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The chemistry of methyl and ethyl radicals on Pt(111) from the decomposition of tri-alkyl bismuth compounds

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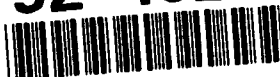
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**The Chemistry of Methyl and Ethyl Radicals on Pt(111) from the Decomposition of
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Abstract

The chemistry of trimethyl and triethyl bismuth compounds adsorbed on Pt(111) have been studied using TDS, AES and HREELS. Alkyl radicals and bismuth atoms are delivered to the Pt(111) surface in a 3:1 (alkyl:bismuth) ratio. In the presence of Bi, it is expected that the alkyl radical chemistry is not perturbed substantially. The tri-alkyl bismuth compounds adsorb molecularly at 110K. Upon heating, the R_3Bi compound decomposes and alkyl radicals are introduced to the surface. Below multilayer coverage, the methyl and ethyl radicals, delivered to the surface by thermal decomposition of the parent, show similar trends. There is some fraction of parent (BiR_3) desorption at ~158K. The remaining methyl or ethyl radicals follow two reaction pathways. The first is hydrogenation which leads to CH_4 or CH_3CH_3 formation, respectively. This pathway leads to reaction rate limited desorption of CH_4 or CH_3CH_3 which occurs at ~285K. The second reaction pathway is dehydrogenation of the methyl or ethyl radical leading to an on-top methylidyne or ethylidyne species, respectively, remaining on the surface.

Introduction

Understanding the chemistry of hydrocarbon reactions on transition metal surfaces is important because these reactions are the basis for several industrial catalytic processes. In addition there is current interest in thin metal CVD on semi-conductor substrates and the reactions which lead to deleterious carbon in the films. Much speculation exists about the intermediates and mechanisms involved and the processes which govern selectivity for the intermediates to follow different reaction pathways.

The chemistry of C_1 and C_2 alkyl fragments is thought to be important in the intermediate reaction steps of hydrocarbon chemistry at metal surfaces. A study of these species is a challenge because methane and ethane gas phase molecules cannot easily be used to deliver C_1 and C_2 alkyl fragments because their adsorption onto metal surfaces is extremely weak. For instance, the heats of adsorption for methane and ethane at 300K onto Pt from the gas phase have been calculated to be -19 kcal/mole and -25 kcal/mole, respectively.¹ Also importantly, CH_4 and CH_3CH_3 adsorbed onto Pt(111) at lower temperatures have energetically high barriers to decomposition which cannot be thermally overcome in competition with desorption.

Previous studies have shown that the dissociation of adsorbed alkyl halides may be used to deliver alkyl groups to the Pt surface. White, et. al.²⁻³ and Zaera, et. al.⁴⁻⁷ in two independent endeavors used the techniques of photochemistry, TPD, XPS, RAIRS, and HREELS spectroscopies to study the geometry and thermal chemistry of alkyl halides on Pt(111) surface. In these studies, the chemistry of methyl and ethyl groups in the presence of halide adatoms is studied. The Zaera work, in particular, show some similarity to the present work in the reaction products after the thermal decomposition of alkyl halide. However, the overall chemical reaction schemes in Zaera's work are significantly more complicated than the alkyl bismuth delivery system discussed here. To date, there is no clear evidence which verify that the electron withdrawing halide does not affect the electronic structure of the Pt surface and thus its reactivity. This may be a

reason there is a difference in the overall chemical reaction schemes between alkyl halides and alkyl bismuth systems. There have also been intricate molecular beam studies of methane and ethane over Pt(111) and Ni (111) such that these molecules have enough translational energy to overcome the barrier to decomposition on the Pt(111) surface.⁸

In the present study, we offer a simple and straightforward means to deliver alkyl radicals to the Pt surface. The thermal decomposition of trimethyl and triethyl bismuth compounds provides a simple method to cleanly generate alkyl radicals on metal surfaces for further study. In the presence of bismuth, it is expected that the alkyl fragment chemistry is not perturbed significantly. Bismuth has previously been found to have unique properties on the Pt surface:^{9a-g} a) it is relatively inert in its surface chemistry on Pt(111); b) it distributes randomly over the surface due to weakly repulsive interactions between Bi adatoms; c) its Pauling electronegativity is very similar to that of Pt (Bi = 2.02; Pt = 2.28); and d) it does not desorb until ~900 - 1200K which is well above the temperature at which we study the alkyl fragment chemistry.

Our results indicate that the methyl and ethyl radicals on Pt(111) display similar chemistry. Some parent desorption occurs at ~158K. The alkyl radicals then undergo either hydrogenation which results to reaction limited desorption of methane or ethane, respectively, at ~280K or dehydrogenation leading to a C_nH_m species. A branching ratio is calculated for hydrogenation vs. dehydrogenation. We identify the C_nH_m species as an on-top methylidyne or ethylidyne, respectively.

Experimental

The TPD, AES, and HREELS experiments were performed in two separate chambers with different Pt(111) crystals. The standardly cut and polished Pt(111) crystals were cleaned in vacuum by oxygen treatment at 1.0×10^{-7} torr O_2 and 900K then flash annealed to ~ 1200K. Cycled Ar^+ sputtering and annealing were performed to

remove calcium or ubiquitous carbon. Cleanliness was determined by AES using a Phi Model 11-010 CMA. The chamber for TPD experiments has a base pressure of 1.0×10^{-10} torr and is equipped with an UTI Model 100-C quadrupole mass spectrometer and the Phi Auger electronics. The TPD experiments were performed at a temperature ramp of 5 K/sec, desorption was in line-of-sight of the mass spectrometer, and a chromel-alumel thermocouple was used. The TPD software is capable of multiplexing 12 masses in one experiment.¹⁰ The second chamber operates at a base pressure of 7.0×10^{-11} torr. It is a double level chamber and is equipped with an UTI quadrupole mass spectrometer, LEED optics, and Phi Auger electronics in the level and a Kesmodel LK 2000 HREELS system in the lower level.

