

## Structure–Reactivity Correlations in the Reactions of Hydrocarbons on Transition Metal Surfaces. 2. Hydrogenation of Norbornene and Bicyclo[2.2.2]octene on Platinum(111)

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**Abstract:** The reactivity of two bicyclic alkenes, bicyclo[2.2.2]octene (BOE) and norbornene (NBE), has been studied on Pt(111) in both the absence and the presence of co-adsorbed hydrogen. The inability of these alkenes to rearrange to alkylidyne species on the surface considerably alters their reaction chemistry. At 130 K, the alkenes are bound molecularly to the surface via two interactions: (1) a  $\pi$  or di- $\sigma$  interaction with a C=C double bond, and (2) an apparent agostic interaction with a C–H bond. The geometries of these bicyclic alkenes strongly suggest that they are interacting with three mutually-adjacent surface Pt atoms, but it is not clear from the data whether the alkene group bridges between two Pt atoms and the agostic interaction involves one Pt atom or vice versa. Several reactions ensue upon thermolysis. At  $\sim$ 250 K, the agostic C–H bond is cleaved and a surface-bound alkyl intermediate is formed. The resulting surface-bound hydrogen atoms do not immediately desorb, but some of them transfer to unreacted BOE and NBE molecules to form the alkanes bicyclo[2.2.2]octane (BOA) and norbornane (NBA), respectively. The rate-determining step for this self-hydrogenation reaction is the dehydrogenation of BOE or NBE; these processes appear to follow first-order rate laws with activation energies of  $\sim$ 16 kcal/mol. If the Pt(111) surface is first treated with hydrogen and then dosed with the bicyclic alkene, alkane is formed at lower temperatures (as low as 190 K) and in significantly greater amounts. In the presence of co-adsorbed D<sub>2</sub>, BOE and NBE are hydrogenated to a distribution of alkane isotopomers with up to four deuterium atoms per molecule; these observations suggest that the surface-bound alkyl intermediates can  $\alpha$ -eliminate and reversibly form alkylidenes. Surface carbon atoms, when present at sufficiently high coverages, inhibit the hydrogenation and self-hydrogenation of these bicyclic alkenes due to the reduced ability of the carbonaceous Pt(111) surface to activate H–H or C–H bonds. At higher temperatures (470–520 K), both BOE and NBE eventually decompose to give benzene (part of which desorbs) and surface C<sub>x</sub>H<sub>y</sub> fragments. The latter decompose by  $\sim$ 620 K to give a partial carbonaceous overlayer and H<sub>2</sub> gas.

### Introduction

The heterogeneous catalytic hydrogenation of unsaturated functional groups is a reaction of paramount industrial importance, and consequently considerable effort has been expended to elucidate the mechanisms of reactions such as the catalytic hydrogenation of alkenes.<sup>1,2</sup> For homogeneous alkene hydrogenation reactions,<sup>2,3</sup> detailed mechanisms have been worked out that have led to the rational design of new catalysts, most notably those effective in promoting the enantiospecific hydrogenation of alkenes.<sup>4–6</sup> In contrast, much less is known about the mechanisms of alkene hydrogenation reactions occurring on surfaces. This situation is partly ascribable to the difficulties in characterizing reactive species and intermediates on a metal

surface. Surface-sensitive spectroscopies often limit studies to reactions that occur under ultrahigh vacuum (UHV) conditions; alkene hydrogenation reactions, because they are associative, are generally disfavored relative to dissociative processes at the low surface concentrations and adsorbate fluxes encountered in a UHV environment.<sup>7</sup>

Despite the obstacles in studying bimolecular reactions under UHV conditions, several significant studies of the hydrogenation of alkenes on platinum surfaces have been described.<sup>8</sup> It has been reported that ethylene can be hydrogenated (albeit in low yield) in two ways: via self-hydrogenation, which involves the sacrificial donation of hydrogen from one ethylene molecule to another, and via hydrogenation, which is promoted by pre-adsorbed hydrogen. The former process occurs at higher temperatures (305 K) and follows a first-order rate law in which the rate-limiting step is the decomposition of ethylene. The hydrogen-promoted process occurs at lower temperatures (252 K) and follows a second-order rate law. It has long been thought that alkene hydrogenation occurs via insertion of the alkene into

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a M-H bond to form a surface alkyl group, followed by reaction of this alkyl intermediate with another surface hydrogen atom to reductively eliminate alkane. However, another mechanism has been proposed that is based on the observation that the platinum-catalyzed hydrogenation of ethylene proceeds at a constant rate after a high coverage of ethylidyne has appeared on the surface.<sup>9</sup> In this mechanism, surface hydrogen first converts two ethylidynes ( $\text{CH}_3\text{C}\equiv$ ) to two ethylidene ( $\text{CH}_3\text{-CH=}$ ) groups. Transfer of hydrogen atoms from two ethylidenes to a weakly adsorbed ethylene molecule then occurs to give ethane and two ethylidyne groups.

Recent elegant studies of the hydrogenation of substituted alkenes catalyzed by Fe(100)-CO surfaces<sup>10,11</sup> have established the activation energies for several of the key steps in the process; these studies have presented a thorough analysis of the dependence of the rate of hydrogenation on the degree of substitution of the alkene and the coverage of carbon monoxide on the surface. The investigations demonstrated that the mechanism of alkene hydrogenation involves insertion of the alkene into a Fe-H bond and that the rate-determining step for the formation of free alkane is the bimolecular reductive elimination of an alkyl and a hydride group.

Another extremely valuable approach to understanding heterogeneous hydrogenation reactions is to prepare and study directly the surface-bound alkyl groups thought to be the central intermediates in the conversion of alkenes to alkanes. These surface-bound alkyl groups can be produced in several ways, most notably by the dissociative chemisorption of alkyl halides and by the use of molecular beams of pre-generated alkyl radicals.<sup>12-16</sup> Studies of these surface-bound alkyl groups have afforded detailed insights into several C-H bond activation processes, including  $\beta$ -hydrogen elimination (which is the

microscopic reverse of the alkene insertion step believed to be important in alkene hydrogenation reactions).

We describe here kinetic and spectroscopic studies of the chemistry of norbornene and bicyclo[2.2.2]octene on Pt(111) single crystal surfaces. These bicyclic internal alkenes are readily hydrogenated on platinum, and thus afford an excellent opportunity to probe the interactions between surface hydrogen and adsorbed alkenes. This work considerably extends previous studies of the decomposition of another bicyclic alkene, norbornadiene, on Pt, Ni, and Pd single crystal surfaces.<sup>17,18</sup>

Our studies are also relevant to the surface reactions that take place during the chemical vapor deposition (CVD) of platinum and platinum-containing thin films from certain organoplatinum precursors. Platinum complexes of bicyclic alkenes (especially norbornadiene)<sup>19,20</sup> are useful precursors for the deposition of platinum under reducing conditions (i.e., with  $\text{H}_2$  as a carrier or reactive gas).<sup>21-25</sup> The mechanism of the heterogeneous hydrogenation of platinum bis(alkene) complexes in solution has been the subject of extensive study;<sup>26-28</sup> interactions between bicyclic alkenes and surface hydrogen atoms are likely to be important to the chemistries that occur during thin film growth as well.

## Experimental Section

The UHV chambers used in this work have been detailed previously,<sup>29</sup> and only will be described briefly here. The mass spectrometric and Auger electron spectroscopic studies were performed in a stainless steel chamber equipped with diffusion, turbomolecular, titanium sublimation, and ion pumps. The base pressure in the chamber was  $2.0 \times 10^{-10}$  Torr. The infrared spectroscopic studies were performed in a stainless steel chamber equipped with a turbomolecular pump (an Auger electron spectrometer was also attached to the chamber); the base pressure was  $3.0 \times 10^{-10}$  Torr.<sup>30</sup> The Pt(111) crystal was

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purchased from Cornell Laboratories and was oriented to within  $0.5^\circ$  and polished to a fine mirror finish by standard metallographic techniques. The crystal was cleaned in both chambers by sputtering with  $\text{Ar}^+$  ions at 1050 K (current to the crystal =  $5 \mu\text{A}$ ), followed by annealing at 1050 K for 8–10 min. AES indicated that there was no detectable carbon on the crystal surface ( $<0.5$  atomic %).

Deuterium and hydrogen were purchased from Matheson and used as received. Norbornene and bicyclo[2.2.2]octene were purchased from Aldrich; gas chromatography indicated that the samples were greater than 98% pure. The samples were degassed before being introduced into the chamber. Dosing was accomplished by backfilling the chamber through a variable leak valve and the amount is given in Langmuirs ( $1 \text{ L} \equiv 10^{-6} \text{ Torr s}$ ).<sup>31</sup>

## Results

The binding and reactivity of two bicyclic alkenes, bicyclo[2.2.2]octene (BOE) and norbornene (NBE), on Pt(111) surfaces at low temperatures ( $<300 \text{ K}$ ) have been elucidated by a combination of techniques, including temperature programmed reaction spectroscopy (TPRS), integrated desorption mass spectrometry (IDMS),<sup>32,33</sup> and reflection-absorption infrared spectroscopy (RAIRS). Comparisons of the behavior of BOE and NBE in the absence and in the presence of pre-adsorbed hydrogen have led to a comprehensive picture of the thermodynamic and kinetic factors that govern the chemistry of bicyclic alkenes on platinum(111) surfaces.

**Temperature-Programmed Reaction Spectroscopy. (a) Reactivity of Bicyclo[2.2.2]octene and Norbornene on Pt(111): Self-Hydrogenation.** When a Pt(111) single crystal is dosed at 100 K with BOE and then heated, several species are detected in the desorbing flux at temperatures lower than 300 K (Figure 1). Foremost among these is BOE itself: a BOE multilayer is formed at exposures of 8 L or greater, and desorbs from the surface at  $T_{\text{max}} \approx 188 \text{ K}$  (Figure 1d). If this multilayer desorption process is assumed to follow a first-order rate law (a qualitative approximation for coverages just exceeding a monolayer) and the pre-exponential factor is assigned a typical value of  $10^{13} \text{ s}^{-1}$  ( $\Delta S^\ddagger = 0$ ), then the activation energy for the sublimation of BOE can be calculated to be  $\sim 10 \text{ kcal/mol}$ .<sup>34</sup>

Interestingly, no BOE desorbs when the exposure is less than 8 L (i.e., from a monolayer or submonolayer coverage). Instead, the molecules remain adsorbed on the surface until, eventually, they react at higher temperatures (262 K) to produce (in part) the hydrogenation product bicyclo[2.2.2]octane (BOA) as shown by the TPRS trace in the  $m/e = 110$  channel (Figure 1e).<sup>35</sup> The identity of the desorbing material was verified by the IDM spectrum collected near this temperature.<sup>36</sup> The peak temperature for the desorption of BOA is independent of the initial coverage of BOE.

