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# Thermal Stability of the $CH_3$ Group Adsorbed on the Pd(100) Surface

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**Abstract:** The adsorption and subsequent dissociation of $CH_3I$ on Pd(100) have been investigated with ultraviolet photoelectron spectroscopy, Auger electron spectroscopy, temperature-programmed desorption, and work function change over the temperature range 85–600 K. We find that $CH_3I$ adsorbs molecularly at 85 K and dissociates at 100–150 K to give adsorbed I and $CH_3$. The latter compound decomposes above 150 K to yield methane. The thermal stability of adsorbed $CH_3$ (250 K) is much lower than that found for $CH_3$ (400 K) formed in the dissociation of $CH_3OH$ on the Pd(111) surface.[2]

Recently, an interesting discussion proceeded in this journal on the question of whether the C–O bond of $CH_3OH$ can be thermally dissociated on a clean Pd surface.[1-3] In contrast with previous studies, where only cleavage of the O–H bond of chemisorbed $CH_3OH$ and formation of the species $CH_3O$ were established,[4-7] Winograd et al.[1,2] reported an efficient C–O bond scission of chemisorbed $CH_3OH$ and formation of the species $CH_3$ on the Pd(111) surface. SIMS (secondary-ion mass spectroscopy) and XPS (X-ray photoelectron spectroscopy) were used to identify the adsorbed $CH_3$. However, Yates et al.[3] subsequently observed no C–O bond scission in the thermal decomposition of $CH_3OH$ on Pd(111), as demonstrated by the absence of isotopic exchange in the desorbing CO and $CH_3OH$ products from coadsorbed $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$.

This controversy prompted us to examine this question further, as the possible activation of the methanolic C–O bond represents a new route for $CH_3OH$ dissociation, which is strongly relevant to the catalytic synthesis and reactions of $CH_3OH$. We wish to contribute to the solution of this problem with a study of the thermal stability of $CH_3$ adsorbed on a Pd surface, as the surface species attributed to $CH_3$ by Winograd et al.[1,2] exhibited an unusually high thermal stability: it was detected even at ~400 K. A surface species displaying such a high thermal stability was also identified by Christmann and Demuth[5] in a study of $CH_3OH$ adsorbed on the Pd(100) surface: this species was ascribed to an adsorbed $CH_3O$ complex.

In the present work, adsorbed $CH_3$ was generated in the dissociation of $CH_3I$. This allowed elimination of the disturbing effects of $CH_3O$ (which was produced in $CH_3OH$ decomposition even in the work of Winograd et al.[1,2]) and led to adsorbed $CH_3$ in much higher concentrations than in the case of $CH_3OH$ adsorption.

## Experimental Section

The Pd(100) sample was cleaned by prolonged cycles of $Ar^+$ ion bombardment (1.0 kV, 2 $\mu A/cm^2$, 1000 K), annealing (1200 K), oxygen treatment (1000 K), and annealing (1200 K), which are sufficient to remove the surface carbon.[3,8] The oxygen, sulfur, phosphorus, and carbon impurities on the cleaned surface were estimated to be less than 0.1% of a monolayer. Experiments were performed in a standard ultra-high-vacuum chamber equipped with facilities for Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), thermal desorption spectroscopy (TDS), and work function measurements.[9]

## Results and Discussion

In the first series of measurements, we examined the adsorption and dissociation of $CH_3I$. Figure 1 shows the thermal desorption spectra of $CH_3I$ obtained after the adsorption of $CH_3I$ at different exposures at 85 K. At low exposures, 0.05–2.0 langmuirs, there was no molecular desorption of $CH_3I$. Above an exposure of 2 langmuirs, a single desorption peak developed at 121 K, which did not saturate even at high $CH_3I$ exposures: this state is assigned to multilayers.

