

# Effects of potassium on the adsorption and dissociation of $\text{CH}_3\text{Cl}$ on Pd(100)

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The effects of potassium on the adsorption and dissociation of  $\text{CH}_3\text{Cl}$  on a Pd(100) surface has been investigated by ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (in the electronic range EELS), temperature-programmed desorption (TPD) and work function change. In contrast to the clean surface, the adsorption of  $\text{CH}_3\text{Cl}$  caused a significant work function increase, 0.9–1.4 eV, of potassium-dosed Pd. Preadsorbed K enhanced the binding energy of  $\text{CH}_3\text{Cl}$  to the surface and induced the dissociation of adsorbed molecules. The extent of the dissociation increased almost linearly with the potassium content. The appearance of a new emission in the UPS spectrum at 9.2 eV, attributed to adsorbed  $\text{CH}_3$  species, and the low-temperature formation of ethane suggest that a fraction of adsorbed  $\text{CH}_3\text{Cl}$  dissociates even at 115–125 K on potassium-dosed Pd(100). At the same time, a significant part of adsorbed  $\text{CH}_3$  radical is stabilized, the reaction of which occurs only at 250–300 K. By means of TPD measurements,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , KCl and K were detected in the desorbing gases. The results are interpreted by assuming a through-metal electronic interaction at low potassium coverage and by a direct interaction of the Cl in the adsorbed  $\text{CH}_3\text{Cl}$  with potassium at high potassium coverage. The latter proposal is supported by the electron excited Auger fine structure of the Cl signal and by the formation of KCl in the desorbing gases.

## 1. Introduction

In the previous paper we reported on the adsorption and decomposition of  $\text{CH}_3\text{Cl}$  on clean Pd(100) [1].  $\text{CH}_3\text{Cl}$  adsorbs molecularly on this surface at 100 K and desorbs before detectable dissociation. In the present work the effect of a potassium adlayer on the adsorption and dissociation of  $\text{CH}_3\text{Cl}$  is examined. Our primary aim is to produce  $\text{CH}_3$  species on Pd by promotion of the cleavage of the C–Cl bond at low temperature, and to determine its reaction on a K-dosed Pd surface.

The adsorption of  $\text{CH}_3\text{Cl}$  on single crystal surfaces has been the subject of several recent electron spectroscopic studies [1–10]. The decomposition of this molecule may yield adsorbed  $\text{CH}_3$  species on reactive surfaces, which is a reaction intermediate in hydrocarbon synthesis from  $\text{H}_2$  and CO, as well as in the oxidative dimerization of methane. As alkali metals are used as promotor

for this catalytic reaction, the evaluation of their role in the reaction of  $\text{CH}_3$  species is of great importance. Apart from our short note [10] the effect of potassium on the dissociation of the C–Cl bond on transition metal single crystals and on the reactivity of  $\text{CH}_3$  species has not yet been investigated.

## 2. Experimental

The experiments were carried out in the same UHV system as those for clean Pd(100) surface [1]. The system was equipped with facilities for AES, LEED, UPS, ELS (in the electronic range), TDS and work function measurements.

Cleaning procedure for Pd was the same as used in our previous paper [1]. For the determination of the exact K coverage we used the cross-experimental results of AES, TDS and LEED measurements. This has been described in detail [11].

We found that a monolayer of potassium on Pd(100) corresponds to a surface density of  $6.7 \times 10^{14}$  potassium atoms/cm<sup>2</sup>, or  $\theta_K = 0.5$ . This value was calculated from the  $c(2 \times 2)$  overlayer structure derived from the LEED pattern at this coverage [11].

### 3. Results

#### 3.1. Auger spectroscopic measurements

The uptake of CH<sub>3</sub>Cl on K-dosed Pd(100) surfaces was followed first by registering the relative Cl Auger signal ( $Cl_{181} + Pd_{190}$ )/ $Pd_{330}$  as a function of the CH<sub>3</sub>Cl exposure. This ratio is 0.02 for the clean surface. In order to minimize the electron beam effects, we worked with a defocused beam, used low beam current ( $\sim 15$  nA) and short time of beam exposure (10–20 s). In addition, the important signal ( $Cl_{181}$ ) was taken first, and then the other part of the spectrum. From the results plotted in fig. 1A it appears that the adsorption of CH<sub>3</sub>Cl on a Pd(100) surface at 100 K was only slightly influenced by potassium adatoms. Fig. 1B shows the effect of temperature on the relative intensity of the chlorine Auger signal at different K coverages. In the case of a clean surface this value markedly decayed between 100 and 200 K and reached its final value at 250 K corresponding

to the clean surface. Similar behaviour was experienced for  $\theta_K = 0.1$  with the difference that the value at 250 K was somewhat higher than that for the clean surface, indicating that a small amount of chlorine remained on the surface after desorption of CH<sub>3</sub>Cl. At  $\theta_K = 0.3$ , and particularly at  $\theta_K = 0.5$ , the initial decay was less and it was followed by a constant region between 200 and 500 K. The relative chlorine signal started to diminish only above this temperature. In all cases of K-dosed surfaces the value for clean Pd was attained at 700–750 K.

As all adsorbed CH<sub>3</sub>Cl and C<sub>x</sub>H<sub>y</sub> compounds desorb from clean and K-dosed Pd(100) below 400 K, the determination of the relative intensity of the Cl Auger signal at this temperature gives information about the extent of the decomposition of adsorbed CH<sub>3</sub>Cl (fig. 1C). We obtained that the decomposition of CH<sub>3</sub>Cl increased almost linearly with an increase of K coverage, at  $\theta_K = 0.5$  a value of 60% was calculated.