The formation of BOA from BOE indicates that a disproportionation reaction is occurring: some portion of the BOE is being dehydrogenated by the Pt(111) surface, and the resulting

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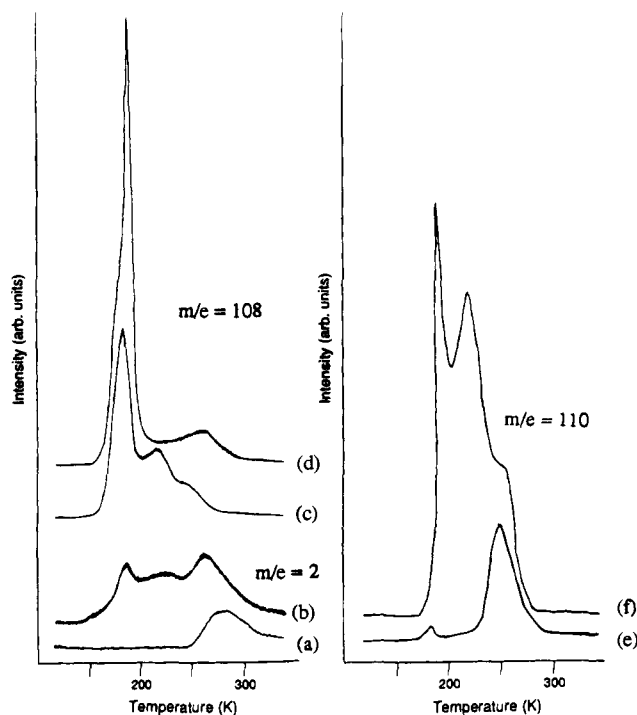
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(33) Compounds were identified by comparing their IDM spectra with those of authentic samples except for BOA, whose assignment is based upon a literature spectrum: *Atlas of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W., Eds.; Interscience: New York, 1969; Vol. 1.

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(35) Coverage dependent studies reveal that the desorption of BOA occurs by a first-order process.

(36) Note for future reference that BOA gives a strong signal in the  $m/e = 108$  channel [ $\text{P} - 2$ ]<sup>+</sup> in addition to the parent peak at  $m/e = 110$ , so that TPRS features in the  $m/e = 108$  channel could indicate either the presence of large amounts of BOA in the desorbing flux or the desorption of BOE, or both. These possibilities can be distinguished by IDMS.

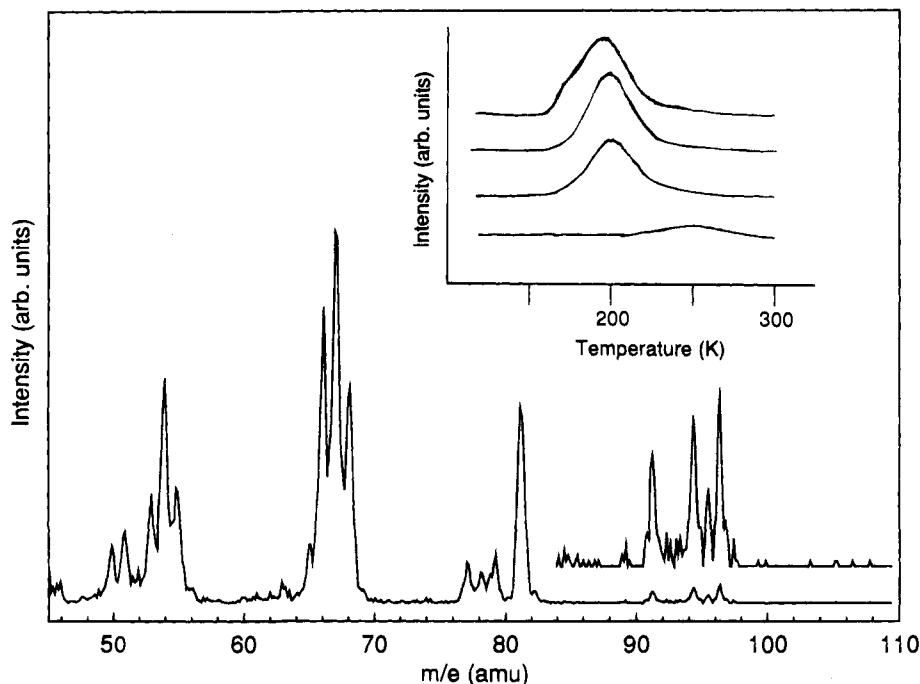


**Figure 1.** Temperature-programmed reaction profiles taken from a Pt(111) surface dosed with either 8 L of bicyclo[2.2.2]octene (BOE) (a, d, e), or 10 L of  $\text{H}_2$  followed by 8 L of BOE (b, c, f):  $m/e = 2$  charts the desorption of  $\text{H}_2$ ,  $m/e = 108$  contains contributions from both BOE and bicyclo[2.2.2]octane (BOA), and  $m/e = 110$  tracks the desorption of BOA.

adsorbed hydrogen is then used to hydrogenate unreacted BOE to BOA. The  $m/e = 2$  TPRS profile exhibits a desorption feature whose rising edge coincides almost exactly with the falling edge of the BOA peak (Figure 1a). Thus, some of the hydrogen atoms generated by the dehydrogenation of BOE desorb as  $\text{H}_2$ ; these data suggest either that BOE loses multiple hydrogen atoms near 262 K or that the reaction of surface hydrogen atoms with BOE to form BOA does not occur with unit efficiency. Infrared studies (see below) suggest that BOE loses only one hydrogen atom below 300 K.

The gross characteristics of the thermal desorption behavior of norbornene (NBE) on Pt(111) closely resemble those of BOE. At doses above 7 L, multilayer desorption of NBE is seen ( $T_{\text{max}} \approx 178 \text{ K}$ ); using the assumption described above, this temperature corresponds to an activation energy for sublimation of  $\sim 11 \text{ kcal/mol}$ . The self-hydrogenation of NBE to norbornane (NBA) also occurs, and can most clearly be detected as a desorption feature at 250 K in the  $m/e = 96$  channel (Figure 2, inset). The identification of the desorbing species as NBA was confirmed by IDMS (Figure 2). The peak temperature for self-hydrogenation is independent of the initial coverage of NBE. Like the situation described for BOE, NBA desorption is followed by hydrogen desorption, with  $T_{\text{max}} \approx 320 \text{ K}$ . IR studies, which are described below, indicate that the hydrogen which is used for NBE self-hydrogenation arises from the cleavage of a specific C–H bond in NBE.

**(b) Reactivity of Bicyclo[2.2.2]octene and Norbornene on a Hydrogenated Pt(111) Surface.** On Pt(111) surfaces, the hydrogenation of BOE and NBE by coadsorbed  $\text{H}_2$  proceeds differently depending on the dosing order. If the crystal is first dosed with 8 L of BOE and then with 10 L of  $\text{H}_2$ , a substantial amount of hydrogen adsorbs on the surface, as shown by the TPRS profile in the  $m/e = 2$  channel. The hydrogen has relatively little effect, however, on the reactions of the adsorbed



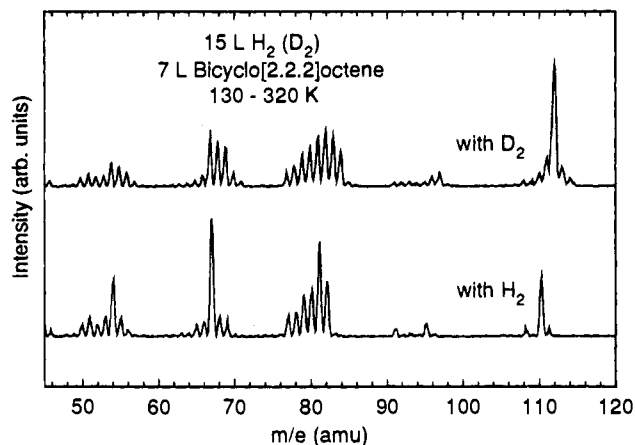
**Figure 2.** Integrated desorption mass spectrum of the species desorbing between 240 and 290 K from a Pt(111) surface dosed with 9 L of norbornene. (Inset) Temperature-programmed reaction profiles taken from Pt(111) surfaces dosed first with various amounts of hydrogen (from bottom, 0–8 L) and 7 L of norbornene:  $m/e = 98$  tracks the desorption of norbornene.

alkene: the TPRS profiles tracking the desorption of BOE and BOA are virtually identical to those observed for 8 L of BOE dosed onto a hydrogen-free surface.

In contrast, if the crystal is first dosed with 10 L of  $H_2$  and then with 8 L of BOE, the ensuing TPRS profiles show a  $\sim 10$  fold increase in the amount of BOA that desorbs from the surface (Figure 1f). Furthermore, the temperature at which BOA desorbs is lowered by about 40 K: the major desorption feature now occurs at 220 K.<sup>37</sup> Clearly, the presence of pre-adsorbed hydrogen promotes the hydrogenation of BOE to BOA.

When the Pt(111) surface is first dosed with  $D_2$  and then with BOE, desorption of BOA containing significant quantities of deuterium occurs with  $T_{max} = 231$  K.<sup>38</sup> This desorption temperature is 11 K higher than that seen when the surface is first dosed with  $H_2$ ; an analysis of the kinetic isotope effect for the hydrogenation reaction will be presented in the Discussion Section. As determined by IDMS, the major desorbing isotopomer is BOA- $d_2$ , but lesser quantities of BOA- $d_3$  and BOA- $d_4$  are also present in the desorbing flux (Figure 3). The formation of the  $d_3$  and  $d_4$  alkane isotopomers suggests that at least one of the steps in the hydrogenation pathway is reversible; the implications of this observation are addressed in the Discussion Section.

The nature of the interactions between co-adsorbed hydrogen and BOE molecules and the influence of these interactions on the production of BOA have been explored in two TPRS studies. In the first study, the amount of hydrogen (10 L) was held constant and the amount of BOE was varied (Figure 4a). At the lowest doses of BOE, BOA desorbs in a peak centered at 246 K; if the BOE exposure is increased, more BOA desorbs ( $T_{max}$  remains essentially constant). Although bulk samples of BOA were not available for independent measurements of its



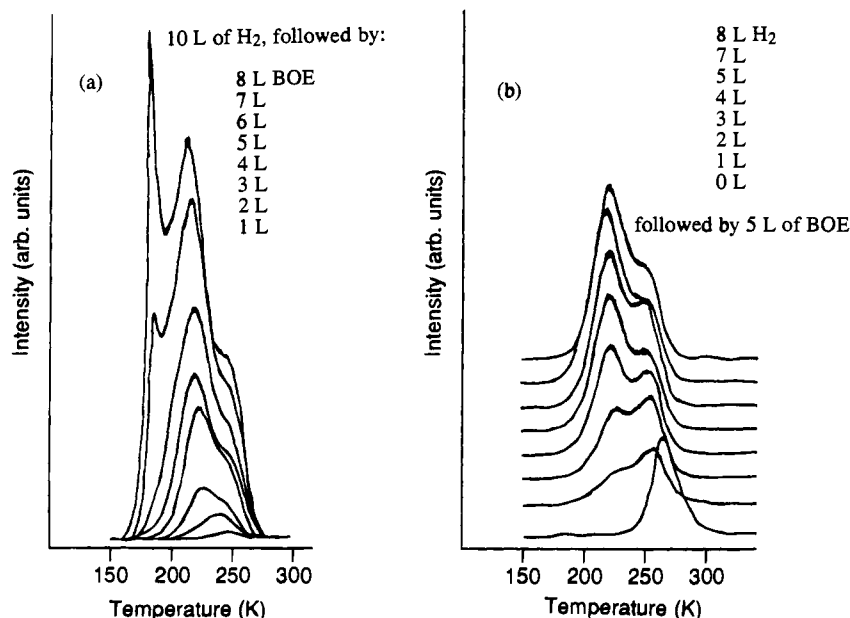
**Figure 3.** Integrated desorption mass spectra of the species desorbing between 130 and 320 K from (bottom) a hydrogen-covered Pt(111) surface dosed with 7 L of bicyclo[2.2.2]octene or (top) a deuterium-covered Pt(111) surface dosed with 7 L of bicyclo[2.2.2]octene.

multilayer and monolayer desorption temperatures, values of  $< 200$  K would be expected as judged from studies of other hydrocarbons of similar size (cyclooctane<sup>29</sup> and norbornane<sup>39</sup>); therefore, a desorption temperature of 246 K is undoubtedly reaction-limited. At BOE doses of 3 L or higher, a second large BOA desorption peak at lower temperature (220 K) becomes evident; at BOE doses of 7 L or higher, a third (but small) BOA desorption peak at  $\sim 188$  K appears. Finally, at a BOE dose of 8 L, the conversion to BOA saturates. IDMS indicates that the only desorbing hydrocarbon under these latter conditions is BOA. Since the addition of more BOE to the  $H_2$ -predosed surface lowers the temperature at which BOA desorption begins, we conclude that addition of BOE forces the adsorbed hydrogen atoms to migrate to more reactive surface sites. The BOA desorption features at 188 and 220 K are evidently desorption-limited and reaction-limited, respectively; the latter conclusion

(37) Although TPRS features are seen in the  $m/e = 108$  channel, IDMS has confirmed that they are due to desorption of BOA and detection of its  $[P - 2]^+$  fragment ion (Figure 3).