The lack of a desorption peak for $CH_3I$ at low coverages indicates that all chemisorbed molecules underwent dissociation during the temperature-programmed desorption (TPD) cycle. The major desorption product was $CH_4$, with $T_p$ = 170 and 215 K (Figure 1). $CH_4$ formation was detected even at very low exposures (0.05 langmuir). Other hydrocarbons, including $C_2H_6$ ($T_p$ = 175 K), $C_2H_4$ ($T_p$ = 240 K), and $H_2$ ($T_p$ = 332 K), were detected only in trace amounts. This fact suggests that the $CH_3$ radical, as a primary dissociation product of $CH_3I$, is decomposed and hydrogenated to form $CH_4$. A great effort was made to detect surface carbon by Auger electron spectroscopy. However, as was pointed out by Musket et al.,[10] the AES detection of less than 0.25 monolayer of carbon is very difficult due to the overlap of the C (KLL) peak at approximately 270 eV and the large Pd (MNN) peak at 279 eV. We found that the $Pd_{279}/Pd_{330}$ ratio for the clean surface agreed well with that measured after the desorption of $CH_3I$ and $CH_4$. This indicates that only a very small amount of C formed in the surface reaction.

The adsorption and dissociation of $CH_3I$ were also followed by Auger electron spectroscopy. Figure 2A depicts the change in the intensity of the relative AES signal ($R_I = I_{511}/Pd_{330}$) as a function of $CH_3I$ exposure. Saturation was attained at about 3.0 langmuirs. The extent of dissociation was calculated by measuring the $R$ value after the adsorbed layer was heated to 150 K, where the molecularly adsorbed $CH_3I$ desorbed completely and no other $CH_xI$ compounds were indicated by UPS. In harmony with the previous speculation, the extent of dissociation was ~100% at saturation during the heating to 150 K. Figure 2B demonstrates that the adsorbed I formed in the dissociation is stable on the surface up to 800 K. The spectrum of the clean surface was attained at about 1100 K.

The work function of Pd(100) decreased linearly up to monolayer coverage ($\Delta\Phi$ = 1.85 eV) and then increased by about 0.25 eV when the multilayer was formed. The decrease in the work function suggests that the adsorbed $CH_3I$ has a positive outward dipole moment. This is consistent with the bonding of molecular methyl halides through the halogen atom.[11] When an adsorbed

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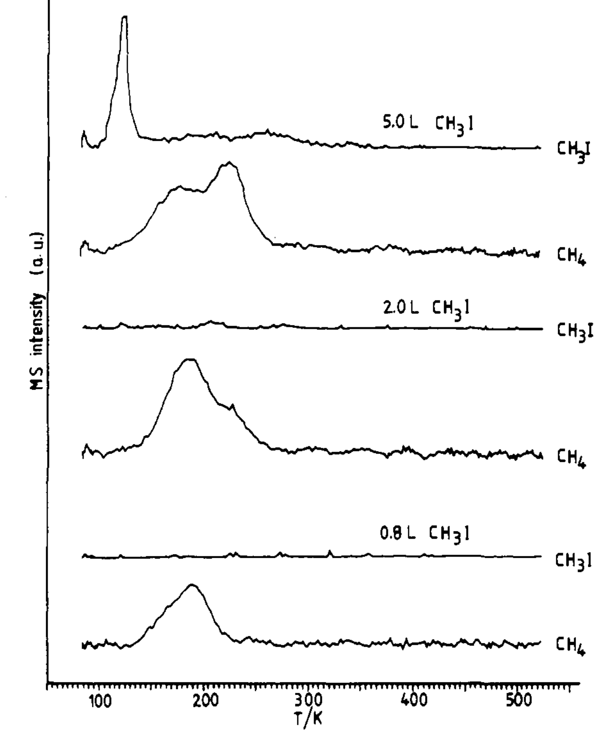

**Figure 1.** Thermal desorption spectra of $CH_3I$ and $CH_4$ from $CH_3I$ adsorbed on Pd(100) at 85 K. Heating rate was 8 K/s.

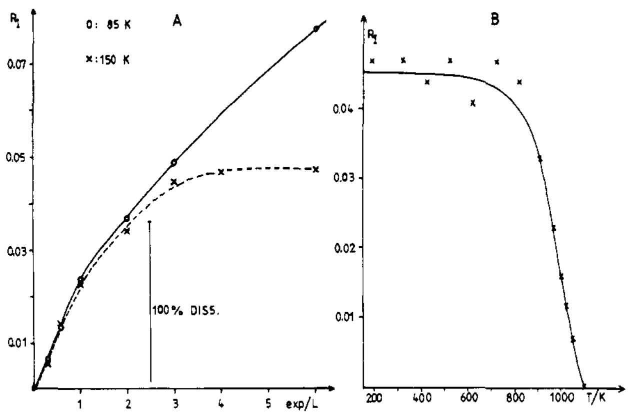

**Figure 2.** (A) Relative intensity of the iodine Auger signal ($R_I = I_{511}/Pd_{330}$) at 85 K and after heating the adsorbed layer to 150 K as a function of $CH_3I$ exposure. (B) Changes of the $R_I$ value upon heating the adsorbed layer to higher temperature.

layer was heated, there was a sudden decrease in the work function at 110–140 K, corresponding to desorption of the multilayer. This stage was followed by a gradual increase up to ~250 K and then by a constant state up to 800 K. In this state, the work function of the sample was 0.28 eV lower than that of the clean surface, which was restored only at 1100 K.