The liquid trialkyl bismuth compounds were produced via a Grignard synthesis and purified by vacuum distillation. After synthesis, purity was confirmed by NMR and IR spectroscopy. During the TPD and HREELS experiments, the compounds were purified for use in vacuum by several freeze thaw cycles, and purity was periodically checked by mass spectroscopy. A directional doser was used to adsorb the room temperature trialkyl bismuth compounds onto the liquid nitrogen cooled Pt(111) crystal at 110K. Exposures were determined by the amount of time the crystal was in front of the doser and reproducible coverages were ascertained by AES.

Results and Discussion

Trimethyl Bismuth

The TPD of trimethyl bismuth shows parent desorption at 158K and CH_4 (16 amu) desorption at 280K which confirms that indeed trimethyl bismuth delivers methyl radicals to the Pt surface. The parent desorption and the HREELS results discussed below verify that molecular adsorption occurs on the 110K Pt (111) crystal. As shown in figure 1, the CH_4 desorption peak at 280K is coverage independent. Auger studies of the Pt(111) crystal past 280K show residual carbon, suggesting that after methyl radicals are

delivered to the Pt(111) surface, accompanying the hydrogenation channel leading to the formation of methane, a dehydrogenation channel is present. This result is also supported by the 2 amu TPD desorption trace, figure 2, which shows two major areas of desorption. One peak is attributed to being part of the fragmentation of CH_4 at 280K and the other peak at 460K is from the decomposition of a species formed from the dehydrogenation of methyl radical.

Figure 3 shows HREELS spectra of a saturation exposure of trimethyl bismuth at various temperatures. At 150K, molecular adsorption still exists which is, within the HREELS instrumental resolution, nicely corroborated with gas phase IR vibrational modes listed in Table 1. As the crystal is heated to 333K up to 373K, figures 3b-c, the 453 cm^{-1} Bi-C, 789 cm^{-1} , 1140 cm^{-1} symmetric and 1388 cm^{-1} asymmetric CH_3 stretches are lost. A C-Pt loss peak appears at 789 cm^{-1} and moves to 760 cm^{-1} with increasing temperature due to a mass effect. The 2913 cm^{-1} CH mode becomes stronger and narrower with increasing temperature which is characteristic of one type of a CH_x species as compared to the broad 2971 cm^{-1} CH_x loss at 150K indicative of CH in various chemical environments. It is not possible to assign the CH_x species as being a CH_3 or CH_2 considering none of the methyl or methylene losses are present between $1000 - 1400\text{ cm}^{-1}$. As a result, we expect the species to be an on-top methylidyne.

Triethyl Bismuth

As in the case of $\text{Bi}(\text{CH}_3)_3$, $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ molecularly adsorbs at 110K. Parent desorption occurs at 158K; CH_3CH_3 and CH_2CH_2 (30 amu and 27 amu TPD signal monitored, respectively) show reaction rate limited desorption peaks at 295K which is shown in figure 4. The 27 amu TPD spectra is a convolution of the electron bombardment fragmentation of CH_3CH_3 and CH_2CH_2 . The H_2 TPD spectra, figure 5, show two major broad regions of desorption. The peak at 295K is attributed to the fragmentation of both CH_3CH_3 and CH_2CH_2 ; the second peak at 470K is from the decomposition of a remaining C_nH_m species on the surface. This species will also be

discussed below. There was no detectable CH_4 or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ moieties, from C-C bond scission or ethyl radical addition reactions, in the $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ TPD.

Ion abundances determined from the mass spectra of $\text{Bi}(\text{CH}_2\text{CH}_3)_3$, CH_3CH_3 , and CH_2CH_2 can be used to understand the origin of the 27 amu desorption trace. Quantification of the 27 amu and 30 amu TPD spectra based on the mass spectra indicate that at very low coverages, the ethyl groups dehydrogenate to form mostly ethylene. As the coverage is increased, both ethylene and ethane desorb from the Pt surface, and the amount of desorbing ethane increases. These observations are schematically shown in figure 6 which is the ethane-to-ethylene branching ratio as a function of dosing time which indicates increasing ethane production with increased triethyl bismuth exposure. This ratio is calculated from ion abundances obtained from the mass spectra. The hydrogenation channel of the ethyl radical becomes more accessible as the ethyl radical coverage increases. This is consistent with more hydrogen being available for ethane production from the ethyl radical dehydrogenation process.

Previous studies of ethylene have shown that when ethylene is adsorbed onto the Pt(111) surface at 110K, 54% molecularly desorbs at 285K, 44% decomposes to form ethylidyne, and approximately 2% hydrogenates to form ethane which desorbs at 295K. Our TPD spectra show that once ethyl radicals are delivered to the surface, part of the species hydrogenates to form ethane and part dehydrogenates to form ethylene as discussed above. The ethylene formed does not re-hydrogenate to form additional ethane. Some of the ethylene dehydrogenates to form an on-top ethylidyne suggested in our HREELS results and the remainder desorbs as ethylene.

Figure 7 shows temperature dependent HREELS spectra following a 120 sec exposure of $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ resulting in a below saturation coverage overlayer. Figure 7a shows the HREELS spectra at 150K; the modes attributed to the vibrational losses are listed in Table 2 along with gas phase IR values. As shown in Table 2, the loss modes are comparable to the IR values and confirm molecular adsorption as in the $\text{Bi}(\text{CH}_3)_3$ case

just discussed. As the sample is heated to 231K, figure 7b, some molecular desorption occurs, however, the spectra indicate that some parent species is still present molecularly adsorbed on the crystal surface.

At 291K, a temperature which is just before ethylene and ethane desorption, the spectra in figure 7c show that a mixture of species exist that will undergo either 1) hydrogenation leading to formation of CH_3CH_3 which desorbs or 2) dehydrogenation leading to formation of CH_2CH_2 which either desorbs or undergoes subsequent decomposition leading to formation of a C_2H_x species. At this temperature, loss of the Bi-C mode at $\sim 400\text{ cm}^{-1}$ starts to occur. The 672 cm^{-1} methylene rocking and 229 cm^{-1} methylene torsion modes also begin to disappear. The C-C vibrational loss at 957 cm^{-1} starts to shift to a higher frequency at 1091 cm^{-1} . Finally, the growth of a new Pt-C stretch at 565 cm^{-1} appears.