(38) In both experiments the surface was first saturated with  $H_2$  ( $D_2$ ); this was followed by an 8 L exposure of BOE. The data in Figure 4 strongly suggest that the 11 K shift is a true kinetic isotope effect and is not a consequence of coverage-dependent desorption kinetics.

(39) Hostetler, M. J.; Girolami, G. S.; Nuzzo, R. G. Manuscript in preparation.



**Figure 4.** Temperature-programmed reaction profiles taken from Pt(111) surfaces dosed with various amounts of hydrogen and BOE; the  $m/e = 110$  channel tracks the desorption of BOA.

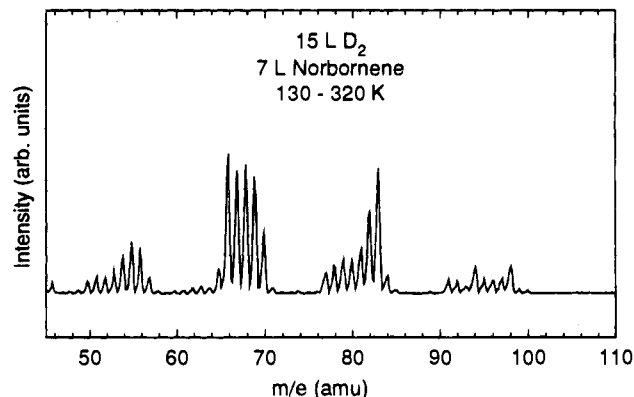
is consistent with the kinetic isotope effect seen for the 220 K feature discussed above.

In the second study of the hydrogenation of BOE to BOA, the amount of hydrogen and the amount of BOE (5 L or  $\sim 1/2$  monolayer) was held constant (Figure 4b). The bottom TPR trace (no added hydrogen) corresponds to the desorption of BOA formed in the self-hydrogenation reaction. At a  $H_2$  dose of 1 L, the TPRS trace changes strikingly: two BOA desorption features are seen, a small one centered at 224 K and a larger one at 254 K. The amount of BOA that desorbs at 254 K is comparable to that generated by self-hydrogenation in the absence of co-adsorbed  $H_2$ . As the hydrogen exposure is increased, both peaks grow in intensity but the lower-temperature feature grows more quickly and becomes the dominant feature at  $H_2$  exposures of 3 L or higher. In addition, both peaks shift lower in temperature to 220 and 246 K, respectively. Hydrogenation of BOE reaches a saturation limit following a dose of 7 L of  $H_2$ . It must be emphasized that even at high  $H_2$  doses, however, a substantial portion of the BOE is *not* hydrogenated and undergoes further reaction at higher temperatures (see below).

In both of these studies, the lowering of the temperature at which BOA desorbs from the  $H_2$ -dosed surface strongly suggests that the rate-determining step for the formation of BOA in the *absence* of co-adsorbed  $H_2$  (i.e., for the self-hydrogenation process) is *not* the reaction of surface-bound hydrogen atoms with BOE. The formation of BOA from BOE under these conditions must instead be limited by the rate at which BOE is sacrificially dehydrogenated.

Results similar to those above have also been obtained for the hydrogenation of NBE to NBA on hydrogenated Pt(111) surfaces. The dependence of the alkane yield on dosing order described for BOE also holds true for NBE. The peak temperature for desorption of alkane again drops dramatically even in the presence of small amounts of hydrogen (Figure 2, inset): 3 L of  $H_2$  causes the NBA desorption temperature to shift from 250 to 194 K ( $m/e = 96$  TPRS trace; 7 L dose of NBE). As expected, larger doses of hydrogen increase the amount of NBA that desorbs (Figure 2, inset).<sup>40</sup>

Analogous experiments were performed by dosing 7 L of NBE onto a Pt(111) surface that had been pre-dosed with



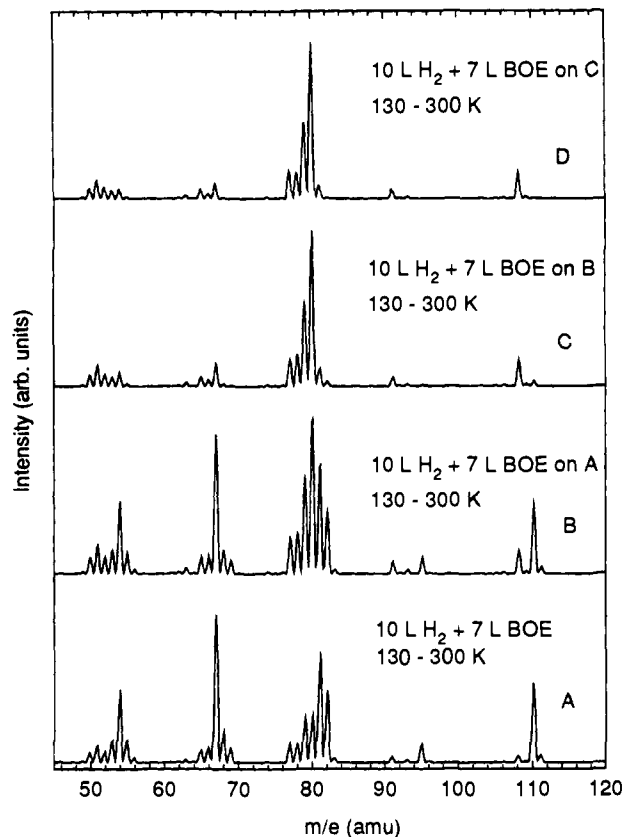
**Figure 5.** Integrated desorption mass spectrum of the species desorbing between 130 and 320 K from a deuterium-covered Pt(111) surface dosed with 7 L of norbornene.

deuterium ( $\theta \approx 0.8\theta_{\text{sat}}$ ). An IDM spectrum collected over the temperature range 130–320 K (Figure 5) shows that most of the NBA formed contains two deuterium atoms ( $m/e = 98$ ); smaller amounts of NBA isotopomers with three and four deuterium atoms are also present. The desorbing flux also contains some NBE- $d_0$  and NBE- $d_1$  as shown by the peaks at  $m/e = 94$  and 95; in contrast, alkene was *not* among the desorption products for the  $D_2$ /BOE experiments.<sup>41</sup>

Three important conclusions can be drawn from these TPRS experiments. First, the rate-limiting step for the self-hydrogenation of alkene to alkane is activation of the C–H bonds of the alkene. Second, the presence of NBE in the desorbing flux from the hydrogen pre-dosed surfaces suggests that NBE is *not* hydrogenated as easily as is BOE. Third, the generation of  $d_3$  and  $d_4$  alkane isotopomers in the deuterium-labeling experiments implies that at least one step in the hydrogenation of alkene to alkane is reversible.

(40) Unlike the series of analogous spectra collected for BOE, there is no shoulder in the NBA desorption feature which corresponds to self-hydrogenation. At very high coverages, a low-temperature shoulder appears at 174 K, which corresponds to the desorption temperature for NBA from the multilayer.

(41) We cannot tell whether the peaks at masses 96 and 97 are due to NBE- $d_0$  and NBE- $d_1$  or to NBE- $d_2$  and NBE- $d_3$ , or a mixture of these species.



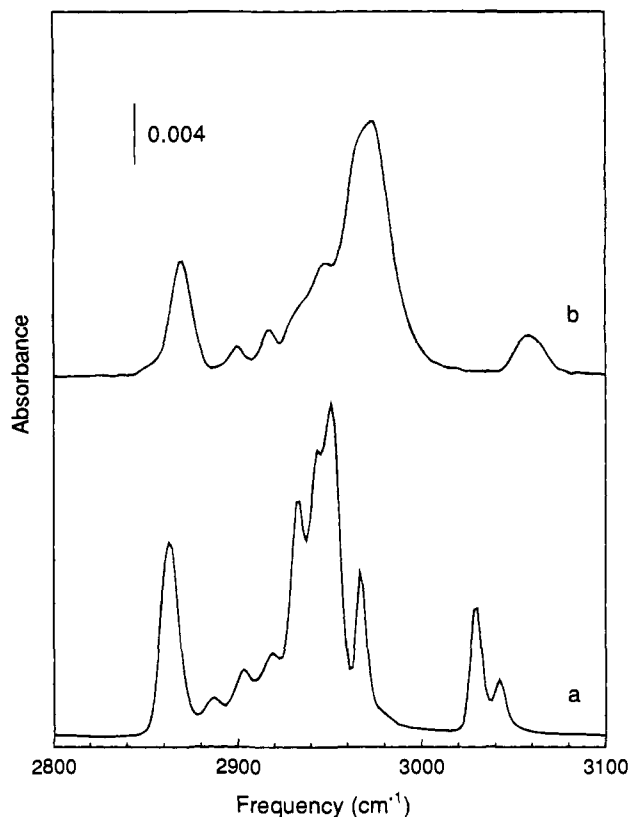
**Figure 6.** Integrated desorption mass spectra illustrating the poisoning effect of the carbonaceous overlayer on the hydrogenation of BOE to BOA.

(c) **Reactivity of Bicyclo[2.2.2]octene on a Carbonaceous Pt(111) Surface.** The hydrogenation of BOE to BOA is inhibited by the presence of surface carbon. This is best illustrated by the series of integrated desorption mass spectra in Figure 6. These spectra were obtained by successively repeating the following procedure: the surface was exposed to 10 L of  $H_2$ , exposed to 7 L of BOE, ramped to 800 K, and then cooled to 100 K. The surface was *not* cleaned between each cycle. We will show below that this procedure leaves a partial carbonaceous overlayer on the surface. As expected from the results described above, the clean Pt(111) surface present during the first cycle is quite active: only BOA is observed in the desorbing flux (Figure 6a). After this first cycle, 30% of a monolayer of carbon is left behind as a carbonaceous overlayer as judged by AES.<sup>42</sup> During the second cycle, both BOA and BOE are present in the desorbing flux (Figure 6b), which indicates that the ability of the surface to hydrogenate BOE has been inhibited. After this cycle, 80% of a monolayer of carbon remains on the surface. By the third cycle, the hydrogenation process is almost completely shut down (Figure 6c); a total of 1.7 monolayers of carbon remains on the surface at this point. Finally, in the fourth cycle, no hydrogenation is observed and only BOE desorbs from the surface (Figure 6d).

When a carbon-covered surface (corresponding to Figure 6d) is exposed to 100 L of  $H_2$  at 100 K and then heated, the desorption of  $H_2$  is not detected. This provides strong evidence that the dissociative adsorption of hydrogen is inhibited on the Pt-C surface.

