A comparative study of the thermal stability and reactions of CH_2, CH_3 and C_2H_5 species on the Pd(100) surface

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Received 23 December 1993; accepted 7 April 1994

Adsorbed CH_2, CH_3 and C_2H_5 moieties were produced on Pd(100) at 90 K by photo-induced dissociation of the corresponding iodo compounds, and their thermal reactions were established.

Keywords: adsorption of CH_3I, C_2H_2I and C_2H_5I; photo-induced formation of CH_3, CH_2 and C_2H_5 species; decomposition and coupling of CH_x fragments on Pd(100)

1. Introduction

Hydrocarbon moieties, C_xH_y, are important reaction intermediates in the catalytic synthesis of hydrocarbons and in the transformation of CH_4 into C_2H_6 [1–3]. The study of their bonding and reactivity on catalysts is hampered by the fact that their reactions occur at relatively high temperatures, where the lifetime of the species C_xH_y on the catalyst surface is very limited. One possibility for the production of a fragment C_xH_y with a desired composition is the thermal dissociation of a corresponding halogenated hydrocarbon [4–9]. However, as demonstrated in previous papers [10–12], the complete dissociation of these compounds on Pd surfaces (even the least stable iodo compounds) requires an elevated temperature at which decomposition of the products proceeds in parallel with their formation. This problem can be circumvented by the photo-induced dissociation of the halogenated compounds at low temperature, following their adsorption on metal surfaces, a process which has been observed on the Pd(100) surface [10–12,14,15].

The aim of the present work is to produce CH_2, CH_3 and C_2H_5 moieties on the Pd(100) surface by photo-induced dissociation of the corresponding iodo com-

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pounds at 90 K, and to compare their thermal reactions by means of photoelectron (XPS and UPS) and thermal desorption (TPD) spectroscopy. It was recently found that methane molecules decompose (presumably through the formation of species CH_x) at well-measurable rates on Pd single crystal on Pd(567) [16], and on supported Pd [17,18]. In the latter case, the formation of ethane was also reported. Supported Pd effectively catalysed the CH_4–CO_2 reaction too, to yield synthesis gas [19,20].

2. Experimental

The experiments were carried out in an ultrahigh vacuum system with a background pressure of 5×10^{-10} mbar. The system was equipped with an electrostatic hemispherical analyser (Leybold–Heraus LHS-10), a differentially pumped UV photon (He I, II) source for UPS, and Al Kα X-ray for XPS. All binding energies are referred to the Fermi level with the Pd($3d_{5/2}$) peak at 335.1 eV. The UV light source was a focussed 100 W Hg lamp. The light passed through a high-purity sapphire window into the vacuum chamber [10–12]. The oriented 4N9 purity, disk-shaped crystal was cleaned by cycles of argon ion bombardment, annealing (1000 K), oxygen treatment and short annealing (1100 K) [10–12]. All the compounds used were the products of Fluka. They were degassed and purified by freeze–pump–thaw cycles prior to use and stored in glass vials shielded from light to prevent photodecomposition.

3. Results and discussion

The easiest way to establish the dissociation of alkyl and alkenyl iodides on metal surfaces is via the binding energy (BE) of I($3d_{5/2}$), as it differs by about 1.5–2.0 eV for molecularly adsorbed iodine compounds and for atomically adsorbed iodine. The intensity of the XPS peak for atomically adsorbed I is unaltered up to the temperature of desorption of I from Pd(100), 700–750 K [10–12].

3.1. THERMAL STABILITY AND REACTIONS OF ADSORBED CH_3

The monolayer adsorption of CH_3I on Pd(100) caused a work function decrease of 1.54 eV. CH_3I adsorbed dissociatively at submonolayer coverages, and molecularly at high coverages. The adsorbed CH_3I monolayer is characterized by a BE of 620.5 eV for I($3d_{5/2}$) and 284.5 eV for C(1s) (fig. 1). As indicated by the BE for adsorbed I, complete dissociation was achieved by illumination for about 20 min. The occurrence of this process caused no shift in the BE for C(1s).

