

Surface photochemistry: Adsorption and dissociation of CH_3Cl on clean and K-promoted Pd(100) surfaces

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The photochemistry of adsorbed CH_3Cl on clean and potassium-dosed Pd(100) surfaces has been studied by illumination with low-intensity UV light from a high-pressure Hg lamp. The effects of illumination were established by post-irradiation thermal desorption, Auger and photoelectron spectroscopic measurements. Evidences are presented for photodissociation of the C-Cl bond to give surface bound methyl group coadsorbed with chlorine. The thermal decomposition of the surface methyl is accompanied by desorption of methane, and small amounts of ethane and ethylene. The presence of preadsorbed potassium greatly enhanced the extent of photodissociation of the C-Cl bond. The efficiency of potassium adatoms depended on its amount, i.e., on the work function of the coadsorbed systems. From the study of the wavelength dependence it is concluded that in the photodissociation of $\text{CH}_3\text{-Cl}$ the optical excitation of the substrate to produce photoelectrons plays a dominant role.

I. INTRODUCTION

In the evaluation of the mechanisms of catalytic reactions, it is of paramount importance to identify the surface complexes (reaction intermediates) formed and to establish their bonding mode, their structure, their reactivity and hence their possible roles in the catalytic processes. In the past decade, we have used different spectroscopic methods to make thorough investigations of the chemistry of NCO, CN, N, C, HCOO, and CH_3O , surface complexes playing important roles in the NO-CO reaction, and in the hydrocarbon and methanol syntheses.¹⁻⁵ The study of the chemistry of these species is relatively easy, as they are formed in catalytic reactions in well-measurable concentrations, or this can be attained by thermal dissociation of their parent molecules, HNCO, C_2N_2 , HCOOH, CH_3OH , and CO.

This cannot be achieved so easily for C_xH_y fragments, as they are thermally unstable and decompose rapidly after their formation. This difficulty can be circumvented by the illumination of adsorbed layers containing C_xH_y with photons, which may cause the dissociation of the adsorbed species at very low temperature.

Although the photochemistry of metal-adsorbate systems is a relatively new subject, a number of studies have recently demonstrated that photodesorption, photodissociation, and other photoinduced reactions readily occur on metal surfaces. The quenching of the electronic excitation of adsorbates is in most cases slow and not efficient enough to prevent the occurrence of the above processes. The results obtained so far are well documented in recent papers.⁶⁻⁸

In this work we report on the photochemistry of CH_3Cl on Pd(100), which is one of the most active catalysts in the synthesis of oxygenated compounds from CO and CO_2 . The central issue of this paper is the photoinduced dissociation of CH_3Cl on Pd, the surface chemistry of the adsorbed CH_3 formed, and finally the effects of potassium, an electropositive additive, on the above processes. Apart from our brief note,⁹ the effects of alkali metals on the photolysis of alkali metal halides have not been investigated so far; alkali metal

additives appear to have been applied only in a work dealing with the photodecomposition of $\text{Mo}(\text{CO})_6$ on the Cu(111) surface.¹⁰ Since potassium, depending on its coverage, markedly changes the work function of Pd metal,¹¹ which influences the energy required for the photoexcitation of substrate electrons, the $\text{CH}_3\text{Cl} + \text{K}/\text{Pd}(100)$ system provided a suitable model for the acquisition of useful information concerning the role of photoexcited electrons in the photolysis of adsorbed molecules.

