# Kinetic Parameters for the Elementary Steps in the Palladium-Catalyzed Synthesis of Vinyl Acetate

**Florencia Calaza · Dario Stacchiola · Matthew Neurock · Wilfred T. Tysoe**

**Abstract** The kinetics of the reaction between gas-phase ethylene and adsorbed acetate species to form vinyl acetate monomer (VAM) on a Pd(111) surface are measured using infrared spectroscopy to monitor the rate of acetate removal, as well as the rates of VAM and ethylidyne formation, at various temperatures. The results are fit using a kinetic model first proposed by Samanos in which ethylene reacts with acetate species to form an acetoxyethyl intermediate that forms VAM via $\beta$-hydride elimination. The results of the kinetic model agree well with the experimental data and Arrhenius plots of the rate constants yield activation energies that are in good agreement with those predicted by density functional theory (DFT) calculations. DFT also predicts that the reaction activation energies should depend on the acetate coverage while the experimental data can be fit by constant values of the rate constants, suggesting that the reaction activation energies are similar for a reaction center surrounded either by acetate species, ethylidynes, or a combination of both. Finally, the kinetic parameters for VAM desorption are in good agreement with the experimental peak temperature measured by temperature-programmed desorption for VAM desorbing from an ethylidyne-covered surface.

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## 1 Introduction

The industrial, palladium-catalyzed synthesis of vinyl acetate monomer (VAM) from acetic acid, ethylene and oxygen:

$$CH_3COOH + C_2H_4 + 1/2O_2 \rightarrow CH_3COOC_2H_3 + H_2O \qquad (1)$$
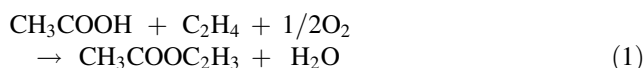
produces approximately 3.5 million tons annually [1]. We have previously shown that gas-phase ethylene reacts with adsorbed $\eta^2$-acetate species on a Pd(111) model catalyst surface and demonstrated, using isotope labeling experiments [2, 3], that the reaction proceeds via the Samanos pathway [4–7]. The acetate removal kinetics by reaction with gas-phase ethylene on Pd(111) were reproduced by a simple kinetic model using a single rate constant that assumed that ethylene adsorption is blocked by the acetate species and that the reaction is first order in both the coverage of acetate and ethylene species [3]. More recent results from density functional theory (DFT) [8] also predict that the reaction proceeds via the Samanos pathway on Pd(111) [9], which has been shown to be active for VAM synthesis [10–12]. The calculated activation energy for the rate-limiting $\beta$-hydride elimination step was found to be close to the experimentally measured value [9]. However, the calculated activation energies of the elementary reaction steps were found to be significantly affected by interadsorbate lateral interactions. Specifically, the activation energy for the reaction between adsorbed acetate and ethylene to form the acetoxyethyl intermediate was calculated to be 103 kJ/mol at a low coverage

($\Theta = 1/9$ ML), while at a higher, acetate-saturation coverage ($\Theta = 1/3$ ML), it decreases to 73 kJ/mol. Furthermore, the calculated activation barrier for the subsequent $\beta$-hydride elimination step increased from +43 kJ/mol at low coverages ($\Theta = 1/9$ ML) to +61 kJ/mol at the higher, saturation coverage ($\Theta = 1/3$ ML). The calculated activation energies at high coverages, where the experiments are performed, were in good agreement with the experimental values. As noted above, the complete acetate removal kinetics could be modeled using a single rate constant [2, 3]. This appears to contradict the DFT results as the surface is depleted of acetate during the titration, which at first glance would be thought to increase the activation barrier. Spectroscopic results, however, show that the surface acetate species are predominantly replaced by ethylidyne species towards the end of the titration reaction. Thus, while the acetate coverage on the surface decreases during a titration experiment, which, according to the above arguments would affect the reaction activation energy, and thus the reaction rate constant, the sum of the coverages of all of the reactants and products remains high. Thus, the environment around each of the acetate + ethylene reaction centers evolves in a relatively complex way as the titration reaction proceeds. The fact that the acetate titration curves can be fit by a single rate constant suggests that these different environments result in reaction activation energies that do not change drastically during the course of the reaction. This correspondingly implies that the influence of the local environments and lateral interactions created by adsorbed acetate and ethylidyne intermediates on the reaction center are quite similar. Thus, while, in principle, any kinetic model should explicitly take into account modifications to the reaction activation energy due to variations in the reaction environment, it may be that, in the case of VAM synthesis, at least, changing the environment from acetates to ethylidyne species, or a combination of these, does not strongly affect the reaction activation energy as long as the surface remains crowded.