In the He II UPS, the species CH_3 formed in the photodissociation of CH_3I at 90 K is characterized by a photoemission line at 8.5 eV [10] (fig. 2A). With increase of the temperature, the peak attenuated above 140–150 K and was detect-

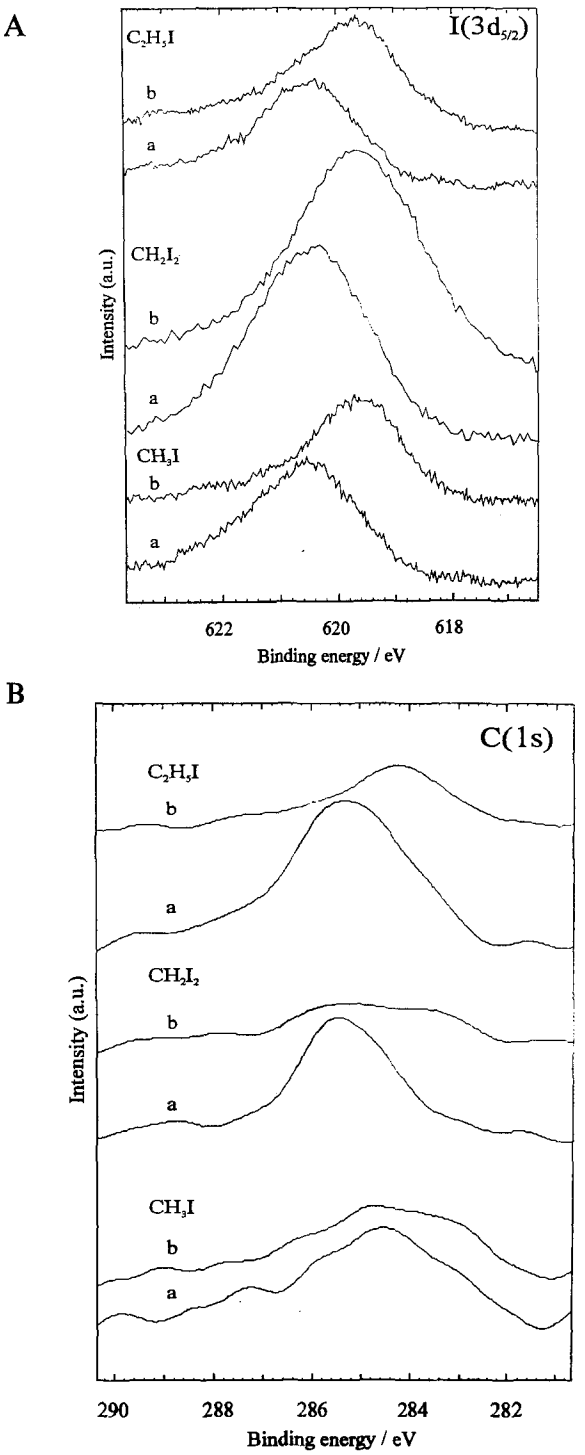

Fig. 1. XPS of $I(3d_{5/2})$ (A) and C(1s) (B) of adsorbed CH_3I, CH_2I_2 and C_2H_5I (monolayer) before illumination (a) and after complete photo-induced dissociation (b).