The interaction of methyl chloride with metal single crystals under UHV conditions has been the subject of several recent works,¹²⁻²⁰ and its surface photochemistry has been examined on Ni and Pt surfaces.²¹⁻²⁴ The adsorption of CH_3Cl on the Pd(100) surface has been investigated in our laboratory.^{15,16} Methyl chloride adsorbs molecularly on clean Pd(100) at 80-100 K and desorbs before any detectable dissociation. Our main contribution to the surface chemistry of CH_3Cl is the finding that a potassium adlayer stabilizes CH_3Cl on Pd(100) and induces C-Cl cleavage even at 125-135 K.^{15,25}

II. EXPERIMENTAL

Methods. Experiments were performed in a standard UHV system equipped with facilities for Auger electron (AES), ultraviolet photoelectron (UPS), x-ray photoelectron (XPS), electron energy loss in the electronic range (EELS) and thermal desorption (TDS) spectroscopies, and work function measurements. UPS studies were carried out by using HeII (40.81 eV) radiation. The photoelectrons were detected with a hemispherical analyzer (Leybold-Heraeus LHS-10). Work function data were obtained from HeI spectra. For TPD, the sample was heated resistively at 7 K s^{-1} from 80 K to a selected temperature determined by the nature of the experiment.

The UV light source was a 700 W Hg arc lamp. The light passed through a high-purity sapphire window in the vacuum chamber wall. The power density at the sample was 6.5

mW cm^{-2} . The incident angle was 30° off the sample normal. When the wavelength dependence was studied, by using different cutoff filters, the lamp output was increased to achieve this energy at the surface. The temperature of the sample during irradiation was about 85 K, which includes about 5 K rise due to radiative heating.

Materials. Pd(100) disk (diameter 8 mm, thickness 1 mm) was cleaned in the same way as described in our previous papers.^{11,16} In most cases, this included Ar^+ ion sputtering (1 keV, 5 $\mu\text{A/cm}^2$) followed by annealing at 1000 K and/or by oxidation at 700 K and annealing at 1000 K. A commercial SAES getter source was used to deposit potassium metal onto the Pd(100) surface, situated 3 cm from the K source. The deposition of potassium was done at 250–300 K. A coverage of $\Theta_K = 0.50, 0.5$ K per surface Pd, was taken for the first saturated layer.^{11,26}

III. RESULTS

The results are presented in two major subsections, one dealing with a clean, and the other with a potassium-dosed Pd surface. For the clean surface, the irradiation of a submonolayer, a monolayer, and a condensed layer is examined. First, the results of TPD are reported, followed by those obtained with other spectroscopic methods.

A. Clean surface

1. TPD measurements

Figure 1(A) shows the effect of irradiation at 85 K on the TPD curves of CH_3Cl at monolayer. Without illumination, CH_3Cl at monolayer desorbs with a peak temperature (T_p) of 136 K. Higher-temperature peaks can also be seen in the TPD spectra ($T_p = 180$ – 248 K), which was attributed to the adsorption at defect sites on the surface.^{15,16} The amount of CH_3Cl adsorbed in this state is about 2–3% of the total amount of adsorbed CH_3Cl . Irradiation with the full arc for 60 min caused a decreased of about 14% in the amount of CH_3Cl desorbed. This value was much less when a 280 nm cutoff filter was inserted. (It is important to mention that in the blank experiments the adsorbed layer was

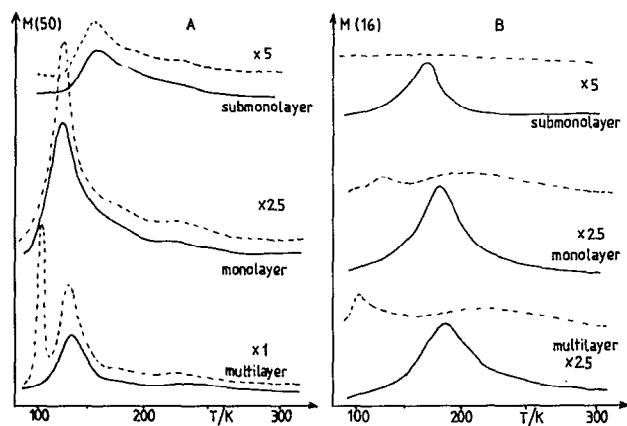


FIG. 1. Postirradiation TPD for CH_3Cl (A) and CH_4 (B) derived from submonolayer, monolayer, and multilayer of CH_3Cl . Irradiation time was 60 min and full arc was used. Dashed line represents the blank experiments: no irradiation but held in vacuum for 1 h.

held under vacuum before TPD and any other experiments for the same period as in normal photolysis.)

