J. Phys. Chem. 1987, 91, 1153-1158

Catalytic Dehydration of Acetic Acid on a Graphitized Platinum Surface

J. J. Vajo, Y.-K. Sun, and W. H. Weinberg*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125 *(Received: July 18, 1986; In Final Form: October 17, 1986)*

Absolute reaction rates have been measured in a continuous flow microreactor for the steady-state, catalytic dehydration of acetic acid to ketene at pressures between 8×10^{-7} and 7×10^{-4} Torr and temperatures between 500 and 800 K. The catalyst was a polycrystalline platinum wire containing approximately a monolayer of graphitic carbon. At 675 K or above, for the entire range of pressures studied, the order of the dehydration reaction is unity with respect to acetic acid pressure. In this regime, the apparent activation energy is 1 ± 1 kcal/mol, and the extrapolated reaction probability at $1/T = 0$ is $(2.5\text{–}10) \times 10^{-4}$. Under these conditions, the rate of dehydration is determined by a competition between the rates of desorption and surface reaction of molecularly adsorbed acetic acid. For temperatures below 540 K and pressures of 3.5×10^{-4} Torr and above, the reaction rate is independent of acetic acid pressure, and the apparent activation energy is 27 ± 2 kcal/mol. Under these conditions, the rate of decomposition of a surface intermediate controls the rate of reaction. A mechanistic model is developed and discussed which describes accurately both the temperature and the pressure dependence of the rate of dehydration.

I. Introduction

It is well-known that carbon overlayers on transition-metal surfaces can affect both the reactivity and the selectivity of many heterogeneously catalyzed surface reactions.[1-11] These effects may have several origins. For example, carbon adatoms may physically occupy specific surface sites that are necessary for a particular reaction to occur, and they may chemically modify unoccupied sites by altering the electronic structure of the surface.[12-14] Both of these phenomena can change the reactivity and/or the selectivity of a heterogeneous catalyst. The effect of adsorbed carbon on both the reactivity and the selectivity of a catalytic reaction may be illustrated by considering the decomposition of formic acid on the Ni(110) surface.[6] Since formic acid decomposition may produce either CO or CO_2, the relative rates of these competing reactions provide a measure of selectivity. On the clean Ni (110) surface, the CO_2 to CO product ratio observed upon heating a saturation coverage of formic acid at 315 K is 1:1. On a carbided Ni(110) surface, formed by the dissociative adsorption of ethylene at 600 K, the product ratio is 10 ± 5:1, whereas the total quantity of formic acid which decomposed is unchanged compared to the clean surface. However, a shift in the temperature corresponding to the maximum rate of CO_2 production from 390 to 440 K indicates that the activation energy for CO_2 production is greater on the carbon-covered surface compared to the clean surface. Upon exposing the Ni(110) surface to ethylene at 800 K, a graphitic overlayer was formed. Decomposition of formic acid on this surface produced only 0.1 as much as on the clean and carbided surfaces, and the product ratio was near unity.

Recently, the decomposition of acetic acid over a polycrystalline platinum wire was studied in our laboratory at a pressure of 7×10^{-4} Torr and at temperatures between 300 and 900 K.[11] Two disparate kinetic regimes were observed. On the initially clean platinum surface, acetic acid decomposed to yield CO, CO_2, H_2, and adsorbed carbon. No water was observed during this transient production of CO, CO_2, and H_2. The adsorbed carbon ultimately poisoned the reaction channels producing CO, CO_2, and H_2, while simultaneously initiating the steady-state, catalytic dehydration of acetic acid to ketene and water. Similar to the results described above for formic acid decomposition on nickel, both the reaction rate and the CO_2 to CO product ratio were found to be dependent on the carbon adatom concentration in the first regime. Since graphitic overlayers on platinum surfaces are formed readily from carbon adatoms at temperatures above 750 K,[15-17] the carbon-covered surface which dehydrates acetic acid and which is formed at 900 K is graphitic.[11] Moreover, the carbon adatom concentration, determined from oxygen titration measurements, corresponds to approximately one monolayer of the basal plane of graphite.

In the work described here, we shall focus on the steady-state dehydration of acetic acid to ketene and water which occurs only on the graphitized platinum surface. Absolute reaction rates have been measured for reactant pressures between 8×10^{-7} and 7×10^{-4} Torr and at temperatures between 500 and 800 K. The steady-state reactivities of acetic anhydride, acetone, methyl acetate, and isopropyl alcohol on the graphitized surface also have been investigated briefly. On the basis of these results, together with those of thermal desorption measurements, a consistent mechanism of the acetic acid dehydration reaction is developed. For completeness, the decomposition of acetic acid on the clean platinum surface is described briefly, whereas a detailed discussion of both this reaction and the nature of the carbon overlayer is presented elsewhere.[11]

The organization of this paper is as follows. In section II the experimental details are described, and the experimental data are presented in section III. The reaction mechanism is developed and discussed in section IV. Finally, the major results of this work are summarized in section V.

II. Experimental Procedures

The experiments were performed over a range of pressures from 8×10^{-7} to 7×10^{-4} Torr in a steady-state flow microreactor that has been described previously.[18,19] The catalyst was a 20-cm

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length of 0.0125-cm-diameter high-purity (99.99%) polycrystalline platinum wire. All reagents were either reagent or research grade and were purified further by freeze–thaw–pump cycles in liquid nitrogen. Isotopically labeled ethylene, $^{13}C_2H_4$ (98 atom % ^{13}C from MSD Isotopes), was used without further purification.