#### 3.2. Thermal desorption measurements

In fig. 2 we present a plot of the molecular desorption of CH<sub>3</sub>Cl adsorbed on K-covered surfaces after 16 L of CH<sub>3</sub>Cl exposure at 100 K. There is a radical change in the form of the desorption curve even in the presence of a very small amount of potassium,  $\theta_K = 0.05$ –0.15. This

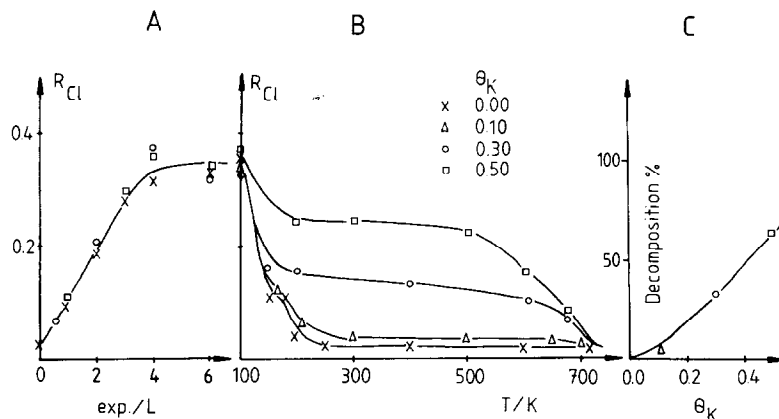


Fig. 1. Changes in the intensity of the relative Auger signal of chlorine at 181 eV as a function of CH<sub>3</sub>Cl exposure at 100 K (A) and after heating the sample gradually to higher temperature (B) at different K coverages. The calculated extent of the decomposition is also shown (C).

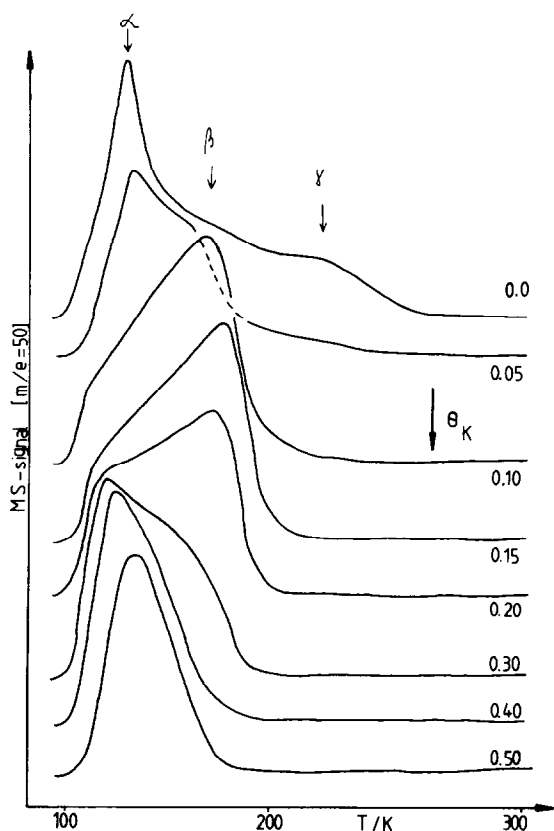


Fig. 2. Effects of potassium coverage on the adsorption of CH<sub>3</sub>Cl on Pd(100) at 100 K. CH<sub>3</sub>Cl exposure was 16 L.

is manifested in reduced  $\alpha$  and  $\gamma$  peaks and in an increase for the  $\beta$  peak. Above  $\theta_K = 0.15$  the  $\alpha$  state developed again, while the amount of CH<sub>3</sub>Cl desorbed in the  $\beta$  state diminished gradually up to  $\theta_K = 0.5$  (monolayer). As the adsorption of CH<sub>3</sub>Cl was performed at 100 K, the peak due to condensed CH<sub>3</sub>Cl observed in our previous paper at  $T_p = 105$  K [1] was not detectable.

It is a common feature for all K coverages that the filling up of the surface with CH<sub>3</sub>Cl begins with the stronger bonded state, the peak temperature of which is only slightly decreased with an increase of CH<sub>3</sub>Cl coverage, as illustrated for  $\theta_K = 0.15$  in fig. 3A. The integrated areas of the desorption spectra of molecular CH<sub>3</sub>Cl are shown as a function of the CH<sub>3</sub>Cl exposure in fig. 3B. It can be seen that above  $\theta_K = 0.15$  no desorption of CH<sub>3</sub>Cl occurs at low exposures which obviously

does not exclude the adsorption of CH<sub>3</sub>Cl on the surface (see later).

Further TPD studies showed that at higher temperatures other products, H<sub>2</sub> and CH<sub>4</sub>, are also formed (fig. 4A). The peak temperature for hydrogen is almost constant at  $\theta_K = 0.05$ – $0.2$ , where the amount of hydrogen evolved increases with an increase of potassium coverage. A drastic change occurs above  $\theta_K = 0.2$ ; in this case hydrogen desorbs in a broad peak between 680 and 950 K. The amount of methane also increased up to  $\theta_K = 0.3$ ; above this value, however, gradually decreased. At around half a monolayer coverage, methane desorbed in a broad peak between 230 and 340 K, with  $T_p = 270$  K (fig. 4B). In a search for other hydrocarbons we identified only ethane and ethylene. Ethane appeared first at  $\theta_K = 0.4$  (fig. 5A). Its peak temperature was rather low, 135 K. Traces of ethylene were detected between 200

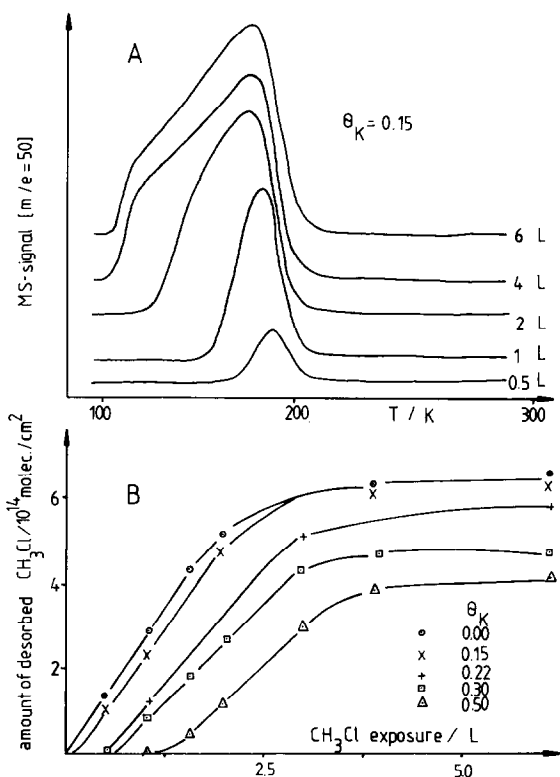


Fig. 3. (A) Thermal desorption of CH<sub>3</sub>Cl from K-dosed Pd(100) at  $\theta_K = 0.15$  as a function of CH<sub>3</sub>Cl exposure at 100 K. (B) The uptake of CH<sub>3</sub>Cl as a function of CH<sub>3</sub>Cl exposure at different potassium coverages at 100 K.

