger extent. For reaction with CHDCHD, there will always be hydrogen at the β-position, so that the intermediate can decompose more rapidly resulting in less blocking of the ethylene adsorption by the intermediate. This suggests that reaction with CD_2CH_2 should be slower than that with CHDCHD as found experimentally (Figure 1). The data in Figure 1 were fit using a simple kinetic model that assumes that ethylene adsorption is blocked by both surface acetate species and the acetoxyethyl-palladium intermediate and that the reaction rate is given by $k \times \theta$(ethylene)$\times\theta$(acetate), where θ refers to the surface coverage, and k is the reaction rate constant. The rate constant is varied depending on the number of deuteriums in the beta position of the acetoxyethyl-palladium intermediate resulting in a change in its coverage and a concomitant change in reaction rate. The results of this simple kinetic model yield the lines plotted in Figure 1. While the fits are not perfect, they effectively reproduce the different rates found for CH_2CD_2 and CHDCHD.

Conclusions

The experimental results provide clear evidence for ethylene insertion into the acetate proceeding *via* a pathway proposed by Samanos (2), that is, by ethylene insertion into an adsorbed acetate species and subsequent β-hydride elimination to form vinyl acetate. First is the identification of a vibrational mode at ~1718 cm^{-1} when reaction is carried out using C_2D_4, which cannot be assigned to vinyl acetate itself and is therefore assigned to the acetoxyethyl-palladium intermediate. Second, the differences in reaction rates for CHDCHD and CH_2CD_2 can only be rationalized by the Samanos route by making the reasonable assumption that the acetoxyethyl-palladium intermediate blocks the adsorption of ethylene. While this model did not yield qualitative agreement with the experimental data, an analysis of this model clearly demonstrates that there is a measurable difference in the reaction rates of these isotopomers.

Acknowledgements

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