In order to determine the acetate titration kinetics explicitly, and to provide a more stringent comparison between experiment and theory, the sequential kinetic equations for both the insertion and $\beta$-hydride elimination steps in the Samanos pathway, and VAM desorption are solved numerically to model the time-dependent coverage of the acetoxyethyl intermediate, the vinyl acetate product and the ethylidyne species. The more rigorous kinetic analysis carried out here allows the rate constants for the formation of the acetoxyethyl species from acetate and adsorbed ethylene, acetoxyethyl dissociation, $\beta$-hydride elimination, and product desorption to be obtained as a function of reaction temperature. The resulting activation energies are compared with theoretical predictions, where good agreement is obtained.

## 2 Experimental Methods

Infrared data were collected using a system that has been described previously [13]. Briefly, the sample could be resistively heated to 1200 K, or cooled to 80 K by thermal contact with a liquid-nitrogen filled reservoir. Infrared spectra were collected using a Bruker Equinox infrared spectrometer and a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path was enclosed and purged with dry, $CO_2$-free air. The $C_2H_4$ (Matheson, Research Grade) and acetic acid (Aldrich, 99.99+%), were transferred to glass bottles, which were attached to the gas-handling line for introduction into the vacuum chamber. Kinetic measurements were carried out by initially saturating the Pd(111) surface with acetate species by exposure to acetic acid. A flux of ethylene impinged onto the sample from a collimated dosing source to obtain an enhanced flux at the Pd(111) single crystal surface while minimizing the background pressure by using an ethylene background pressure of $1 \times 10^{-4}$ Torr [2, 3]. This ethylene pressure was selected to be sufficiently high that no variation in acetate reaction rate was observed as a function of ethylene pressure. The acetate removal kinetics were measured by monitoring the acetate asymmetric OCO vibrational mode at $\sim 1414$ cm$^{-1}$ [2], the vinyl acetate mode (at $\sim 1788$ cm$^{-1}$ [3]) and the ethylidyne mode (at $\sim 1330$ cm$^{-1}$ [14–17]). The acetoxyethyl intermediate (which would occur at $\sim 1718$ cm$^{-1}$ [3]) was not detected in experiments carried out using $C_2H_4$.

The temperature-programmed desorption (TPD) experiments were carried out in a separate ultrahigh vacuum chamber that has been described in detail elsewhere [18]. The Pd(111) single crystal was cleaned using a standard protocol and its cleanliness monitored using Auger spectroscopy and TPD collected following oxygen adsorption.

## 3 Theoretical Methods

### 3.1 Kinetic Analysis

The important elementary C–O bond forming and C–H bond breaking steps associated with the Samanos pathway are depicted in Scheme 1 [4–7]. The rate constant for the
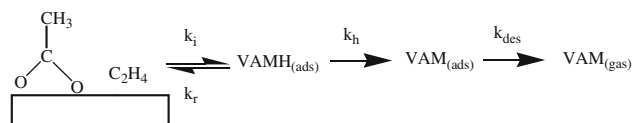


**Scheme 1** Depiction of the reactions occurring on the surface during titration of acetate species by ethylene in the Samanos pathway and the rate constants used in the fit to the reaction kinetics

insertion of ethylene into the palladium–acetate bond to form the acetoxyethyl intermediate (designated $VAMH_{(ads)}$) is given by $k_i$, and the reverse reaction has a rate constant $k_r$. The acetoxyethyl intermediate resembles ethyl acetate bonded to the surface via the terminal carbon on the ethyl group and its structure is shown in reference [9]. The rate of $\beta$-hydride elimination from this intermediate to form adsorbed vinyl acetate monomer ($VAM_{(ads)}$) is $k_h$, and the rate at which this desorbs from the surface to produce gas-phase vinyl acetate monomer is $k_{des}$. A detailed structure of the adsorbed vinyl acetate monomer is shown in reference [9].

An initial fit was carried out using a simple analytical model for the removal of acetate that assumes that only the acetate species block ethylene adsorption in order to obtain preliminary parameters for the full fit. The final fitting procedure includes blocking by the acetoxyethyl intermediate and the adsorbed VAM [2, 3, 9]. For the initial fit, it is assumed that the acetoxyethyl intermediate is in equilibrium with the reactants, ethylene and acetate species so that:

$$\Theta_{VAMH} = \frac{k_i}{k_r} \Theta_{acetate} \Theta_{ethylene} \qquad (2)$$

where $\Theta_{VAMH}$ refers to the coverage of the acetoxyethyl intermediate on the surface. For simplicity, we write $k_i/k_r = K$. It is assumed that ethylene adsorption is blocked only by the acetate species so that $\Theta_{acetate} + \Theta_{ethylene} = 1$. This yields:

$$\Theta_{VAMH} = K\Theta_{acetate}(1 - \Theta_{acetate}). \qquad (3)$$

Since the adsorbed acetate species react directly to form the acetoxyethyl intermediate, to a good approximation:

$$-\frac{d\Theta_{acetate}}{dt} \cong \frac{d\Theta_{VAMH}}{dt} \qquad (4)$$

so that the rate of acetate removal can be written as:

$$-\frac{d\Theta_{acetate}}{dt} = k_h K\Theta_{acetate}(1 - \Theta_{acetate}). \qquad (5)$$