The reaction products, which were sampled via a capillary tube from the main chamber of the reactor, were monitored continuously by a microcomputer-interface EAI 1200 quadrupole mass spectrometer, located in a high-vacuum chamber of the reactor of which the base pressure is below 10^{-8} Torr. Absolute reaction rates for the steady-state dehydration of acetic acid were determined by monitoring the change in the parent ion signal at 60 amu and using the appropriate continuous stirred tank reactor (CSTR) formalism.[18,19] The reactor was well characterized as a CSTR by a series of step-response experiments.[18] Average conversions were below 5% except for temperatures above 600 K at 7×10^{-4} Torr, where average conversions were $\lesssim 20\%$. However, separate measurements in which the average conversions were below 8% for all conditions gave identical results.[20]

For thermal desorption measurements, the bellows valve separating the main reaction chamber from the high-vacuum section was opened, and the sample was translated into the high-vacuum section (see Figure 2 of ref 18). Heating was accomplished with a constant-current power supply which produced a nearly linear temperature ramp of 20 K/s over the temperature range 350–650 K. Temperatures were measured with a W-5% Re/W-26% Re thermocouple which was spot-welded near the center of the platinum wire.

Two different platinum wires were used in this study. Initially, each one was heated in 0.1 Torr of oxygen (99.99%) at 1000 K for 3 h and then reduced in 0.1 Torr of hydrogen (99.995%) under the same conditions. Approximately ten cycles of this procedure led to reproducible, steady-state rates of acetic acid dehydration. A single oxidation–reduction cycle at 10^{-3} Torr and 1000 K for 30 min was conducted prior to each experiment to remove carbon that had been deposited during previous acetic acid decomposition. This treatment was found to produce a clean platinum surface, as judged by the reproducible rates of the acetic acid decomposition reactions which occur on the initially clean surface[11] and the steady-state rates of dehydration of acetic acid after formation of the graphitic overlayer. After the initial cleaning treatment at 0.1 Torr, longer oxidation–reduction cycles at 10^{-3} Torr did not change the measured rates.

III. Experimental Results

1. Acetic Acid Decomposition. Relative rates of production of CO, CO_2, H_2, H_2O, and CH_2CO (ketene), uncorrected for mass spectrometric sensitivities and pumping speeds, from an initially clean platinum surface are shown in Figure 1 as a function of time during a constant flow (average residence time of 3.6 s) of acetic acid at a pressure of 7×10^{-4} Torr and a surface temperature of 900 K. It is apparent that the rates of production of CO, CO_2, and H_2 pass through a maximum and decline nearly to their respective background values. Coincident with the decrease in the CO, CO_2, and H_2 signals, the rates of formation of both ketene and water rise to steady-state values.[21] These steady-state rates have been observed for more than 2 h, corresponding to well over 100 catalytic "turnovers" per surface site, without significant change. Under these steady-state conditions, no reaction products were detected other than ketene and water. The minimum in the ketene signal, which coincides with the maximum for CO, CO_2, and H_2 in Figure 1, is a consequence of the fact that mass 42 is also a fragmentation product of acetic acid. The minimum, therefore, is associated with the decomposition of acetic acid to CO, CO_2, and H_2, and it is unrelated to ketene.

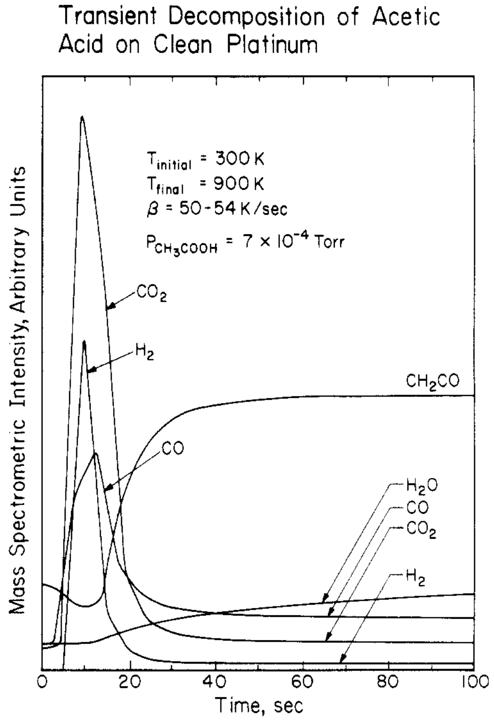

Figure 1. Time evolution curves for the production of CO, CO_2, H_2, H_2O, and CH_2CO (42 amu) during the constant exposure of an initially clean platinum surface to acetic acid at 7×10^{-4} Torr. At $t = 0$, the surface temperature was increased at a rate of 50–54 K/s from 300 to 900 K and thereafter held constant at 900 K. The data are uncorrected for fragmentation, mass spectrometric sensitivities, and pumping speeds.

The relatively slow rise in the water signal, compared with the ketene signal, is due to adsorption of water on the walls of the vacuum system. This has been confirmed by independent step-response experiments. After correction for mass spectrometric sensitivities and pumping speeds, the mass 42 and mass 18 steady-state signals shown in Figure 1 correspond to a 1:1 molar ratio of ketene to water.

