rather than the hydrophobic tail part. An interesting result of this work is that the orientation of PNP in the close-packed monolayer that is obtained by assuming a sharp distribution of θ is almost the same as the reported orientation angle of C–OH bond.[9] This might indicate the existence of an orienting interaction between PNP and the C–OH part of the monolayer.

A further interesting result in these SH studies of fatty acids with PNP is our observation of huge fluctuations in the SH signal at low lipid densities, 150, 300, and 600 Å[2]. These fluctuations reflect the interfacial inhomogeneity due to aggregates and isolated fatty acid molecule domains and are expected to be present in a gas–liquid coexistence region. Orientational and dynamic information on these aggregates as deduced from the observed time-dependent fluctuations will appear in a separate publication.

Conclusions

In summary, we have shown how SHG may be employed in the study of the structure and population of a solute molecule at an interface containing long-chain molecules. With increasing packing density of fatty acid at the air/water interface, (1) the population of PNP at air/water interface first increases and then decreases, (2) the long axis of PNP is increasingly aligned toward the surface normal, and (3) the behavior of *p*-nitrophenol in pentadecanoic and hexadecanoic acid monolayers is insensitive to the π–A phase diagram in the liquid-expanded–liquid-condensed region. This implies that the coadsorption or "penetration" of PNP happens preferentially in the polar head group of a fatty acid monolayer. Furthermore, huge time-dependent fluctuations in the SH signal were observed at low lipid coverages and are attributed to the inhomogeneity of the interface as expected in the lipid gas–liquid coexistence region.

Effects of Illumination on the Surface Behavior of CH₃Cl on Clean and K-Dosed Pd(100) Surfaces

Frigyes Solymosi,* János Kiss, and Károly Révész

Institute of Solid State and Radiochemistry and Reaction Kinetics Research Group, The University of Szeged, P.O. Box 105, Szeged, 6701, Hungary (Received: October 30, 1989; In Final Form: January 1, 1990)

Irradiation of adsorbed CH₃Cl on Pd(100) at 90 K with low-intensity ultraviolet light from a high-pressure Hg lamp induced the cleavage of C–Cl bond to give adsorbed CH₃ and Cl on a clean Pd surface and significantly enhanced the extent of dissociation of CH₃Cl for a K-dosed surface.

Introduction

In previous papers we showed that CH₃Cl adsorbs weakly and molecularly on a clean Pd(100) surface under ultra-high-vacuum conditions.[1,2] However, potassium adatoms markedly influenced its adsorption and caused C–Cl bond cleavage even at around 131 K. The effect of potassium was attributed to enhanced electron donation from the Pd to the adsorbed molecule (at low K coverage) and to a direct interaction between CH₃Cl and K (at and above monolayer). The present work demonstrates that irradiation of the adsorbed layer with UV light produces a profound effect on both surfaces.

Experimental Section

Experiments were carried out in a standard ultra-high-vacuum chamber equipped with facilities for AES, UPS, XPS, TDS, and work function measurements. Sample preparation and cleaning and potassium deposition were described in a previous communication.[3] A coverage of $\Theta_K = 0.5$ (0.5 K atoms per surface Pd atom) was taken for the first saturated layer. The UV light generated from a 700-W Hg arc lamp passed through a high-purity sapphire window in the vacuum chamber. The power density at the sample was estimated to be about 50 mW/cm². The incident angle was approximately 30° off the sample normal. The

temperature of the sample during irradiation was about 90 K, which includes a ~4 K rise due to radiative heating. The sample was cleaned by Ar⁺ ion bombardment and high temperature treatment (at ~1200 K) between runs, which are sufficient to remove the surface carbon.