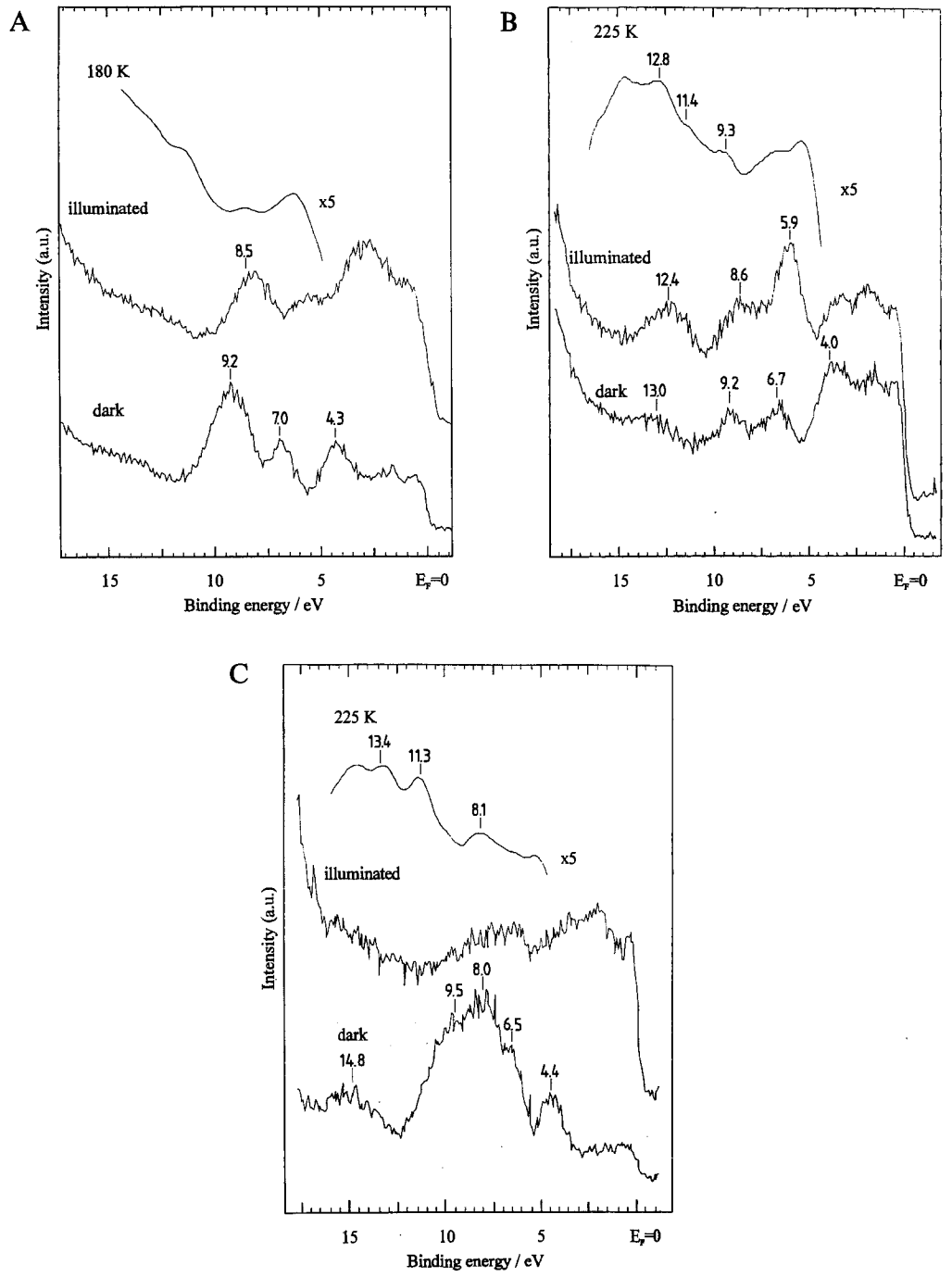

Fig. 2. He II UPS spectra of adsorbed CH_3I (A), CH_2I_2 (B) and C_2H_5I (C) at monolayer, after their complete photo-induced dissociation at 90 K and after subsequent heating. The uppermost spectra are difference spectra. In order to see clearly the characteristic signals of CH_3I in UPS, its coverage was higher than monolayer.

able up to 250 K. There was no spectral indication of the transitory existence of the species CH_2 or CH, which means that if they were formed they decomposed further rapidly.

Post-irradiation TPD revealed that the main product of the decomposition of adsorbed CH_3 was methane ($T_p = 170$ K). Coupling of the CH_3 and that of CH_2 formed in its decomposition was very limited, as indicated by the small amount of ethane and ethylene desorbed ($T_p = 175$ K). The amount of C_2 compounds formed was only 3.5% of that of methane.

3.2. THERMAL STABILITY AND REACTIONS OF ADSORBED CH_2

The monolayer adsorption of CH_2I_2 results in a work function decrease of 0.85 eV. The adsorption was molecular at and above the monolayer, but the dissociation of CH_2I_2 on Pd(100) occurred at low coverage. The BE values for $I(3d_{5/2})$ and C(1s) at monolayer coverage were 620.4 and 285.5 eV, respectively (fig. 1). A shift in I BE occurred even at the shortest irradiation time, $\sim$ 1 min, but the BE value characteristic for atomically adsorbed I was reached only after irradiation for 5–7 min. In this case, the C(1s) peak was at 283.6 eV.

He II photoelectron spectra of the adsorbed layer after completion of the photo-induced dissociation of CH_2I_2 are displayed in fig. 2B. The characteristic photoemission signal for adsorbed CH_2 at low coverage was at 5.5 eV, which is in agreement with the value given for this species by Steinbach et al. [21]. When a monolayer of adsorbed CH_2I_2 was illuminated for 5 min, all the signals characteristic of adsorbed CH_2I_2 disappeared, an intense peak developed at 5.9 and weaker ones at 8.6 and 12.4 eV. As the positions of these photoemission lines approximated well to those observed following ethylene adsorption on Pt metals [16–18], we may conclude that a significant proportion of the CH_2(a) produced in the photo-induced dissociation process dimerized into adsorbed C_2H_4 species even at 90 K. Annealing the adsorbed layer showed the characteristic features of di-σ-bonded ethylene, which consists of the transient formations of both vinyl and ethylidyne [11].