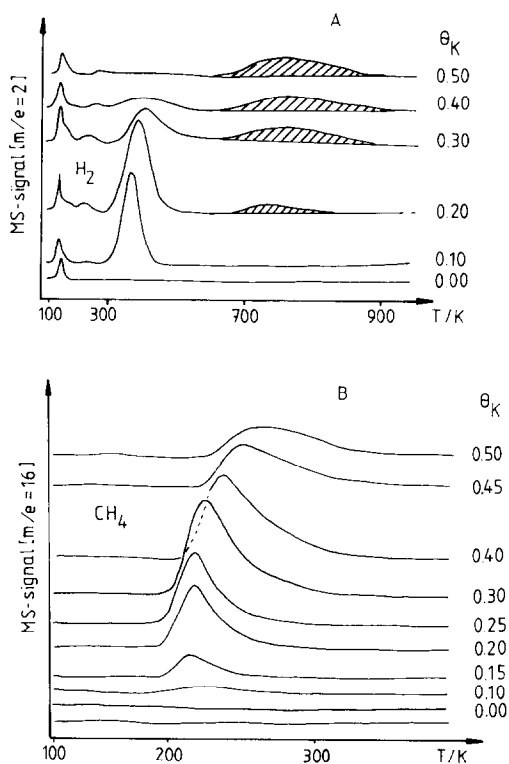


Fig. 4. Effects of potassium coverage on the formation of H<sub>2</sub> (A) and CH<sub>4</sub> (B) following 16 L of CH<sub>3</sub>Cl exposure at 100 K.

and 300 K (fig. 5A). Its production temperature exhibited a great variance with K coverage; ethylene formed at lower temperature at higher K content. As regards the desorption of chlorine-containing compounds we found KCl above 650 K. The small amount of chlorine atoms detected is likely the result of fragmentation of CH<sub>3</sub>Cl and KCl. Potassium also desorbed at high temperatures; at  $\theta_K = 0.5$  the peak temperature is  $\sim 700$  K (fig. 5).

The surface concentration of adsorbed CH<sub>3</sub>Cl was calculated from the measured intensity of the chlorine Auger signal at saturation taking into account this value obtained after chlorine adsorption on a clean Pd(100) surface [1,12]. In this way we obtained that the approximate surface concentration of adsorbed CH<sub>3</sub>Cl on a clean surface at 100 K is  $6.5 \times 10^{14}$  CH<sub>3</sub>Cl molecules/cm<sup>2</sup> [1].

In fig. 6 we have plotted the amount of adsorbed CH<sub>3</sub>Cl (total) and its decomposition products found by TPD measurements. In the calcula-

tion we have taken into account the following: (i) the number of dissociated CH<sub>3</sub>Cl molecules is a linear function of the potassium coverage (see AES measurements), (ii) there are no other desorbing products containing C and H atoms, but CH<sub>3</sub>Cl, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, (iii) the amount of desorbed H<sub>2</sub> can be calculated taking into account its saturation value ( $1.8 \times 10^{15}$  hydrogen atoms/cm<sup>2</sup>) on a Pd (100) surface [13]. The amount of CH<sub>4</sub> was calculated taking into account the amount of CH<sub>3</sub>Cl decomposed and the amount of hydrogen formed. When other hydrocarbons were also produced we determined the relative sensitivity of our mass spectrometer to the CH<sub>x</sub> compounds. In spite of this effort, we consider the data for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> plotted in fig. 6 only informative.

At low potassium coverage ( $\theta_K < 0.10$ ) only hydrogen desorbs indicating that CH<sub>3</sub>Cl underwent total dissociation to surface carbon. The amount of methane always exceeds that of ethane, with an exception at  $\theta_K = 0.5$ , where they formed in equal concentration. The results plotted in fig. 6B demonstrate that at low CH<sub>3</sub>Cl coverages mostly hydrogen is formed, methane evolution occurs at higher surface concentration of CH<sub>3</sub>Cl.

### 3.3. Work function measurements

As was reported before the deposition of potassium on a Pd(100) surface drastically decreased the work function of Pd [11]. The initial linear decrease was completed around  $\theta_K = 0.2$ ; the maximum decrease was  $\Delta\phi = -4.15$  eV. Above this coverage the work function increased by about 0.65 eV as a result of depolarization and metallization of K ions.

In the case of a clean Pd surface the adsorption of CH<sub>3</sub>Cl at 100 K caused a work function decrease of 0.91 eV; the original value was regained upon heating the adsorbed layer to 250 K [1]. In the presence of potassium we observed a much more complex behaviour. For more detailed measurements we selected two coverages:  $\theta_K \approx 0.25$  and  $\theta_K \approx 0.5$ . Work function changes are displayed in fig. 7. In contrast to the clean surface the adsorption of CH<sub>3</sub>Cl caused a work function increase of 1.4 eV for  $\theta_K = 0.25$  and 0.9 eV for