Figure 7d shows the HREELS spectra at 354K, a temperature just after ethylene and ethane desorption, but before any further dehydrogenation which can be identified in the 2 amu desorption trace of figure 5. At this temperature, all methylene vibrations have been lost. Also, there is the strong Pt-C stretch at 565 cm^{-1} , a C-C loss at 1091 cm^{-1} , and a CH_3 loss at 1301 cm^{-1} . There appears to be some detectable C-H loss at 2918 cm^{-1} . This spectrum cannot be attributed to a hollow-site ethylidyne species because previous HREELS studies have shown that hollow-site ethylidyne on Pt(111) displays no loss frequency at 565 cm^{-1} and the 1300 cm^{-1} mode dominates the spectra of that species.¹¹⁻¹² However, the 565 cm^{-1} mode can be assigned to the molecule metal (Pt-C) stretch of an on-top ethylidyne or ethylidene species. This species being present is also consistent with studies of the characterization of Bi on Pt(111) which show that Bi adatoms tend to occupy three-fold hollow sites thus leaving only on-top sites available for adsorption.^{2b} The existence of a C_2 species with methylene groups is ruled out due to no detectable methylene loss frequencies in the region $1100 - 1400\text{ cm}^{-1}$.

Summary

After the thermal decomposition of BiR_3 and the delivery of $\cdot\text{R}$ radicals to the Pt(111) surface ($\text{R} = \cdot\text{CH}_3$ or $\cdot\text{CH}_2\text{CH}_3$), similarities in the alkyl radical chemistry is observed on the Pt(111) surface. Molecular adsorption occurs at 110K. Parent desorption occurs at $\sim 158\text{K}$. Thermal decomposition of the parent leads to two reaction pathways taken: 1) hydrogenation leading to desorption, and 2) dehydrogenation leading to desorption and/or C_nH_m species remaining on the surface. These two reaction pathways are shown schematically in figure 8.

Acknowledgements

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Tables

1. HREELS loss frequencies of $\text{Bi}(\text{CH}_3)_3$ on $\text{Pt}(111)$ compared to gas phase IR vibrational modes.
2. HREELS loss frequencies of $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ on $\text{Pt}(111)$ compared to gas phase IR vibrational modes.

Figures

1. CH_4 (16 amu) TPD desorption trace at various exposures below multilayer formation which is coverage independent. Desorption peak occurs at 280°K.
2. H_2 (2 amu) TPD for trimethyl bismuth at various exposures below multilayer coverage.
3. HREELS spectra of multilayer coverage of trimethyl bismuth at various temperatures.
4. a) CH_2CH_2 (27 amu monitored) and b) CH_3CH_3 (30 amu) desorption trace at various exposures below multilayer coverage.
5. H_2 (2 amu) TPD desorption trace of triethyl bismuth.
6. Ethane-to-Ethylene branching ratio versus exposure time up to multilayer formation.
7. HREELS spectra of below multilayer coverage of triethyl bismuth at various temperatures.
8. Reaction scheme for $\text{Bi}(\text{CH}_3)_3$ and $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ chemistry on the Pt(111) surface.

Bi(CH₃)₃ Vibrational Spectral Assignments

	Gas/Liquid (IR/cm ⁻¹)	On Pt(111) (HREELS/cm ⁻¹)
δ (C-Bi-C)	171	---
ν (Bi-C)	460	453
ρ (CH ₃)	780	789
δ_s (CH ₃)	1160	1140
δ_{as} (CH ₃)	1383	1388
ν_s (CH)	2994	2971
ν_{as} (CH)	3054	

Table 1. HREELS loss frequencies of Bi(CH₃)₃ on Pt(111) compared to gas phase IR vibrational modes.