Whereas no other desorbing products were detected for the unirradiated sample, the formation of methane and minute amounts of hydrogen was observed following irradiation [Fig. 1(b)]. Traces of C_2H_6 and C_2H_4 were also detected. The peak temperature for methane was 167–172 K. The size of the methane peak was the largest at irradiation with full arc; it decreased significantly when a 280 nm cutoff filter was used. No methane formation occurred when a 360 nm cutoff filter was inserted (Fig. 2).

Similar features were established at submonolayer coverage 0.18 ML, where a larger percentage of adsorbed CH_3Cl was transformed into CH_4 following illumination than at monolayer coverage. This is illustrated in Fig. 1.

When a condensed layer was also present, the illumination caused its total desorption (Fig. 1). However, the remaining monolayer underwent dissociation to give methane in almost the same amount as in the illumination at monolayer.

2. AES and UPS measurements

The results of TPD measurements qualitatively indicate that nonthermal photochemical rupture of the C–Cl bond occurs. To confirm this, and to establish the nature of the adsorbed species formed, the adsorbed layer was examined after irradiation. Two methods were used: AES to detect the atomic Cl, and UPS to identify C_xH_y fragments formed in the dissociation of CH_3Cl . Auger analysis was performed after heating of the sample to 300 K to desorb all the adsorbed species except Cl, while for UPS measurements the sample was heated gradually to higher temperatures.

Following this procedure, in the case of the unirradiated surface, no signals attributable to adsorbed species were seen

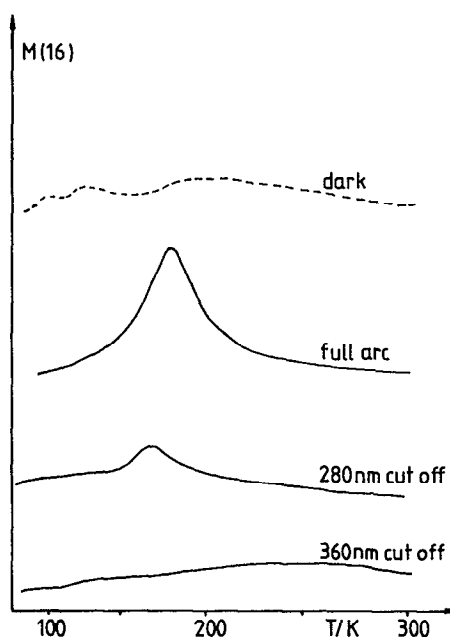


FIG. 2. Postirradiation TPD for CH_4 for monolayer CH_3Cl irradiated for 60 min using different filters.

in the AES. However, an intense peak was detected at 181 eV after illumination, which relates to the Cl (LMN) AES signal (Fig. 3). (The chlorine AES signal was measured together with the weak Pd AES transition at 189.0 eV. For the clean surface, the intensity of this Pd transition relative to that of the main Pd peak at 330.0 eV is 0.02.) The chlorine Auger peak began to attenuate only at 650 K, and was eliminated above 950 K. The same behavior was experienced when the Cl_2 molecule was adsorbed on the Pd(100) surface.²⁷ This result clearly indicates that cleavage of the C–Cl bond occurred following irradiation, to give adsorbed Cl species.

Registration of the intensities of the Cl Auger signal before and after irradiation gave a possibility for determination of the extent of the photoinduced dissociation of CH_3Cl and its dependence on various factors. These values could be influenced by the thermal or photoinduced desorption of Cl adsorbed on the Pd(100) surface. Control experiments, however, showed that the desorption of Cl is negligible under the experimental conditions.