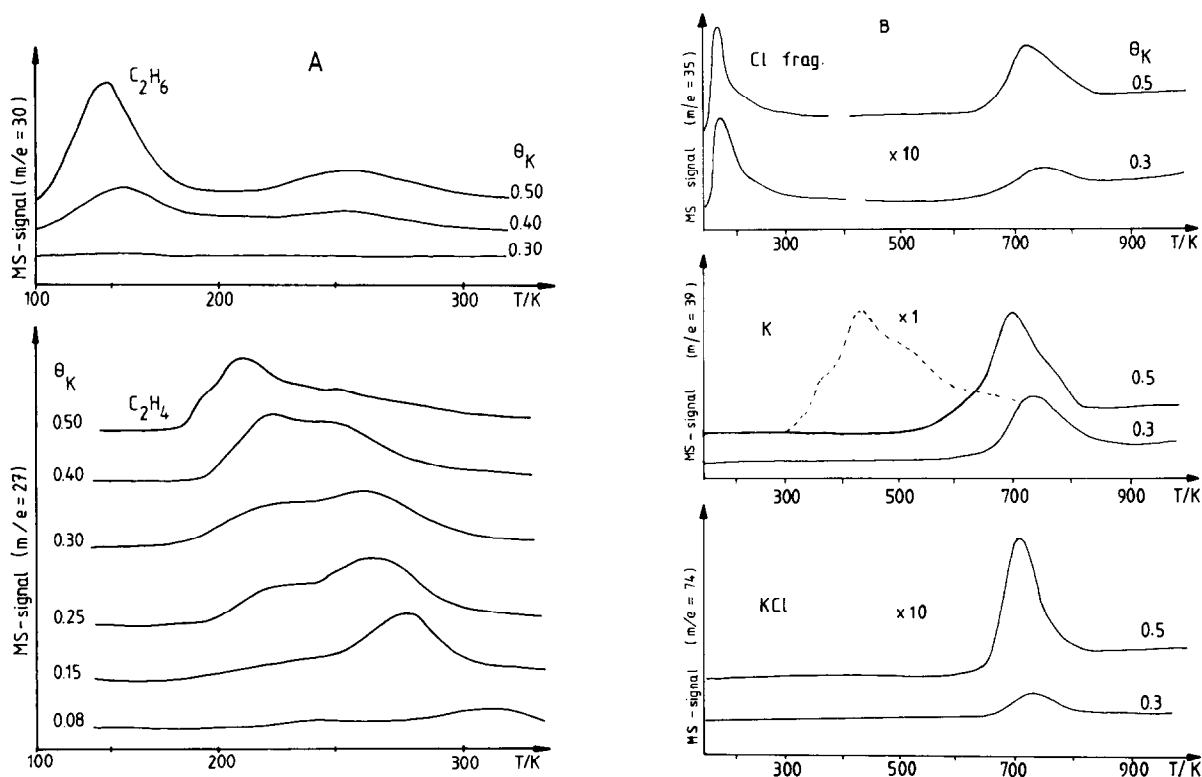


Fig. 5. Desorption of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, Cl fragment, K and KCl from CH<sub>3</sub>Cl + K coadsorbed layer on Pd(100) following 16 L of CH<sub>4</sub>Cl exposure at 100 K. The K desorption without CH<sub>3</sub>Cl coadsorption is also shown at  $\theta_K \approx 0.5$  (dotted line).

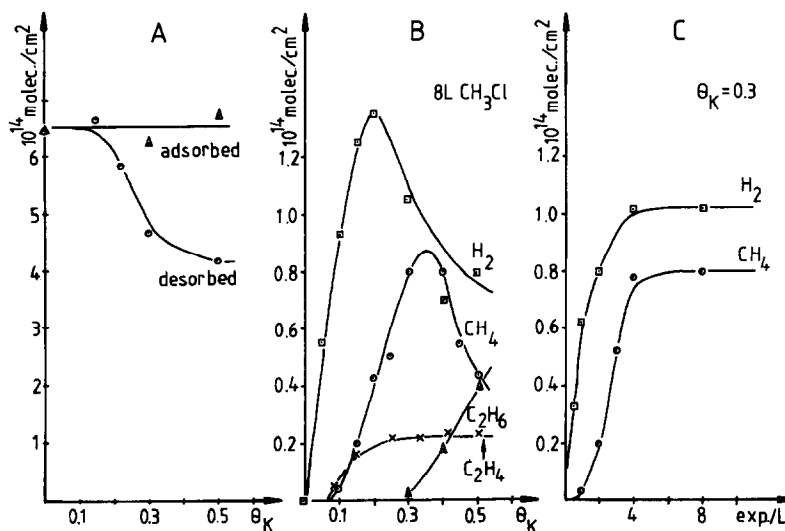


Fig. 6. The concentration of adsorbed CH<sub>3</sub>Cl (A) and its decomposition products as a function of K coverage (B) and CH<sub>3</sub>Cl exposure at  $\theta_K = 0.30$  (C). The adsorption temperature was 100 K.

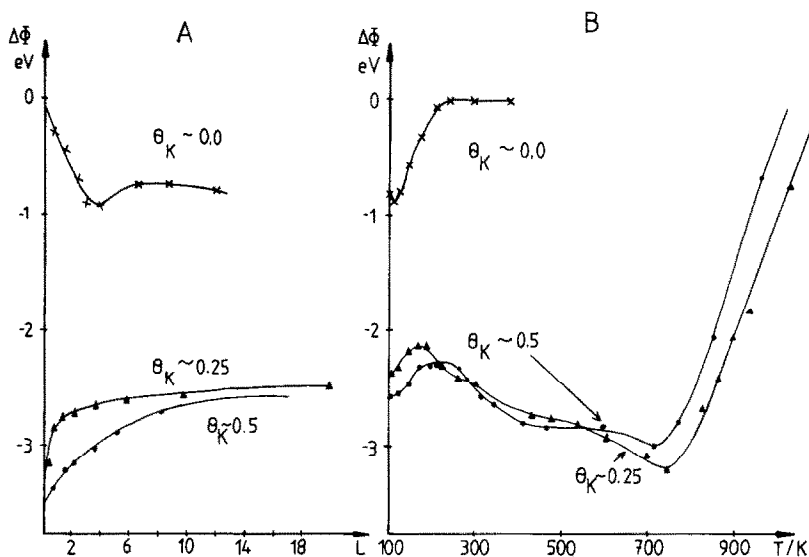


Fig. 7. Changes in the work function of clean and potassium-dosed Pd(100) as a function of CH<sub>3</sub>Cl exposure at 100 K and during subsequent heating to higher temperatures.

$\theta_K = 0.5$ . On warming up the coadsorbed layer, the work function underwent a transitory increase up to 170 K, then a decrease (from 204 K for  $\theta_K \approx 0.25$  and 260 K for  $\theta_K \approx 0.5$ , respectively) to 700 K. This was followed by a gradual increase up to about 1000 K, when the value characteristic for a clean Pd(100) surface was restored.