This series of experiments suggests that both hydrogen-induced hydrogenation and self-hydrogenation of BOE are

(42) The carbon coverage was calculated using the calibration parameters described in: Rodriguez, J. A.; Campbell, C. T. *J. Phys. Chem.* **1989**, *93*, 826–835.



**Figure 7.** Reflection-absorption infrared spectrum of a multilayer of (a) bicyclo[2.2.2]octene and (b) norbornene on Pt(111).

inhibited by the carbonaceous overlayer. However, some of the BOE molecules still undergo C-H bond activation as indicated by the increase in the amount of carbonaceous overlayer from cycle to cycle and by the presence of a weak  $H_2$  desorption feature at 510 K even during the fourth dosing cycle. Thus, surface hydrogen atoms are generated but are not transferred to other BOE molecules.

#### Reflection-Absorption Infrared Spectroscopic Studies.

(a) **RAIR Spectra of Bicyclo[2.2.2]octene on Pt(111).** The infrared spectrum of a multilayer coverage of BOE on Pt(111) is given in Figure 7a; the peak assignments are presented in Table 1. Although an analysis of the vibrational modes of BOE does not appear to be available, both norbornane<sup>43</sup> and norbornadiene<sup>43–45</sup> have been analyzed and our interpretation of the RAIR data is based upon this work. A detailed discussion of the assignments is presented in the Appendix.

The RAIR spectrum obtained from a submonolayer coverage of BOE on Pt(111) at 130 K is shown in Figure 8 (mode assignments are given in Table 1). Also included in Figure 8 are the spectra obtained after the surface was annealed to a series of temperatures relevant to the reactions responsible for the formation of alkane (130 K corresponds to the lowest temperature we could achieve in our system; 170 K is just below the temperature where the hydrogen-promoted hydrogenation of BOE occurs; 220 K is above the temperature where hydrogen-promoted hydrogenation takes place but below where self-hydrogenation of BOE occurs; 300 K is higher than the BOE self-hydrogenation temperature).

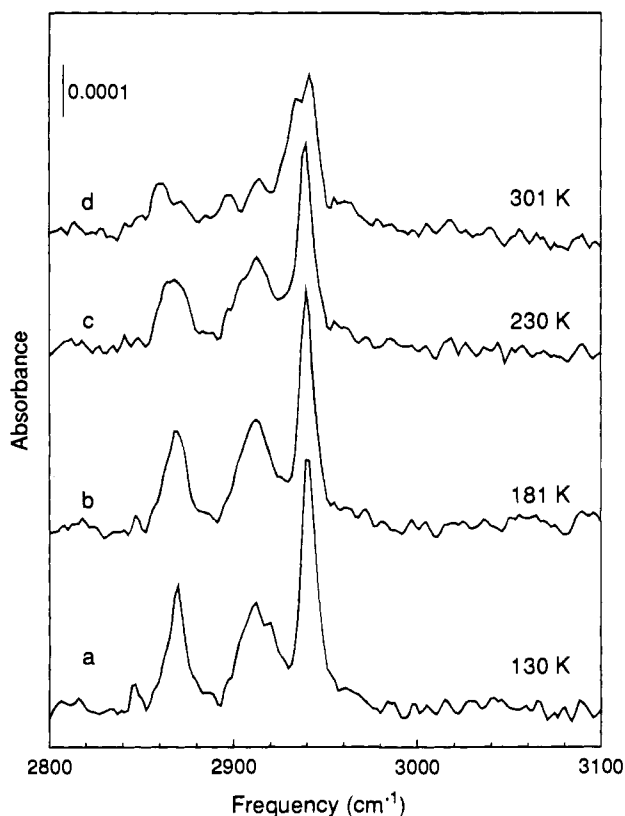
(43) Levin, I. W.; Harris, W. C. *Spectrochim. Acta* **1973**, *29A*, 1815–1834.

(44) Aleksanyan, V. T.; Garbuzova, I. A.; Pryanishnikova, M. A.; Paturyan, I. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1973**, 756–760.

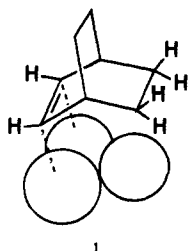
(45) Maslowsky, E., Jr. *Vibrational Spectra of Organometallic Compounds*; John Wiley & Sons: New York, 1977; p 468–477.

**Table 1.** Vibrational Assignments for BOE on Pt(111)

assignment	multilayer 132 K	submonolayer			
		130 K	181 K	230 K	301 K
vinyllic $\nu_a(\text{C-H})$	3042				
vinyllic $\nu_s(\text{C-H})$	3030				
tertiary $\nu_a(\text{C-H})$	2966				
$\text{CH}_2\text{CH}_2$ $\nu_a(\text{C-H})$	2951, 2943				
near surface $\text{CH}_2\text{CH}_2$ $\nu_a(\text{C-H})$		2940	2940	2940	2941, 2934
$\text{CH}_2\text{CH}_2$ $\nu_a(\text{C-H})$	2934				
$\text{CH}_2\text{CH}_2$ $\nu_s(\text{C-H})$	2918	2912	2912	2912	2914
$\text{CH}_2\text{CH}_2$ $\nu_s(\text{C-H})$	2903, 2887			2906, 2897	2897
combination band	2862	2870	2870	2868, 2864	2872, 2862

**Figure 8.** Reflection-absorption infrared spectra from a Pt(111) surface dosed at 130 K with a submonolayer coverage of bicyclo[2.2.2]-octene and then annealed to the indicated temperatures.

At 130 K, the vinyllic C-H stretches above  $3030\text{ cm}^{-1}$  are absent; this result suggests that the alkene binds to the surface through its C=C double bond. In order for the  $\pi$ -system of the double bond to coordinate to the surface, the BOE molecule must be oriented in a specific fashion: one of the  $\text{CH}_2\text{CH}_2$  groups must be pointed almost directly away from the surface, but the other  $\text{CH}_2\text{CH}_2$  group *must* be brought near the surface (structure I).



This view of the binding of the conformationally rigid BOE molecule to the surface allows us to interpret other features of

the RAIR spectra shown in Figure 8. When BOE interacts with the surface, its effective symmetry is reduced from  $C_{2v}$  to  $C_s$  (ignoring the site symmetry of the surface itself), and the molecule should exhibit one tertiary C-H stretch and a total of four C-H stretching vibrations for the two inequivalent  $\text{CH}_2\text{CH}_2$  groups. Although all of these modes are IR-active by symmetry, several of these will be weak either because their transition moments are small or because their transition directions are nearly perpendicular to the surface normal (and thus not observable in a RAIR experiment).<sup>46</sup> Specifically, the tertiary C-H stretch and two of the four C-H stretches of the  $\text{CH}_2\text{CH}_2$  groups will be absent or weak; thus, only two C-H stretching bands should be observable.

Indeed, this is what we observe. Figure 8a (130 K) reveals the presence of two bands in the C-H stretching region besides the low-frequency peak at  $2870\text{ cm}^{-1}$  that is assigned to the combination band (see Appendix). The frequency of one of the two C-H stretching bands is only slightly perturbed from the position of a symmetric  $\text{CH}_2\text{CH}_2$  stretch in the spectrum of a BOE multilayer; this band, at  $2912\text{ cm}^{-1}$ , is therefore assigned to one of the C-H stretching modes of the  $\text{CH}_2\text{CH}_2$  group that is *not* interacting with the surface. Specifically, we assign this mode as the in-phase combination of two local symmetric  $\text{CH}_2$  stretching motions. We assign the other C-H stretching band at  $2940\text{ cm}^{-1}$  to an antisymmetric stretching vibration for the  $\text{CH}_2\text{CH}_2$  group that is nearest to the surface.

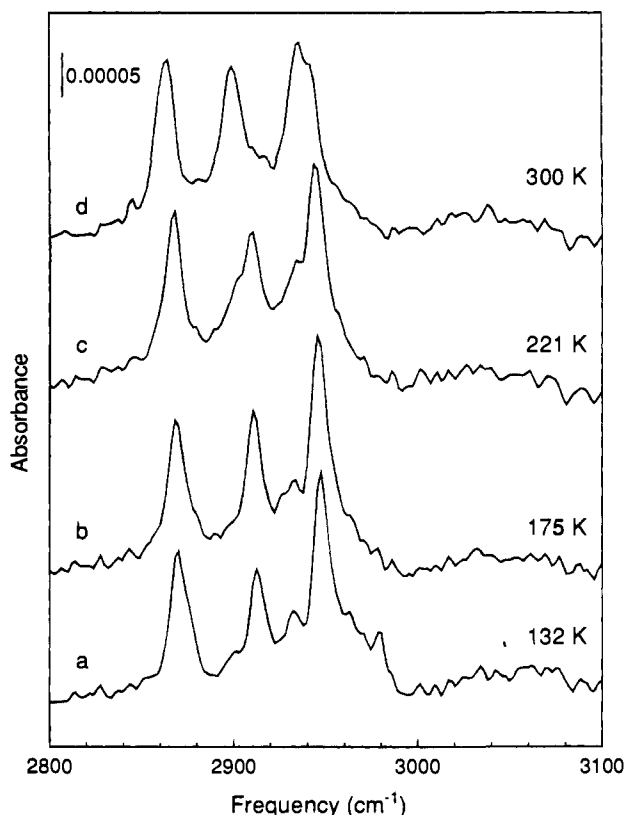
The RAIR spectrum obtained upon annealing the BOE-dosed surface to 181 K (Figure 8b) contains the same three bands in the C-H stretching region and it is evident that the BOE molecules are still intact. When the surface is further heated to 230 K (Figure 8c), which is just below the temperature where self-hydrogenation is seen, changes in the RAIR spectrum become apparent that signal the initiation of the BOE decomposition process. By 301 K, the spectrum is significantly different: the bands due to BOE have nearly disappeared, and several new bands now dominate. These changes are consistent with the contention that BOE is dehydrogenated at these temperatures.

It is of interest to determine how many hydrogen atoms are lost per molecule when BOE is dehydrogenated, because this number will dictate the stoichiometry of the BOE self-hydrogenation process. Several possibilities exist: loss of one hydrogen could occur to give a bicyclo[2.2.2]octenyl group, loss of two hydrogens could occur to give the diene bicyclo[2.2.2]octadiene (BOD), or loss of more than two hydrogens could occur. The RAIR spectra suggest that bicyclo[2.2.2]octadiene is not the initial dehydrogenation product. If BOD were formed, the only band which should be seen would be a symmetric C-H stretching vibration near  $2915\text{ cm}^{-1}$  for the unbound  $\text{CH}_2\text{CH}_2$  group (if the BOD molecules were bound to the surface via both C=C double bonds) or a prominent vinyllic C-H stretch

**Table 2.** Vibrational Assignments for NBE on Pt(111)

assignment	multilayer 132 K	submonolayer			
		132 K	175 K	221 K	300 K
vinyl $\nu_s(\text{C-H})$	3042				
tertiary $\nu_a(\text{C-H})$	2972 <sup>a</sup>	2978			
$\text{CH}_2 \nu_a(\text{C-H})$	2972 <sup>a</sup>	2947	2947	2945	2947
$\text{CH}_2\text{CH}_2 \nu_a(\text{C-H})$	2947				
$\text{CH } \nu(\text{C-H})$			2936	2936	2941
$\text{CH}_2\text{CH}_2 \nu_s(\text{C-H})$	2916	2912	2913	2913, 2906 <sup>b</sup>	2899 <sup>b</sup>
not assigned	2899, 2935	2901			
overtone	2870	2870	2870	2870	2864

<sup>a</sup> Unresolved component. <sup>b</sup> Norbornenyl intermediate, structure V.