Figure 3 shows the UP spectra of the Pd(100) surface at low and at high exposures of $CH_3I$ at 85 K. At 0.6 langmuir (and below), only one new emission developed, at 8.5 eV, which is attributed to the 1e orbital of the pyramidal $CH_3$ radical.[12] In the photoinduced dissociation of $CH_3Cl$, the characteristic photoemission of the adsorbed $CH_3$ species was observed at practically the same energy, 8.2 eV.[13,14] At higher exposure, other photoemission peaks appeared at 4.3, 6.6, and 9.0 eV, which we attribute to molecularly adsorbed $CH_3I$. These emissions were eliminated when the adsorbed layer was heated to 150 K, where only an intense signal remained at 8.5 eV, due to the $CH_3$ group.

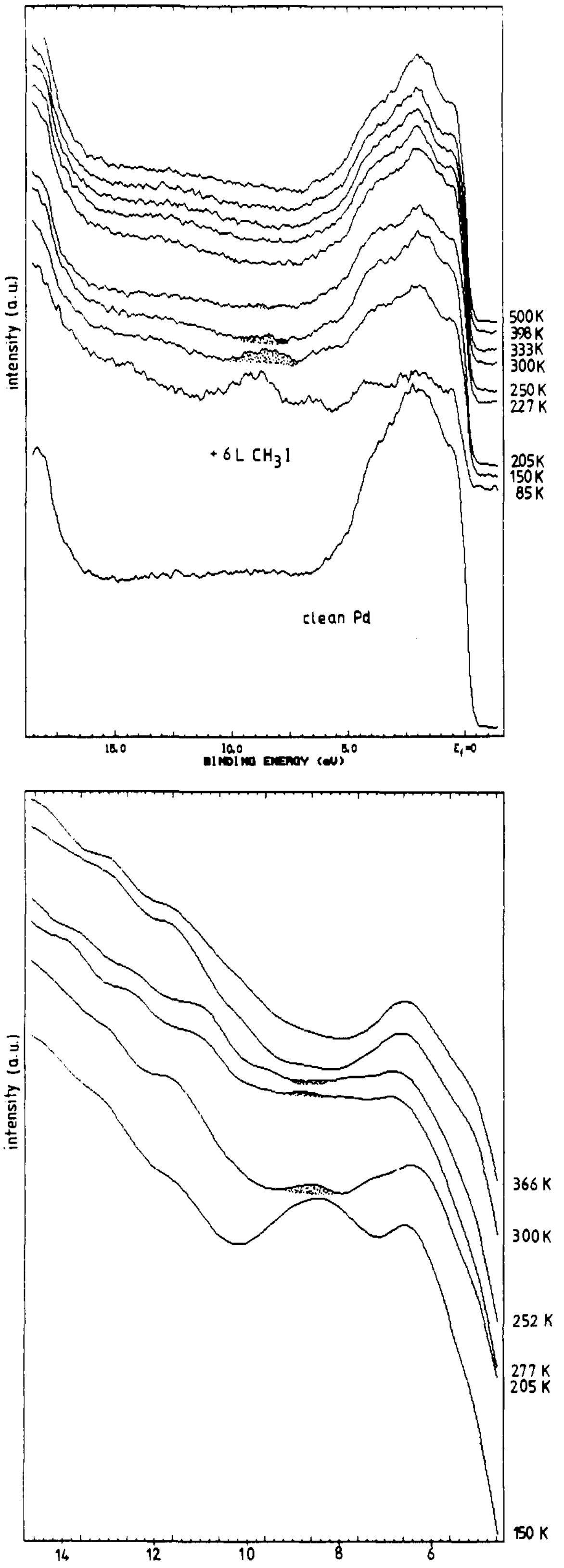

**Figure 3.** He II photoelectron spectra (A, top) following $CH_3I$ adsorption on Pd(100) at 85 K and (B, bottom) after heating the adsorbed layer to different temperatures. The spectra in part B are difference spectra smoothed by the fast Fourier transform method.[13]