This equation can be integrated, and it is assumed that there is an initial coverage of vacancies in the acetate overlayer $\delta$ to allow ethylene adsorption on the surface so that the initial acetate coverage is taken to be $1 - \delta$. This yields an analytical expression for the time-dependent acetate coverage in the titration experiment given by:

$$\Theta_{acetate}(t) = \frac{1}{1 + \delta \exp(Kk_h t)}, \qquad (6)$$

which has been shown previously to fit well to the experimental titration curves of acetate removal, and similarly good fits were found to all of the curves in this work [2, 3, 9].

These initial results are used to provide input parameters for a more complete kinetic model described in the following for the experimentally determined Samanos pathway (Scheme 1). The change in acetate coverage is given by:

$$-\frac{d\Theta_{acetate}}{dt} = k_i \Theta_{acetate} \Theta_{ethylene} - k_r \Theta_{VAMH} \qquad (7)$$

and the change in the coverage of the acetoxyethyl intermediate is given by:

$$\frac{d\Theta_{VAMH}}{dt} = k_i \Theta_{acetate} \Theta_{ethylene} - k_r \Theta_{VAMH} - 2k_h \Theta_{VAMH}, \qquad (8)$$

where the acetoxyethyl dehydrogenation rate is given by $2k_h$ to account for the presence of two $\beta$-C–H bonds that can break to form vinyl acetate. Finally, the vinyl acetate coverage is given by:

$$\frac{d\Theta_{VAM}}{dt} = 2k_h \Theta_{VAMH} - k_d \Theta_{VAM}. \qquad (9)$$

This constitutes a series of coupled differential equations that are solved iteratively using an initial saturation acetate coverage and integrating over small time steps. The value of the time step was decreased until no discernible differences in the solution were found. A time step of 0.2 s was used for the integration of the differential equations. The total coverage of all adsorbates was set to unity to account for site blocking where it was assumed that both the acetoxyethyl intermediate and adsorbed vinyl acetate can block the adsorption of two ethylene molecules, while the acetate species can block only one. More detailed kinetic Monte Carlo calculations will be carried out to explore this site-blocking effect further. This finally yields:

$$\Theta_{acetate} + \Theta_{ethylene} + 2\Theta_{VAMH} + 2\Theta_{VAM} = 1, \qquad (10)$$

and this equation was used to calculate the ethylene coverage. Since ethylene converts to ethylidyne species as the surface becomes depleted of acetate species under the experimental conditions used here [19], the calculated ethylene coverage is compared to the experimental ethylidyne coverage during the reaction. Thus, the final comparison with the experimental data includes the time dependence of the acetate, adsorbed vinyl acetate and ethylidyne coverages.

## 4 Results

### 4.1 Experimental Results

Figure 1 displays a series of typical infrared spectra collected as a function of time for a Pd(111) surface initially saturated by acetate species and pressurized by $1 \times 10^{-4}$ Torr of ethylene at a sample temperature of
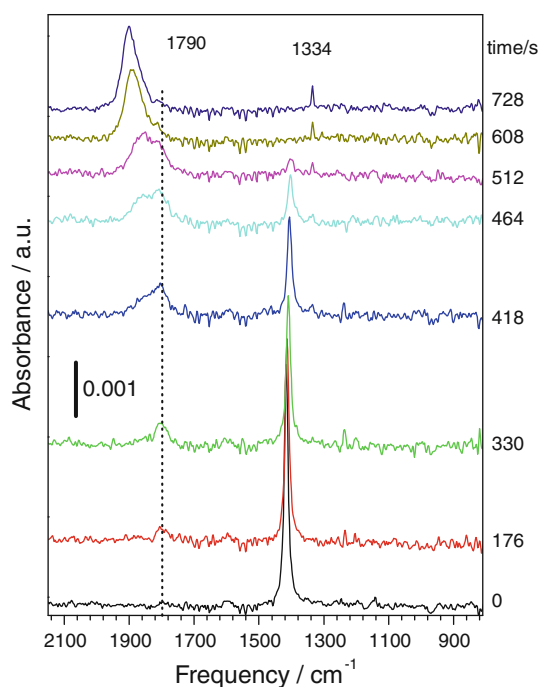
**Fig. 1** A sequence of infrared spectra collected for an initially acetate-covered Pd(111) surface pressurized with $1 \times 10^{-4}$ Torr of ethylene at 327 K as a function of time