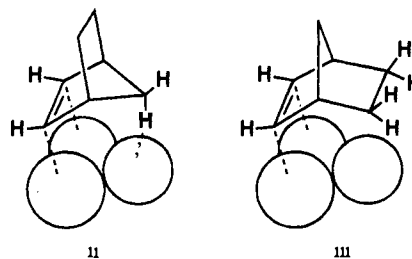
**Figure 9.** Reflection-absorption infrared spectra from a Pt(111) surface dosed with a submonolayer coverage of norbornene and then annealed to the indicated temperatures.

(if they were bound via one C=C double bond and one CH<sub>2</sub>-CH<sub>2</sub> group). Since a much more complex spectrum is obtained when BOE is heated to 301 K, we conclude that BOE is *not* the major dehydrogenation product; in the next section we will show that norbornene behaves similarly—it does not give norbornadiene when it is heated to 300 K. Instead, we propose that dissociative processes involve the loss of only *one* hydrogen atom initially (see below).

**(b) RAIR Spectra of Norbornene on Pt(111).** The infrared spectrum of a multilayer of NBE on Pt(111) is presented in Figure 7b, and mode assignments are included in Table 2. The assignment of this spectrum (see Appendix) follows directly from our previous description for BOE and the aforementioned assignments for norbornane and norbornadiene.

The RAIR spectrum which is obtained from a submonolayer coverage of NBE on Pt(111) at 132 K is shown in Figure 9a (mode assignments are given in Table 2). Also included in Figure 9 are the spectra obtained after the surface was annealed to various temperatures.<sup>47</sup> It is clear that at 132 K essentially all of the norbornene molecules are bound to the surface via the C=C double bond; this conclusion is most clearly supported

by the lack of any bands in Figure 9 assignable to vinyl C-H stretches. Given that NBE is bound to the surface via its C=C bond, there are two possible orientations for this molecule on the surface: in one orientation, the CH<sub>2</sub> group is near the surface (structure II), while in the other orientation, the CH<sub>2</sub>CH<sub>2</sub> group is near the surface (structure III):



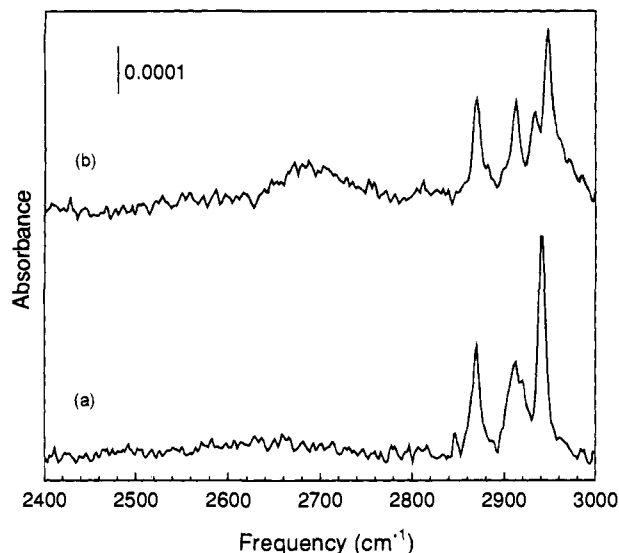
These two orientations should be distinguishable spectroscopically. If the CH<sub>2</sub> group is in contact with the surface, then the only bands that should be observable would be the symmetric stretching vibration of the CH<sub>2</sub>CH<sub>2</sub> group (~2915 cm<sup>-1</sup>) and a stretching mode for the C-H bond of the CH<sub>2</sub> group that points away from the surface (~2960 cm<sup>-1</sup>). If the CH<sub>2</sub>CH<sub>2</sub> group is in contact with the surface, then the only bands that should be detected by RAIRS would be the symmetric stretching vibration for the CH<sub>2</sub> group (2940 cm<sup>-1</sup>) and a stretching mode for the C-H bonds of the CH<sub>2</sub>CH<sub>2</sub> group that point away from the surface (~2950 cm<sup>-1</sup>).

The two dominant features in the spectrum (Figure 9b) are the bands at 2913 and 2947 cm<sup>-1</sup> (the feature at 2860 cm<sup>-1</sup> is a combination band). The frequency of the former peak strongly suggests that NBE is oriented with the CH<sub>2</sub> group near the surface: the 2913 cm<sup>-1</sup> band is too low in frequency to be assignable to a symmetric CH<sub>2</sub> stretching vibration of this strained bicyclic molecule and therefore must be an in-phase local symmetric C-H vibration of the CH<sub>2</sub>CH<sub>2</sub> group. Given that the NBE molecules are oriented with the CH<sub>2</sub> group in contact with the surface, the band at 2947 cm<sup>-1</sup> can be assigned to the stretching vibration for the C-H bond of the surface-bound CH<sub>2</sub> group that is pointing away from the surface.

We also note that the RAIR spectra of adsorbed NBE molecules contain a broad band centered at 2680 cm<sup>-1</sup> (Figure 10b); if such a "soft" mode is present in the RAIR spectrum of adsorbed BOE molecules, it is exceedingly broad and weak (Figure 10a). We believe that this difference reflects the fact that different groups are brought near the surface: a CH<sub>2</sub>CH<sub>2</sub> group in BOE and a CH<sub>2</sub> group in NBE. Consequently, the saturated C-H bonds of the two molecules interact with

(47) Unlike the situation observed for BOE, absorption of NBE in submonolayer quantities on Pt(111) at 132 K gives a spectrum that contains "extra" features (Figure 9a) that disappear when the surface is heated to 175 K (Figure 9b). The extra features in the low-temperature spectrum (especially near 2980 cm<sup>-1</sup>) probably arise either from the presence of small amounts of physisorbed NBE or from molecules that are chemisorbed but oriented differently with respect to the surface.





**Figure 10.** Reflection-absorption infrared spectra of (a) bicyclo[2.2.2]octene and (b) norbornene on Pt(111) at 130 K.

different high-symmetry surface sites (see the Discussion section). As discussed in a number of recent publications, the appearance of vibrational bands in this region has been correlated with the presence of a weakened C–H bond.<sup>48–50</sup> This mode softening is thought to arise from the interaction of the surface orbitals at the Fermi level with an antibonding C–H orbital. This metal-to-adsorbate back-bonding interaction weakens the C–H bond to the hydrogen atom that points toward the surface, and lowers the energy of the corresponding C–H stretching vibration.

When the NBE-dosed surface is heated to 221 K, some subtle changes in the RAIR spectrum become apparent, and these changes become more pronounced at 300 K (Figure 9, spectra c and d): in particular, a band at 2936  $\text{cm}^{-1}$  and a low-frequency shoulder at 2913  $\text{cm}^{-1}$  appear. These changes are *not* consistent with the dehydrogenation of NBE to norbornadiene (NBD), since the new peaks seen do not match those observed when authentic samples of NBD are dosed onto Pt(111) at this temperature.<sup>51</sup>

One other significant change in the spectrum occurs between 130 and 300 K: the soft mode at 2680  $\text{cm}^{-1}$  disappears. This result strongly suggests that when NBE dehydrogenates, the “agostic” C–H bond involving the  $\text{CH}_2$  group of norbornene is cleaved by the surface to generate a norbornenyl intermediate.<sup>52,53</sup> The new band at 2936  $\text{cm}^{-1}$  is assigned to the C–H stretching vibration for the remaining hydrogen atom on the (former)  $\text{CH}_2$  unit.

(48) Raval, R.; Parker, S. F.; Chesters, M. A. *Surf. Sci.* **1993**, *289*, 227–236.

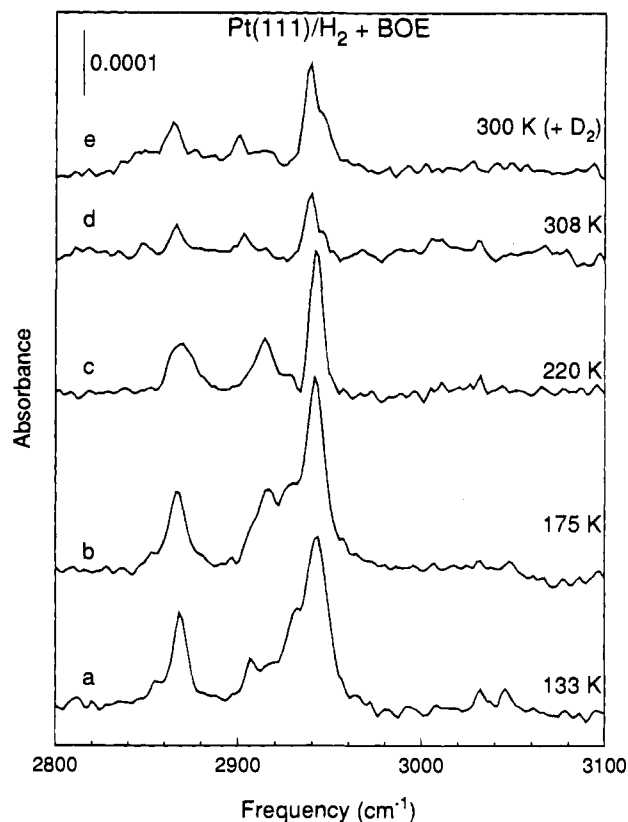
(49) Land, D. P.; Erley, W.; Ibach, H. *Surf. Sci.* **1993**, *289*, 237–246.

(50) Chesters, M. A.; Gardner, P. *Spectrochim. Acta* **1990**, *46A*, 1011–1015.

(51) The RAIR spectrum of norbornadiene on Pt(111), over the identical temperature range as that used for our NBE studies, is markedly different from that described in this paper for any product arising from the decomposition of NBE. See ref 17c.

(52) The term “agostic” refers to a  $\text{M}\cdots\text{H}-\text{C}$  interaction, irrespective of the nature of the bonding responsible for the interaction. It should be noted, however, that molecular examples of agostic interactions usually involve donation of H–C  $\sigma$  bonding electrons into an empty metal orbital, whereas on surfaces the agostic interactions principally involve donation of electrons in the metal near the Fermi level into the H–C  $\sigma^*$  orbital.

(53) For studies of agostic bonds in homogeneous transition metal systems, see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299–338. (c) Brookhart, M.; Green, M. L. H.; Wong, W.-W. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.



**Figure 11.** Reflection-absorption infrared spectra from (a–d) a hydrogen-covered Pt(111) surface or (e) a deuterium-covered Pt(111) surface dosed with a submonolayer coverage of bicyclo[2.2.2]octene and then annealed to the indicated temperatures.

**(c) RAIR Spectra of Bicyclo[2.2.2]octene on a Hydrogenated Pt(111) Surface.** Hydrogenated platinum(111) surfaces were generated by dosing at 130 K with 40 L of  $\text{H}_2$  (to ensure complete saturation of the surface with atomic hydrogen). Subsequent addition of 5 L of BOE and examination of the surface by RAIR spectroscopy gives the spectrum shown in Figure 11 (mode assignments are given in Table 3). Essentially identical spectra are obtained if the surface is pre-dosed with deuterium. Figure 11 also contains spectra obtained after the surface was annealed to temperatures that approximate those used in the study of BOE on a clean surface.

