THERMAL DECOMPOSITION OF C_2H_5I ON Ag(111)

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The decomposition of C_2H_5I on Ag(111) has been studied using temperature programmed desorption (TPD), work-function change measurements ($\Delta\Phi$) and X-ray photoelectron spectroscopy (XPS). Adsorption of C_2H_5I at 100 K is mostly molecular with little dissociation. C-I bond cleavage starts around 110 K. Below 1 monolayer coverage, all adsorbed C_2H_5I(a) dissociates to C_2H_5(a) and I(a) during TPD. C_2H_5(a) undergoes only recombination, producing gas phase butane (C_4H_{10}) around 190 K. No C-H or C-C bond cleavage takes place. On D/Ag(111), hydrogenation of C_2H_5(a) to C_2H_5(g) occurs readily between 150 and 220 K.

1. Introduction

The thermal and photochemistry of alkyl halides on metal surfaces has received considerable attention in this group [1–12], as well as in others [13–20]. An inherent property of these compounds is that their thermal dissociation or photodissociation produces adsorbed C_xH_y fragments. Since these fragments play an important role in CO hydrogenation and in heterogeneous hydrocarbon catalysis, the surface chemistry of these compounds is especially interesting. As a part of our continuing investigation of alkyl halides on a variety of metal surfaces, we report in this paper the thermal dissociation of ethyl iodide on Ag(111) studied using TPD, $\Delta\Phi$ and XPS. The unique property of Ag(111), compared to Group A transition metal surfaces, is that CH_3 [5] and C_2H_5 fragments on it undergoes only recombination and hydrogenation, if surface H is present, but not dehydrogenation.

2. Experimental

All experiments were performed in an ion-pumped UHV chamber, which has been described previously [21]. The chamber was equipped with a Perkin-Elmer double-pass CMA with coaxial electron gun, a VG Instruments dual-anode X-ray source, a helium discharge lamp, a sputtering gun and a UTI 100C quadrupole mass spectrometer (QMS). The chamber had an auxiliary 170 l/s turbomolecular pump and a titanium sublimation pump. The base pressure was 4×10^{-10} Torr.

The mounting and cleaning procedure of the Ag(111) crystal has been reported previously [22]. The sample was cooled to 100 K with liquid nitrogen. The temperature was measured with a chromel-alumel thermocouple spot-welded to a Ta loop that was pressed into a hole drilled in the edge of the crystal. For TPD, a temperature ramp rate of 2.5 K/s was generated by a home-made controller. XPS was referenced to the Ag($3d_{5/2}$) binding energy of 367.9 eV [23] and utilized 1253.6 eV MgKα incident radiation and a band pass of 50 eV on the CMA. $\Delta\Phi$ was measured from the low kinetic energy threshold of secondary electron emission of HeI UPS spectra.

Ethyl iodide (99.5%, Matheson) was further purified using several freeze-pump-thaw cycles in liquid nitrogen prior to use. It was dosed through a microchannel doser about 7 mm away from the sample. The pressure rise during dosing was 2×10^{-10} Torr at the ion gauge with the sample facing away from the doser. The absolute exposure of Langmuirs with this method of dosing was unknown. Surface deuterium was prepared by dosing atomic D, generated from the QMS filament, to the surface.

3. Results

3.1. TPD

Molecular C_2H_5I desorption was not observed in TPD below monolayer (ML) exposures. Multilayer C_2H_5I desorbs at 140 K. TPD was used to monitor m/e's corresponding to H_2 and C_{1-4} hydrocarbons. However, no H_2, CH_4, C_2H_6 or C_3H_8 was observed. The other m/e's observed all track one another and are typical of those for butane (C_4H_{10}), with $m/e = 43$ the strongest and $m/e = 29$ the next most intense. After TPD to 300 K, AES showed iodine, but no carbon, left on the surface. These results show that there is no C-H and C-C bond cleavage for C_2H_5I on Ag(111).

Figure 1 shows the C_4H_{10} TPD spectra after dosing various amounts of C_2H_5I on Ag(111) at 100 K. The peak temperature shifts to slightly higher temperature and the peak broadens as C_2H_5I coverage increases. At monolayer coverage (fig. 1e), two shoulders, one at lower temperature (175 K) and the other at higher temperature (220 K), appear. At C_2H_5I coverages > 1 ML, C_4H_{10} TPD does not differ from fig. 1e, and the AES intensity of surface iodine does not increase. This indicates that the thermal dissociation of C_2H_5I occurs only at the first monolayer.