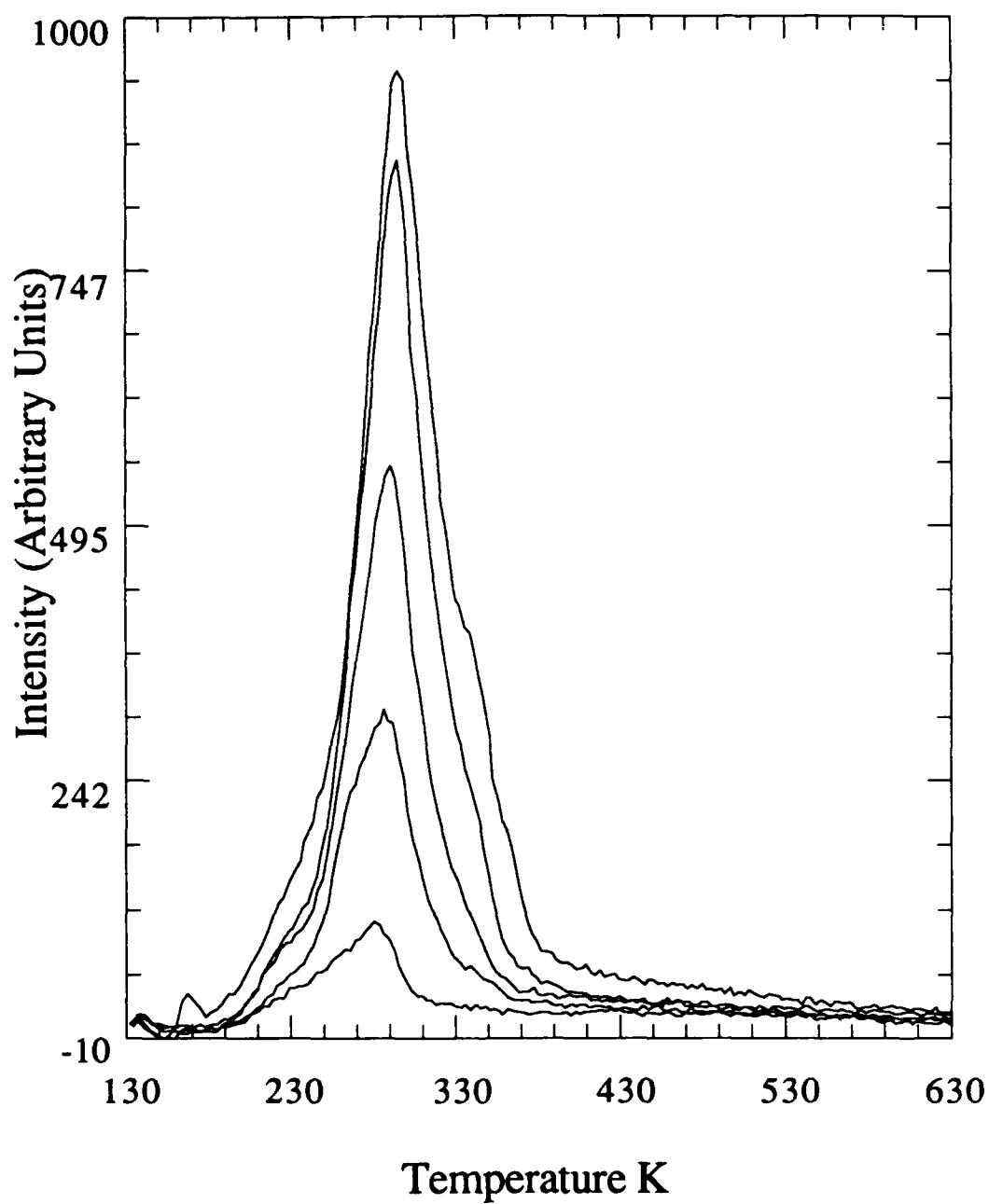


Figure 1. CH_4 (16 amu) TPD of $\text{Bi}(\text{CH}_3)_3$ at 20,50,100,200,400 sec exposures