Results and Discussion

Figure 1 shows the effects of illumination at 90 K on the desorption of CH₃Cl below monolayer coverage. In this case the amount of CH₃Cl desorbed with $T_p = 162$ K decreased by about 50%. While no methane formation was observed on the unirradiated surface, an easily detectable methane peak was found at $T_p = 167$–172 K. At monolayer CH₃Cl coverage, a very small additional methane peak appeared at $T_p = 375$–390 K. No other hydrocarbons (ethane, ethylene) were identified in the desorbing gases. Hydrogen desorption occurred above 400 K. After heating of the sample to 400 K (to desorb the molecularly adsorbed CH₃Cl), a Cl Auger signal was found at 181 eV. This signal started to attenuate only at 700 K and was eliminated above 950 K. No residual Cl signal could be seen for the unirradiated surface after desorption of CH₃Cl at 250–280 K. These features clearly indicate that C–Cl bond cleavage occurred following irradiation to give adsorbed CH₃ and Cl. Photoinduced dissociation of a halogen–carbon bond was also observed by White et al.[4–6] in
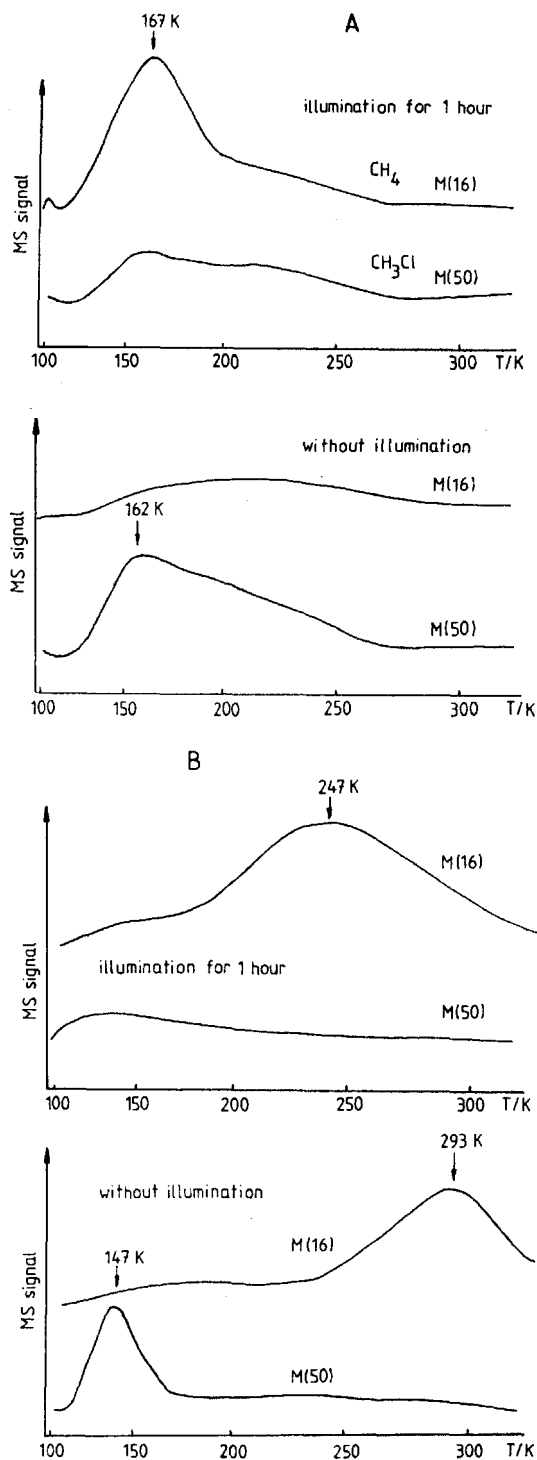
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Figure 1. Thermal desorption spectra of unirradiated and irradiated CH_3Cl adsorbed on a clean (A) and a K-dosed Pd(100) ($\Theta_K = 0.5$) (B) at 90 K. Irradiation was performed for 1 h with the full arc of Hg lamp. In the blank experiment the adsorbed layer was left in the dark for 1 h. No reactions attributed to photoinduced effect was observed.

CH_3Br and CH_3Cl on a Pt(111) surface.

Determination of the intensities of the Cl Auger signal before and after irradiation at 100 K demonstrated that less than 10% of a monolayer of adsorbed CH_3Cl was desorbed due to illumination. Further calculation showed that more than 15% of the strongly adsorbed CH_3Cl underwent dissociation as a result of irradiation with the full arc of a mercury lamp.

The absence of ethane from the desorbing products and the production of methane at low temperature indicate that CH_3 (a)

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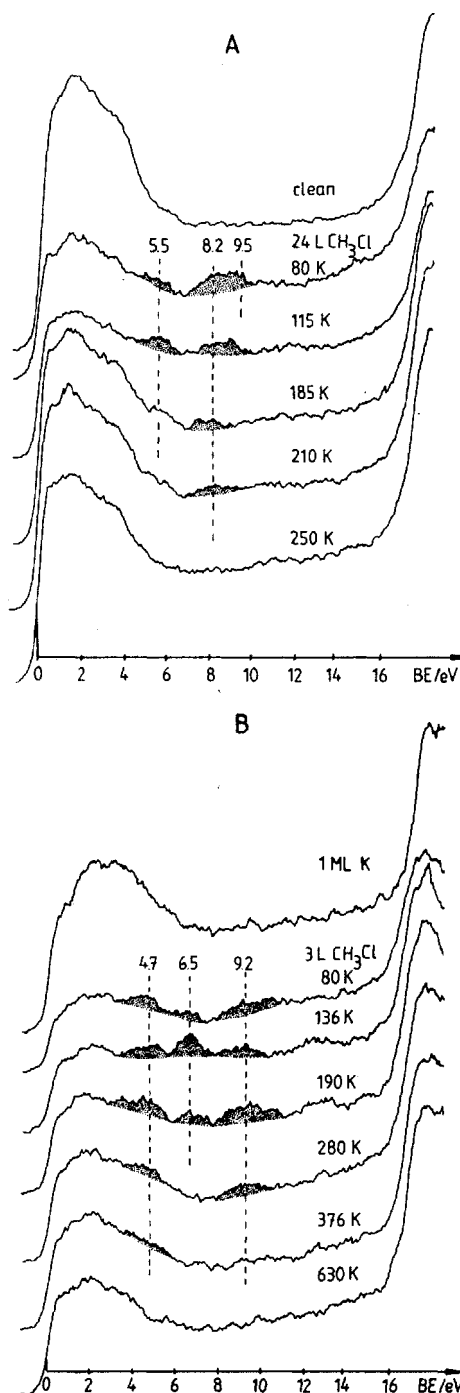
Figure 2. Ultraviolet photoemission spectra following irradiation of adsorbed CH_3Cl at monolayer on a clean (A) and a K-dosed Pd(100) ($\Theta_K = 0.5$) (B) surfaces at 90 K.