Figure 2 shows the TPD results after dosing about 1 ML C_2H_5I on atomic D preadsorbed Ag(111). The D_2 desorption, peak at 190 K, is in agreement with a previous report [24]. With D(a), a significant amount of ethane is produced

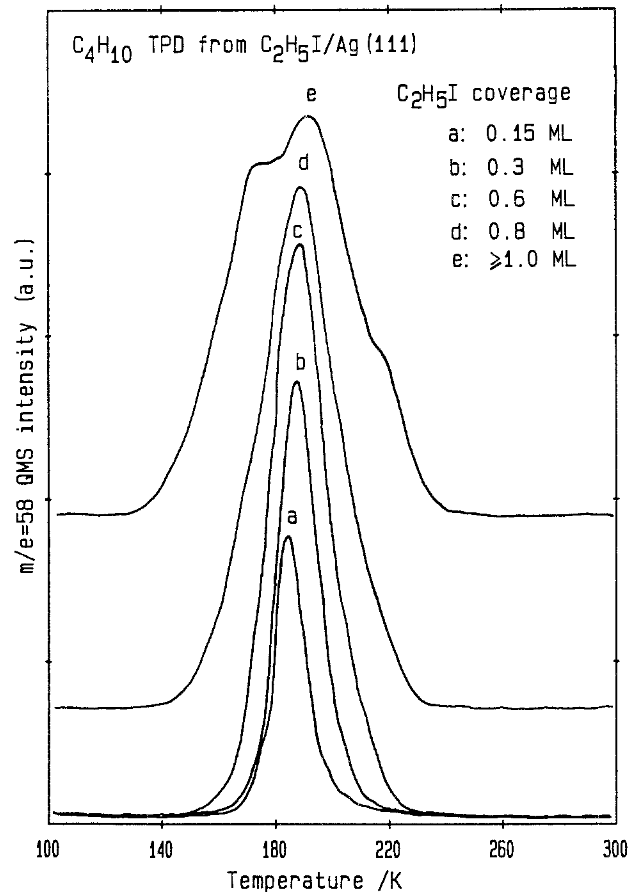

Fig. 1. TPD spectra of butane (C_4H_{10}) from Ag(111) exposed with various amounts of C_2H_5I at 100 K. The temperature ramping rate was 2.5 K/s.

between 150 and 220 K and the major peak for C_4H_{10} almost disappears (a peak remains at 220 K). This peak matches the higher temperature shoulder found in the absence of D(a) (fig. 1e). As on the clean surface, no molecular C_2H_5I desorbs and neither dehydrogenation nor C-C bond cleavage take place on D/Ag(111), as evidenced by the absence of HD and methane in TPD and the absence of carbon on the surface after TPD. C_2H_5D is the only hydrogenation product.

3.2. $\Delta\Phi$

Figure 3 shows $\Delta\Phi$ as a function of annealing temperature for the surfaces dosed with 0.5 and 1 ML C_2H_5I at 100 K. $\Delta\Phi$ at 100 K is -1.0 eV at 0.5 ML and -1.1 eV at 1 ML coverage of C_2H_5I. The surface work function increases monotonically with increasing temperature and becomes constant with $\Delta\Phi = 0.57$