The low-temperature RAIR spectrum of BOE on a hydrogen- or deuterium-covered surface (Figure 11a) is similar to that seen for BOE on a clean Pt(111) surface except that there are weak peaks due to vinylic C–H stretches. The vinylic peaks are not due to a BOE multilayer, since peaks at 2966 and 2951  $\text{cm}^{-1}$  are not observed. Thus, at least some of the BOE molecules do *not* interact strongly with the surface via their C=C bonds and the substrate interactions responsible for the perturbation of the methylene modes are no longer present. For purposes of clarity, we will refer to these molecules as being “weakly-bound”. Evidently, some of the sites which bind the C=C double bond are blocked by hydrogen, or the work function of the metal is changed sufficiently by the presence of co-adsorbed hydrogen so that the affinity of the surface for alkene functional groups is reduced.

Heating the surface to 175 K (Figure 11b) causes a significant decrease in the intensity of the vinylic bands. This indicates that the weakly-bound BOE molecules either have desorbed, have reoriented to BOE molecules bound via their C=C bonds, or have been hydrogenated to BOA. We know from TPRS and AES studies that, on hydrogenated Pt(111) surfaces, a substantial fraction of the BOE is removed from the surface via hydrogenation.

**Table 3.** Vibrational Assignments for BOE on Hydrogen- (or Deuterium) Covered Pt(111)

assignment	H at 133 K	D at 133 K	H at 175 K	D at 175 K	H at 220 K	D at 221 K	H at 308 K	D at 300 K
vinyl $\nu_a(\text{C-H})$	3046	3050						
vinyl $\nu_s(\text{C-H})$	3032							
near surf $\text{CH}_2\text{CH}_2 \nu_a(\text{C-H})$	2943	2943	2941	2941	2941	2941	2940	2940
$\text{CH}_2\text{CH}_2 \nu_a(\text{C-H})$	2932		2930		2928	2926		
$\text{CH}_2\text{CH}_2 \nu_s(\text{C-H})$	2920	2918	2916	2918	2914	2914	2903	2901
$\text{CH}_2\text{CH}_2 \nu_s(\text{C-H})$	2908	2909						
combination band	2868, 2954	2870	2866	2868	2870	2868	2866	2864

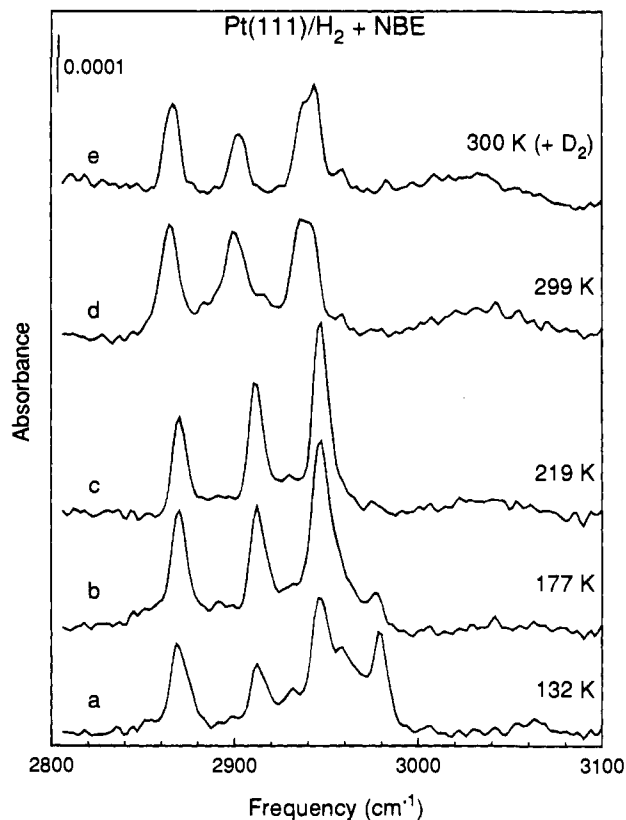
tion to BOA. The RAIR results are consistent with this conclusion. Further heating to 220 K (Figure 11c) results in the complete disappearance of the bands due to the weakly-bound BOE molecules. In all of these higher-temperature spectra, the peaks at 2941,  $\sim$ 2917, and  $\sim$ 2867  $\text{cm}^{-1}$  are readily assignable to BOE molecules bound to platinum in the same fashion as that described for the clean surface, viz., via their C=C double bonds.

At  $\sim$ 300 K, the spectrum of BOE on a hydrogen-dosed surface (Figure 11d) has changed and now resembles that seen for dehydrogenated BOE molecules generated by heating a clean Pt(111) surface dosed with BOE to this temperature (Figure 8d). This result indicates that even on a hydrogen-covered surface, some adsorbed BOE is still converted into the proposed bicyclo[2.2.2]octenyl intermediate.

The RAIR data also reveal that the adsorbed fragments which remain do not easily undergo extensive H/D exchange. This is most clearly demonstrated by comparison of spectra d and e in Figure 11, which were taken under identical conditions except that the crystal was pre-dosed with  $\text{H}_2$  and  $\text{D}_2$ , respectively. This result does not necessarily mean that formation of the inferred bicyclo[2.2.2]octenyl intermediate proceeds irreversibly; it is possible that bicyclo[2.2.2]octene and the bicyclo[2.2.2]octenyl intermediate are rapidly interconverting, but that the same C-H bond is made (and broken) every time.

**(d) RAIR Spectra of Norbornene on a Hydrogenated Pt(111) Surface.** The RAIR spectrum obtained after Pt(111) is treated first with 40 L of hydrogen and then with 3 L ( $\sim$ 1/2 monolayer) of NBE is shown in Figure 12a (mode assignments are given in Table 4). Similar spectra are seen when the surface is pre-dosed with deuterium. Figure 12 also contains spectra obtained after the surface was annealed to different temperatures.

The behavior of NBE on a hydrogen-dosed Pt(111) surface is similar to that of BOE under similar circumstances. In particular, the low-temperature RAIR spectrum contains peaks that may be due to "weakly-bound" NBE molecules: weak vinyl C-H stretching bands and tertiary C-H and  $\text{CH}_2\text{CH}_2$  antisymmetric are present. However, most of the peaks can be readily assigned to NBE molecules bound to the Pt(111) surface via their C=C double bonds. When the sample is warmed to 177 K (Figure 12b), the IR bands due to the weakly-bound molecules disappear. At 300 K (Figure 12d), most of the molecules remaining on the surface are dehydrogenated NBE fragments; these spectra are similar to those of the "norbornenyl" intermediate seen when a clean Pt(111) surface dosed with NBE is heated to this temperature. The band intensities seen for NBE on a hydrogenated Pt(111) surface remain largely unaffected up to 300 K; this behavior contrasts with that of BOE on a hydrogenated Pt(111) surface, where desorption of BOA and a consequent substantial decrease in band intensity occurs upon heating (compare spectra b, c, and d in Figure 11). Thus, in support of our TPRS results, the hydrogenation of NBE to NBA must be less efficient than the hydrogenation of BOE to BOA, and instead dissociative dehydrogenation of NBE to norbornenyl fragments must be the kinetically dominant process.



**Figure 12.** Reflection-absorption infrared spectra from (a-d) a hydrogen-covered Pt(111) surface or (e) a deuterium-covered surface dosed with a submonolayer coverage of norbornene and then annealed to the indicated temperatures.

As shown above, the dehydrogenated intermediates derived from BOE do not undergo isotopic exchange with  $\text{D}_2$ ; similarly, the data shown in spectra d and e in Figure 12 suggest that the dehydrogenation of NBE also occurs without isotopic exchange.

**(e) High-Temperature Reactions of Adsorbed Bicyclo[2.2.2]octenyl and Norbornenyl Intermediates on Pt(111).** When either of the species derived from the low-temperature decomposition of BOE or NBE is heated from 300 to 800 K, a series of reactions occurs. TPRS and IDMS data (see Supplementary Material) suggest that both of these alkenyl intermediates persist on the surface to  $\sim$ 400 K. The bicyclo[2.2.2]octenyl fragment is further transformed between 400 and 450 K as judged from the appearance of  $\text{H}_2$  desorption features over this temperature range. The norbornenyl group is less reactive and remains intact until temperatures above 450 K. The reactivity difference evidenced here is entirely consistent with the assignment of these intermediates as alkenyl species. A bicyclo[2.2.2]octenyl fragment can undergo  $\beta$ -hydride elimination to form bicyclo[2.2.2]octadiene; in contrast, a norbornenyl fragment (possessing a metal-carbon bond to the former  $\text{CH}_2$  carbon) cannot eliminate its  $\beta$ -hydrogen since this reaction would generate a C=C double bond involving a bridgehead carbon (a process which is forbidden according to Bredt's rule).

**Table 4.** Vibrational Assignments for NBE on Hydrogen- (or Deuterium) Covered Pt(111)

assignment	H at 132 K	D at 132 K	H at 175 K	D at 175 K	H at 219 K	D at 220 K	H at 299 K	D at 300 K
vinyllic $\nu_s(\text{C-H})$	3053	3053						
tertiary $\nu_a(\text{C-H})$	2978	2978	2976	2978				
$\text{CH}_2 \nu_a(\text{C-H})$	2959	2962	2947	2947	2947	2947	~2940 <sup>a</sup>	~2940 <sup>a</sup>
$\text{CH}_2\text{CH}_2 \nu_a(\text{C-H})$	2945	2949						
$\text{CH}_2 \nu_s(\text{C-H})$	2932	2937			2930			
$\text{CH}_2\text{CH}_2 \nu_s(\text{C-H})$	2912	2912	2912	2912	2911	2912	2901 <sup>b</sup>	2903 <sup>b</sup>
overtone	2868	2868	2870	2872	2870	2870	2866	2866

<sup>a</sup>Contains contribution from CH  $\nu(\text{C-H})$  of the norbornenyl intermediate; see Table 2. <sup>b</sup> $\text{CH}_2\text{CH}_2 \nu_s(\text{C-H})$  of the norbornenyl intermediate.

Between 450 and 550 K, the adsorbed species decompose further: benzene desorption is seen at 495 (shoulder) and 510 K for BOE and at 485 K for NBE. The remaining  $\text{C}_x\text{H}_y$  fragments produced by these processes dehydrogenate to give  $\text{H}_2$  (which desorbs at 620 K) and a carbonaceous overlayer. The final carbon coverages are low (~30% of a monolayer), with the exact quantity depending on the amount of alkene and  $\text{H}_2$  originally dosed onto the surface.

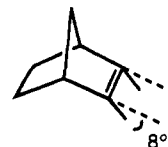
## Discussion

**Binding of Bicyclic Alkenes to Pt(111).** The low-temperature (130 K) infrared spectra of BOE and NBE on Pt(111) indicate that both adsorbates are bound to the surface via their C=C double bonds. This conclusion, which is supported by the absence of bands assignable to vinyllic C-H stretching vibrations, is consistent with the behavior of a variety of other alkenes on platinum surfaces.<sup>54,55</sup>

The bicyclic structures of BOE and NBE guarantee that, when these molecules are bound to the surface via their C=C double bonds, other atoms must be near the surface as well. For BOE, these secondary interactions involve two C-H bonds of one of the  $\text{CH}_2\text{CH}_2$  groups. Owing to the symmetry of BOE, the same secondary interactions are generated irrespective of which  $\text{CH}_2\text{CH}_2$  group is brought near the surface (structure I). In contrast, there are two kinds of secondary interactions possible for NBE: a C-H bond of the  $\text{CH}_2$  group can be brought near the surface (structure II), or two C-H bonds of the  $\text{CH}_2\text{CH}_2$  group can be brought near the surface (structure III). At 175 K, the RAIR spectrum of NBE strongly suggests that structure II is adopted. This conclusion is supported by the presence of essentially unperturbed bands for the  $\text{CH}_2\text{CH}_2$  group, and by the presence of two perturbed C-H stretching bands for the bridging  $\text{CH}_2$  group. The first of these perturbed bands appears at  $2947 \text{ cm}^{-1}$ ; this band is assigned to a stretching mode involving the C-H bond of the  $\text{CH}_2$  group that points away from the surface. The second perturbed band is a so-called "soft mode" and appears at  $2680 \text{ cm}^{-1}$ ; this band is assigned to a stretching mode involving the C-H bond of the  $\text{CH}_2$  group that points toward the surface. The low frequency of this latter band is characteristic of a strong "agostic" interaction with the surface.