327 K. This ethylene pressure has been shown to be sufficiently large that no change in acetate removal rate with ethylene pressure was observed [2, 3, 9]. The sequential spectra were each collected for 200 scans. These results show that the coverage of the acetate species, indicated by the presence of a strong mode at 1414 cm$^{-1}$, decreases with time, as found previously [2, 3, 9]. Additional features grow as the reaction proceeds. A 1334 cm$^{-1}$ mode appears as the surface is almost totally depleted of acetate species and has been observed previously for the reaction between ethylene and acetate on Pd(111) and is assigned to the formation of ethylidyne species on the surface [14–17]. The maximum absorbance of this feature after a reaction time of 728 s ($5 \times 10^{-4}$ absorbance units) indicates that the ethylidyne coverage is $\sim 0.2$ ML compared to a saturation coverage on clean Pd(111) of 0.25 ML [19, 20]. Another feature grows at $\sim 1790$ cm$^{-1}$ in the C=O stretching region and has been assigned to vinyl acetate adsorbed on an ethylidyne-saturated surface [3]. Note that the acetoxyethyl intermediate, which exhibits a feature at 1718 cm$^{-1}$ [3], is not detected indicating that the coverage of this species during the reaction is sufficiently low that its signal intensity is below the noise level of the spectra. At even longer times, another feature grows at $\sim 1900$ cm$^{-1}$, which is due to the adsorption of some CO from the background on the ethylidyne-covered surface because of the relatively long times required to follow the kinetics.

The intensity of the 1790 cm$^{-1}$ mode decreases once again at even longer times due to vinyl acetate desorption.

It has been shown previously that the integrated intensities of the acetete and ethylidyne infrared peaks scale well with their coverages [2]. Typical reaction profiles are shown in Fig. 2, which plots the integrated intensities of the features due to acetate species, vinyl acetate monomer and ethylidyne, normalized to the acetate intensity, for various reaction temperatures. The lines through these data represent fits to the model described above and are discussed in greater detail below.

Since the vinyl acetate product desorbs from a surface that is predominantly covered by ethylidyne species, vinyl acetate adsorption was explored both on clean and ethylidyne-saturated Pd(111) at 300 K by temperature-programmed desorption. The ethylidyne-saturated overlayer was prepared by exposing a clean Pd(111) sample to 60 Langmuirs of ethylene at 300 K [19]. The results are summarized in Fig. 3, where Fig. 3a, for adsorpion on clean Pd(111), reveals that no 43 amu signals, characteristic of VAM, are detected. In addition, no 45 amu signal (acetic acid) is found and only $CO_2$ is detected (44 amu) in addition to CO and methane (data not shown). This indicates that VAM decomposes on clean Pd(111) in accord with previous studies for vinyl acetate on a clean Pd(111) surface [21, 22]. Figure 3b displays the results for VAM adsorbed on an ethylidyne-saturated surface. In this case, a rather broad feature is detected at 43 amu centered at $\sim 380$ K. Neither $CO_2$ nor acetic acid are detected over this temperature range, thus confirming that this feature is due to molecular VAM desorption. This is confirmed by detecting other masses corresponding to VAM fragmentation pattern (at 26 and 29 amu).

## 5 Discussion

The kinetic data are analyzed using the model outlined above and by assuming that the reaction rate constants (Scheme 1) do not change during the course of the reaction. As emphasized above, the calculated activation energies for acetoxyethyl intermediate formation ($k_i$) and $\beta$-hydride elimination reactions ($k_h$) are found to depend on acetate coverage so that the rate constants would a priori be expected to vary during the course of the titration reaction. If a fit to the kinetic model can be achieved using coverage-independent rate constants, this will imply that lateral interactions with surrounding ethylidyne species mimic those for surrounding acetate species.

In order to limit the initial range of input values for the full fit to the numerical model, analytical fits were made to the acetate removal kinetics using the simpler model (Eq. 6). The resulting values of $Kk_h$ are summarized in