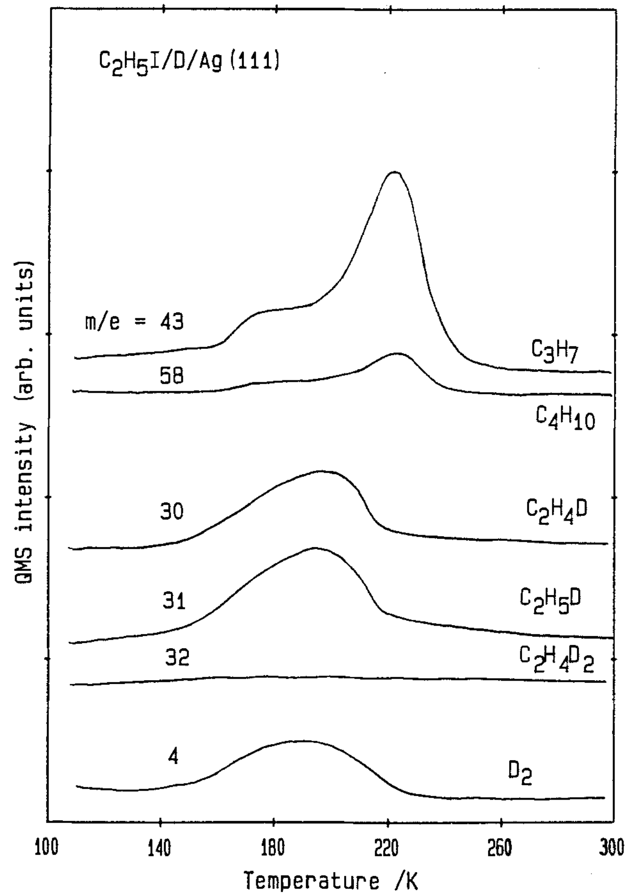

Fig. 2. TPD spectra of $m/e = 43$ ($C_3H_7^+$), 58 ($C_4H_{10}^+$), 32 ($C_2H_4D_2^+$), 31 ($C_2H_5D^+$), 30 ($C_2H_4D^+$) and 4 (D_2^+) after dosing about 1 ML C_2H_5I on D/Ag(111) at 100 K. The temperature ramping rate was 2.5 K/s.

eV at 230 K for 0.5 ML C_2H_5I/Ag (111) and $\Delta\Phi = 0.9$ eV at 260 K for 1 ML C_2H_5I/Ag (111). Since no molecular C_2H_5I desorbs at coverages below 1 ML and since no C_4H_{10} desorbs below 140–160 K, depending on the C_2H_5I coverage, the change in surface work function reflects the processes of C_2H_5I dissociation below 140–160 K and both C_2H_5I dissociation and C_4H_{10} desorption above 140–160 K. The work function decrease upon the adsorption of C_2H_5I indicates that the adsorption is probably through the I atom; both the permanent dipole orientation and charge redistribution involving the lone pair electrons centered on the I atom cause the drop.

That $\Delta\Phi$ is positive when there is only I(a) on the surface indicates that I(a) withdraws electron density from the surface. The increase in surface work function when the temperature of C_2H_5I/Ag is increased signals the conversion

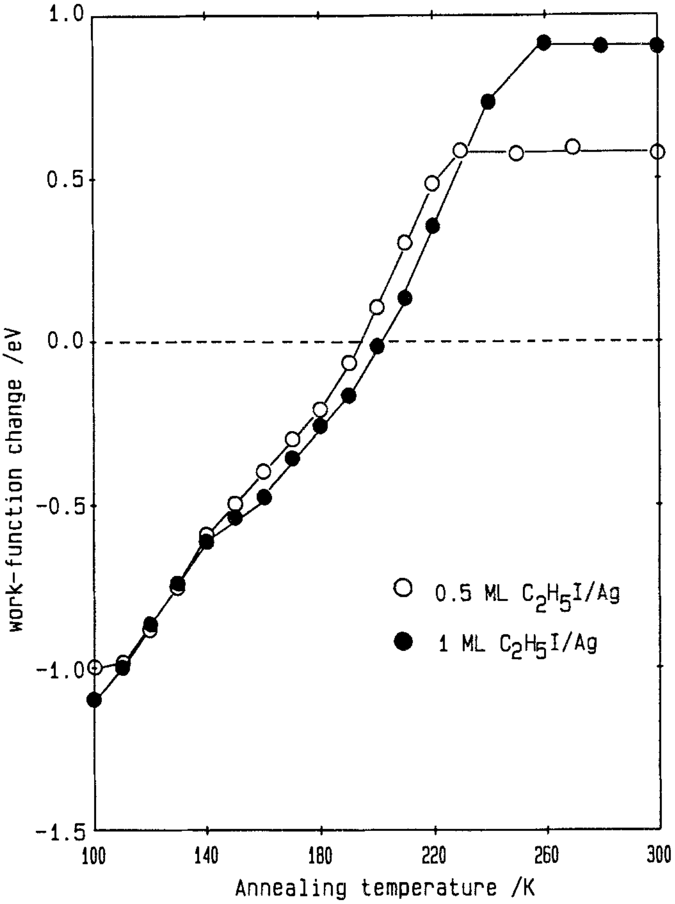

Fig. 3. $\Delta\Phi$ as a function of annealing temperature for the Ag(111) surface dosed with 0.5 ML (open circle) and 1 ML (filled circle) C_2H_5I at 100 K.

from $C_2H_5I(a)$ to I(a). Thus, we conclude that the dissociation of C_2H_5I starts at 110 K and is complete at 230 and 260 K for 0.5 and 1 ML C_2H_5I, respectively.