In Fig. 3(A) we present data on the quantitative time dependence, based on the relative intensity of the Cl Auger signal at 181 eV. With increasing illumination time, the Cl yield increased slowly. Saturation could not be reached even after irradiation for 240 min. Postirradiation TPD measurements showed that a decreasing amount of intact CH_3Cl remained on the surface after irradiation [Fig. 3(B)]. In the inset of Fig. 3, the amount of chlorine produced in the photolytic process is plotted vs that of CH_3Cl remaining intact and desorbed as such after irradiation. The linear correlation obtained may suggest that the decrease in the amount of CH_3Cl desorbed is mainly a result of its dissociation. Determination of the intensities of the Cl Auger signal before and after irradiation at 100 K demonstrated that less than 5% of a monolayer of adsorbed CH_3Cl was desorbed due to illumination. The extent of decomposition of CH_3Cl was calculated by taking into account the value of

$R_{\text{Cl}} (= (\text{Cl}_{181} + \text{Pd}_{189})/\text{Pd}_{330})$ before and after irradiation. In the latter case the coadsorbed layer was heated up to 300 K to desorb all the adsorbed species except Cl. For an irradiation time, 60 min, the photoinduced dissociation was estimated to be 13%. From the knowledge of the absolute coverage of CH_3Cl at monolayer (6.5×10^{14} CH_3Cl molecules/ cm^2),^{15,16} we obtain that the amount of decomposed CH_3Cl is 0.8×10^{14} CH_3Cl molecules/ cm^2 . The results obtained using different cutoff filters are collected in Table I.

An attempt was made to detect the C (KVV) Auger signal following irradiation and after the desorption of CH_3Cl and CH_4 . Although this is particularly difficult on Pd, due to the overlapping with the Pd signals, we did observe a small and variable shoulder due to C at 271 eV.

Although AES measurements clearly confirmed the occurrence of cleavage of the C–Cl bond, it did not give information on other products formed in the dissociation of CH_3Cl . An answer was expected from UPS measurements. Figure 4 shows the UPS spectra of adsorbed CH_3Cl on a clean Pd(100) surface produces photoemission peaks at 5.7, 8.3, and 9.5 eV at 85 K, which practically do not vary as a function of exposure.¹⁶ They disappeared at 189 K, without producing any new signals [Fig. 4(A)]. Illumination of the monolayer apparently produced very little change in the photoemission spectrum; a slight broadening of the peak at 8.3 eV to lower energy may be noticed. An important result was obtained after heating of the adsorbed layer to 185–200 K (above the desorption temperature of CH_3Cl), when well-detectable features remained in the spectrum at 8.2 and 5.5 eV. These emissions could be seen even at 210 K, but vanished at 250 K. We tentatively attribute these photoemission signals to adsorbed CH_3 and CH_x species formed in the photoinduced dissociation process. The above photoinduced features were not present after irradiation through a cutoff filter which removed all radiation below 360 nm.

