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A Study of the Stereoselectivity in the Dimerization of Ethylidene To Form 2-Butene on Ag(111)

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Received February 18, 2000

Abstract: The reaction products formed from 1,1-diiodoethane adsorbed on clean Ag(111) have been investigated by using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) and compared to *cis*- and *trans*-2-butene adsorbed on the same Ag(111) surface. Ethylidene species synthesized from 1,1-diiodoethane adsorbed on Ag(111) dimerize to form 2-butenes. The TPD profiles of the reactively formed 2-butenes resemble those of *cis*- and *trans*-2-butenes directly adsorbed on Ag(111) exhibiting a sharp peak at ∼140 K and a broad feature at ∼184 K. The surface infrared spectra of *cis*- and *trans*-2-butene are distinguishable where monolayer *cis*-2-butene/Ag(111) exhibits peaks at 1445, 1434, and 1030 cm^{-1} whereas the trans isomer has features at 1429, 973, and 959 cm^{-1}. It is found that the surface infrared spectrum collected after 1,1-diiodoethane adsorption on Ag(111) is very close to that of *trans*-2-butene on Ag(111). This demonstrates that the stereoselectivity of ethylidene dimerization on Ag(111) surfaces is controlled by the initial approach of the carbenes rather than the desorption of the 2-butene product.

Introduction

Previous work has demonstrated that the metathesis of propylene catalyzed by metallic molybdenum foils at high temperatures (>650 K) proceeds via an initial dissociative formation of carbenes ($CH_2=$ and $CH_3-CH=$) which recombine on the surface to form ethylene and 2-butene.[1] It was found that the ratio of *cis*-2-butene to *trans*-2-butene formed by ethylidene recombination exceeded that expected thermodynamically by a factor of 2 to 3.[1] In contrast, ethylidene recombination to form alkenes in organometallic compounds generally favors the formation of *trans*-2-butene.[2−7] This difference can be rationalized by assuming that the adsorbed ethylidene species approach each other in such a way that their carbene planes are parallel. Such a geometry facilitates overlap between the carbene π orbitals and the formation of π and σ bonds between α-carbons. In this case, steric hindrance between the methyl groups of the approaching ethylidenes will favor the formation of a trans intermediate. In many cases on transition metals, and in particular on molybdenum, alkenes are substantially rehybridized, and adsorb in a di-σ configuration with ca. sp^3 hybridized carbons.[8−13] In this geometry, the methyl groups of the *cis*- or *trans*-2-butene are oriented away from the surface.

The next step in alkene formation is the reductive elimination of this intermediate, involving carbons 2 and 3 rehybridizing from sp^3 to sp^2, and the molecule becoming planar. When the intermediate is bonded to an isolated metal center, this involves no steric hindrance; the stereoselectivity is controlled by the initial carbene approach leading to a predominance of *trans*-2-butene in the gas phase. In contrast, when the intermediate is strongly bonded to a planar substrate, interaction of the methyl groups with the surface will prevent the adsorbate from rehybridizing in the case of a trans intermediate. For the cis intermediate, the adsorbed molecule can rotate slightly around the C(2)−C(3) bond thus minimizing steric interference with the surface hence favoring the formation of the cis product, as found on molybdenum.[1] The work described in this paper explores the stereoselectivity of ethylidene recombination on Ag(111) to further test this model. Alkenes bond weakly to silver, predominantly via van der Waals' interactions.[14−17] It is anticipated that the heat of adsorption of *trans*- and *cis*-2-butene on Ag(111) will be very similar implying that the stereoselectivity on silver, in contrast to the behavior on molybdenum, will *not* be controlled by the desorption of 2-butene. Alkyl species adsorbed on silver dimerize to form alkanes[18−21] and adsorbed carbenes yield alkenes.[21−23] Furthermore, these reactions proceed at relatively low temperatures thus accentuating energy differences due to steric interactions between the methyl species. The above considerations suggest that the formation

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of *trans*-2-butene rather than *cis*-2-butene should be favored from ethylidene recombination on Ag(111). This conjecture is borne out by the results presented below. Finally, alkylidene species can be conveniently grafted onto metals by exposure to the corresponding iodine-containing molecule in ultrahigh vacuum.[24] The relatively weak carbon—iodine bond compared to the corresponding carbon—metal bond favors C—I bond cleavage to graft the hydrocarbon fragment to the surface, along with chemisorbed iodine. In this work, ethylidene species are formed by dosing a clean Ag(111) surface with 1,1-diiodoethane. The reaction appears to be facile on silver where it has been demonstrated that CH_2 species are formed from methylene iodide at relatively low temperatures and there is significant (20—30%) thermal decomposition even at ~130 K.[25]

The chemistry is followed using a combination of temperature-programmed desorption (TPD) and reflection—absorption infrared spectroscopy (RAIRS). Temperature-programmed desorption is used to monitor the nature and kinetics of the desorbing species and reflection—absorption infrared spectroscopy reveals the nature and, in favorable cases, the geometry of adsorbed species. RAIRS is particularly useful in this case since *cis*- and *trans*-2-butene exhibit very different infrared spectra.[26]