3.3. XPS

To gain further information about the dissociation process of C_2H_5I, we measured binding energies (BE) at 100 K of I($3d_{5/2}$) (fig. 4) and C(1s) (fig. 5) as a function of annealing temperature for the surfaces dosed with 0.5 ML (left panels) and 1 ML (right panels) C_2H_5I. The binding energy of I($3d_{5/2}$) is very sensitive to the dissociation of the C-I bond [5]. At 100 K, the BE of I($3d_{5/2}$) is 620.4 eV for 0.5 ML and 620.3 eV for 1 ML C_2H_5I coverage. After annealing to 120 K, the I($3d_{5/2}$) XPS peak broadens at lower BE. As the surface temperature further increases, the whole peak shifts to lower BE. After annealing to > 250 K, I($3d_{5/2}$) XPS shows only a single peak at 618.5 eV, and no further changes in BE

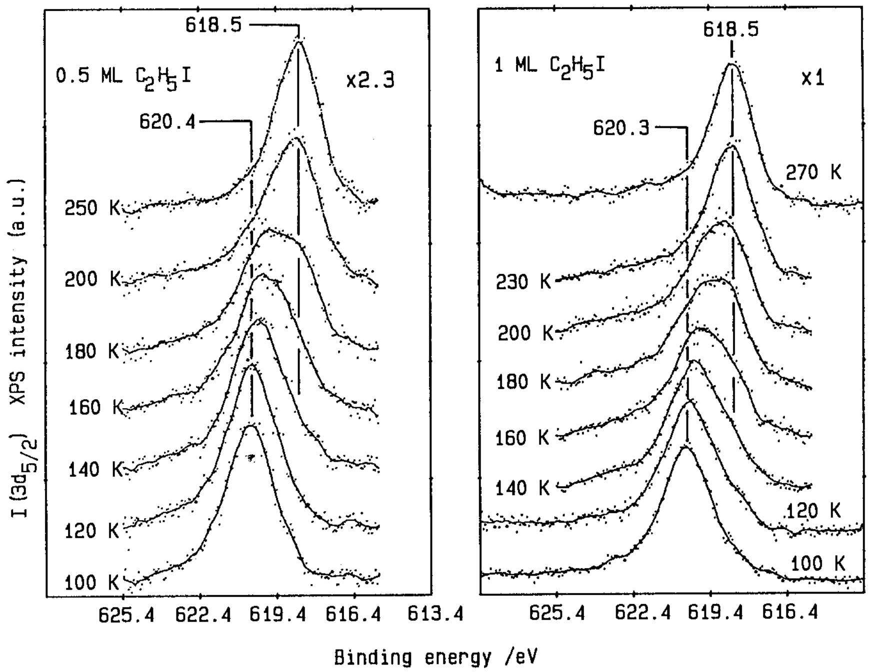

Fig. 4. I($3d_{5/2}$) XPS spectra for surfaces exposed with 0.5 ML (left panel) and 1 ML C_2H_5I (right panel) at 100 K and annealed to the indicated temperatures.