After exposure to acetic acid, the platinum surface contains a substantial concentration of carbon adatoms, as judged from oxygen titration experiments in which predominantly CO_2 is formed.[11] The concentration of surface carbon atoms following a 90-s exposure to acetic acid at 7×10^{-4} Torr and a temperature of 900 K was $(2.6–3.5) \times 10^{15}$ cm^{-2}. Exposure of the platinum surface to acetic acid at 1000 K for 5 min did not alter the carbon adatom concentration. Although the surface that results from exposure to acetic acid at temperatures below 900 K was not examined extensively, it appears that for surface temperatures above 700 K an identical surface may be prepared with a sufficiently long exposure (annealing) time. The carbon adatom concentration produced from exposure to acetic acid at 0.1 Torr for 90 s at 900 K was 5.9×10^{15} cm^{-2}. Other pressures were not investigated in detail. A similar concentration of carbon, 2.4×10^{15} cm^{-2}, was produced from a 90-s exposure of the surface at 900 K to 7×10^{-4} Torr of ethylene. For comparison, the surface atom densities of Pt(111) and of the basal plane of graphite are 1.5×10^{15} cm^{-2} and 3.8×10^{15} cm^{-2}, respectively.[22]

To summarize, on an initially clean platinum surface, acetic acid decomposes to CO, CO_2, and H_2 and produces a graphitic overlayer. The surface becomes poisoned to these decomposition reactions, and subsequently, on the graphitic surface, acetic acid dehydrates catalytically to ketene and water.

2. Steady-State Dehydration Kinetics. Absolute steady-state reaction rates for the dehydration of acetic acid to ketene and water over the graphitized platinum surface are shown in Figure

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[20] For these experiments, the conversion was lowered by placing an additional pump on the outlet of the reactor, thereby decreasing the residence time of the acetic acid.

[21] The existence of ketene was confirmed by monitoring the parent ion signal at 42 amu and the fragmentation products at 41, 28, and 14 amu. Water was monitored at 18 amu. For the fragmentation intensities of ketene, see: Cornu, A.; Masut, R. *Compilation of Mass Spectral Data*, 2nd ed.; Heydon and Son: New York, 1975; Vol. 1.

[22] These values result from assuming a hexagonally close-packed surface and an atom–atom distance of 2.746 and 1.42 Å for platinum and graphite, respectively.

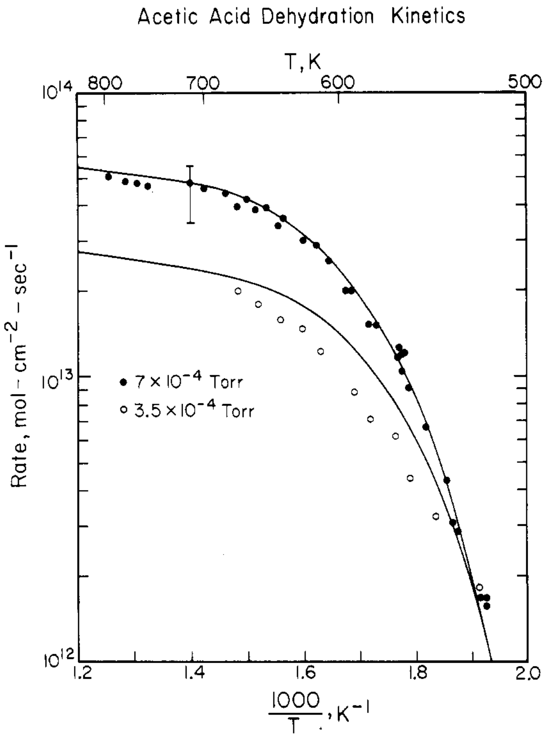

Figure 2. Arrhenius plots of the rate of dehydration of acetic acid at 7 × 10^{-4} and 3.5 × 10^{-4} Torr. For each pressure, a graphitic overlayer was first prepared by exposing a clean platinum surface to 7 × 10^{-4} Torr of acetic acid at 900 K for 90 s. The error bar at $10^3/T = 1.4$ indicates the variation in the rate observed by repeatedly removing and depositing the graphitic overlayer. The lines are the results of model calculations which are described in the text.

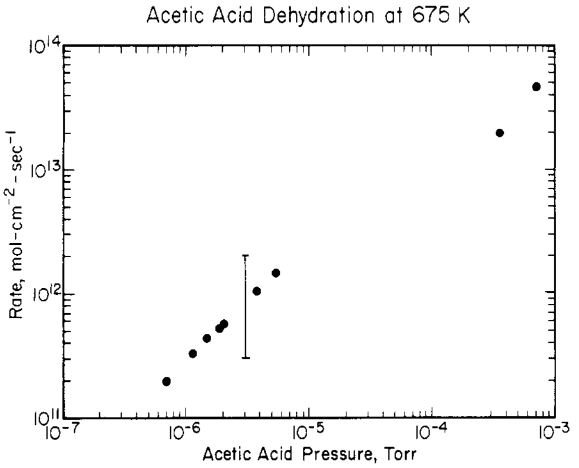

Figure 3. Absolute reaction rates for the dehydration of acetic acid at 675 K as a function of acetic acid pressure. The error bar at 3 × 10^{-6} Torr indicates the systematic error in calibration of the rates for all pressures below 10^{-5} Torr.