Experimental Section

The experiments were carried out in a stainless steel, ultrahigh vacuum chamber operating at base pressures of ~8 × 10^{-11} Torr following bakeout which has been described in detail elsewhere.[27] Infrared data were collected from an Ag(111) single crystal sample mounted in a modified 2 3/4 in. six-way cross equipped with infrared-transparent, KBr windows. The sample could be resistively heated to1000 K or cooled to 80 K using liquid nitrogen. Light from a Bruker Equinox infrared spectrometer passes through a polarizer and is focused on the sample at an incidence angle of ~80° and the reflected light steered onto a liquid nitrogen cooled, mercury—cadmium—telluride detector. The complete light path is enclosed and purged with dry, CO_2-free air. The spectrometer typically operated at 4 cm^{-1} resolution and data were collected for 1000 scans.

The infrared cell was attached to the main 12 in. diameter ultrahigh vacuum chamber and the sample could be moved from the cell into the main chamber on a transfer rod. The chamber was equipped with a single-pass, cylindrical-mirror analyzer that was used to collect Auger spectra of the sample.

Temperature-programmed desorption data were collected using a heating rate of ~3 K/s and desorbing species detected using a Dycor quadrupole mass spectrometer located in the main ultrahigh vacuum chamber and interfaced to a PC allowing five masses to be monitored sequentially during the same desorption sweep.

The sample was cleaned using a standard procedure[16,28] which consisted of bombarding with Argon ions (1 keV, 2 μA/cm^2) at 300 K and annealing to 1000 K in vacuo to remove any remaining surface species.

The 1,1-diiodoethane used for these experiments was synthesized from ethyl iodide and 1,1-dichloroethane according to a literature procedure[29] and its purity was checked using nuclear magnetic resonance spectroscopy. The product was transferred to glass vials, attached to the gas-handling line of the vacuum system, and further purified by repeated freeze—pump—thaw cycles and its cleanliness was monitored mass spectroscopically. The *cis*- and *trans*-2-butene (Aldrich
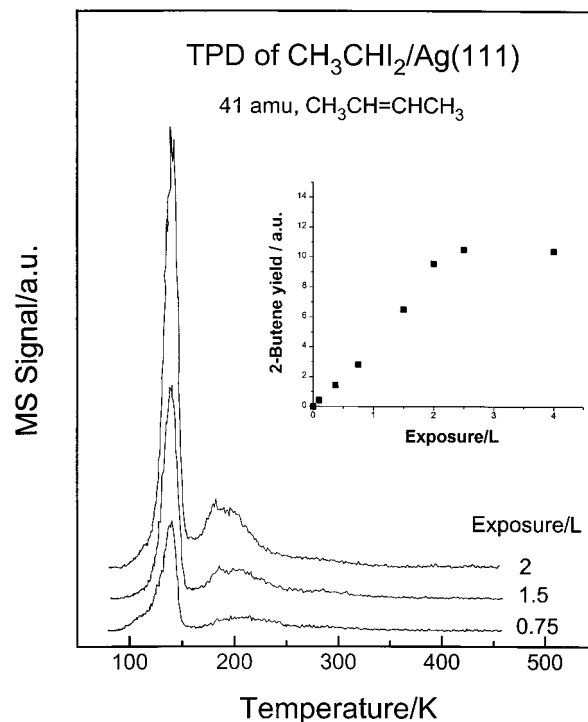
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Figure 1. Temperature-programmed desorption spectra taken at 41 amu (2-butene) following the adsorption of 1,1-diiodoethane on Ag-(111) at 80 K as a function of exposure. The exposures are marked adjacent to the corresponding spectrum. Shown as an inset is the 2-butene desorption yield as a function of exposure.

Chemicals, 99+% purity) were transferred from their cylinders into glass bottles and were further purified using several freeze—pump—thaw cycles. Their purities were also verified mass spectroscopically.

Results

It has been shown previously that alkyl species adsorbed onto Ag(111) using iodine-containing precursors couple to form the corresponding alkane so that exposing a surface to an alkyl iodide, RI, yields adsorbed alkyl (R) species and iodine.[18-21] The alkyl species react to form an R—R alkane in temperature-programmed desorption.[18-21] The corresponding chemistry for adsorbed alkylidene species forming alkenes has also been studied.[21-23,25] The 41-amu temperature-programmed desorption spectra collected after exposing clean Ag(111) to 1,1-diiodo-ethane are displayed in Figure 1 as a function of 1,1-diiodoethane exposure (in Langmuirs; 1 L = 1 × 10^{-6} Torr·s). Note that exposures are not corrected for ionization gauge sensitivities. This mass corresponds to a fragment of 2-butene[30] and is not due to 1,1-diiodoethane which was not observed to desorb for exposures up to 2 L. Multilayer 1,1-diiodoethane desorption was detected for higher (>2 L) exposures. Measuring the desorption spectra at other masses (56, 39, and 27 amu) shows that their relative desorption intensities agree very well with the mass spectrometer ionizer fragmentation pattern of 2-butene (both *cis*- and *trans*-2-butene), which cannot be distinguished mass spectroscopically.[30] The exposure of 2 L corresponds to the saturation of the overlayer (Figure 1, Inset). Iodine desorption was detected at ~850 K (not shown) in accord with the results of others.[18-23] The spectra exhibit two distinct desorption states with a narrow feature at 140 K and a broader peak at 184 K (Figure 1). A Redhead analysis, assuming a preexponential factor of 1 × 10^{13} s^{-1}, yields desorption