**Fig. 2** Titration curves for the reaction of ethylene with acetate species at **a** 303, **b** 327 and **c** 332 K showing the time dependence of the acetate (■), vinyl acetate (▲) and ethylidyne (●) signals as a function of time. The lines through these data are the results of kinetics fits
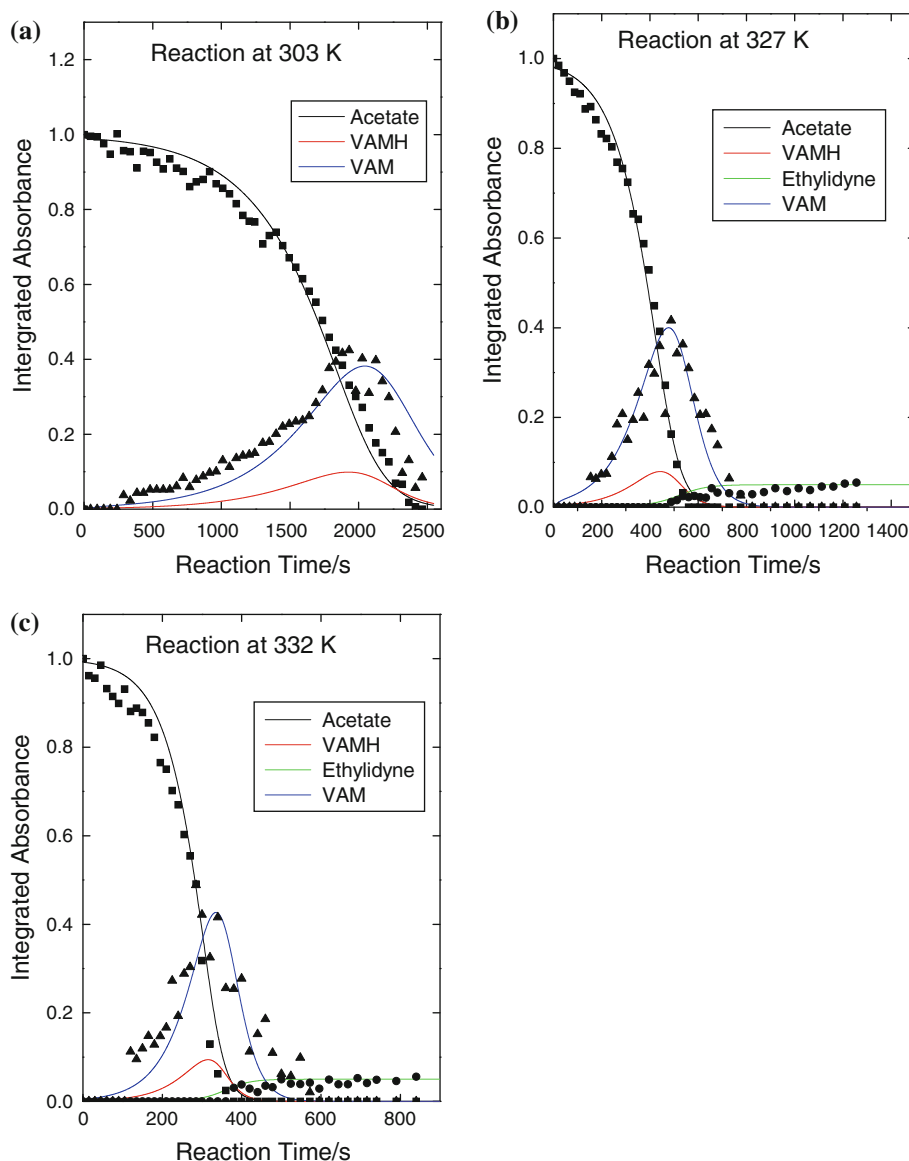


Table 1, and an Arrhenius plot of these data yields an energy of $55 \pm 5$ kJ/mol as found previously [9]. This activation energy arises from the temperature dependence of a number of rate constants, $k_i$, $k_r$ and $k_h$. Using the values for $E_i$ and $E_h$ from DFT calculations [9] allows a value of $E_r$ to be estimated as $73 \pm 5$ kJ/mol, similar to the value of $E_i$. This implies that the formation of the acetoxyethyl intermediate is approximately thermoneutral with respect to the reactants, adsorbed ethylene and acetate. Since the activation energies of $k_i$ and $k_r$ are almost identical, this suggests that the rate constants for the insertion of ethylene into the acetate species to form the acetoxyethyl intermediate and the reverse reaction should be almost the same. In addition, since, from the data shown in Table 1, $Kk_h$ is of the order of $10^{-2}$, $k_h$ should be less than either $k_i$ or $k_r$.

These constraints are used to select initial parameters for the fitting to a more complete model.

It should also be noted that, while it is possible to derive a simple analytical form for the titration of acetate species from the surface as shown above, the subsequent analysis to derive the coverages of the acetoxyethyl intermediate and of the vinyl acetate monomer is more difficult and the kinetics are thus solved iteratively.