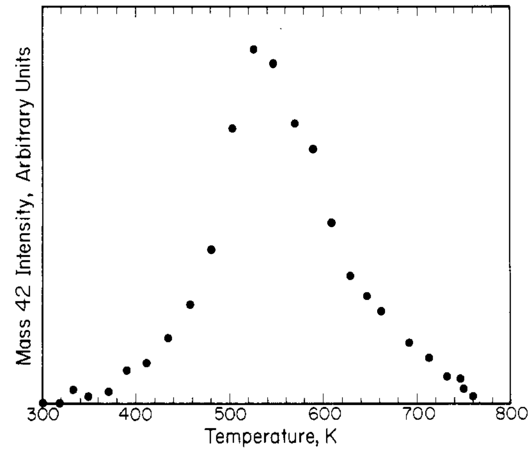

Figure 4. Thermal desorption spectrum of ketene following either reaction at elevated temperatures (500–700 K) and cooling to 300 K in the presence of acetic acid or exposure of the graphitic overlayer to acetic acid at 300 K. The heating rate was 20 K/s, and the maximum desorption rate occurs at 520 K.

2 as a function of reciprocal temperature for pressures of 7 × 10^{-4} and 3.5 × 10^{-4} Torr. The kinetics displayed in Figure 2 are essentially identical for all the methods that were used to prepare the graphitic overlayer, including graphite formation from ethylene (cf. section III.1). In addition, annealing the graphitized surface under vacuum at 1000 K did not change the observed kinetics. For the data presented explicitly here, however, each of the graphitic overlayers was prepared by exposing the initially clean platinum surface to 7 × 10^{-4} Torr of acetic acid for 90 s at 900 K. At low temperatures (≲540 K), the steady-state reaction rate is independent of acetic acid pressure. Under these conditions, the apparent activation energy is 27 ± 2 kcal/mol, with an extrapolated intercept at $1/T = 0$ of (0.2–1.6) × 10^{24} molecules/(cm^2 s). At higher temperatures (≳675 K), the reaction rate scales linearly with the acetic acid pressure, and the activation energy decreases to 1 ± 1 kcal/mol. In this regime, the extrapolated intercept at high temperatures is (0.7–2.8) × 10^{17} molecules/(cm^2 s Torr). This corresponds to a reaction probability per surface collision of acetic acid of (2.5–10) × 10^{-4}. The error bar at $10^3/T = 1.4$ in Figure 2 indicates the variation in the measured rate after repeatedly cleaning the surface and redepositing the graphitic overlayer. The dehydration of perdeuterioacetic acid showed no detectable isotope effect under any conditions, although the uncertainty in the measured activation energy would have obscured any change in the activation energy that is less than 1–2 kcal/mol. Thus, a primary isotope effect involving cleavage of a C–H bond with a vibrational frequency of 3000 cm^{-1} would not be observed, since the expected increase in the activation energy is only 1.1 kcal/mol for C–D bond cleavage.

At the lowest temperatures studied (≲540 K), the steady-state CO signal, which is a fragmentation product of ketene, increased relative to the ketene mass spectrometric intensity. Since the mass spectrometric intensities at these low temperatures are approaching our detection limit, it was not possible to quantify this behavior. However, this may represent another steady-state decomposition mechanism which competes with dehydration to ketene at low temperatures where the overall rate of decomposition is very small (e.g., the reaction probability at 540 K and 7 × 10^{-4} Torr is approximately 10^{-5}).

Figure 3 shows the steady-state rate of dehydration of acetic acid as a function of pressure from 8 × 10^{-7} to 7 × 10^{-4} Torr at 675 K. The reaction order with respect to acetic acid pressure, measured from the data that were recorded below 10^{-5} Torr, is 0.95 ± 0.05. While the *relative* rates determined at these low pressures are quite accurate, the calibration that is necessary to calculate absolute rates is difficult at low pressures. The error bar at 3 × 10^{-6} Torr indicates the absolute error present in all the data at pressures below 10^{-5} Torr. Considering this rather large absolute error and the much smaller uncertainties for measurements at higher pressures, a first-order dependence of the rate on pressure is suggested at 675 K over the entire range of pressures studied, i.e., for pressures below 10^{-3} Torr.

Steady-state dehydration of acetic acid was also conducted on a graphitic surface composed of ^{13}C to ascertain the stability of the graphitic overlayer. The ^{13}C-labeled surface was prepared by exposing the clean platinum surface to 7 × 10^{-4} Torr of $^{13}C_2H_4$ for 90 s at 900 K. Comparison of the ^{13}C surface concentration, determined by oxygen titration, following dehydration of acetic acid at 7 × 10^{-4} Torr and 675 K for 20 min with the ^{13}C surface concentration measured without reaction revealed that the ^{13}C atoms remain on the surface during the dehydration of acetic acid. Hence, the dehydration of acetic acid over graphitized platinum is a "catalytic" reaction in the strictest sense; i.e., no component of the "catalyst" is incorporated into the reaction product.

3. Thermal Desorption Measurements. A thermal desorption spectrum of ketene following exposure of the graphitized platinum surface to 7 × 10^{-4} Torr of acetic acid for 240 s at 300 K is shown in Figure 4. A single peak occurs at a temperature of 520 K. The desorption spectrum is independent of the delay time associated with transferring the sample from the reaction chamber to the high-vacuum chamber. Moreover, the desorption spectrum is independent of exposure time (>4 min) and surface temperature (between 300 and 700 K), provided the surface is cooled to 300 K before the acetic acid is evacuated. Exposures at pressures below 7 × 10^{-4} Torr were not investigated. An approximate calibration using the mass spectrometric sensitivity and the pumping speed for CO_2 indicates the desorption of (0.1–5) × 10^{13} molecules/cm^2 of ketene. Although the desorption of neither acetic acid nor H_2O was observed, these species would not be detected for surface concentrations below approximately 5 × 10^{13} cm^{-2} due to the adsorption of acetic acid and H_2O on the system walls.