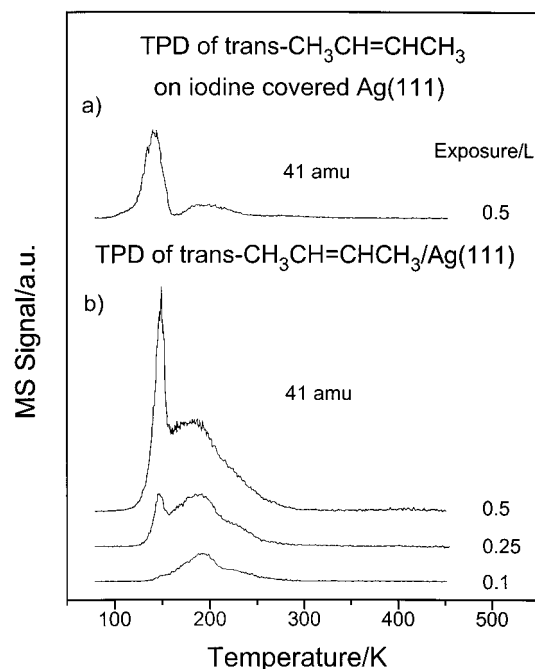(30) NIST Mass Spectroscopy Data Center, http://webbook.nist.gov/chemistry.

Figure 2. (a) Temperature-programmed desorption spectra of *trans*-2-butene adsorbed on iodine-covered Ag(111). Iodine was adsorbed on the surface by exposure to 2 L of 1,1-diiodoethane and heating to 500 K. (b) Temperature-programmed desorption spectra taken at 41 amu (2-butene) following the adsorption of *trans*-2-butene on clean Ag(111) at 80 K as a function of exposure. The exposures are marked adjacent to the corresponding spectrum.
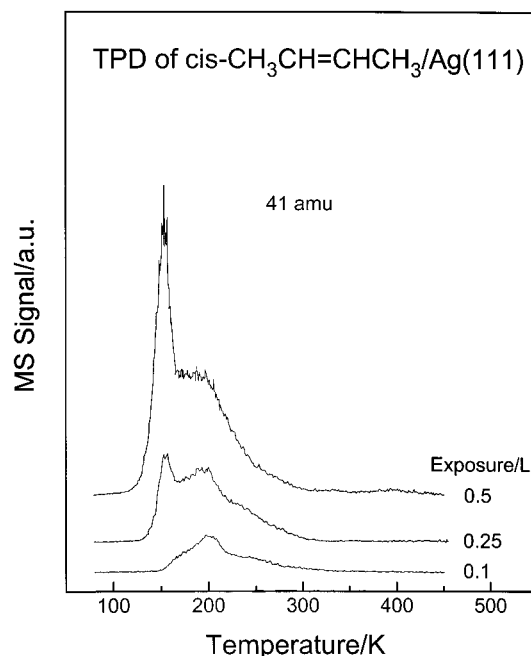

Figure 3. Temperature-programmed desorption spectra taken at 41 amu (2-butene) following the adsorption of *cis*-2-butene on Ag(111) at 80 K as a function of exposure. The exposures are marked adjacent to the corresponding spectrum.

activation energies of ∼8.4 and 11.2 kcal/mol respectively for these states.[31] Since 2-butene is proposed to arise from a recombinative reaction, a first-order Redhead analysis is apparently not warranted. However, data presented below indicate that these states reflect the activation energy for desorption rather than recombination, justifying this analysis. Note also that the asymmetric line shape and constant peak position, particularly of the 140 K state, suggests first-order desorption processes since a second-order desorption state would have a more symmetric peak and peak temperature that decreases with increasing coverage.[31] This notion is confirmed by the data of Figure 2b, which display the temperature-programmed desorption spectra of *trans*-2-butene itself from Ag(111) as a function of exposure, following adsorption at 80 K. The spectra display two desorption peaks in the 41-amu spectrum, the first a sharp feature centered at 146 K, the second a broader peak at 188 K, temperatures extremely close to those found for the desorption of 2-butene from Ag(111) following exposure to 1,1-diiodoethane (Figure 1). No other desorption products were detected. Note also that the relative intensity ratios of the 146 and 188 K features for *trans*-2-butene adsorbed directly on Ag(111) (Figure 2b) are different from the corresponding ratios following 1,1-diiodo-ethane adsorption (Figure 1). The temperature-programmed desorption data for *trans*-2-butene adsorbed on iodine-precov-ered Ag(111) are shown in Figure 2a. It desorbs in two states at 140 and 184 K where relative peak intensities and positions now agree well with the data in Figure 1. The peak intensities are modified while the desorption temperatures are only slightly affected by the presence of iodine indicating that 2-butene still adsorbs on the silver surface but that sites are blocked by iodine. A similar effect has been observed for the adsorption of 1,3-butadiene on Ag(111) and for the formation of 1,3-butadiene from C₂H₃I.[21] In addition, 1,1-diiodoethane adsorbed onto