Information on the vinyl acetate desorption kinetics are available from the TPD data for vinyl acetate adsorbed on a (crowded) ethylidyne-covered surface (Fig. 3). Vinyl acetate desorbs with a peak temperature of $\sim 383$ K (with a heating rate of 3.7 K/s) and this result will serve as a check on the kinetic parameters for VAM desorption obtained by the fit.
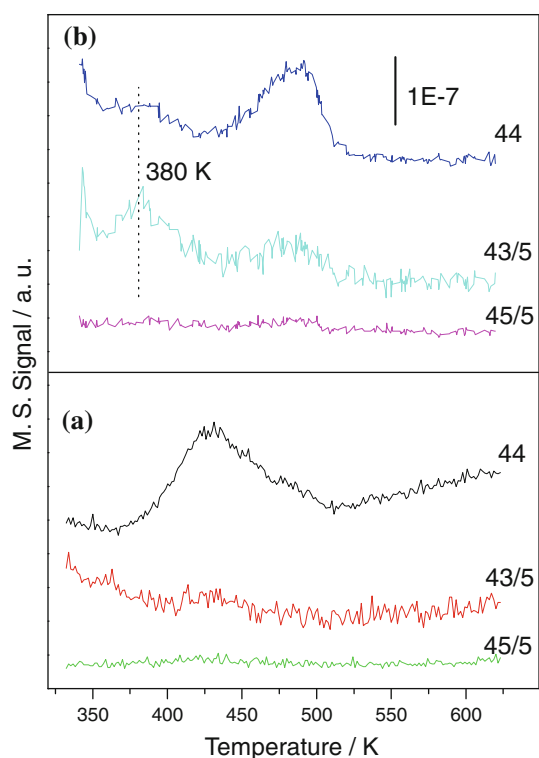
**Fig. 3** Temperature-programmed desorption data for 0.3 L VAM dosed at 300 K onto **a** clean Pd(111) and **b** an ethylidyne-saturated Pd(111) surface monitoring 43, 44 and 45 amu, where the detected masses are displayed adjacent to the corresponding desorption profiles. The 43 and 45 amu signals are scaled by a factor of 5 compared to the 44 amu signal as indicated adjacent to the 43 and 45 amu profiles

**Table 1** Fitting parameters for analytical function shown in Eq. 6

| Temperature (K) | $Kk_h$ |
|---|---|
| 303 | $2.98 \times 10^{-3}$ |
| 311 | $3.72 \times 10^{-3}$ |
| 327 | $1.12 \times 10^{-2}$ |
| 332 | $2.06 \times 10^{-2}$ |
| 340 | $4.20 \times 10^{-2}$ |
| 352 | $6.76 \times 10^{-2}$ |

Kinetic measurements were carried out at 303, 311, 327, 332, 340 and 352 K. The maximum temperature was determined by the stability of acetate species on the surface since it undergoes some thermal decomposition at temperatures higher than $\sim$360 K [23, 24]. The long reaction times at temperatures lower than 303 K resulted in low-quality spectra due to baseline shifts. The coupled kinetic Eqs. 7–9 were integrated iteratively in small time steps and compared with the experimental data. The kinetic data, examples of which are shown in Fig. 2, plot the integrated absorbances of the acetate, VAM and ethylidyne signals as a function of time relative to that of the acetate signal.

In order to fit the calculated coverages to the experimental integrated absorbance data, the absorbances of ethylidyne and VAM relative to those of the acetate species are required. The value for ethylidyne is obtained simply by comparing the integrated absorbances for saturated acetate and ethylidyne overlayers and results in a value of 0.05, so that integrated ethylidyne absorbances are calculated by multiplying the ethylidyne coverage by 0.05. In order to obtain the corresponding values for VAM, the initial a decrease in acetate signal is taken to result entirely in VAM formation and allows a similar sensitivity factor for VAM to be estimated as 2.7. The values of the kinetic parameters (Scheme 1) were adjusted manually until the best-fit values were obtained. Typical fits to the kinetic data are displayed in Fig. 2 (at 303, 327 and 323 K), which compares the calculated, time-dependent absorbances of acetate species, VAM and ethylidyne with the experimental data, and the agreement between the fitted curves and the experimental data is good. Since no VAMH was detected in the experiment, the relative sensitivity of the absorbance of this species compared with the acetate species is not known, so that the uncorrected VAMH coverage is plotted in Fig. 2. The predicted coverage of the acetoxyethyl intermediate (VAMH) is, in all cases, low in accord with the lack of detection of this intermediate when using $C_2H_4$ as the reactant. In addition, lowering the $\beta$-hydride elimination rate ($k_h$) yields a significant isotope effect as found experimentally [2].

Similar good fits were obtained for all temperatures, allowing the kinetic data to be plotted in Arrhenius form to determine the corresponding activation energies, for comparison with theory, as well as allowing the pre-exponential factors to be obtained. The resulting Arrhenius plots for all of the rate constants are displayed in Fig. 4, where good straight lines are obtained in all cases. The activation energies and pre-exponential factors are obtained from linear fits to these data and the results are displayed in Table 2 and compared with the values calculated by DFT [9].