#### 3.4. UPS measurements

The adsorption of CH<sub>3</sub>Cl on a clean Pd(100) surface produced photoemission peaks at 5.7, 8.3 and 9.5 eV at 85 K which practically did not vary with exposure [1]. They disappeared when the surface was heated to 189 K.

On a potassium-dosed Pd(100) surface the orbitals of adsorbed CH<sub>3</sub>Cl appeared at higher binding energies: at 6.1, 9.7 and 10.7 eV for  $\theta_K = 0.25$ , and at 7.1, 10.8 and 11.8 eV for  $\theta_K = 0.5$  (figs. 8 and 9).

Upon heating the coadsorbed layer to higher temperatures the intensity of the observed emissions markedly decreased between 85–115 K and disappeared at  $\sim 200$  K at all potassium coverages. In the case of  $\theta_K = 0.5$  new photoemission peaks developed at 5.0 and 9.2 eV at 115–136 K.

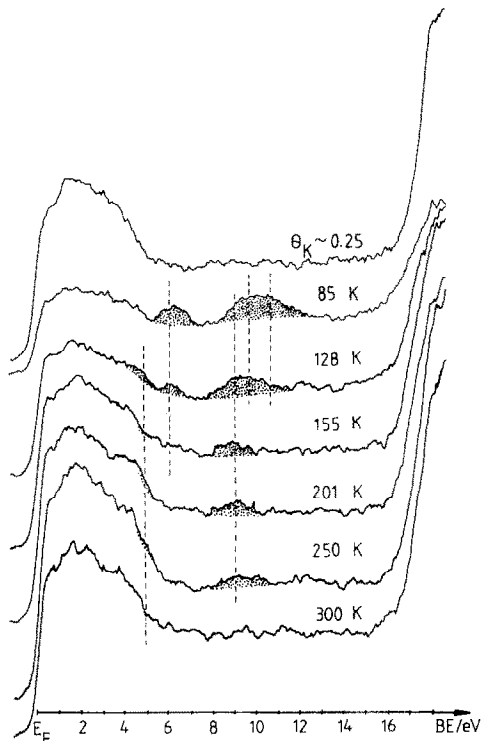


Fig. 8. HeII photoelectron spectra following CH<sub>3</sub>Cl adsorption and after heating the adsorbed layer to different temperatures.  $\theta_K \approx 0.25$ ,  $T_a = 85$  K.

Their intensities increased up to 200 K. The peak at 9.2 eV disappeared between 300 and 350 K. The emission at 5.0 eV decreased above 200 K, remained constant between 400–600 K and vanished at around 700 K. These new signals, particularly that at 5.0 eV, were much weaker at lower potassium content. In this case the peak at 9.2 eV was eliminated at lower temperature, at ~ 275 K.

### 3.5. ELS measurements

The deposition of K on the Pd(100) surface produced one new peak at 20.2 eV, and suppressed the most intensive loss of Pd between 4 and 9 eV.

On a K-dosed surface at  $\theta_K = 0.5$  the adsorption of CH<sub>3</sub>Cl at 150 K produced new losses at 6.2, 10.1 and 13.5 eV (fig. 10). On increasing the exposure, the intensity of all these peaks increased

simultaneously, which suggests that they are due to the same surface species. Note, that in the case of a clean surface the two main losses appeared at higher energies, at 11.3 and 14.6 eV. At higher exposures, losses can be also detected at 3.9 and 25.0 eV. Upon heating the coadsorbed layer to higher temperatures, the 10.1 and 13.5 peaks were present up to 300 K. The feature at 6.2 eV underwent more significantly changes, it became broader and larger at 300–500 K and disappeared only above 700 K.

The weak losses at 13.8–14.0 and 25.0 eV, observed even up to 900 K, are very likely due to CO adsorbed from background during cooling [14]. The spectrum of the clean surface was restored over 1000 K.

## 4. Discussion

### 4.1. General characteristics

In the study of the adsorption of CH<sub>3</sub>Cl on a clean Pd(100) surface at 100 K we came to the conclusion that – similarly as an other metals – CH<sub>3</sub>Cl binds with its chlorine end to the Pd atoms. The activation of CH<sub>3</sub>Cl on Pd at 100 K was not sufficient to cause the dissociation of the molecule before its complete desorption at 250–270 K [1]. However, preadsorbed potassium induced a drastic change in the behaviour of CH<sub>3</sub>Cl on the Pd(100) surface. The main features are as follows:

- (i) an increase in the binding energy of CH<sub>3</sub>Cl,
- (ii) an occurrence of the dissociation of CH<sub>3</sub>Cl,
- (iii) an increase in the work function,
- (iv) production of new spectral features in UPS, ELS and CILMM Auger fine structure.

The adsorption of CH<sub>3</sub>Cl on the clean Pd(100) surface at 80 K produced photoemission peaks at 5.7, 8.3, 9.5 and 15.5 eV below the Fermi level attributed to the 2e, 3a<sub>1</sub>, 1e, and 2a molecular orbitals of CH<sub>3</sub>Cl [15]. In the presence of preadsorbed potassium these orbitals shifted to higher binding energy with potassium coverage. The shift of CH<sub>3</sub>Cl peaks parallels the shift in work function which indicates that the proper reference levels for this species is the vacuum level. From

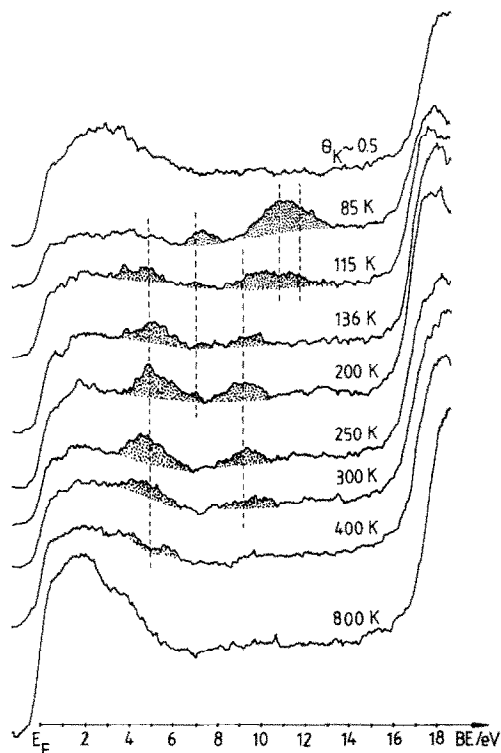


Fig. 9. He II photoelectron spectra following CH<sub>3</sub>Cl adsorption and after heating the adsorbed layer to different temperatures.  $\theta_K \approx 0.5$ ,  $T_a = 85$  K.