iodine-covered Ag(111) forms no 2-butene confirming that the chemistry takes place on the metal surface.

The corresponding 41-amu desorption spectra collected after adsorbing *cis*-2-butene on Ag(111) are displayed in Figure 3, also as a function of exposure. The spectra also show a sharp low-temperature peak (at 152 K) with a broader, higher-temperature state (at 196 K). Analogous Redhead analyses of these desorption states reveal that they correspond to desorption activation energies of 9.2 (152 K state) and 11.9 (196 K state) kcal/mol.[31] These data provide the first suggestion that *trans*-2-butene forms following adsorption of 1,1-diiodoethane since the 41-amu desorption peak temperatures in Figure 1 more closely resemble those of *trans*- (Figure 2) than *cis*-2-butene (Figure 3). However, the infrared spectrum is more sensitive to *cis*−*trans* isomerization.[26] Figure 4 displays the RAIRS spectra of monolayers of *cis*- and *trans*-2-butene adsorbed on Ag(111) at 80 K. *trans*-2-Butene exhibits peaks at 1429 and 959 cm⁻¹ with a shoulder at 973 cm⁻¹ whereas the spectrum for *cis*-2-butene has peaks at 1434 cm⁻¹, a shoulder at 1445 cm⁻¹, and a peak at 1030 cm⁻¹. It is clear from these spectra that they are sufficiently different to allow the two isomers to be distinguished on the surface.

The RAIRS spectra collected following 1,1-diiodoethane adsorption on Ag(111) at 80 K are displayed in Figure 5 as function of exposure, where an exposure of 2 L (Figure 5d) corresponds to the saturation of the overlayer (Figure 1). At low exposures (0.5 L; Figure 5a), the spectrum consists of a feature at 967 cm⁻¹. As the exposure increases to 1 L (Figure 5b), the 967-cm⁻¹ feature is still present but an additional feature appears at 957 cm⁻¹. The single feature at 958 cm⁻¹ continues to grow up to completion of the monolayer (Figure 5d). To confirm that these are not due to 1,1-diiodoethane itself, this was condensed onto the surface by the addition of two more langmuirs to yield the spectrum shown in Figure 5e. The feature present at 958 cm⁻¹ in Figure 5d is still present in Figure 5e, but slightly shifted to 964 cm⁻¹, presumably due to the presence of the condensed overlayer. Clearly evident in Figure 5e are
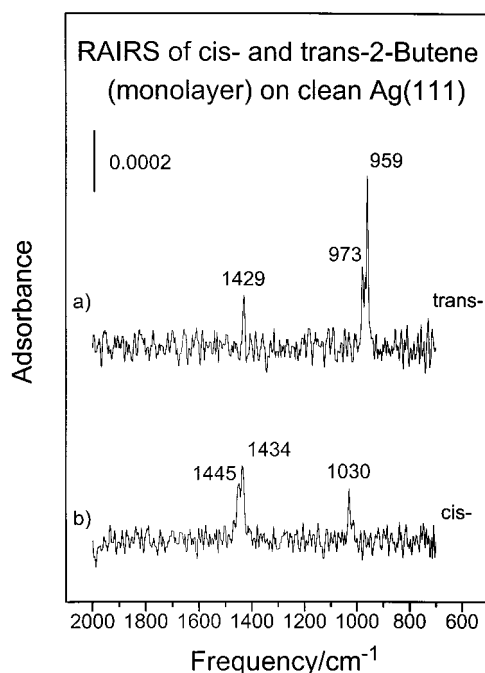
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Figure 4. Reflection-absorption infrared spectra of a monolayer of (a) *trans*-2-butene and (b) *cis*-2-butene adsorbed on Ag(111) at 80 K. The absorbance scale is indicated as a vertical line on the figure.
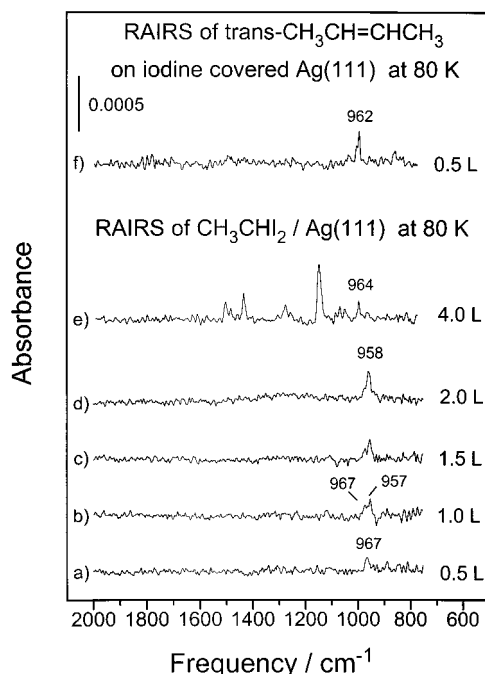