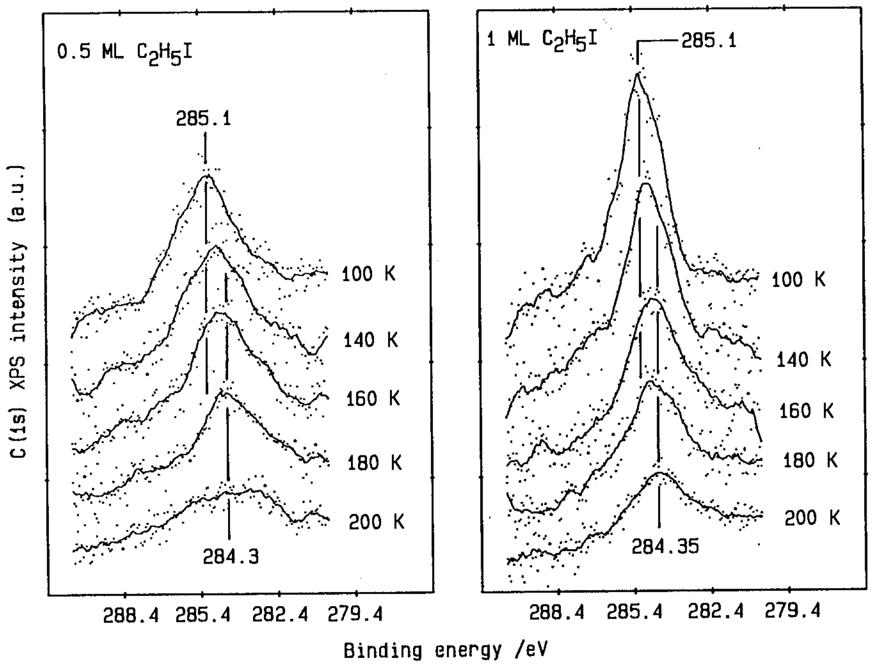

Fig. 5. C(1s) XPS spectra for surfaces exposed with 0.5 ML (left panel) and 1 ML C_2H_5I (right panel) at 100 K and annealed to the indicated temperatures.

take place. The peak at 618.5 eV has been attributed to surface I(a) [5]. The change in BE of I($3d_{5/2}$), therefore, indicates the dissociation of the C-I bond.

We conclude from fig. 4 that the dissociation of C_2H_5I is not complete until about 250 K for both 0.5 and 1 ML C_2H_5I, which is consistent with $\Delta\Phi$ results, as well as TPD results which show C_4H_{10} desorption ending just below 250 K. Comparing the peak at 100 K with that after annealing to 250 K, we find that the peak at 100 K is slightly broader. This probably indicates that slight dissociation of C_2H_5I takes place even at 100 K. However, such slight dissociation may be induced by X-ray and secondary electron emission during XP spectra acquisition. Other factors, such as extraatomic relaxation or related phenomena in molecularly adsorbed C_2H_5I, may also account for the broader peak for I($3d_{5/2}$) at 100 K than at 250 K. The I($3d_{5/2}$) XPS area does not change with increasing surface temperature, consistent with the TPD result indicating no molecular C_2H_5I desorption below 1 ML coverages.

The BE for C(1s) is 285.1 eV at 100 K. The peak for C(1s) also shifts to lower BE as the surface temperature increases. The peak area decreases above 160 K for 0.5 ML and 140 K for 1 ML C_2H_5I. These temperatures are consistent with the onset of C_4H_{10} desorption. Since TPD indicates that no C-H or C-C bond cleavage takes place, the shift in BE of C(1s) at a temperature where no C_4H_{10} desorbs is attributed to the conversion of C_2H_5I(a) to C_2H_5(a). In a recent photochemical study of C_2H_5Cl on Ag(111), we also found a shift of C(1s) to lower BE when C_2H_5Cl was photolyzed [9].

4. Discussion

Although adsorption of C_2H_5I on Ag(111) at 100 K is mainly molecular, no chemisorbed C_2H_5I desorbs in TPD. This is in contrast with the CH_3I/Ag(111) system, in which most of the chemisorbed CH_3I desorbs reversibly around 200 K with only 35% of the monolayer undergoing dissociation. The reactions of chemisorbed CH_3I and C_2H_5I during TPD involve two competing channels, molecular desorption and dissociation. The reaction rates depend on the activation energies of these two channels. CH_3I starts to dissociate around 130 K [5], higher than C_2H_5I. By way of comparison, chemisorbed C_2H_5Cl on Ag(111) desorbs at 154 K [9], while CH_3Cl desorbs at 126 K [5], indicating stronger binding of C_2H_5Cl to Ag than CH_3Cl. The binding of chemisorbed C_2H_5I to Ag is, therefore, also expected to be stronger than CH_3I. Thus, the difference in activation energy between molecular desorption and dissociation is larger for C_2H_5I than for CH_3I, accounting for more dissociation of C_2H_5I than CH_3I.

Molecular C_4H_{10} dosed onto Ag(111) at 100 K desorbs in a peak at 153 K. Therefore, the C_4H_{10} desorbing with a peak near 180 K and setting in near 160 K (fig. 1) does not form at low temperatures; rather, it is limited by C_2H_5(a) recombination. This is consistent with XPS results, (figs. 4 and 5), which show major changes after annealing at 160 K. Above 160 K, further dissociation of C_2H_5I and desorption of C_4H_{10} take place simultaneously. The C(1s) and I($3d_{5/2}$) XP spectra also indicate that $C_2H_5I(a)$ and $C_2H_5(a)$ coexist above 160 K.