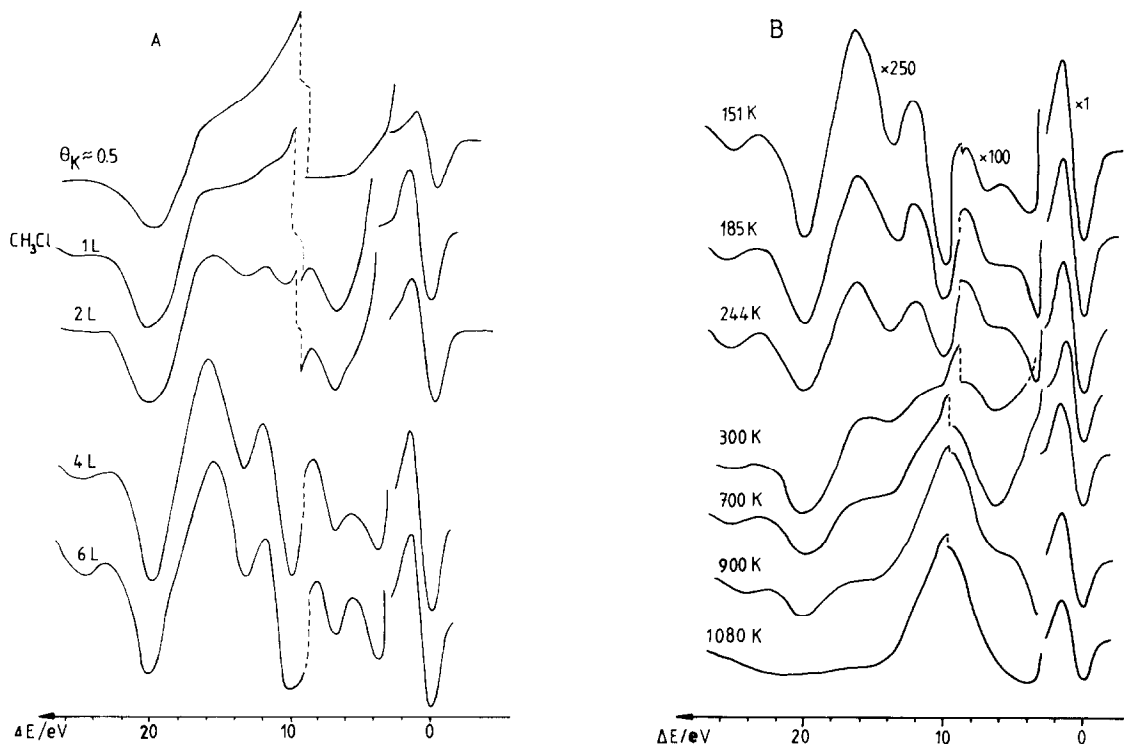


Fig. 10. Electron energy loss spectra of K-dosed Pd(100) at  $\theta_K \approx 0.5$  as a function of CH<sub>3</sub>Cl exposure at 100 K (A) and after subsequent heating to higher temperatures (B).

the losses observed in the EEL spectrum, the 6.2, 10.1 and 13.5 eV losses are assigned to electron transitions involving the 2e, 3a<sub>1</sub> and 1e levels of adsorbed CH<sub>3</sub>Cl near the Fermi level. The stable loss feature at 6.2 eV (being present between 300 and 700 K) is very likely due to electron transition from the 3p orbital of adsorbed Cl, which strongly interacts with potassium. The 3.9 eV loss, which was not observed on a clean surface, is tentatively attributed to CH<sub>x</sub> groups stabilized by potassium.

The total amount of adsorbed CH<sub>3</sub>Cl was practically independent on the potassium coverage. However, the extent of decomposition of adsorbed CH<sub>3</sub>Cl increased with increasing K coverage. As the most stable peak ( $\gamma$ ) of CH<sub>3</sub>Cl desorption is completely missing in the presence of preadsorbed K ( $\theta_K > 0.05$ ), we may assume that it is the chemisorbed CH<sub>3</sub>Cl which underwent dissociation. However, the amount of CH<sub>3</sub>Cl bonded in this state on a clean surface is about 22% of the total adsorbed CH<sub>3</sub>Cl, while the extent of decomposi-

tion on K-dosed surface approaches a value of 40%. This suggests that a significant fraction of less strongly bonded CH<sub>3</sub>Cl has also been stabilized by potassium and underwent dissociation.

Another important feature is that the effect of potassium clearly differs at low ( $\theta_K = 0.05-0.2$ ) and high ( $\theta_K = 0.3-0.5$ ) coverages [11]. At low K coverage the work function of Pd(100) linearly decreased with increasing K coverage. It is assumed that in this range potassium metal is completely ionized and, due to the repulsive interaction, the K<sup>+</sup> ion is dispersed homogeneously on the Pd surface. In this state potassium is considered as mainly ionic. Above  $\theta_K = 0.3$ , the depolarization of K<sup>+</sup> ions sets in and the metallization proceeds. A potassium coverage of about one monolayer is regarded as mainly metallic [11]. This difference in the state of potassium was exhibited in several features of the adsorption of CO<sub>2</sub>, CH<sub>3</sub>OH and HCOOH on potassium dosed metals [16-21], and it seems to be important in



the present case, too. Therefore the results are discussed separately.