Carbon monoxide was also observed to desorb from the graphitized platinum surface following exposure to acetic acid. The peak temperature was approximately 540 K and showed the same independence of surface temperature and delay time in transfer as ketene. The amount of CO that desorbed corresponded to approximately half the amount of ketene that desorbed and (as verified by independent measurements) was not due to adsorption from the background. This desorption of CO may be related to the increase in the mass 28:mass 42 ratio observed at low temperatures during the steady-state reaction (cf. section III.2). Due to the lack of quantitative steady-state data concerning this reaction pathway, however, the origin of the CO was not investigated further.

4. Steady-State Reaction of Related Compounds. To gain further insight into the mechanism of the steady-state dehydration of acetic acid, the reactions of four functionally related model compounds, namely, acetic anhydride, isopropyl alcohol, acetone, and methyl acetate, were investigated briefly. In each case, the graphitic overlayer was prepared in a manner identical with that used for the steady-state measurements of acetic acid dehydration, i.e., an exposure of 7 × 10^{-4} Torr f acetic acid for 90 s at 900 K. The rates of decomposition of each compound were measured at a pressure of 7 × 10^{-4} Torr. Acetic anhydride decomposed predominantly to ketene and acetic acid, with an activation energy of 12–15 kcal/mol which was constant over the temperature range 420–650 K. A minor amount of water, <1% of the acetic acid signal, was observed above 535 K. Isopropyl alcohol dehydrated to propylene and water, with an activation energy decreasing from approximately 16 kcal/mol at temperatures between 450 and 500 K to approximately 3 kcal/mol at 625 K. Qualitatively, the observed steady-state kinetics for the dehydration of isopropyl alcohol are similar to those for acetic acid dehydration. Acetone and methyl acetate showed no reaction at any temperature studied (≲700 K).

IV. Discussion

1. Reaction Kinetics and Adsorbed Intermediates. For temperatures below approximately 570 K and pressures between 10^{-3} and 10^{-4} Torr, the steady-state rate of dehydration of acetic acid to ketene on graphitized platinum exhibits a linear Arrhenius behavior and a diminishing dependence on acetic acid pressure as the temperature decreases (cf. Figure 2). These observations suggest that under these conditions the catalytic surface is nearly saturated with either acetic acid, a reaction intermediate, or a reaction product. Since the heat of adsorption of acetic acid, water, and ketene on graphitized platinum is expected to be ≲5 kcal/mol,[23] a mechanism in which the surface is saturated with an intermediate in the dehydration reaction species is implicated. For example, the intramolecular elimination of water from molecularly adsorbed acetic acid is not a viable mechanism of dehydration, since *molecular* acetic acid would be adsorbed reversibly at 300 K. Moreover, the thermal desorption of ketene at 520 K following both exposure of the surface to acetic acid at 300 K and the reaction of acetic acid at elevated temperatures is identical, provided the surface is cooled in the presence of acetic acid. This result implies that the adsorbed intermediate in the reaction is stable and readily formed at 300 K.

Information concerning the reaction intermediate is provided by the observed reactivities of methyl acetate, acetone, and isopropyl alcohol. On the basis of both these results and those pertaining to acetic acid, we suggest that the physically most reasonable intermediate which leads to ketene from acetic acid dehydration is a monodentate acetate, designated η^1-CH_3COO(a), formed by the dissociation of the oxygen–hydrogen bond of acetic acid. As discussed below, this intermediate is consistent with the observed reactivity (or lack thereof) of methyl acetate, acetone, and isopropyl alcohol, as well as that of acetic acid on the graphitized platinum surface. The observed lack of reactivity of methyl acetate in which the hydroxyl hydrogen of acetic acid is replaced with a methyl group indicates the importance of the acidic hydrogen. Since the oxygen–carbon bond is substantially more difficult to cleave than the oxygen–hydrogen bond, dissociation of the acidic hydrogen is implicated in the formation of the surface intermediate. Note that since the heats of reaction for both the dehydration of acetic acid and the elimination of methanol from methyl acetate are approximately 34 kcal/mol,[24] arguments based solely on thermochemistry cannot account for the observed differences in reactivity. Similarly, acetone, in which the hydroxyl group is replaced with a methyl group, is unreactive.

The relative importance of the acidic hydrogen is also illustrated by the dehydration of isopropyl alcohol, which exhibits kinetics that are qualitatively similar to those of acetic acid. Although much less acidic than that of acetic acid, the hydroxyl hydrogen or 2-propanol can dissociate, forming an alkoxy intermediate. This alkoxy intermediates that is formed by cleavage of the oxygen–hydrogen bond of 2-propanol is analogous to the monodentate acetate intermediate that is formed from cleavage of the acidic hydrogen from acetic acid. Since the intermediates are analogous, similar kinetics may be expected. In addition, the measured apparent activation energies at low temperatures of 27 and 16 kcal/mol for the dehydration of acetic acid and 2-propanol vary consistently with the C–OH bond energies of 107 and 92 kcal/mol for acetic acid and isopropyl alcohol, respectively.[25] Assuming the same relative C–O bond energies in the adsorbed intermediates, the observed activation energies indicate that the cleavage of the C–O bond can be important in controlling the rate of decomposition of the surface intermediate.