The agreement between the calculated and measured values of the activation energies of $k_i$ ($\Delta E_i^*$ (DFT) = 73 and $\Delta E_i^*$ (Expt) = 74 $\pm$ 4 kJ/mol) and $k_h$ ($\Delta E_h^*$ (DFT) = 60.7 and $\Delta E_h^*$ (Expt) = 59 $\pm$ 3 kJ/mol) is excellent and is within the experimental errors of the measured values. The activation energy for the rate constant, $k_r$, the reverse reaction of the acetoxyethyl intermediate to reform acetate and ethylene ($\Delta E_r^*$ (DFT) = 65 and $\Delta E_r^*$ (Expt) = 67 $\pm$ 5 kJ/mol), appears to be slightly lower than that for the insertion reaction, although the difference is within the error limits for these measurements.

Finally, the pre-exponential factor for the desorption of vinyl acetate from the surface is much lower than the typical values of desorption pre-exponential factors, which
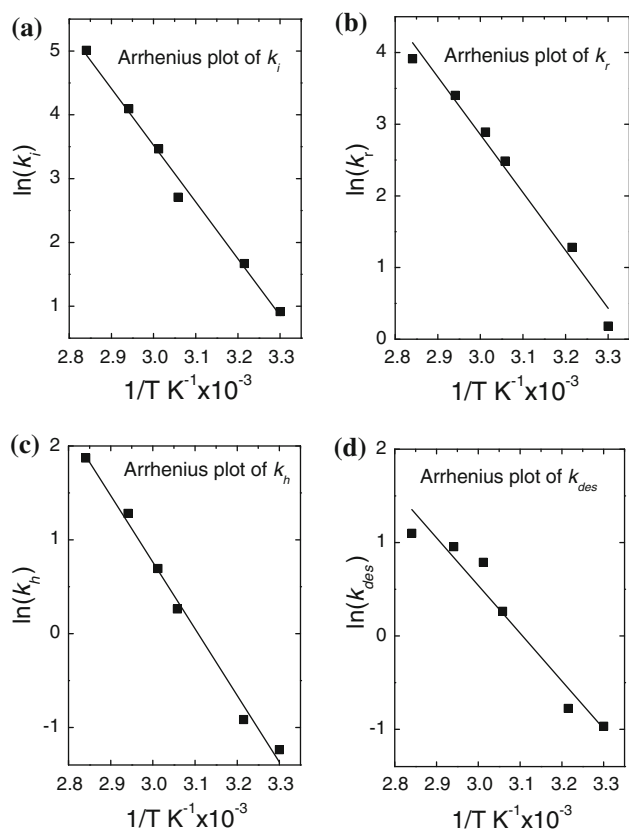
**Fig. 4** Arrhenius plots for the rate constants **a** $k_i$, **b** $k_r$, **c** $k_h$ and **d** $k_{des}$ obtained from fits to the titration curves

**Table 2** The activation energies and pre-exponential factors for the rate constants $k_i$, $k_r$, $k_h$ and $k_{des}$ obtained from the Arrhenius plots displayed in Fig. 4

|  | $E_{act}$ (kJ/mol) | $E_{act}$(calc) (kJ/mol) | $A$ (s$^{-1}$) |
|---|---|---|---|
| $k_i$ | $74 \pm 4$ | 73 | $2.0 \pm 0.4 \times 10^{10}$ |
| $k_r$ | $67 \pm 5$ | 65 | $9 \pm 2 \times 10^{9}$ |
| $k_h$ | $59 \pm 3$ | 60.7 | $6.3 \pm 0.8 \times 10^{7}$ |
| $k_{des}$ | $43 \pm 5$ | – | $1.3 \pm 0.4 \times 10^{5}$ |

Thus, a full kinetic fit using an analytical model that assumes that ethylene adsorption is blocked by the acetate, acetoxyethyl and vinyl acetate species, is in good agreement with the experimental titration curves and yields activation energies for the elementary steps that are in excellent agreement with those calculated using DFT. Such a mean-field kinetic analysis is possible in this case because the effect on the activation energy of a reaction center surrounded either by acetate or ethylidyne species is very similar and because the surface remains saturated throughout the course of the reaction. However, it has been shown theoretically that the reaction activation energies are strongly affected by coverage so that reaction conditions that result in lower surface coverages will lead to large local effects that cause significant activation energy changes [9].

The results further suggest that the acetoxyethyl intermediate formed on the crowded surface during reaction is close to thermoneutral with respect to the reactants. They also indicate that the VAM desorbs with an activation of $\sim 43$ kJ/mol, both from the titration curves and from temperature-programmed desorption, but with a very low pre-exponential factor. It should be noted that the shape of the titration curve of the vinyl acetate coverage is very sensitive to changes in desorption activation energy, so that the desorption rate constants are quite precisely determined by the fitting procedure. Presumably the low pre-exponential factor for desorption arises because the VAM desorbs from a crowded surface.