#### 4.2. Low potassium coverage, $\theta_K \leq 0.25$

In addition to the elimination of the high temperature  $\gamma$  state, the stabilization of CH<sub>3</sub>Cl was exhibited by a significant decrease in the height of the  $\alpha$  peak and at the same time by an intensification of the  $\beta$  peak. Adsorption of CH<sub>3</sub>Cl on this surface at 100 K caused an increase in the work function that may mean that a charge flows from K + Pd to CH<sub>3</sub>Cl. This is in complete contrast to the clean surface, where CH<sub>3</sub>Cl adsorption resulted in a decrease ( $-0.9$  eV) in the work function. The stabilization of the CH<sub>3</sub>Cl molecule on this surface may be attributed to a through-metal electron transfer which strengthens the Pd–Cl bond. The strengthening of this bond may lead to

the weakening of Cl–C bond, which can result in the dissociation of adsorbed CH<sub>3</sub>Cl at higher temperature. Analysis of UPS spectra suggests that the rupture of the Cl–C bond on this surface occurs around 128 K as indicated by the appearance of a new emission at 9.2 eV (fig. 8). This signal may be attributed to the 1e orbital of pyramidal CH<sub>3</sub> radical [22]. This consideration seems to be supported by the results obtained following CH<sub>3</sub>I adsorption on a clean Pd(100) surface [23]. In this case the dissociation of CH<sub>3</sub>I to adsorbed CH<sub>3</sub> and I was complete already at 100 K. This process produced an emission at 8.5 eV which disappeared above 210 K, when the reaction of adsorbed CH<sub>3</sub> groups occurred.

The dehydrogenation of CH<sub>3</sub>(a) takes place very likely immediately after its formation, as no desorption of CH<sub>3</sub> was observed among the desorbing products. If we assume that the dehydrogenation of CH<sub>3</sub> and its subsequent hydrogenation are fast reactions,

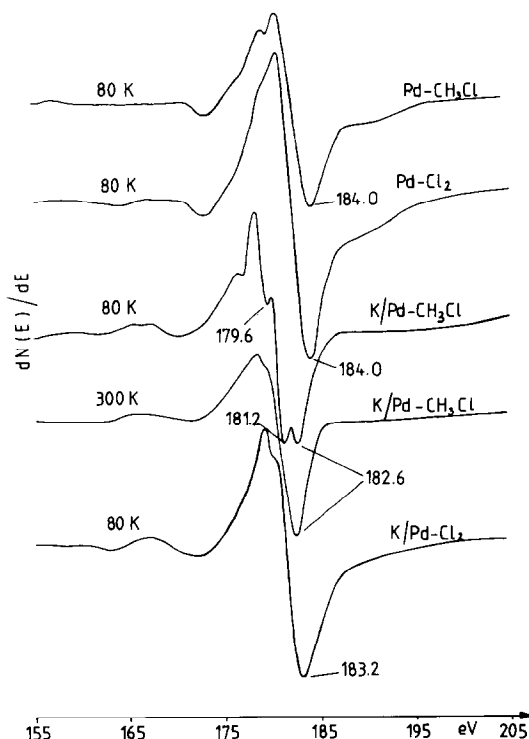
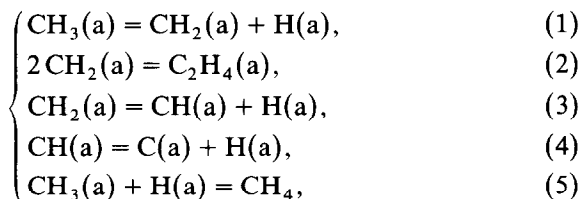
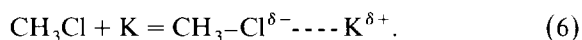


Fig. 11. CILMM Auger Line shape after adsorption of CH<sub>3</sub>Cl and Cl<sub>2</sub> on clean and potassium-dosed Pd(100).  $\theta_K = 0.5$   $E_p = 2.5$  kV;  $I_B = 1$   $\mu$ A, modulation voltage:  $0.5$   $V_{p-p}$ .

and take also into account the observation that CH<sub>4</sub> desorbs from clean and K-dosed surfaces below 150 K [10], the temperature range of CH<sub>4</sub> formation should not significantly differ from that of CH<sub>3</sub>Cl dissociation. As the data of fig. 3B demonstrates, the evolution of methane starts above 190 K and reaches its maximum at  $\sim 230$  K for this K coverage range. This consideration is also supported by the fact that in this case no ethane formation was noticed, which may mean that the steps (1)–(5) are fast enough to produce methane, compared to the recombination of CH<sub>3</sub> to give C<sub>2</sub>H<sub>6</sub>. In this case a significant amount of hydrogen was produced; its formation is clearly a desorption-limited process. We note here that the UPS signals (6.1, 9.7 and 10.7 eV) attributed to molecularly adsorbed CH<sub>3</sub>Cl were eliminated at 155–200 K.

### 4.3. High potassium coverage, $\theta_K \geq 0.3$

From  $\theta_K = 0.3$  different features were established. The concentration of adsorbed CH<sub>3</sub>Cl was practically the same as the lower K coverage, but the relative extent of the dissociation was higher. The adsorption state,  $\beta$ , did not appear and the dominant feature on the TPD curve of CH<sub>3</sub>Cl was at  $T_p = 130\text{--}140$  K. This was very much the same as for a clean sample. As at monolayer K coverage 50% of surface Pd atoms are covered by potassium, we may assume that an increasing fraction of CH<sub>3</sub>Cl is bonded directly to metallic potassium:



The formation of highly ionic K–Cl<sup>−</sup> can cause the dissociation of this surface complex at relatively low temperature.

If this assumption is true we may expect a significant difference in the electron-excited Auger fine structure of the ClLMM signal following adsorption of CH<sub>3</sub>Cl on a clean and K-promoted Pd surface. Spectra obtained are displayed in fig. 11. On a clean Pd surface the main Auger electron signal appeared at 184 eV, a shoulder is also seen at 179.6 eV. The same features were produced by the adsorption of Cl<sub>2</sub>. The absence of any difference between the two Auger spectra is probably the result of the electron-induced dissociation of adsorbed CH<sub>3</sub>Cl as experienced in our former paper [1].