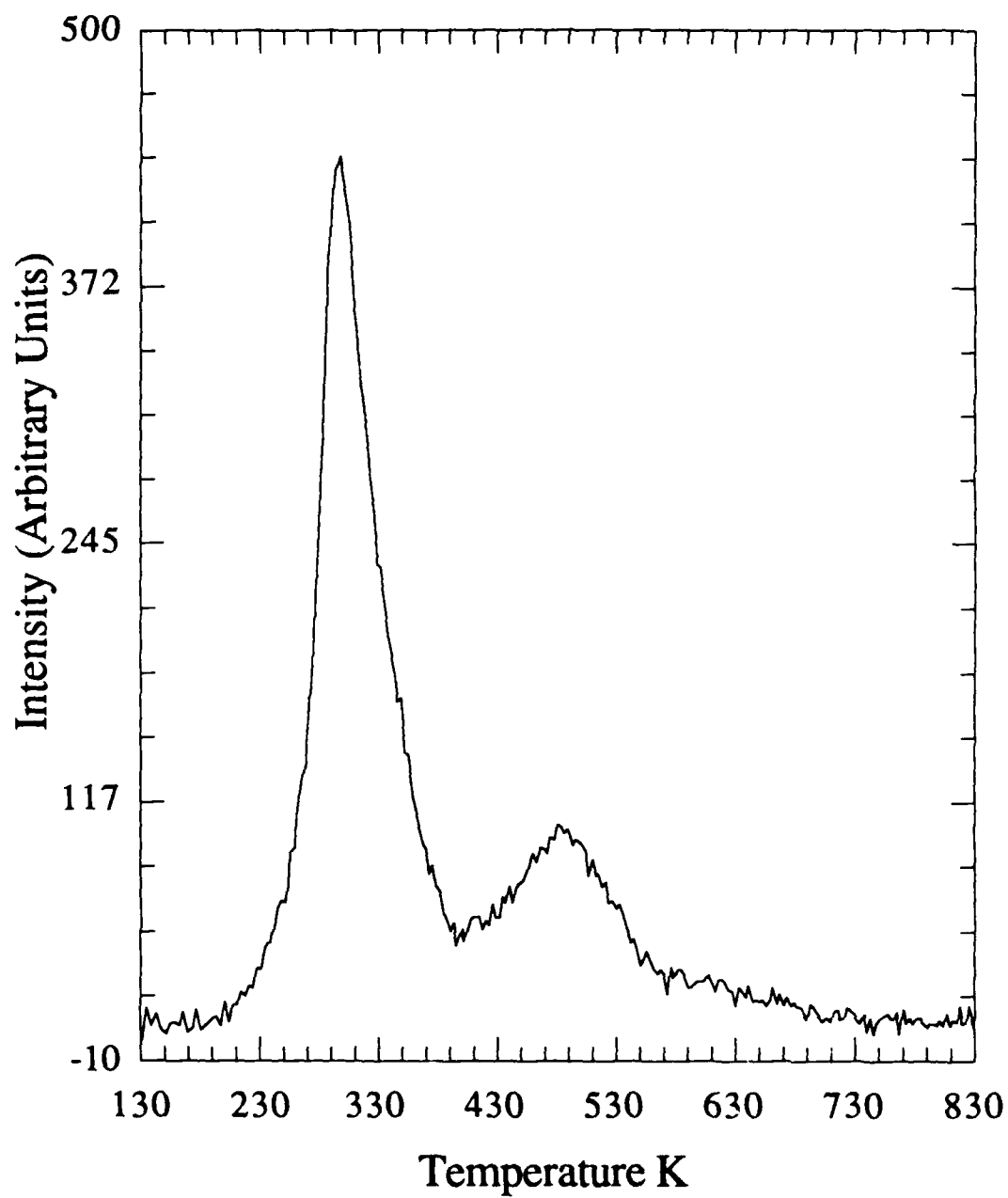


Figure 2. H_2 (2 amu) TPD of $\text{Bi}(\text{CH}_3)_3$
at 50 sec exposure

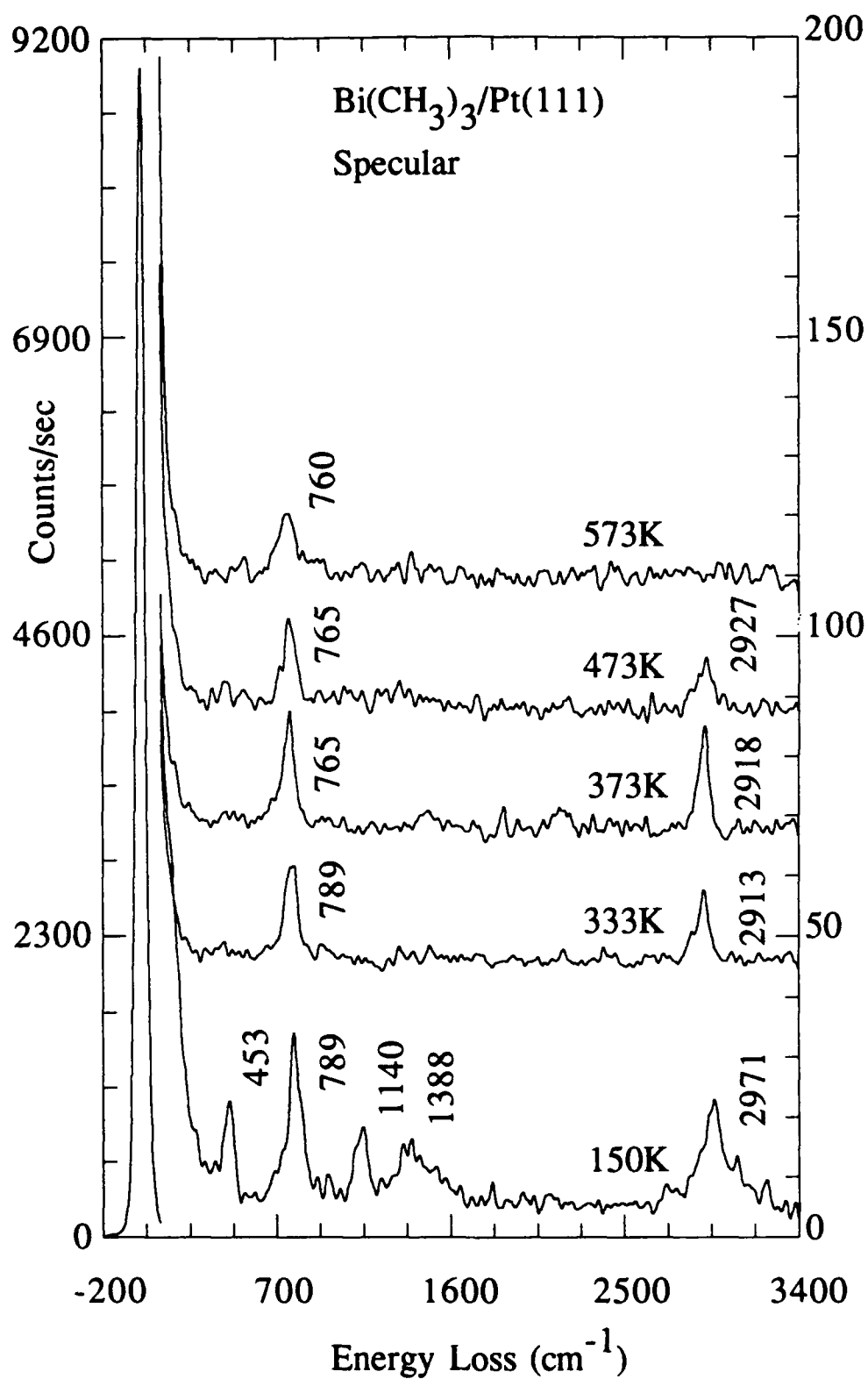


Figure 3. HREELS spectra of multilayer coverage of Bi(CH₃)₃ at various temperatures.