In contrast to the kinetics observed at low temperatures (≲570 K), at high temperatures (≳675 K) the rate of dehydration of acetic acid is first-order in acetic acid pressure, and the reaction probability approaches (2.5–10) × 10^{-4}. This low reaction probability indicates that the vast majority of acetic acid molecules which adsorb (weakly) on the surface subsequently desorb without reacting. Hence, the steady-state surface coverage of acetic acid is essentially equal to the equilibrium value in the absence of any decomposition. A low reaction probability of acetic acid is also consistent with our measurements of the decomposition of acetic anhydride. Although acetic anhydride decomposes readily to ketene and acetic acid, only a small fraction (<1%) of the acetic acid that is formed on the surface reacts further via dehydration.

2. Mechanistic Modeling. The steady-state reaction kinetics and the thermal desorption measurements, taken together, imply that the dehydration of acetic acid proceeds via an irreversibly adsorbed intermediate. Although the mechanistic model described below postulates that this adsorbed intermediate is a monodentate acetate, *the numerical results are insensitive to the structure of the intermediate provided it is readily formed at 300 K and stable*

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(23) Kouznetzov, A. V.; Shcherbakova, K. D. *J. Chromatogr.* **1970**, *49*, 21.

(24) This result is based on the following values for the various heats of formation: ΔH_f(acetic acid) = −106.7, ΔH_f(methyl acetate) = −98, ΔH_f(ketene) = −14.6, ΔH_f(water) = −57.8, and ΔH_f(methyl alcohol) = −48.1. All quantities are in kcal/mol for the gas phase at 298 K.

(25) *Handbook of Chemistry and Physics*, 51st ed.; Weast, R. C., Ed.; Chemical Rubber Co.: Cleveland, OH, 1970; p F-166.

TABLE I: Model Parameters for the Dehydration of Acetic Acid on a Graphitized Platinum Surface

S^0	1	E_3	0 kcal/mol[a]
$k_2^{(0)}$	1×10^{10} s^{-1}	$E_1 - E_d$	2 kcal/mol
E_2	27.5 kcal/mol	$k_1^{(0)}/k_d^{(0)}$	10^{-3}
$k_3^{(0)}$	7×10^{-10} cm^2/s[a]	n_s	10^{14} cm^{-2}[b]

[a] Reference 27. [b] Reference 26.

upon heating to approximately 520 K.

Assuming a monodentate acetate intermediate, the dehydration of acetic acid may be written mechanistically as follows

$$CH_3COOH(g) \underset{k_d}{\overset{S(\theta)F}{\rightleftharpoons}} CH_3COOH(a) \qquad (1)$$

$$CH_3COOH(a) \xrightarrow{k_1} \eta^1\text{-}CH_3COO(a) + H(a) \qquad (2)$$

$$\eta^1\text{-}CH_3COO(a) \xrightarrow{k_2} CH_2CO(g) + OH(a) \qquad (3)$$

$$OH(a) + H(a) \xrightarrow{k_3} H_2O(g) \qquad (4)$$

where $S(\theta)$ represents the functional dependence of the probability of adsorption of acetic acid on the fractional coverage of each surface species; F is the molecular flux of acetic acid to the surface; and k_d, k_1, k_2, and k_3 are the reaction rate coefficients for the desorption of acetic acid and the three surface reactions. The probability of adsorption of acetic acid may be written as

$$S(\theta) = S^0(1 - \sum_i \theta_i) \qquad (5)$$

where S^0 is the probability of adsorption on the graphitized platinum surface in the limit of zero adsorbate coverage, θ_i is the fractional surface coverage of species i, and the sum is over all surface species. Each of the reaction rate coefficients may be written as $k_i = k_i^{(0)} \exp(-E_i/k_BT)$ with (assumed) coverage-independent preexponential factors $k_i^{(0)}$ and activation energies E_i. To calculate the steady-state rate of acetic acid dehydration via this mechanism, the steady-state material balance equations for each surface species were solved. Since only three of the mass balance equations are linearly independent, the additional assumption that $\theta_{\eta^1\text{-}CH_3COO}$ is equal to θ_H was invoked. As discussed below, the rate of reaction 4 is rapid compared to that of reaction 3, validating this assumption. The probability of molecular adsorption of acetic acid on the clean graphitic surface S^0 was taken to be unity, and the surface site density n_s, which is necessary to calculate absolute rates, was taken to be 10^{14} cm^{-2}.[26] For the recominative desorption of water, reaction 4, the preexponential factor and the activation energy have been determined from a molecular beam investigation of the $H_2O + D_2O$ exchange reaction on pyrolytic graphite.[27,28] Thus, the model described by the elementary reactions 1–4 contains four parameters, namely $k_2^{(0)}$ and E_2 and the composite quantities $E_1 - E_d$ and $k_i^{(0)}/k_d^{(0)}$. These parameters were adjusted until the best description of the experimental data was obtained. The values for each of the variables used in the model calculations are given in Table I, and the model results for the dehydration of acetic acid at 7×10^{-4} and 3.5×10^{-4} Torr are compared with the experimental data in Figure 2. Obviously, the model accurately describes both the temperature and the pressure dependence of the reaction rate.