In accord with this, post-irradiation TPD showed that the major product of the reactions of adsorbed CH_2 at monolayer was ethylene, which desorbed in two peaks, $T_p = 230$ and 320 K. The formation of methane, indicative of self-hydrogenation of the species CH_2, also occurred ($T_p = 178$–238 K). The ratio C_2H_4/CH_4 in the post-irradiation experiment was 3.0–3.5. These features are in harmony with the theoretical calculation, which showed that the activation energy of coupling of the species CH_2 on metal surfaces is only 6–9 kcal/mol [22].

3.3. THERMAL STABILITY AND REACTIONS OF ADSORBED C_2H_5

The work function decrease of the Pd(100) surface following the adsorption of C_2H_5I amounted to 2.00 eV. Independently of the coverage, C_2H_5I adsorbed molecularly on Pd(100) at 90 K. The $I(3d_{5/2})$ and C(1s) binding energies for the

C_2H_5I monolayer were 620.4 and 285.2 eV (fig. 1). The C(1s) peak clearly consisted of two overlapping peaks at 285.7 and 285.0 eV: the higher value can be ascribed to the carbon directly bonded to the iodine. Complete dissociation of the C_2H_5I required illumination for 7 min. In this case the C(1s) signal was at 284.1 eV. On the assumption that the fragment C_2H_5 produced in the photodissociation of C_2H_5I is stable at 90 K, we attribute this peak to the C_2H_5 species. At the same time, photoemission lines appeared at 5.5–9.0 and 12.5 eV in the He II photoelectron spectra (fig. 2C). When the illuminated layer was heated, an observable change occurred at 169 K: the photoemission peaks moved to 6.2, 8.8 and 12.8 eV, which are nearly the same as observed for adsorbed ethylene. Further changes in the spectra correspond well to those observed during annealing of adsorbed ethylene.

Post-irradiation TPD indicated the formation of ethylene above 150 K (T_p = 190 and 280 K) and also ethane (T_p = 180 K). However, no methane or C_4 compounds were detected in the desorbing products. Accordingly, the species C_2H_5 started to dehydrogenate on the Pd(100) surface even above 150 K, to give adsorbed C_2H_4. This process was complete at around 200 K. A competitive reaction was the hydrogenation of C_2H_5 moieties by the hydrogen in the background and by that produced in the dehydrogenation.

A dramatic change occurred in the reaction of C_2H_5 species in the presence of Zn atoms produced by thermal- and photodissociation of $(C_2H_5)_2Zn$. In this case significant amounts of butene and butane were formed in addition to ethane and ethylene (fig. 3). We may assume that Zn adatoms, occupying the most active sites on Pd surface, inhibit its dehydrogenation effect on adsorbed CH_3, thereby facilitating the coupling of C_xH_y fragments. Further studies on the effects of Zn adatoms are in progress in our laboratory.

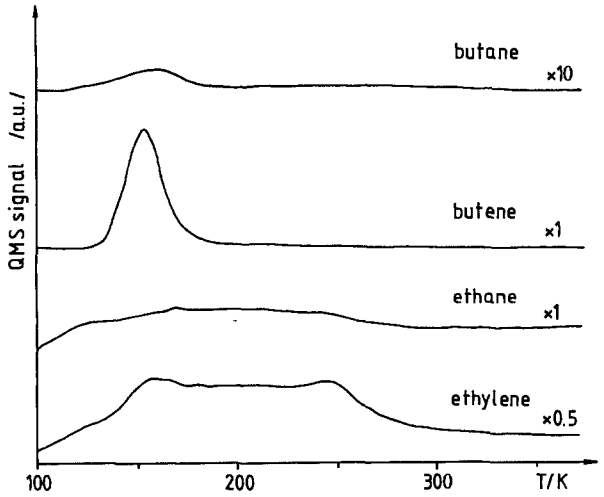

Fig. 3. TPD spectra for the products formed in the reactions of C_2H_5 produced by illumination of adsorbed $(C_2H_5)_2Zn$ (monolayer) at 90 K for 60 min.

4. Conclusions

(i) The species CH_3 is stable on the Pd(100) surface up to 150 K, and undergoes self-hydrogenation at 150–250 K to yield methane. Its coupling to give ethane is very limited. (ii) The species CH_2 is also self-hydrogenated to methane at 150–170 K, but, in contrast with CH_3, at high concentration it readily dimerizes to ethylene, even at 90 K. (iii) C_2H_5 is stable up to 150–160 K. Above this temperature, both the dehydrogenation of C_2H_5 to ethylene and its hydrogenation to ethane occur, without any sign of its coupling. However, the presence of Zn atoms greatly promoted the coupling reaction to butane and butene.

Acknowledgement

This work was supported by the Hungarian Academy of Sciences through Grant OTKA 95700.

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