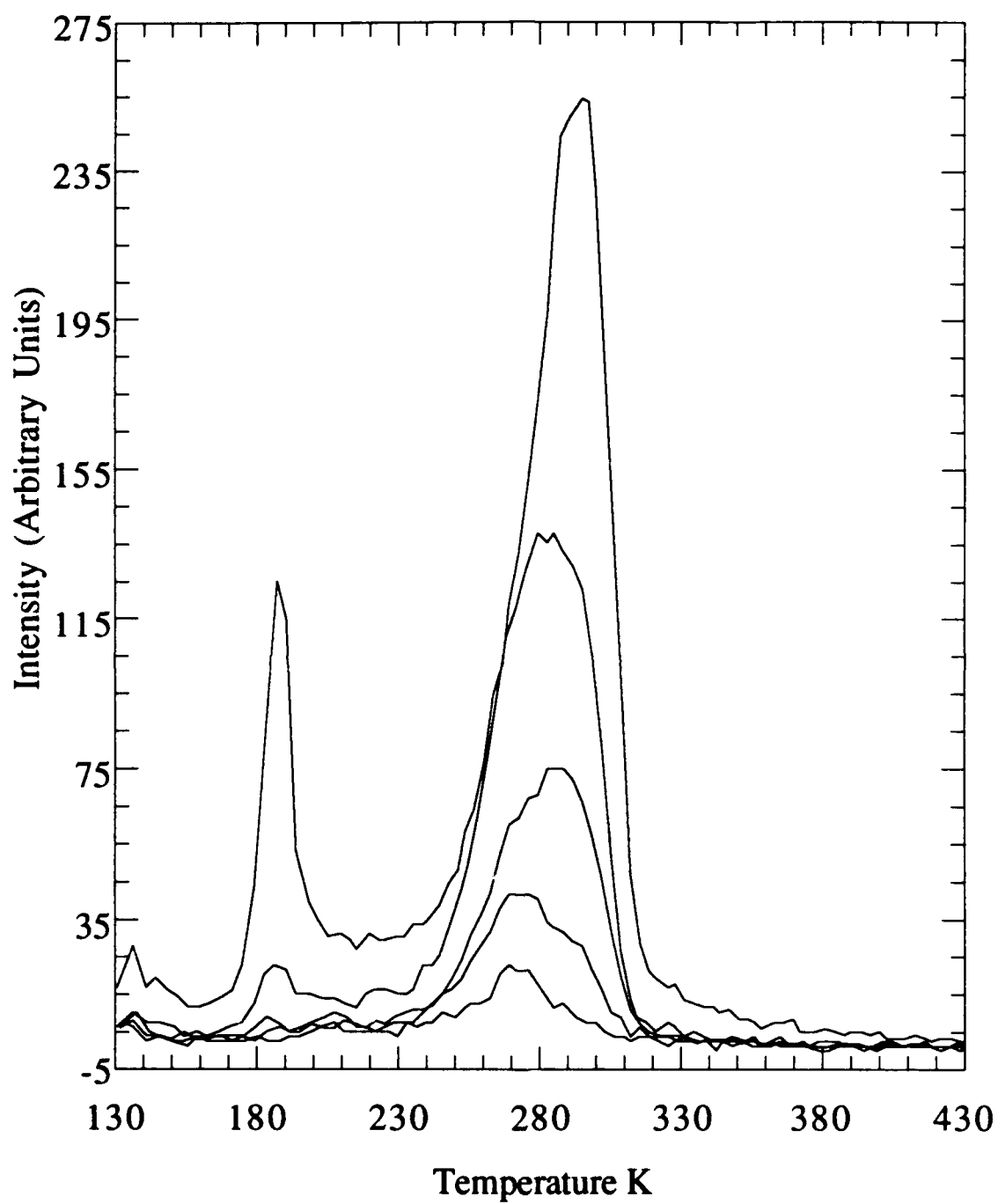


Figure 4a. CH_2CH_2 (27 amu monitored) TPD of $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ 20, 30, 40, 60, 100, 200 sec exposure.

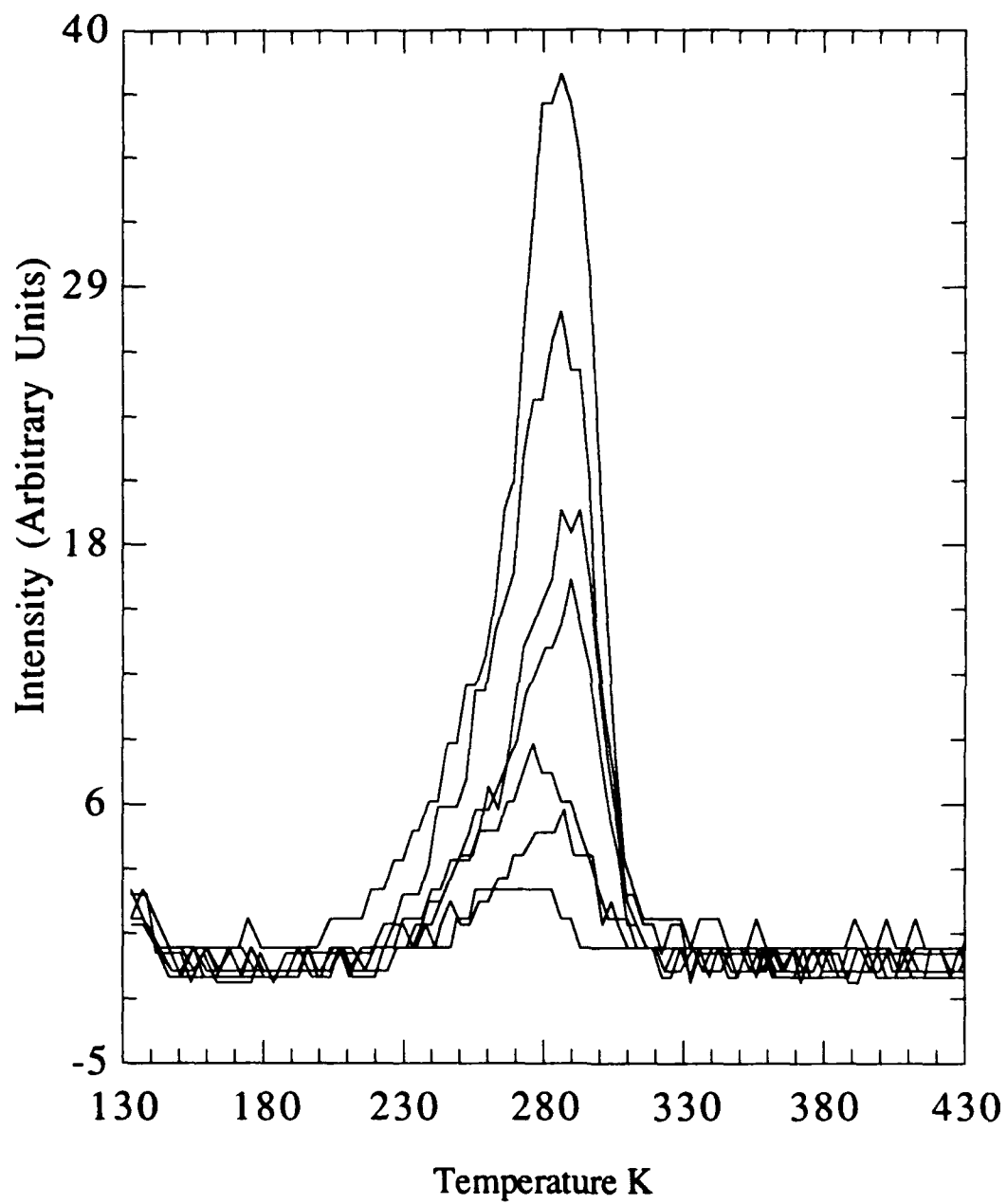


Figure 4b. CH_3CH_3 (30 amu) TPD of $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ at 20, 30, 40, 50, 60, 80, 100 sec exposures