Figure 5. Reflection−absorption infrared spectra of 1,1-diiodoethane adsorbed on Ag(111) at 80 K as a function of exposure: (a) 0.5, (b) 1, (c) 1.5, (d) 2, and (e) 4 L. Shown for comparison in (f) is the infrared spectrum of *trans*-2-butene adsorbed on iodine-covered Ag(111). The absorbance scale is indicated as a vertical line on the figure.

additional peaks at 1106, 1225, 1374, and 1440 cm^{-1} due to diiodoethane. The peak assignments are summarized in Table 1.

To gauge the effect of coadsorbed iodine on the infrared spectrum of adsorbed *trans*-2-butene, this was adsorbed onto an iodine-covered surface that had been formed by exposing it to 1,1-diiodoethane (2 L) and heating to 500 K. The sample was allowed to cool to 80 K and exposed to 0.5 L of *trans*-2-butene. This gave rise to the spectrum shown in Figure 5f which

Table 1. Comparison of the Spectrum Formed by Exposing Ag(111) to 4 L of 1,1-Diiodoethane at 80 K (Figure 5e) with That of Liquid 1,1-Diiodoethane[24]

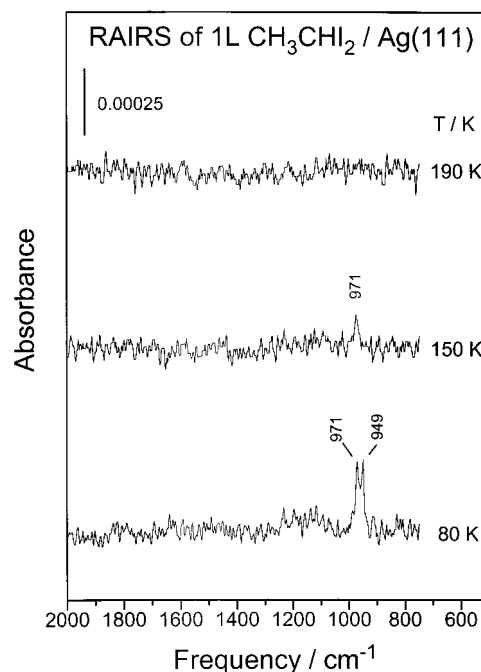| mode	freq/cm^{-1} 1,1-diiodoethane/Ag(111)	freq/cm^{-1} liquid 1,1-diiodoethane
$\delta_{op}(CH)/\delta_{op}(CH_3)$	1106	1101 (vs)
$\delta_{ip}(CH)/\nu(C-C)$	1225	1228 (s)
$\delta_s(CH_3)$	1374	1372 (s)
$\delta_a(CH_3)$	1440	1436 (s)

Figure 6. Reflection−absorption infrared spectra of 1 L of 1,1-diiodoethane adsorbed on Ag(111) at 80 K and annealed to various temperatures where the annealing temperatures are marked adjacent to the corresponding spectrum. The absorbance scale is indicated as a vertical line on the figure.

has a single peak at 962 cm^{-1} corresponding to the 959-cm^{-1} peak shown for *trans*-2-butene adsorbed on clean Ag(111) (Figure 4), so that the vibrational modes are only slightly affected by the presence of coadsorbed iodine.

Shown in Figure 6 is the temperature evolution of the RAIRS spectra following adsorption of 1 L of 1,1-diiodoethane on Ag-(111). The spectrum formed following adsorption at 80 K reproduces that shown in Figure 5b. Heating to 190 K removes all infrared features, corresponding to the complete desorption of all 2-butene in temperature-programmed desorption (Figure 1). Heating to 150 K causes the 949-cm^{-1} feature to disappear and the 971-cm^{-1} peak to attenuate in intensity.

The corresponding temperature evolution of the RAIRS spectrum of *trans*-2-butene is displayed in Figure 7 showing identical peak positions following adsorption at 80 K as found in Figure 4a. Annealing to 150 K causes the 959-cm^{-1} feature to attenuate substantially in intensity suggesting that this is associated with the low-temperature desorption state (Figure 2b). The 973-cm^{-1} feature persists at 150 K but is completely removed by heating to 190 K.