The thermal stability of the adsorbed $CH_3$ species was determined at low (0.1 monolayer) and high $CH_3$ coverage. In the

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latter case, the surface was saturated with $CH_3$ (and I) via multiple adsorption/desorption cycles for $CH_3I$ (adsorption at 85 K and desorption at 150 K). Afterward, the adsorbed layer was gradually heated to higher temperature. To avoid the readsorption of $CH_3I$ from the background, the UPS spectrum was always recorded at 150 K. In order to increase the sensitivity of the measurements, the data collection time for the UPS spectra was extended to 30 min. For the detection of weak signals due to the adsorbed $CH_3$ species at higher temperature, we used the difference spectra (these were produced by subtracting the spectrum of a clean Pd(100) surface from each subsequent spectrum obtained after heating the adsorbed layer to different temperatures). Results are plotted in Figure 3.

It appears that the intensity of the signal at 8.5 eV at high $CH_3$ coverage is greatly decreased above 150 K, where the transformation of $CH_3$ into $CH_4$ proceeded. The emission at this energy can be detected up to 250 K. A signal of the same intensity was observed when the adsorbed $CH_3$ group was heated to 250 K immediately after its preparation.

The same features were observed at low $CH_3$ coverage with the difference that the initial attenuation of the $CH_3$ signal at 8.5 eV was smaller. The obvious reason is that the rate and the probability of the recombination of $CH_3$ groups at low $CH_3$ concentration are significantly reduced. The results suggest that the $CH_3$ decomposition does depend on the availability of surface sites, but the details of the site requirements remain an open question.

All these results suggest that the adsorbed $CH_3$ species exists on the Pd(100) surface, but its thermal stability is much less than that of the species produced by a low exposure of $CH_3OH$ on Pd(111) and assigned as $CH_3$.[1,2] In that case, the intensity of the $CH_3^+$ ion in SIMS was detected even at 400 K.

Before going further, we have to consider that the dissociation of $CH_3OH$ should lead to adsorbed OH together with the $CH_3$ species, which may exert a stabilizing influence on $CH_3$(a). This would not be surprising if OH(a) behaves like O(a), which increases the stability of a number of surface species on the Pt metals. However, our experiments in this context demonstrated that O coadsorbed at different coverages exerts no or only a slight stabilizing influence on the $CH_3$ group adsorbed on the Pd(100) surface.

It may be said that the XPS and SIMS methods applied by Winograd et al.[1,2] are more sensitive than the UPS used in the present work, and they were able to detect a very small amount of adsorbed $CH_3$. In this respect, we mention that the accuracy of measurements with the isotopic-mixing method is such that, if >1% of adsorbed $CH_3OH$ dissociates by C–O bond fission, it can be detected by the production of $^{13}C^{18}O$ or an isotopically mixed $CH_3OH$ species.[3] In spite of this very sensitive technique, Yates et al.[3] found no indication of the rupture of the C–O bond.

In the light of these results, and of those obtained by Yates et al.,[3] we may speculate that the species attributed to $CH_3$ by Winograd et al.[1,2] was not in fact adsorbed $CH_3$ but rather $CH_3O$. In a study of the decomposition of $CH_3OH$ on the Pd(100) surface, Christmann and Demuth[5] observed three kinds of $CH_3O$, one of which was stable even at ~450–500 K, which apparently supports the above speculation. Although this is a tempting conclusion, great care should be taken before a final conclusion is reached. The possibility cannot be excluded that the Pd(111) surface used by Winograd et al.[1,2] contained certain defects which could activate the methanolic C–O bond. Alternatively, the coadsorbed iodine on our crystal decreased the stability of adsorbed $CH_3$ in the present case. Further investigations are clearly needed on this subject.

**Note Added in Proof.** Our attention was recently called to the work of Kruse et al.,[15] who also studied the decomposition of methanol on the Pd(111) surface. They found that the dominant route in the dissociation of $CH_3OH$ involves O–H bond breaking. Adsorbed $CH_3$ was also detected, but this species does not represent a major reactive intermediate.

**Registry No.** Pd, 7440-05-3; $CH_3I$, 74-88-4; $CH_3$, 2229-07-4.

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