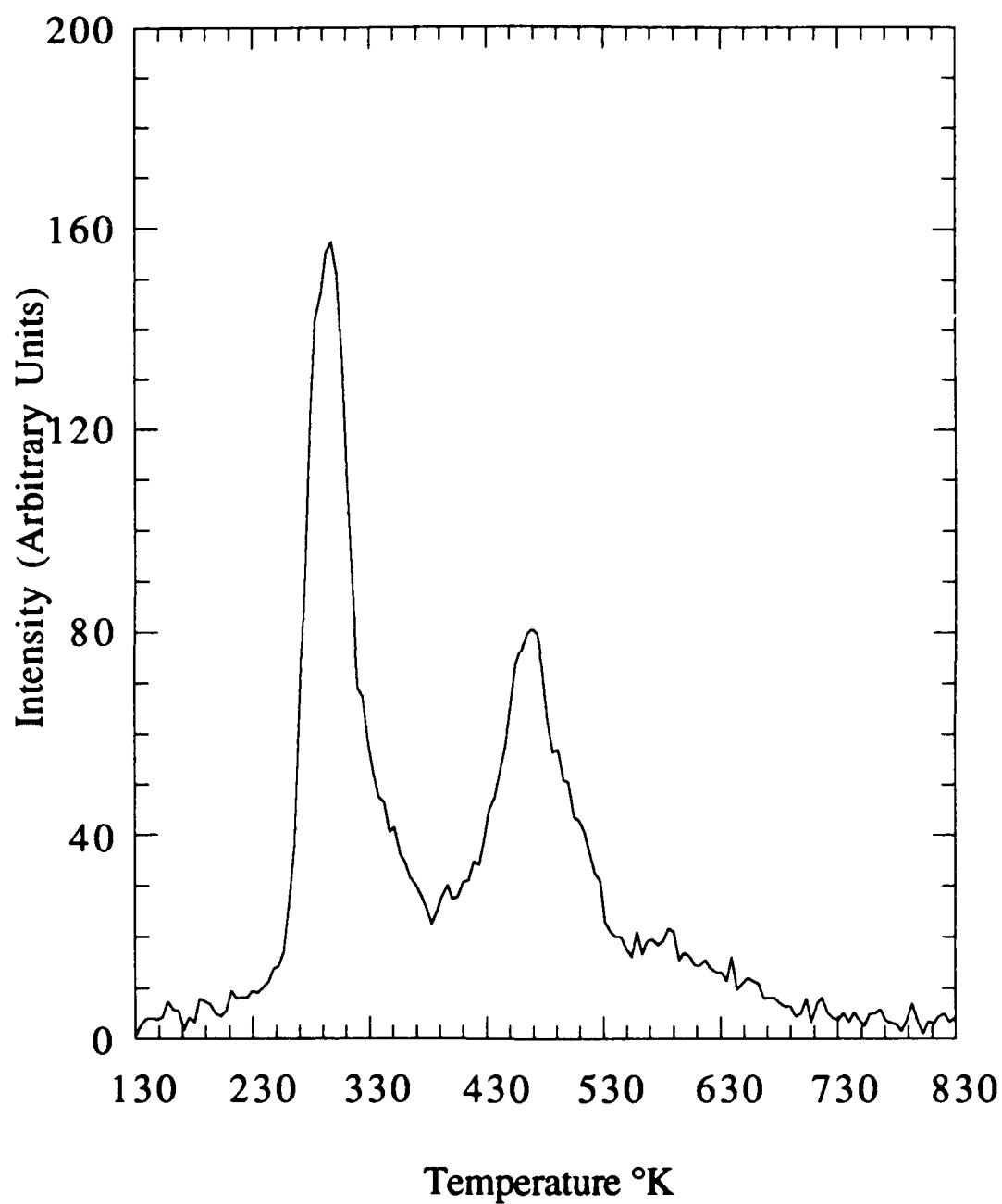


Figure 5. H_2 (2 amu) TPD of $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ at 50 second exposure, below multilayer coverage.

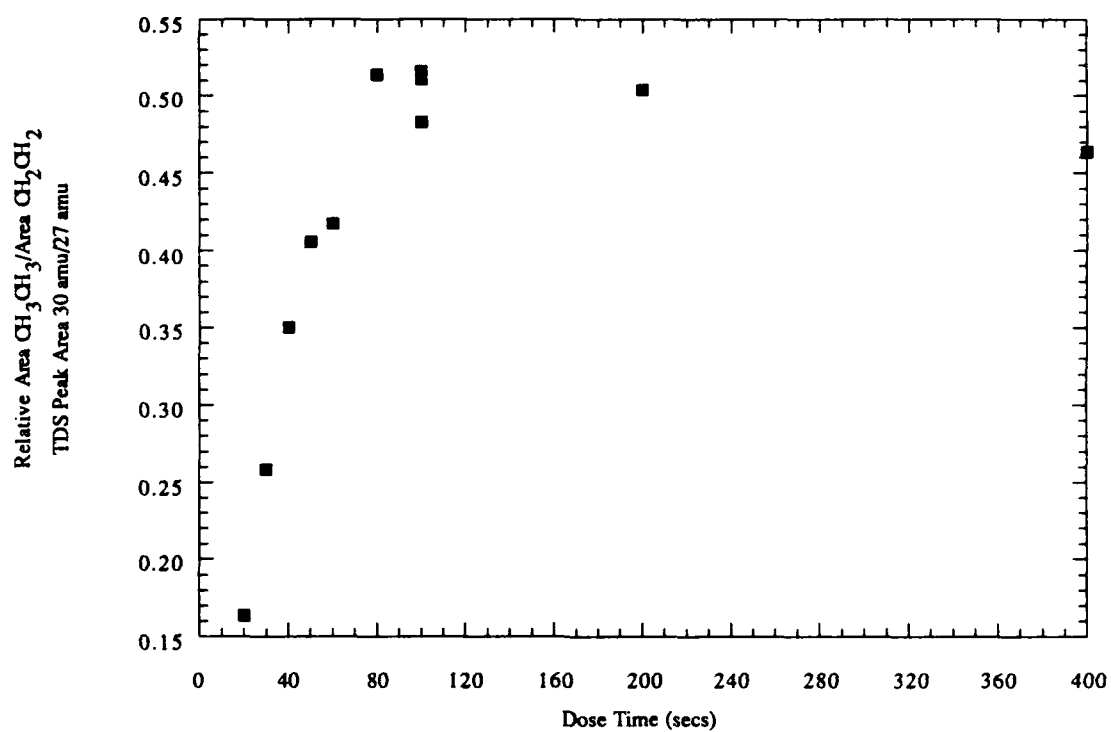


Figure 6. Ethane-to-Ethylene Branching Ratio vs. $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ exposure time.