These data are most consistent with a preferred orientation in which NBE is bound to the surface via its C=C double bond and one agostic bond between the hydrogen atom of the  $\text{CH}_2$  unit and the surface (structure II). In conventional nomenclature, it is the "exo" face of the NBE skeleton that is bound to the surface. Many studies have shown that norbornene is preferentially attacked on the exo face by a wide range of reagents.<sup>56-59</sup> This preference is thought to reflect the fact that

this is the most sterically accessible face: calculations and crystal structure determinations of NBE derivatives have shown that the vinyllic hydrogens are bent as much as  $8^\circ$  away from the exo face, thus sterically occluding the other (endo) face.<sup>60</sup>



This facial selectivity is also corroborated by the organometallic chemistry of NBE; NMR studies of (NBE) $\text{PtL}_2$  complexes indicate that the platinum atom is bound to the exo face of NBE.<sup>61</sup>

Two further questions remain to be addressed: how are the C=C bonds of BOE and NBE interacting with the surface, and why is a pronounced "soft" C-H mode observable for NBE but not for BOE? These two questions are in fact closely related, owing to the rigidity of the BOE and NBE skeletons.

It is well-known that alkenes can be bound to a single surface atom or can bridge between two surface atoms; the available data from several HREELS studies suggest the latter bonding mode is strongly preferred on Pt(111).<sup>54,55,62,63</sup> We have used molecular models with optimized structures for BOE, NBE, and a triangular  $\text{Pt}_3$  unit to explore these two possibilities.

For NBE, the molecular models show that if its C=C double bond interacts with a single Pt atom (i.e.,  $\pi$  bonded), one C-H bond of the  $\text{CH}_2$  group of NBE will point toward a bridge site between two adjacent Pt atoms. In contrast, if the C=C double bond of NBE bridges between two Pt atoms (i.e., di- $\sigma$  bonded) then one C-H bond of the  $\text{CH}_2$  group will point nearly directly toward a nearby atop site.

For BOE, molecular models show that if its C=C double bond is bound to only one Pt atom, then two C-H bonds of the  $\text{CH}_2\text{CH}_2$  group point nearly directly toward atop sites on nearby surface Pt atoms. Alternatively, if the C=C double bond of BOE bridges between two Pt atoms, then both C-H bonds of the near-surface  $\text{CH}_2\text{CH}_2$  group point toward bridge sites.

The key point is the following: if the C=C bonds of NBE and BOE both bind to similar sites on the platinum surface, then the different skeletal geometries of BOE and NBE demand that their near-surface C-H bonds must interact with different sites on the Pt(111) surface; this difference is reflected in the appearance of an intense soft mode for NBE, but not for BOE (Figure 10). If we assume that the C=C double bonds of NBE and BOE both bridge two platinum atoms (as suggested from HREELS studies of other alkenes), then we can be more specific: the C-H bonds are projected toward atop sites for

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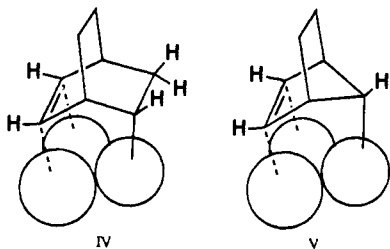
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NBE, but toward bridge sites for BOE, and thus the presence of a strong soft mode is the result of an interaction of a C–H bond with an atop site.

Calculations performed independently by Baetzold<sup>64</sup> and Saillard and Hoffman<sup>65</sup> suggest the largest perturbations of the C–H bond strength occur when the C–H bond can interact with the largest number of metal atoms. On the other hand, calculations reported by Kang and Anderson indicate that the strongest agostic interaction will occur between a C–H bond and an atop metal site.<sup>66</sup> Depending on how the alkene C=C bond interacts with the surface, our data can be made consistent with both views. Continuing studies in this laboratory are being undertaken to further clarify these issues and will be reported at a later time.<sup>39</sup>

**Mechanism of Self-Hydrogenation.** When BOE- or NBE-dosed surfaces are heated, alkene hydrogenation products are generated even in the absence of added hydrogen. The alkane products, bicyclo[2.2.2]octane and norbornane, are formed as a result of a self-hydrogenation process in which some of the alkene molecules are sacrificially dehydrogenated. The infrared spectra of BOE and NBE show that this dehydrogenation process commences at temperatures as low as 220 K. The hydrogen atoms so released combine with other surface-bound alkene molecules to produce the observed alkane products. For both BOE and NBE, the RAIR spectra suggest that only one hydrogen atom is lost at this temperature, since the IR features of the corresponding diene are not observed.<sup>51</sup> Possibly, one of the near-surface hydrogen atoms is lost to form bicyclo[2.2.2]-octenyl (structure IV) and norbornenyl intermediates (structure V) from BOE and NBE, respectively.



Several pieces of evidence indicate that the rate-determining step for the formation of the desorbed alkane (NBA or BOA) on clean Pt(111) surfaces is the dehydrogenation of the adsorbed alkene. First, the reaction rate has an apparent first-order dependence on the coverage of alkene (recall that the  $T_{\max}$  of 262 K for BOA desorption via self-hydrogenation is independent of  $\theta_{\text{BOE}}$ ); this is consistent with a unimolecular rate-determining step. Second, the 262 K desorption temperature is far higher than expected for a desorption-limited process; this strongly suggests that other steps must limit the rate of self-hydrogenation. Third, the addition of small amounts of hydrogen results in a substantial lowering of the temperature at which the product alkanes desorb. All of these observations clearly indicate that, in the absence of added  $\text{H}_2$ , the rate-limiting step for the desorption of alkane is the production of surface hydrogen via alkene dehydrogenation.

The activation energies for the dehydrogenation of BOE and NBE can be calculated from the TPRS profiles for the mass channel corresponding to the product alkane. We start by noting that the peak maxima for desorption of alkane are 262 and 250 K for BOA and NBA, respectively. Using Redhead's method,<sup>34</sup>

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and assuming that both processes follow first-order rate laws and that the pre-exponential factors are  $\sim 1 \times 10^{13} \text{ s}^{-1}$ , we estimate that the activation energies are  $\sim 16 \text{ kcal/mol}$  for the dehydrogenation of BOE and  $\sim 15 \text{ kcal/mol}$  for the dehydrogenation of NBE. These values are similar to the 18 kcal/mol activation energy reported for the self-hydrogenation of ethylene on Pt(111).<sup>8c</sup>

Although self-hydrogenation reactions take place when BOE and NBE are adsorbed on a clean Pt(111) surface, they are strongly inhibited on a carbon-covered Pt(111) surface. The decreased ability of carbon-decorated platinum surfaces to promote self-hydrogenation reactions is presumably related to the fact that the necessary alkene dehydrogenation processes are slower, and occur with reasonable rates only at temperatures of 510 K and higher. Since the rate of  $\text{H}_2$  desorption from platinum surfaces is fast at temperatures above 300 K, it is unlikely that other multistep associative reactions (alkene hydrogenation requires two distinct hydrogen addition steps) will compete effectively with hydrogen desorption at high temperatures.

Self-hydrogenation reactions have been observed in other systems: these include butadiene and 1-butene on Mo(100), Mo(100)–C, and Mo(100)–S;<sup>67</sup> ethylene on W(110) and W(112),<sup>68</sup> butadiene on Re(0001)–C;<sup>69</sup> ethylene on Pd(100), Pd(110), and Pd(111);<sup>70</sup> and ethylene on Pt(111).<sup>8</sup> The conclusion that sacrificial dehydrogenation of alkene is the rate-limiting step for the formation of alkane has been reached previously.<sup>8</sup>

**Hydrogen-Promoted Hydrogenation.** The RAIRS and TPRS studies indicate that, in the presence of pre-adsorbed hydrogen, BOE is hydrogenated more efficiently than NBE; this result probably reflects differences in the relative rates of hydrogenation and dehydrogenation.

When a Pt(111) surface is first dosed with  $\text{D}_2$  and then with BOE at 100 K, subsequent heating leads to the desorption of at least three deuterated isotopomers of the corresponding alkane: BOA- $d_2$ , BOA- $d_3$ , and BOA- $d_4$ . Similarly, IDMS studies indicate that when a Pt(111) surface is first dosed with  $\text{D}_2$  and then with NBE at 100 K, subsequent heating leads to the desorption of NBA- $d_2$ , NBA- $d_3$ , and NBA- $d_4$ . The formation of the  $d_3$  and  $d_4$  alkane isotopomers demonstrates that one of the C–H bond making or breaking processes these alkenes undergo is reversible. Three possibilities exist for this reversible step: addition of hydrogen to the alkene to form a surface alkyl intermediate, loss of hydrogen from the alkene to form a surface alkenyl intermediate, or loss of hydrogen from an alkyl intermediate to form a surface alkylidene.

The reversible insertion of the alkene into the M–D bond cannot be the process directly responsible for the formation of the  $d_3$  and  $d_4$  isotopomers in the deuterium labeling experiments. These bicyclic adsorbates are conformationally rigid and the principle of microscopic reversibility guarantees that insertion of the alkene into a Pt–D bond to give a surface alkyl will not lead to further H/D exchange;  $\beta$ -hydride elimination will only lead to the formation of the unlabeled alkene.

At first glance it might seem that deuterium exchange must be occurring via the reversible dehydrogenation of the alkenes to surface alkenyl intermediates. If so, this would mean that desorbing BOA- $d_3$  and BOA- $d_4$  arise from bicyclo[2.2.2]octenyl intermediates. Likewise, BOA- $d_4$  could result from either a

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bicyclo[2.2.2]octadiene intermediate or two consecutive, reversible dehydrogenations to bicyclo[2.2.2]octenyl intermediates. We cannot rule out this possibility. We believe however that  $\alpha$ -hydrogen elimination from surface alkyl intermediates (to form alkylidene species) is a more likely pathway for the observed isotopic exchange. Such  $\alpha$ -hydrogen elimination reactions can effect isotopic exchange even in these conformationally locked adsorbates and are entirely consistent with the available literature.<sup>12d,13q,71</sup> A similar  $\alpha$ -hydrogen elimination mechanism involving reversible formation of an alkylidene intermediate can also explain the  $d_3$  and  $d_4$  alkane isotopomers seen in the NBE + D<sub>2</sub> experiments.

The hydrogenation reaction exhibits an apparent primary kinetic isotope effect: the reaction-limited desorption temperature for BOA is 220 K when the reaction is carried out with H<sub>2</sub>, and 231 K when the reaction is carried out with D<sub>2</sub>. If we assume that a common rate-determining step operates in each and that the desorption kinetics can be modeled by a simple first-order rate law, this 11 K shift in desorption temperature can be used to calculate the magnitude of the kinetic isotope effect  $k_H/k_D$ . This analysis assumes that the ratio of the preexponential factors,  $A_H/A_D$ , is near unity and exhibits little temperature dependence over this narrow range of temperatures. In the absence of significant tunneling contributions, which we do not believe are important here, this should be a reasonable approximation. With these approximations, we obtain a kinetic isotope effect of  $\sim 6$ , which indicates that the rate-determining step involves the transfer of a hydrogen atom. In principle, there are two possible steps in the hydrogenation pathway that could be responsible for this isotope effect: the insertion of BOE into a Pt-H bond to form a bicyclo[2.2.2]octyl intermediate, or the reductive elimination of the bicyclo[2.2.2]octyl intermediate and a surface hydrogen atom to give BOA. A similar value (KIE = 5 at 180 K) has been measured in a study of the hydrogenation of ethylene on a Fe(100) surface in the presence of coadsorbed CO.<sup>73</sup> In this system, the rate-limiting step was proposed to be reductive elimination of Fe-Et and Fe-H groups to give ethane.