Discussion

2-Butene Adsorption on Clean and Iodine-Covered Ag-(111). Both *cis*- and *trans*-2-butene adsorb on clean Ag(111) at 80 K where *trans*-2-butene desorbs at 140 ($E_{act} = 8.4$ kcal/mol) and 184 K ($E_{act} = 11.2$ kcal/mol) (Figure 2) and *cis*-2-
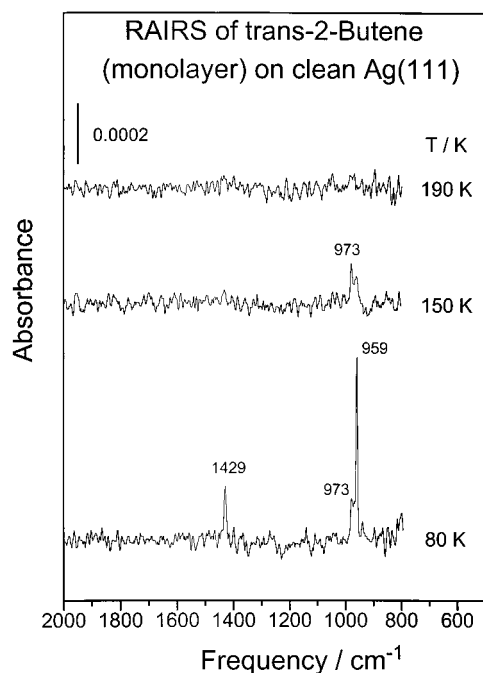
Figure 7. Reflection–absorption infrared spectra of 1 monolayer of *trans*-2-butene adsorbed on Ag(111) at 80 K and annealed to various temperatures where the annealing temperatures are marked adjacent to the corresponding spectrum. The absorbance scale is indicated as a vertical line on the figure.

Table 2. Comparison of Adsorbed and Gas-Phase Infrared Frequencies for *cis*-2-Butene

mode	symmetry	matrix isolated *cis*-2-butene,[26] cm^{-1}	*cis*-2-butene Ag(111), cm^{-1}
ν(C–C)	b$_2$	970	
ρ(CH$_3$)	b$_1$	1037	1030
δ_i(CH)	b$_2$	1408	
δ_a(CH$_3$)	b$_2$	1445	
δ_a(CH$_3$)	b$_1$	1456	1434
δ_a(CH$_3$)	a$_1$	1459	(1445)

Table 3. Comparison of Adsorbed and Gas-Phase Infrared Frequencies for *trans*-2-Butene

mode	symmetry	matrix isolated *cis*-2-butene,[26] cm^{-1}	*cis*-2-butene/ Ag(111), cm^{-1}
δ_a(CH$_3$)	b$_u$	1456	-
δ_a(CH$_3$)	a$_u$	1444	1429
δ_s(CH$_3$)	b$_u$	1397	-
ρ(CH$_3$)	b$_u$	976	(973)
δ_o(CH)	a$_u$	967	959

butene desorbs at 152 ($E_{act} = 9.2$ kcal/mol) and 196 K ($E_{act} = 11.9$ kcal/mol) (Figure 3). In both cases, the high-temperature state populates prior to the low-temperature state as expected. The corresponding infrared spectra of monolayers of *cis*- and *trans*-2-butene are shown in Figure 4. Since the molecules remain intact and the vibrational modes are only likely to be weakly perturbed from the corresponding gas-phase values, spectral assignments can be made by direct comparison with the infrared frequencies for matrix-isolated molecules[26] and are summarized in Tables 2 and 3. The 1030-cm^{-1} mode of adsorbed *cis*-2-butene is unequivocally assigned to the CH$_3$ rocking mode (at 1037 cm^{-1} for the isolated molecule). The appearance of a mode with b$_1$ symmetry is consistent with a molecular plane oriented essentially parallel to the surface. On this basis, the 1434-cm^{-1} mode is assigned to the asymmetric methyl bending mode (1456 cm^{-1} in the isolated molecule).

Assignment to the b$_2$ mode (at 1445 cm^{-1} for matrix-isolated *cis*-2-butene) is excluded since no other modes of b$_2$ symmetry are detected. The 1445-cm^{-1} mode may be due to another adsorption geometry or to an a$_1$ asymmetric methyl bending mode (at 1459 cm^{-1} for matrix-isolated *cis*-2-butene). The presence of this mode would be consistent with a tilting of the molecular plane to yield slightly better π overlap with the surface resulting in a slightly higher desorption energy for *cis*-2-butene than for *trans*-2-butene.