Although the model contains four adjustable parameters, a consideration of the analytic form of the reaction rate in the limits of high and low temperature illustrates that the values of these "adjustable" parameters are actually quite severely constrained by the data. In the limit of high temperature, where the coverage of all surface species approaches zero, the reaction rate becomes

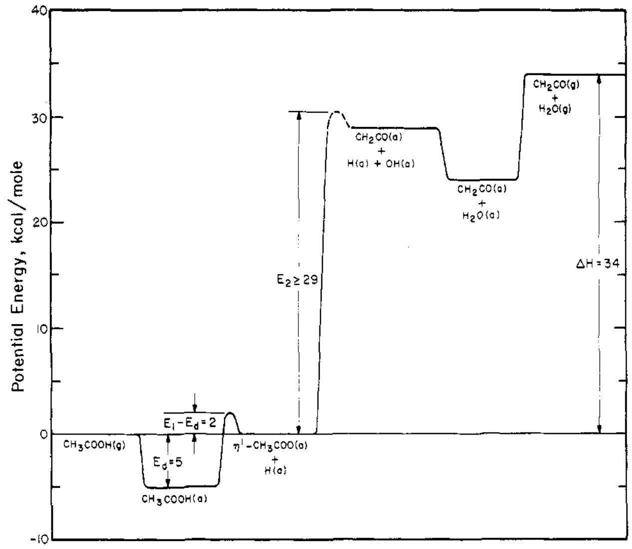

Figure 5. One-dimensional potential energy diagram illustrating the catalytic dehydration of acetic acid to ketene over a graphitized platinum surface. The energy levels have been calculated by choosing acetic acid in the gas phase as the reference level and using the bond energies listed in Table II.

$$R = \frac{S^0Fk_1^{(0)}}{k_d^{(0)}} \exp[-(E_1 - E_d)/k_BT] \qquad (6)$$

Thus, the activation energy observed at high temperature, 1 ± 1 kcal/mol, is equal to $E_1 - E_d$, and the reaction probability at $1/T = 0$ is $S^0k_1^{(0)}/k_d^{(0)}$. At low temperature, the surface becomes saturated with the reaction intermediates η^1-$CH_3COO(a)$ and H(a). Since for all the reaction conditions studied the fractional surface coverages of molecular acetic acid, ketene, and water are negligible, $\theta_{\eta^1\text{-}CH_3COO} = \theta_H = 0.5$, and the reaction rate at low temperature may be written as

$$R = 0.5n_sk_2^{(0)} \exp(-E_2/k_BT) \qquad (7)$$

The observed activation energy, 27 ± 2 kcal/mol, is therefore equal to E_2, and the extrapolated intercept at $1/T = 0$, $(0.2\text{–}1.6) \times 10^{24}$ molecules/(cm^2 s), is equal to $0.5n_sk_2^{(0)}$.

An analysis of the thermal desorption measurements provides *independent* determinations of $k_2^{(0)}$ and E_2. Calibration of the ketene thermal desorption spectrum indicates the desorption of $(0.1\text{–}5) \times 10^{13}$ molecules/cm^2, $0.5n_s$, of ketene. Using this range of values together with the measured result $n_sk_2^{(0)} = (0.4\text{–}3.2) \times 10^{24}$ molecules/(cm^2 s) yields $k_2^{(0)} = (0.04\text{–}16) \times 10^{11}$ s^{-1}. Since we are postulating that ketene originates from the unimolecular decomposition of an adsorbed intermediate, a first-order Redhead analysis[29] applied to the thermal desorption spectrum of ketene using $T_p = 520$ K and $k_2^{(0)} = (0.04\text{–}16) \times 10^{11}$ s^{-1} is appropriate. This gives $E_2 = 23\text{–}29$ kcal/mol, which agrees well with the value of E_2 determined independently from the steady-state kinetics.

In order for the mechanism embodied by reactions 1–4 to describe the experimental data correctly, the rate coefficient for the recombinative desorption of molecular hydrogen must be small compared to that for the production of water. The desorption of molecular hydrogen following both the adsorption of atomic hydrogen and the dissociative adsorption of water has been studied on pyrolytic graphite.[27,28] These results indicate that hydrogen is produced from dissociatively adsorbed water only at temperatures above 2000 K, and even under these conditions, the rate of production of water is an order of magnitude larger than that of hydrogen desorption.[27] An analysis of our model indicates that $k_3n_s^2 >> k_2n_s$ for all conditions studied; e.g., a "worst" case occurs

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(26) Based on the excluded area of an acetic acid molecule, the saturation surface density is approximately 10^{14} cm^{-2}.

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TABLE II: Bond Energies for the Dehydration of Acetic Acid on a Graphitized Platinum Surface

bond	bond energy, kcal/mol	note
CH_3COO–H	107	*a*
CH_3CO–OH	107	*b*
CH_3COOH–S	5	*c, d*
CH_2CO–S	5	*d*
H_2O–S	5	*d*
H–S	61	*e*
HO–S	58	*f*
η^1-CH_3COO–S	52	*g*
η^1-CH_3CO–O(a)	101	*g*