is rather unstable on a clean Pd surface. A fraction of it dehydrogenates to give hydrogen, which hydrogenates the remaining CH_x fragments to methane. Further, it cannot be excluded that hydrogen adsorbed from the unavoidable background of H_2 also participates in the hydrogenation of CH_x (a) to methane. When the adsorption and desorption behavior of methane on a clean Pd(100) surface[7] are considered, it can be concluded that the evolution of methane is a reaction-limited process.

The formation of CH_3 (a) was indicated by UPS measurements. A new photoemission peak was produced at 8.2 eV after illumination at 90 K for 60 min and subsequent heating to 185 K (Figure 2). (This warming-up of the adsorbed layer was required to desorb the remaining CH_3Cl from the surface, which hampered detection of the photoemission signal of adsorbed CH_3 by UPS.)

(7) Unpublished results.

This assignment is further supported by the results obtained for CH_3I adsorption on a clean $Pd(100)$ surface.[8] In this case the majority of the adsorbed CH_3I dissociated even at 100 K, producing an intense photoemission peak at 8.2 eV. In harmony with the results of TD studies, the 8.2-eV peak was eliminated at 210 K. Without illumination, only the photoemission signals due to molecularly adsorbed CH_3Cl (5.5, 8.2, and 9.5 eV attributed to $2e$, $3a_1$, and $1e$ orbitals, respectively)[2,9,10] were observed, which were eliminated at 189 K without the production of new photoemission signals. The above photoinduced features were not present after irradiation through a cutoff filter which removed all radiation below 280 nm.

As mentioned in the Introduction, potassium adatoms exerted a marked influence on the behavior of adsorbed CH_3Cl, and the details of the surface reaction depended on the potassium coverage.[1] At monolayer coverage, the degree of K-induced dissociation of CH_3Cl during heating of the coadsorbed layer was 37%: the decomposition products were methane, ethane, ethylene, hydrogen, and chloride.

As a result of illumination at 90 K, the amount of CH_3Cl desorbed at monolayer coverage decreased by about 80% and the amount of methane formed was doubled. Surprisingly, the peak temperature of methane formation was shifted to lower temperature, from 293 to 247 K, and the high-temperature methane peak observed in postirradiation TPD for clean Pd was missing (Figure 1B).

Following illumination of the coadsorbed layer at 90 K, an intense photoemission peak, very probably due to $CH_3(a)$ perturbed by K, appeared at 9.2 eV, at somewhat higher energies than for a clean surface. Further photoemission peaks were registered at 6.5 and 4.7–5.0 eV (Figure 2). The former is assigned to a $CH_2(a)$ species,[9] while the latter is mostly due to adsorbed Cl attached to K. The intensity of the 6.5 eV emission slightly increased between 136 and 150 K, and the peak disappeared at around 220 K. The 9.2-eV peak vanished when the adsorbed layer was heated to 325 K. The emission at 4.7–5.0 eV shifted to 5.2 eV at higher temperatures, and was eliminated above 600 K.

With regard to this feature, we assume that another very unstable and/or reactive surface species, possibly CH or C, also contributes to the emission at 4.7–5.0 eV. This species can be formed in the complete decomposition of adsorbed CH_x.

To explain the influence of the irradiation on the reactivity of the adsorbed layer, several factors have been considered.[4–6,11,12] We assume that the main effect in the present case is the photoexcitation of substrate electrons, which attach to an adsorbed CH_3Cl molecule, to form a negatively charged species that dissociates more easily. This process, the excitation of substrate electrons, obviously occurs more favorably from metallic potassium on a Pd surface than from clean Pd, which explains the more dramatic effect of irradiation at monolayer K coverage. This explanation is in harmony with the observations that the bombardment of adsorbed methyl halides with electrons facilitates halogen–carbon bond rupture and subsequent secondary reactions on several surfaces.[2,13]

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