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 $\theta$ is almost the same as the reported orientation angle of C=OH bond. 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 $\pi$-$\pi$ 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 liquid gas–liquid coexistence region.

Acknowledgment. We thank Prof. M. J. Rosen of CUNY Brooklyn College for the use of the Langmuir film balance in his lab. This work was made possible by the support of the National Science Foundation, the Air Force Office of Scientific Research, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Effects of Illumination on the Surface Behavior of CH$_3$Cl on Clean and K-Dosed Pd(100) Surfaces

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Irradiation of adsorbed CH$_3$Cl 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 CH$_3$ and Cl on a clean Pd surface and significantly enhanced the extent of dissociation of CH$_3$Cl for a K-dosed surface.

Introduction

In previous papers we showed that CH$_3$Cl adsorbs weakly and molecularly on a clean Pd(100) surface under ultra-high-vacuum conditions. 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 CH$_3$Cl 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. 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 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 CH$_3$Cl below monolayer coverage. In this case the amount of CH$_3$Cl 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 CH$_3$Cl 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 the sample to 400 K (to desorb the molecularly adsorbed CH$_3$Cl), 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 CH$_3$Cl at 250–280 K. These features clearly indicate that C–Cl bond cleavage occurred following irradiation to give adsorbed CH$_3$ and Cl. Photoinduced dissociation of a halogen–carbon bond was also observed by White et al.$^1$ in

Letters


Figure 1. Thermal desorption spectra of unirradiated and irradiated CH$_3$Cl 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$_3$Br and CH$_3$Cl 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$_3$Cl was desorbed due to illumination. Further calculation showed that more than 15% of the strongly adsorbed CH$_3$Cl underwent dissociation as a result of illumination 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) is rather unstable on a clean Pd surface. A fraction of it dehydrogenates to give hydrogen, which hydrogenates the remaining CH$_2$ 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$_2$ (a) to methane. When the adsorption and desorption behavior of methane on a clean Pd(100) surface 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$_3$Cl from the surface, which hampered detection of the photoemission signal of adsorbed CH$_3$ by UPS.)

Figure 2. Ultraviolet photoemission spectra following irradiation of adsorbed CH$_3$Cl at monolayer on a clean (A) and a K-dosed Pd(100) ($\Theta_K = 0.5$) (B) surfaces at 90 K.


(7) Unpublished results.
This assignment is further supported by the results obtained for CH$_3$I adsorption on a clean Pd(100) surface. In this case the majority of the adsorbed CH$_3$I 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$_3$Cl (5.5, 8.2, and 9.5 eV attributed to 2e, 3a$_1$, and 1e orbitals, respectively) 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$_3$Cl, and the details of the surface reaction depended on the potassium coverage. At monolayer coverage, the degree of K-induced dissociation of CH$_3$Cl 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$_3$Cl 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, 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. We assume that the main effect in the present case is the photoexcitation of substrate electrons, which attach to an adsorbed CH$_3$Cl 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.

(8) Kiss, J.; Révész, K.; Solymosi, F. To be submitted for publication.