[a] See ref 30. [b] See ref 25. [c] "S" denotes bonding to the graphitized platinum surface. [d] The adsorbate–surface bond energy for each physically adsorbed species is *estimated* to be 5 kcal/mol. [e] The activation energy for the recombinative desorption of hydrogen from the basal plane of graphite is 18 kcal/mol,[28] which implies a bond energy of 61 kcal/mol. [f] The activation energy for the recombinative desorption of water from the basal plane of graphite is 0 kcal/mol.[27] Given an H–S bond energy of 61 kcal/mol, this implies an HO–S bond energy of 58 kcal/mol. [g] Typically, substitution of the hydrogen in an alcohol or a carboxylic acid with an alkyl group reduces the C–O bond energy by 10 kcal/mol, from approximately 90 to 80 kcal/mol.[25] Given the reduced HO–S (carbon) bond energy of 58 kcal/mol, linear scaling implies that the reduction here is approximately 6 kcal/mol.

at 800 K for which $k_3 n_s^2 > 100 k_2 n_s$. Consequently, the steady-state coverages of η^1-CH_3COO(a) and H(a) are equal, since water is produced rapidly after the decomposition of η^1-CH_3COO(a) into ketene and OH(a).

3. Potential Energy Diagram for Acetic Acid Dehydration. A mechanistic model was developed in section IV.2 which describes the observed kinetics for the dehydration of acetic acid to ketene over a graphitized platinum surface. The energetics of this reaction implied by this model are shown in Figure 5 in the form of a potential energy diagram along the "reaction coordinate". The reference energy level of acetic acid in the gas phase is defined to be zero.

To evaluate the energy levels for each of the other points along the reaction coordinate, the bond energies tabulated in Table II were utilized. Note that the predicted energy levels are consistent with the known endothermicity of the overall reaction, namely, 34 kcal/mol.[24] In addition, for temperatures above 675 K, the observed activation energy is 1 ± 1 kcal/mol, which is consistent with the potential energy level for η^1-CH_3COO(a) + H(a). The measured value for E_2 is 27 ± 2 kcal/mol, which is in good agreement with the predicted value of $E_2 \gtrsim 29$ kcal/mol.

Although carbon–hydrogen bond energies in hydrocarbons are typically 100 kcal/mol, following Balooch and Olander,[28] a hydrogen–surface bond energy of 61 kcal/mol was used to construct the potential energy diagram shown in Figure 5. However, identical energy levels would be calculated by assuming that the hydrogen–surface bond energy is 100 kcal/mol with a concurrent reduction of approximately 80 kcal/mol in the carbon–carbon bond energy of the graphite overlayer for each dissociatively adsorbed acetic acid molecule. In this case, the HO–surface and η^1-CH_3COO-surface bond energies would become approximately 90 and 80 kcal/mol, respectively. This alternate formulation is equally consistent with the measured activation energies for both the desorption of hydrogen and the recombinative desorption of water from the basal plane of graphite.[27,28]

V. Synopsis

The results of this study may be summarized as follows:

1. On a polycrystalline platinum surface containing approximately a monolayer of graphitic carbon, the catalytic dehydration of acetic acid to ketene and water proceeds at steady state.
2. For reactant pressures above 3.5×10^{-4} Torr and temperatures below 540 K, the reaction rate is independent of acetic acid pressure, and the apparent activation energy is 27 ± 2 kcal/mol. Under these conditions the rate of decomposition of an irreversibly adsorbed intermediate controls the rate of reaction.
3. The reaction intermediate is formed from acetic acid on the graphitized platinum surface at 300 K and, upon heating, decomposes at 520 K with the accompanying desorption of ketene. Dissociation of the acidic hydrogen of acetic acid appears to be important in the formation of the intermediate.
4. For reactant pressures below 7×10^{-4} Torr and at temperatures above 675 K, the reaction rate is linearly dependent on acetic acid pressure, and the apparent activation energy is 1 ± 1 kcal/mol. In this regime, the reaction rate is determined by a competition between the rates of desorption and surface reaction of molecularly adsorbed acetic acid.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. DMR-8500789

Registry No. Acetic acid, 64-19-7; carbon, 7440-44-0; platinum, 7440-06-4.

Behavior of Four Anthracene-Linked Dimeric Metalloporphyrins as Electrocatalysts for the Reduction of Dioxygen

Ching-Long Ni,[†] I. Abdalmuhdi,[‡] C. K. Chang,*[‡] and Fred C. Anson*[†§]

Arthur Amos Noyes Laboratory, Division of Chemistry and Chemical Engineering,[§] California Institute of Technology, Pasadena, California 91125, and Department of Chemistry, Michigan State University, East Lansing, Michigan 48824 *(Received: July 31, 1986)*

Four new dimeric metalloporphyrins have been prepared in which the two porphyrin rings are linked by an anthracene bridge attached to meso positions. The electrocatalytic behavior of the diporphyrins toward the reduction of O_2 at graphite electrodes has been examined for the following combination of metal centers: Co–Cu, Co–Fe, Fe–Fe, Fe–H_2. The Co–Cu diporphyrin catalyzes the reduction of O_2 to H_2O_2 but no further. The other three catalysts all exhibit mixed reduction pathways leading to both H_2O_2 and H_2O. However, the pathways that lead to H_2O do not involve H_2O_2 as an intermediate. A possible mechanistic scheme is offered to account for the observed behavior.

Significant progress in the catalysis of the electroreduction of O_2 to H_2O by metalloporphyrins has been achieved in recent years.[1-19] The best catalysts from this class have involved pairs of transition-metal centers in dimeric porphyrins,[1-3] but di-

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[†] California Institute of Technology.
[‡] Michigan State University.
[§] Contribution No. 7452.

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