UHV studies of the hydrogenation of alkenes have almost invariably found that the yield of alkane is strongly dependent on the order in which the reagents are dosed onto the surface. In nearly all reports which specifically describe the dosing protocol, the yield of hydrogenation products is enhanced when the alkene is added after the hydrogen.<sup>8a,c-f,74</sup> One explanation of this behavior is suggested by related experiments described by both Madix and Campbell. In the former, hydrogenation of alkenes only occurs on Fe(100) when CO is added to the surface;<sup>10</sup> in the latter, reductive elimination of methane from Pt(111) is promoted by the addition of Bi atoms to the surface.<sup>72</sup> These data suggest that the dosing order dependence observed in our studies may be related to the formation of "activated" hydrogen. Addition of an alkene (or CO or Bi) to a hydrogen-covered surface may force the hydrogen atoms to move from their preferred binding sites onto sites where they are less firmly bound and thus more reactive. Alternatively, adsorption of NBE or BOE onto the hydrogen-covered surface may lead to the formation of an "activated" alkene.<sup>8c,f</sup> These structural pictures, while intriguing, are not the only possible models. It may well be that lateral segregation (islanding) processes might affect how efficiently surface-bound alkenes react with hydrogen atoms via the sequential steps needed to produce alkanes.

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**Comparisons with Other Alkene Hydrogenation Studies: How Are Bicyclic Alkenes Different?** Alkene hydrogenation has been studied under UHV conditions on a number of transition metal surfaces, ranging from tungsten to copper.<sup>8,10,11,73-78</sup> These studies have shown that alkene hydrogenation proceeds in two steps: conversion of alkene to a surface alkyl group, and conversion of surface alkyl groups to alkane. On Fe(100) surfaces, activation energies of approximately 6 kcal/mol have been determined for the first step.<sup>73</sup> Essentially identical activation barriers have been measured on group 10 metals (Ni, Pd, Pt).<sup>74-76</sup>

Several trends are evident in these studies. First, alkene hydrogenation is at best a low-yield reaction (1-14% of a monolayer) when examined in UHV. Competing side reactions, such as  $\beta$ -hydride elimination or alkylidyne formation, often limit the catalytic efficacy of the hydrogenation process. Second, the reactions occur at low temperatures (170-250 K). Third, surface carbon can affect (raise or lower) the yield of alkene.

In the present studies, we find that the hydrogenation of bicyclic alkenes (especially BOE) occurs readily at temperatures as low as 188 K. As described above, this is much lower than the temperatures at which ethylene hydrogenation occurs on the same surface ( $\sim 256$  K). We believe that the enhanced reactivity of NBE and BOE in this regard may be a result of the ring strain which is relieved upon conversion of these alkenes to alkanes. In addition, the observed yields of alkane ( $\sim 50\%$  for BOE) are higher than those measured for acyclic alkenes, regardless of the nature of the surface. We believe it is likely that the structure of these bicyclic alkenes makes them less susceptible to decomposition reactions leading to intermediates which are not amenable to hydrogenation. For example, the propensity of ethylene to decompose to ethylidyne at 200 K on Pt(111) must severely limit the yield of ethane on this surface (since ethylidyne cannot be hydrogenated to ethane).<sup>9b</sup> In contrast, alkenes such as NBE and BOE, which lack primary carbon atoms, cannot form alkylidyne intermediates without reorganization of the C-C skeleton. The conformational rigidity, ring strain, and skeletal architecture of these bicyclic alkenes all help to promote the sequential bond forming steps that are necessary to effect (or inhibit the reactions that block) the conversion to alkane.

Finally, we should point out that the inability of these bicyclic alkenes to form alkylidyne intermediates means that the hydrogenation to alkane cannot proceed according to an alkylidyne hydrogen-transfer mechanism.

## Conclusions

1. The bicyclic alkenes bicyclo[2.2.2]octene (BOE) and norbornene (NBE) bind to platinum(111) surfaces at two points: via their C=C double bonds and via an additional "agostic" interaction with a saturated C-H bond. For BOE, the second point of attachment is a CH<sub>2</sub>CH<sub>2</sub> group. For NBE, there are two choices for the second point of attachment, the CH<sub>2</sub>CH<sub>2</sub> group or the CH<sub>2</sub> group; geometric factors (the exo face of NBE is  $\sim 8^\circ$  more open than its endo face) favor the latter.

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2. If the alkene C=C double bonds in BOE and NBE bridge between two Pt atoms, then the following correlation is drawn: an agostic interaction between a C-H bond and an atop site on the Pt(111) surface gives a well-defined "soft" mode of lowered frequency, whereas an agostic interaction between a C-H bond and a bridge site on the Pt(111) surface gives a soft mode that is very weak or entirely absent.

3. Upon thermolysis, BOE and NBE undergo dehydrogenation, although in neither case to the diene, but evidently to unconjugated ene-yl structures. Evidently, the "agostic" hydrogen atom is the one that is transferred to the surface. Some of the hydrogen generated from the dehydrogenation of these molecules is used to hydrogenate other intact molecules (self-hydrogenation).

4. The rate-determining step for self-hydrogenation is dehydrogenation of the alkene, which has an activation energy of  $\sim 16$  kcal/mol for BOE and  $\sim 15$  kcal/mol for NBE.

5. Co-adsorption of H<sub>2</sub> or D<sub>2</sub> results in a substantial increase in the amount of the alkane hydrogenation products. In addition, the temperature at which the alkane desorbs is lowered substantially. The alkene hydrogenation reaction exhibits a significant primary kinetic isotope effect ( $k_H/k_D$ ) of 6.

6. The formation of multiply-deuterated alkanes from the reactions of BOE and NBE with D<sub>2</sub> indicates that one of the C-H bond-making or bond-breaking reactions is reversible. We suggest that the reversible process responsible for H/D exchange is the elimination of an  $\alpha$ -hydrogen from a surface alkyl intermediate to form a surface alkylidene species.

7. The absence of primary carbon atoms in BOE and NBE means that these alkenes cannot transform into alkylidyne intermediates on the surface; thus the hydrogenation of these alkenes (which occurs readily) cannot occur via the alkylidyne hydrogen-transfer mechanism that has been proposed by Somorjai.<sup>9</sup> In fact, the inability of BOE and NBE to form alkylidyne intermediates (which cannot be hydrogenated to alkane) is undoubtedly responsible for the much higher yields of alkane from BOE and NBE than seen for the hydrogenation of ethylene and other acyclic alkenes on platinum surfaces.

8. The hydrogenation of BOE and NBE is significantly inhibited by surface carbon. This is in part due to the inability of the carbon decorated surface to activate either C-H or H-H bonds in the temperature regime in which hydrogenation reactions are energetically favored.

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## Appendix

Reflection-absorption infrared spectroscopy (RAIRS) is a very useful tool for establishing both the structures and the orientations of surface adsorbates. The structures of adsorbates can be established by comparisons of the RAIR spectra with IR spectra of bulk samples; their orientations can be determined by taking advantage of the rigorous selection rule that only modes whose dipoles have a non-zero projection along the surface normal will be observable (the intensity of the mode drops with the square of the cosine).<sup>46</sup> As a consequence, if an adsorbate monolayer consists of coherently-oriented molecules, fewer bands will be present in the RAIR spectrum than in a transmission IR spectrum of a bulk sample or in a RAIR spectrum of a randomly-oriented multilayer.

**Assignment of the RAIR Bands of a Bicyclo[2.2.2] Multilayer on Pt(111).** The following discussion will refer to Figure 7a and Table 1. The bands appearing at 3042 and 3030 cm<sup>-1</sup> can be readily assigned to the antisymmetric and symmetric stretching vibrations for the vinylic C-H bonds, respectively. The tertiary (i.e., bridgehead) C-H bonds are expected to exhibit only one band (the antisymmetric stretch) in the IR spectrum; the symmetric stretch leaves the dipole moment of the molecule virtually unchanged and is therefore expected to be extremely weak. We assign the band at 2966 cm<sup>-1</sup> to the antisymmetric C-H stretch of the bridgehead groups.

The next six bands are due to stretching vibrations of the two CH<sub>2</sub>CH<sub>2</sub> groups: the C<sub>2v</sub> symmetry of the molecule dictates that there should be six IR-active modes (2a<sub>1</sub>, 2b<sub>1</sub>, and 2b<sub>2</sub>; the 2a<sub>2</sub> modes are IR-inactive). In analogy to the assignments for norbornane, the 2918 cm<sup>-1</sup> band can be assigned to the a<sub>1</sub> mode consisting of the in-phase combination of local symmetric CH<sub>2</sub> stretching motions of the four CH<sub>2</sub> groups. Specific assignments of the remaining five IR bands at 2951, 2943, 2934, 2903, and 2887 cm<sup>-1</sup> cannot be made with the information we have, except that we expect modes consisting of combinations of local antisymmetric CH<sub>2</sub> stretching motions to be higher in frequency.

The frequency of the band at 2862 cm<sup>-1</sup> is too low to be due to a C-H stretching mode. In analogy with previous work,<sup>43,46</sup> we assign this band to a combination (1470 + 1371 = 2841 cm<sup>-1</sup>) of two C-H deformation modes. The remaining lower frequency bands (data not shown) are numerous, but for the most part do not contribute information about the structure of BOE at lower coverages. Thus, these data will not be described.

**Assignment of the RAIR Spectrum of Norbornene Multilayer on Pt(111).** The following discussion will refer to Figure 7b and Table 2. The NBE molecule possesses one mirror plane and thus falls into the C<sub>s</sub> point group; accordingly, all of its C-H stretching modes are IR-active, although some (like the symmetric stretch of the two tertiary C-H bonds) will be weak owing to a small change in the transition moment. The band at 3042 cm<sup>-1</sup> can clearly be assigned to a vinylic C-H stretch. The next lower energy band at 2972 cm<sup>-1</sup> is broad and data at lower coverages (see below) suggest that this feature is actually an envelope of several modes: the tertiary C-H symmetric stretch, the CH<sub>2</sub> antisymmetric stretch, and combinations of local CH<sub>2</sub> antisymmetric stretches of the CH<sub>2</sub>CH<sub>2</sub> group. The 2947 cm<sup>-1</sup> band is assigned to an antisymmetric CH<sub>2</sub>CH<sub>2</sub> stretching vibration, based on comparisons with the spectra of norbornadiene and norbornane. The next peak (2916 cm<sup>-1</sup>) can be reasonably assigned to in-phase combinations of local symmetric CH<sub>2</sub> stretches of the CH<sub>2</sub>CH<sub>2</sub> group (this band appears at 2916 cm<sup>-1</sup> in norbornane). Finally, the band at 2870 cm<sup>-1</sup> is assigned to an overtone of the CH<sub>2</sub> bending vibration (presumably the scissoring mode at 1447 cm<sup>-1</sup>).

**Supplementary Material Available:** Temperature-programmed reaction profiles charting the desorption of benzene and dehydrogen and integrated desorption mass spectra (Figures S-1 to S-3) (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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