The corresponding assignments for the RAIRS spectra for *trans*-2-butene are shown in Table 3. The 1429-cm^{-1} feature is assigned to the asymmetric methyl bending mode (at 1444 cm^{-1} for matrix-isolated *trans*-2-butene) consistent with a *trans*-2-butene molecular plane oriented parallel to the surface. The intense 959-cm^{-1} peak is assigned to the out-of-plane CH bending mode (967 cm^{-1} for the matrix-isolated molecule). The 973-cm^{-1} mode could be assigned to the methyl rocking mode (b$_u$ symmetry) although no other modes of b$_u$ symmetry are detected. A more likely explanation is offered by the data of Figure 7 which displays the RAIRS spectra of *trans*-2-butene collected as a function of temperature, where the 959-cm^{-1} peak is removed on heating to 150 K whereas the 973-cm^{-1} feature persists and is only removed on heating to 190 K. The 959-cm^{-1} mode is associated with the low-temperature (140 K) desorption state and the 971-cm^{-1} peak with the 184 K state (Figure 3). This is also consistent with the temperature-programmed desorption spectrum of *trans*-2-butene adsorbed on iodine-covered Ag(111) formed by exposure to 2 L of 1,1-diiodoethane and heated to 500 K to desorb hydrocarbon species (Figure 2a), which shows that the 184 K desorption state is substantially diminished in intensity while the low-temperature (140 K) state is not strongly affected. This indicates that iodine blocks the high-temperature adsorption state, consistent with the infrared spectrum displayed in Figure 5f. These results also imply that the sites that are *not* blocked are not substantially affected by the presence of coadsorbed iodine. It has been shown that iodine adsorbs on Ag(111) at the 3-fold hollow site from an analysis of the $\sqrt{3} \times \sqrt{3}$ *R*30° LEED pattern[32] suggesting that this site is occupied by the more stable *trans*-2-butene.

1,1-Diiodoethane Adsorption and Reaction on Ag(111). The temperature-programmed desorption data of Figure 1 confirm that adsorbed 1,1-diiodoethane reacts on Ag(111) to form 2-butene. No other desorption products are detected so that this reaction appears to be rapid and quantitative. The similarity between desorption peak positions of molecularly adsorbed 2-butenes (Figures 2 and 3) and those for the formation of 2-butene from 1,1-diiodoethane (Figure 1) indicates that 2-butene formation from 1,1-diiodoethane is desorption- rather than reaction-rate limited. This indicates that 2-butene has already formed on the surface below $\sim$120 K. This conclusion is confirmed by the RAIRS data of Figure 6, which shows peaks at 949 and 971 cm^{-1}, close to the frequencies of *trans*-2-butene on clean and iodine-covered Ag(111) (Figure 5). The relatively low intensity of the high-temperature state for 2-butene formed from 1,1-diiodoethane, following the above discussion, is due to site blocking by coadsorbed iodine. Based on previous studies of methylene iodide on Ag(111) which show that methylene species are formed at $\sim$130 K,[25] this reaction is proposed to take place by the initial formation of adsorbed CH$_3$–CH= species that rapidly dimerize to form 2-butene. As noted above, the stereoselectivity of this reaction can be controlled either by the initial approach of the two carbenes or by the interaction of the cis or trans products with the surface as depicted in Scheme 1. It is assumed that the carbenes approach each other such that

(32) Gerenser, L. J.; Baetzold, R. C. *Surf. Sci.* **1980**, *99*, 259.

Scheme 1
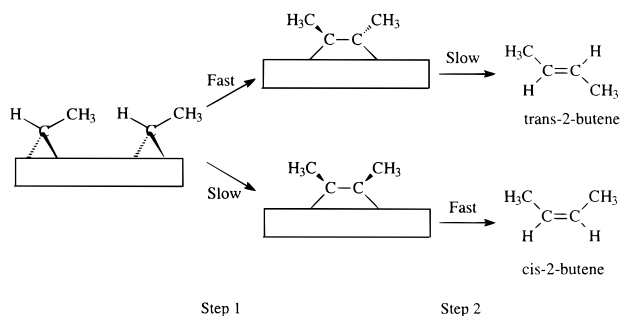
the planes defined by the α- and β-carbons and the α-hydrogen are parallel. In this case, the formation of the *trans*-2-butene intermediate minimizes the steric interaction between the approaching methyl groups. Since there is no steric hindrance in the desorption of the 2-butene intermediate in organometallic species, in the homogeneous phase this chemistry invariably leads to the formation of *trans*-2-butene.[2−7] In contrast, when the 2-butene is strongly adsorbed on a planar substrate, the interaction of the trans methyl groups with the surface inhibits product formation leading to cis stereoselectivity[1]. The situation on Ag(111) is somewhat different since both *cis*- and *trans*-2-butene have almost identical heats of adsorption where *trans*-2-butene desorbs in two states with activation energies of ∼8.4 and 11.2 kcal/mol and *cis*-2-butene desorbs with corresponding activation energies of 9.2 and 11.9 kcal/mol, so that the energy difference between these states is ∼0.7 kcal/mol (Figures 2 and 3). Note, however, that *cis*-2-butene does desorb with a slightly higher activation energy than *trans*-2-butene due to the steric effect depicted in Step 2, Scheme 1. The infrared features due to the adsorption of *cis*- and *trans*-2-butene on Ag(111) (Figure 4, Tables 1 and 2) are very close to those observed in matrix isolation indicating that the 2-butenes maintain their gas-phase geometries on the surface so that the 2- and 3-carbons are still sp^2 hybridized. This implies that a significant portion of the bonding to the surface is due to van der Waals' interactions.[14−17] These observations confirm that the second step in Scheme 1 is not likely to lead to any substantial degree of stereoselectivity which is likely to be controlled on Ag(111) by the initial approach of the carbenes (Step 1, Scheme 1).