A drastic change in the AES spectra was observed when CH<sub>3</sub>Cl was adsorbed on K-dosed Pd(100) at  $\theta_K = 0.5$ . The main signal was split into two peaks located at 181.2 and 182.6 eV and the shoulder at 179.6 eV became more intense. When the adsorbed layer was warmed to 320 K, where all adsorbed CH<sub>3</sub>Cl and C<sub>x</sub>H<sub>y</sub> compounds desorbed, the peak at 181.2 eV disappeared, but the feature at 182.6 eV remained unchanged: it was eliminated only above 700 K. As the absorption of Cl<sub>2</sub> produced only one Auger signal at 183.2 eV on the K-dosed surface, this signal is attributed to the potassium-perturbed electronic level of adsorbed Cl atom. On the other hand, the new Auger peak at 181.2 eV is very likely associated with the strong interaction with potassium of

the Cl in the CH<sub>3</sub>Cl molecule, which appears to be more resistant to the electron beam than adsorbed CH<sub>3</sub>Cl on a clean Pd surface. We note that in the case of adsorption of Cl<sub>2</sub> on a K-dosed Ag(100) surface, a shift of the negative excursion of the ClLMM Auger peak was also observed and it was ascribed to the strong perturbation of the Cl electronic level [24].

A decisive evidence for the direct interaction of CH<sub>3</sub>Cl and metallic K on the Pd(100) surface is provided by the detection of KCl in the desorbing products at high temperature following the adsorption of CH<sub>3</sub>Cl on K-promoted Pd at  $\theta_K = 0.3$  and 0.5 (fig. 5).

The evolution of ethane above 110 K with  $T_p = 135$  K clearly shows that the CH<sub>3</sub>–Cl bond has been activated to such a great extent that dissociation occurs around this temperature. The appearance of the peak at 9.2 eV in UPS at  $\sim 115$  K is consistent with this picture.

The fact that the evolution of methane was observed at significantly higher temperature ( $T_p > 270$  K), and its amount was smaller than at  $\theta_K = 0.2$ , where  $T_p$  was 220 K, may indicate that a fraction of CH<sub>3</sub>Cl is stabilized on this surface and decomposes only at 230–340 K. An alternative explanation for this phenomenon is the stabilization of CH<sub>3</sub> radical (formed at lower temperature) by potassium. The stabilization of CH<sub>3</sub> radical by potassium is not an unlikely process as CH<sub>3</sub>K is a known compound [25], and even its structure has been determined [26]. UPS studies demonstrated that the molecular orbitals of adsorbed CH<sub>3</sub>Cl drastically decayed below 136 K, while the emission at 9.2 eV for CH<sub>3</sub> radical decreased only at 300–350 K (fig. 9), which strengthens the second explanation.

The formation and stabilization of CH<sub>3</sub> groups may be supported by  $\Delta\phi$  measurements. Upon heating the coadsorbed layer,  $\Delta\phi$  first increases by about 0.25 eV at 120–180 K, in spite of the fact that a significant amount of CH<sub>3</sub>Cl desorbs in this temperature range. A decrease in  $\Delta\phi$  starts by 60 K higher at monolayer K coverage than at lower potassium content.

The formation of C<sub>2</sub>H<sub>4</sub> in a wide temperature range suggests the dehydrogenation of CH<sub>3</sub> species, too. The development of an UPS peak at

5.0 eV points to the accumulation of C or CH species [27]. A decrease in the intensity of this emission between 200 and 275 K indicates that a certain fraction of more reactive CH species is hydrogenated to give unsaturated hydrocarbons (C<sub>2</sub>H<sub>4</sub>).

The fact that most of the hydrogen formed in the decomposition of CH<sub>3</sub>(a) is strongly bonded to K/Pd(100) (no desorption of hydrogen was observed below 700 K for  $\theta_K = 0.5$ ), could also contribute to the low-temperature formation of ethane, to the decrease in methane production and to its shift to higher temperatures. To confirm this point the adsorption and decomposition of CH<sub>3</sub>Cl are being investigated on the K-dosed Rh(111) surface, where the diffusion of hydrogen in the subsurface region can be discarded.

As regards the high temperature formation of hydrogen we mention that similar features were observed for the H + K/Pd(100) coadsorbed system [28]. Although a potassium adlayer leads to the stabilization of adsorbed hydrogen in the case of other metals, e.g. Ni [29], Pt [30] and Rh [31], the highest peak temperature for hydrogen desorption was much lower, ~ 500 K, than in the H + K/Pd(100) system. It was suggested that the evolution of hydrogen at such a high temperature is associated with its ability to penetrate into the subsurface area or in the bulk of Pd(100) [28]. It appears that metallic potassium in some way facilitates the penetration of hydrogen into Pd to a great extent, perhaps due to an increase of the lifetime of adsorbed hydrogen at higher temperature, when the diffusion of hydrogen occurs easier.

An interesting feature of the interaction between CH<sub>3</sub>Cl and metallic potassium is that potassium is strongly stabilized on the surface by the adsorbate. This is now a generally observed phenomenon; it was registered for CO + K [14,32,33,34], CO<sub>2</sub> + K [16], CH<sub>3</sub>OH + K [17–20] and HCOOH + K [21] systems, and was attributed to a formation of a stable surface species involving potassium. The coincident desorption temperature reflects the stability of this compounds. In the present case the stabilizing species for K was found to be the chlorine. In contrast to the previous cases, we even detected KCl in desorbing gases,  $T_p = 700$  K.

## 5. Conclusions

(1) Preadsorbed potassium markedly influenced the adsorption and reactions of CH<sub>3</sub>Cl on Pd(100) surfaces. Its main effects are as follows: (i) an increase in the binding energy of CH<sub>3</sub>Cl, (ii) an occurrence of the cleavage of the C–Cl bond, (iii) production of new spectral features in UPS, ELS and Cl LMM Auger fine structure.

(2) Potassium adatoms stabilized the adsorbed CH<sub>3</sub> which was present on the surface up to 250–300 K.

(3) A strong interaction between Cl and K was also detected, which led to a significant stabilization of potassium at monolayer coverage: both species desorbed in a coincident peak,  $T_p \approx 700$  K.

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