Reaction Scheme of the Thermal Decomposition of $\text{Bi}(\text{CH}_3)_3$

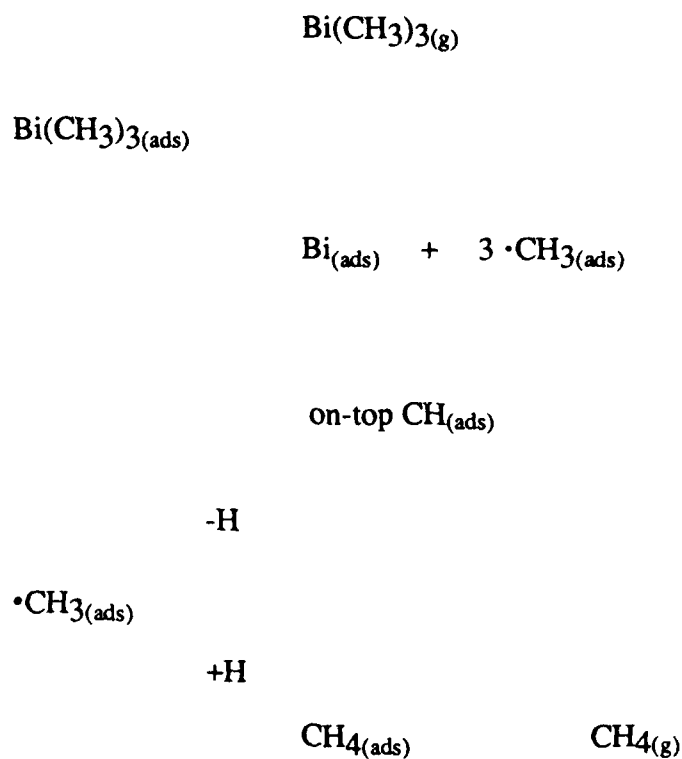


Figure 8a. Reaction scheme for $\text{Bi}(\text{CH}_3)_3$ chemistry on the Pt(111) surface. $\text{Bi}(\text{CH}_3)_3$ is molecularly adsorbed onto the 110K Pt(111) surface. At 158K, there is some fraction of parent desorption. The remaining methyl radical follows two reactions pathways at approximately 280K. The first is dehydrogenation leading to the formation of an atop methylidyne species. The second is hydrogenation leading to the reaction rate limited desorption of methane.

Reaction Scheme of the Thermal Decomposition of $\text{Bi}(\text{CH}_2\text{CH}_3)_3$

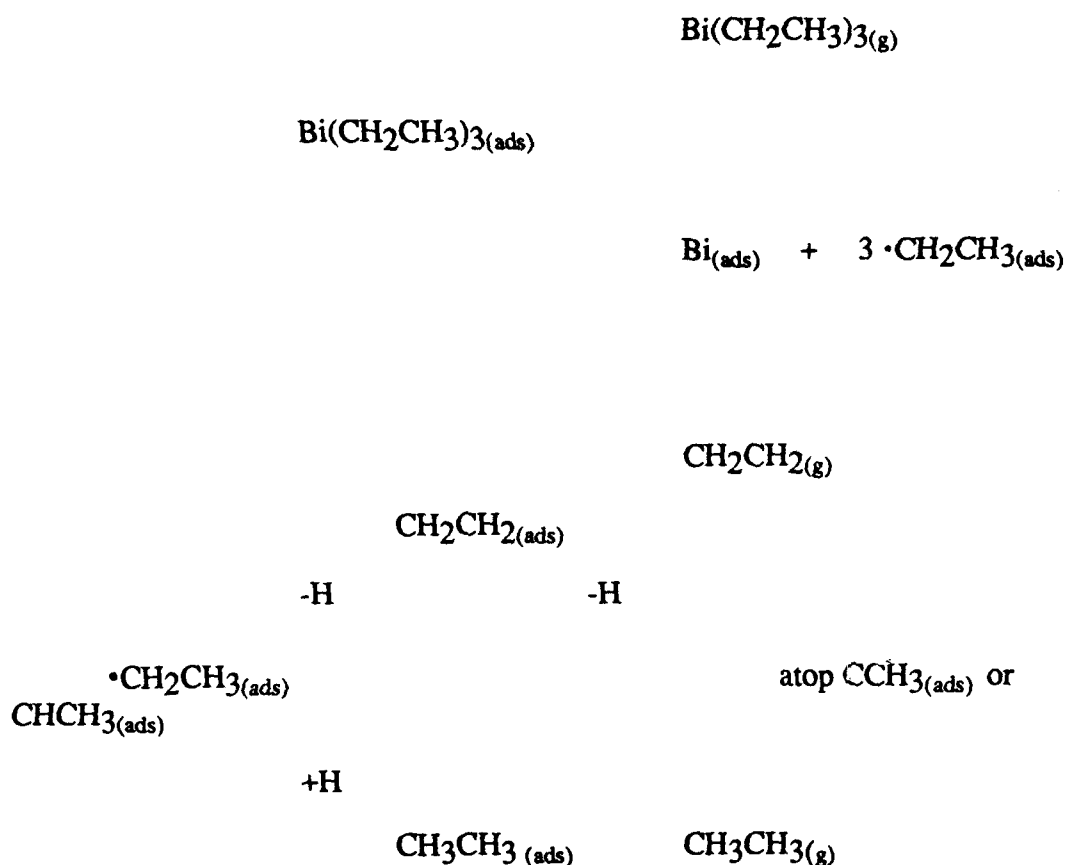


Figure 8b. Reaction scheme for $\text{Bi}(\text{CH}_2\text{CH}_3)_3$ chemistry on the Pt(111) surface.

$\text{Bi}(\text{CH}_2\text{CH}_3)_3$ is molecularly adsorbed onto the 110K Pt(111) surface. At 158K, there is some fraction of parent desorption. The remaining ethyl radical follows two reactions pathways at approximately 285K. The first is dehydrogenation leading to the formation of ethylene. The ethylene formed will either desorb into the gas phase or dehydrogenate to form an atop CCH_3 or CHCH_3 species. The second pathway that ethyl radical may undergo is hydrogenation leading to the reaction rate limited desorption of ethane.