This conjecture is borne out by the infrared data in Figure 5. First, these show that there is no 1,1-diiodoethane on the surface even following adsorption at 80 K, implying that both iodines are removed very rapidly from the 1,1-diiodoethane, in accord with the chemistry found by others for iodine-containing hydrocarbons on silver.[18−23,25] Further, there is no evidence for the presence of the carbenes on the surface since these would have vibrational frequencies reasonably close to the iodine-containing precursor. Comparison to the spectra in Figure 4 of both *cis*- and *trans*-2-butene adsorbed on Ag(111) clearly indicates that the feature is due to *trans*-2-butene. This confirms that the product forms rather rapidly on the surface and rationalizes the similarity between the 2-butene (41 amu) desorption spectrum following adsorption of 1,1-diiodoethane (Figure 1) and that for *trans*-2-butene desorption; the *trans*-2-butene has already formed at or below ∼140 K by carbene recombination, so that the kinetics of Figure 1 merely reflect product desorption. It also justifies the first-order Redhead analysis carried out above.

The data in Figure 5 confirm that the trans isomer is strongly preferred to the cis isomer since only features due to the trans isomer are detected suggesting that, within the sensitivity of RAIRS, the selectivity approaches 100%. To confirm that the peak formed between 957 and 967 cm^{-1} following exposure to

1,1-diiodoethane is not strongly perturbed by the presence of iodine on the surface, the RAIRS spectrum was collected for *trans*-2-butene adsorbed on iodine-covered Ag(111) (Figure 5f). In this case, the iodine was deposited by dosing with 2 L of 1,1-diiodoethane at 80 K and annealing to 500 K. All hydrocarbon fragments desorb to leave just iodine on the surface. This procedure was used since it deposits exactly the same amount of iodine as is present during carbene recombination and desorption. The peak is indeed slightly shifted by ∼4 cm^{-1} (from 958 cm^{-1} for clean Ag(111) to 962 cm^{-1} for the iodine-covered surface). The small shift does not affect the conclusions arrived at above.

To prove that the observed RAIRS features at between 950 and 970 cm^{-1} are indeed associated with adsorbed *trans*-2-butene, RAIRS data were collected after exposing Ag(111) to 1,1-diiodoethane (1 L) and annealing to various temperatures. The resulting spectra are shown in Figure 6 where the annealing temperatures are marked adjacent to the corresponding spectrum. All surface species are removed by heating to 190 K corresponding to the completion of the desorption spectrum in Figure 1, confirming that these vibrational modes are associated with the formation of 2-butene. The preferential removal of the 949-cm^{-1} state on heating to 150 K suggests that this infrared mode is associated with the low-temperature (140 K) desorption state in Figure 1, further demonstrating the correspondence between the infrared and temperature-programmed desorption data.

Finally, alkene formation from other iodine-containing surface species is extremely unlikely since these all would involve the formation of carbon−carbon single bonds between carbons (2) and (3). In this case, any stereoselectivity due to the initial approach would be lost due to rotation around the carbon−carbon single bond. For example, 2-butene could be formed by dimerization of 1-iodoethyl species to yield 2,3-diiodobutane. Subsequent iodine removal would form 2-butene. It could also be formed by a migratory insertion of an ethyldidene into 1-iodoethyl species and subsequent iodine abstraction.[22] Rotation about the single C−C bond between carbons (2) and (3) in all of these alternative reaction pathways would result in a lower stereoselectivity whereas a trans-stereoselectivity approaching 100% is found experimentally (Figure 5), implying that 2-butene is not formed via these routes. Reaction between ethylidene and adsorbed 1,1-diiodoethane can further be excluded since molecular 1,1-diiodoethane adsorbs onto the surface following a 4-L exposure (Figure 5e) while the 2-butene yield remains constant for exposures above 2 L (Figure 1).

Conclusions

Ethylidene species formed on Ag(111) by dosing 1,1-diiodoethane at 80 K dimerize to form *trans*-2-butene which desorbs in two states at 140 and 184 K. Both *cis*- and *trans*-2-butene adsorbed on Ag(111) desorb with almost identical activation energies (within 0.7 kcal/mol), suggesting that the dimerization stereoselectivity is not controlled by product desorption but by the approach of the carbenes as illustrated in Scheme 1. This postulate is borne out experimentally both by temperature-programmed desorption and reflection−absorption infrared spectroscopies where the desorption temperature of 2-butene adsorbed on the surface agrees well with that for 2-butene formed by carbene dimerization, and where the infrared spectrum is due to *trans*-2-butene, not *cis*-2-butene.