Based on TPD and XPS results, we propose the following reaction mechanism for chemisorbed $C_2H_5I(a)$,

$$C_2H_5I(a) \rightarrow C_2H_5(a) + I(a) \tag{1}$$

$$C_2H_5(a) + C_2H_5(a) \rightarrow C_4H_{10}(g) \tag{2}$$

$$C_2H_5(a) + C_2H_5I(a) \rightarrow C_4H_{10}(g) + I(a) \tag{3}$$

When chemisorbed C_2H_5Cl on Ag(111) photodissociates, a C_4H_{10} desorption peak is observed between 175 and 190 K, depending on the coverage [9]. Since C_2H_5Cl does not thermally dissociate during TPD, and since molecular C_2H_5Cl desorbs below 175 K, the C_4H_{10} desorbed is from the recombination of surface $C_2H_5(a)$. Therefore, reaction (2) above is facile. Reaction (3) gains support from the fact that C_2H_5I is used as a trapping agent for surface hydrocarbon fragments [25]. We believe that reactions (2) and (3) take place simultaneously below intermediate C_2H_5I coverages because there is only one C_4H_{10} desorption peak. At higher C_2H_5I coverages, the surface becomes crowded so that $C_2H_5(a)$ recombines at lower temperature, accounting for the shift of C_4H_{10} TPD onset to lower temperature, and producing the lower temperature shoulder (175 K) at very high coverages (fig. 1e). At very high coverages, some $C_2H_5I(a)$ may be preserved to dissociate at higher temperature. This may account for the higher temperature shoulder (220 K) in fig. 1e. This shoulder is $C_2H_5I(a)$ decomposition limited, that is, $2C_2H_5I(a) \rightarrow C_4H_{10}(g) + I(a)$. This is supported by the TPD results for C_2H_5I/D/Ag(111). On D/Ag(111), most C_4H_{10} desorption (220 K) takes place after the surface D and C_2H_5D desorbs. This undeuterated C_4H_{10} is attributed to reaction $C_2H_5I(a)$ which is preserved to temperatures above 220 K.

The desorption of C_4H_{10} does not follow second order kinetics which is expected for the recombination of $C_2H_5(a)$. The desorption of C_4H_{10} formed from $C_2H_5(a)$ derived from photodissociation of C_2H_5Cl/Ag(111) [9] and the desorption of C_2H_6 from CH_3I/Ag(111) [5] do not follow second desorption kinetics either. Even for the desorption of surface H on Ag(111) [24], fractional order kinetics instead of second order kinetics was observed. The deviation of C_4H_{10} desorption from second order kinetics is probably due to island formation of $C_2H_5(a)$, just as for H(a) [24]. The determination of kinetic parameter is, therefore, not attempted here.

It is interesting that C_4H_{10} is the only product of $C_2H_5(a)$ on Ag(111), unlike $C_2H_5(a)$ on Pt(111) [11,12], which undergoes both dehydrogenation and hydrogenation, producing $C_2H_4(g)$, $C_2H_6(g)$ and $H_2(g)$ with surface $CH_3C\equiv$ and H as intermediates. Accordingly, the dehydrogenation of $C_2H_5(a)$ on Ag(111) is much slower than its recombination to give C_4H_{10}. This conclusion is consistent with the catalytic properties of silver, which exhibits much lower activity in dehydrogenation reactions than, for example, the transition metals [26]. In contrast to its dehydrogenation activity, hydrogenation of C_2H_5(a) on Ag(111) is fairly easy, occurring below 200 K. Other studies of C_xH_y fragments on Ag(111) also indicate that the recombination or polymerization and hydrogenation, if surface H is present, of these fragments occur readily [27].

Adsorbed CH_3(a) from CH_3I dissociation on Ag(111) also undergoes only recombination to give ethane [5]. However, the recombination of CH_3(a) takes place at 257 K, much higher than C_2H_5(a), indicating that CH_3(a) is more stable than C_2H_5(a) on Ag(111). This difference in stability probably arises from the differences in size between the two groups or perhaps differences in steric repulsive interaction.

In summary, chemisorbed C_2H_5I on Ag(111) at 100 K dissociates to C_2H_5(a) and I(a) during TPD with no detectable molecular desorption. C_2H_5(a) is less stable than CH_3(a). C_2H_5(a) recombines around 190 K, producing C_4H_{10}. No hydrogenation and dehydrogenation are involved in the reaction of C_2H_5(a). On D/Ag(111), C_2H_5(a) is readily hydrogenated to C_2H_5D(g).

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