It is also evident that the vinyl acetate that is formed on the crowded surfaces does not thermally decompose, while on the clean surface it does (Fig. 3, [21, 22]). It has been shown that vinyl acetate decomposes by C–O bond scission on the clean Pd(111) surface, so that just as surface crowding facilitates the coupling between ethylene and acetate species, it similarly inhibits decomposition of the product. Thus, in the case of VAM synthesis catalyzed by supported palladium particles, where the majority of the exposed facets are likely to be closed-packed (111) surfaces, part of the origin of the high selectivity of these catalysts is the result of the surface being saturated by acetate, ethylidyne or other unsaturated hydrocarbon fragments that inhibit VAM decomposition. It has been demonstrated that acetate species decompose by the molecular plane tilting such that the methyl groups can access the surface to initiate a dehydrogenation reaction [24]. This suggests that non-selective reactions on supported palladium catalysts must be due to ethylene combustion and this has been observed experimentally [5, 28]. This could either be due to the direct combustion of ethylene [29, 30] or to the oxidation of ethylidyne species. This latter reaction must necessarily occur to create new reaction sites for vinyl acetate formation. Disentangling such details will require a more complete (Monte Carlo) kinetic analysis of the reaction under realistic conditions.

are usually taken to be $\sim 10^{13}$ s$^{-1}$. This may imply that the desorption transition-state partition function is much lower than that of the adsorbed state. This is likely to be an effect of the presence of the surroundings that must constrain the transition state to desorption. However, calculating precise pre-exponential factors is rather complex [25, 26].

As noted above, vinyl acetate desorbs from an ethylidyne-saturated surface at $\sim 380$ K, when using a heating rate of $\sim 3.7$ K/s. A first-order Redhead analysis [27] of the desorption peak temperature of 380 K using the experimental pre-exponential factor of $1.3 \times 10^5$ s$^{-1}$ (Table 2) yields a desorption activation energy of 41 kJ/mol, entirely consistent with the activation energy measured from the kinetic data (Table 2).

These results may also provide an understanding of why mean-field kinetic analyses of catalytic reaction data often work well. Metal catalysts are generally sufficiently reactive that, under most conditions, their surfaces are saturated by reactants, reaction intermediates and products. Thus, while the environment around the reaction center may change as the reaction conditions change, if the coverage effects of these various reaction ensembles on the elementary-step reaction kinetics are similar, then a mean-field approximation may well be adequate to describe the kinetics. It should, however, be emphasized that, while the experimental results show that this situation pertains to the titration experiments carried in this work, this may not be true for all reaction steps and reaction conditions. Thus, in general it will be important when describing the reaction kinetics of metal-catalyzed systems to explicitly take account of the myriad of reaction environments on the catalyst's surface. Such complexity will not generally be evident from experimental results, which measures an average of the whole system, but can only be captured by a detailed theoretical exploration of the energetics of the reaction with different local environments. If changes in the environment are found to affect the reaction activation energy, these will have to be explicitly accounted for in the kinetic model and precludes mean-field kinetic analyses being used, and this problem must necessarily be addressed using other strategies such as kinetic Monte Carlo methods.

Finally, DFT calculations concluded that VAM is formed on Pd(111) by the Samanos pathways [9] in agreement with the results of experiment [2, 3]. The agreement between the values of activation energy predicted by DFT and the experimental results presented here indicate that DFT can rather precisely predict activation energies and thus provides additional confirmation that the VAM formation reaction proceeds on Pd(111) via the Samanos route.

# 6 Conclusions

The kinetic data for the reaction of a saturated overlayer of acetate species on Pd(111) with gas-phase ethylene are fit to a model that, in addition to modeling the removal of acetate species, includes the formation of both VAM and ethylidyne species. The results of the model fit well to the experimental data and yield rate constants for the reaction of ethylene with acetate species to form an acetoxyethyl palladium intermediate, its reverse reaction to reform ethylene and acetate species, $\beta$-hydride elimination from the acetoxyethyl intermediate to form VAM, and VAM desorption. The activation energies measured for the elementary steps are in good agreement with values calculated using density functional theory, and the rate constant for VAM desorption is also in good agreement with the results

of the TPD experiment for VAM on ethylidyne-saturated Pd(111). While DFT showed that the reaction activation energies depend on acetate coverage, the fact that each titration curve collected at various temperatures can be fit by constant values of the rate constants suggests that the activation energies are similar for a reaction center surrounded either by acetate species, ethylidynes, or a combination of both.

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