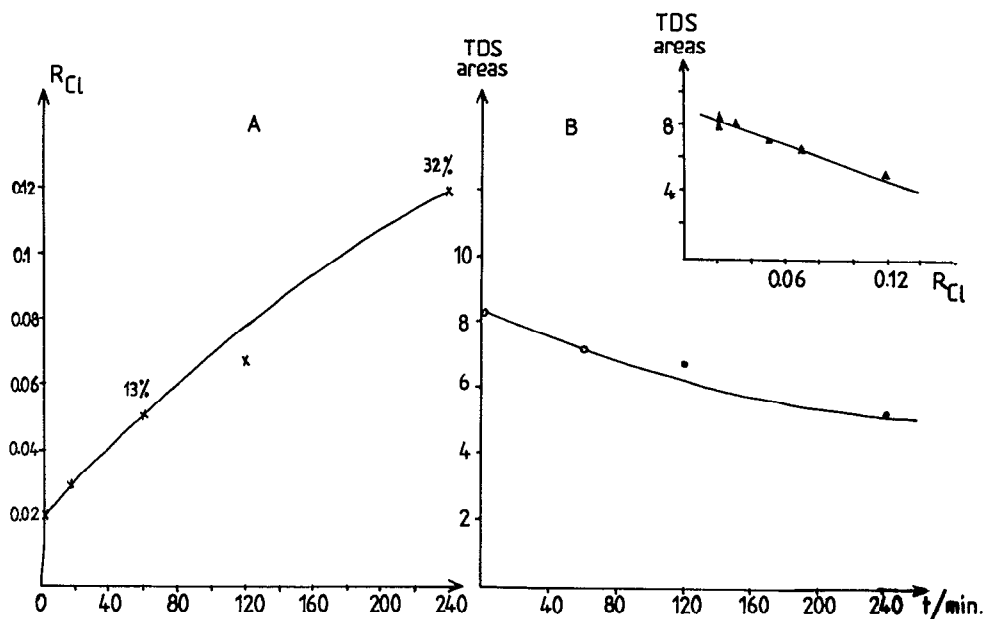


FIG. 3. The photolysis yield (with constant light power) vs illumination time for monolayer CH_3Cl adsorbed on Pd(100). (A) Retained chlorine atom (after desorbing the undecomposed CH_3Cl) determined by AES, (B) the amount of desorbing CH_3Cl . The full Hg arc was used. In the inset, the amount of retained chlorine is plotted against that for desorbed CH_3Cl . $R_{\text{Cl}} = (\text{Cl}_{181} + \text{Pd}_{189})/\text{Pd}_{330}$.

TABLE I. Wavelength dependence of the photolysis of adsorbed CH₃Cl on clean and K-promoted Pd(100) surface.

Sample	Work function of coadsorbed layer, eV	Cutoff filter, nm	Maximum incident photon energy, eV	Extent of the dissociation of C-Cl bond, ^a %	Cross section for the 254 nm line, cm ²
Pd(100)	4.55	Dark	0	0.0	2.14 × 10 ⁻²⁰
		360	3.45	0.0	
		280	4.44	4.0	
		Full	4.89	13.0	
Θ _K = 0.1	3.77	Dark	0	8.2	
		500	2.48	8.3	
		360	3.45	12.3	
		280	4.44	26.8	
		Full	4.89	39.8	
Θ _K = 0.2	3.12	Dark	0	23.0	
		500	2.48	23.8	
		360	3.45	32.9	
		280	4.44	49.5	
		Full	4.89	60.2	
Θ _K = 0.5	2.45	Dark	0	40.0	5.39 × 10 ⁻²⁰
		500	2.48	39.3	
		360	3.45	59.6	
		280	4.44	60.9	
		Full	4.89	69.2	

^aThe accuracy of the determination of the extent of the dissociation is ± 2%. The extent of the dissociation of CH₃Cl was determined by taking into account the value of R_{Cl} [= (Cl₁₈₁ + Pd₁₈₉)/Pd₃₃₀] before and after irradiation. In the latter case the coadsorbed layer was heated up to 300 K to desorb all the adsorbed species except Cl.

B. Effect of preadsorbed Cl

Preadsorbed Cl markedly influenced the adsorption of CH₃Cl; (i) it eliminated the bonding of the CH₃Cl in the γ state (desorbing between 150 and 270 K), even at low coverage of CH₃Cl, (ii) it slightly destabilized the adsorbed CH₃Cl in the α state and eliminated this state above $\Theta_{Cl} = 1.0$ ML; and, (iii) it facilitated the formation of a condensed layer desorbing with $T_p = 103$ K.¹⁶ This latter feature provided a possibility for study of the effects of illumination separately on the condensed layer without having more strongly adsorbed CH₃Cl.

Following illumination at 85 K for 60 min, the amount of condensed CH₃Cl decreased by about 50%. The amount of CH₃Cl desorbed was practically the same as observed for the clean surface, where less CH₃Cl went into the condensed phase at the same exposure. Postirradiation TPD showed that neither methane nor other hydrocarbons were formed. AES analysis for the additional Cl deposition was out of the question on this highly chlorinated surface, but UPS studies revealed no adsorbed species formed in the irradiation. Careful analysis of the gas phase during illumination did not disclose any photofragmentation of the CH₃Cl molecule. (This latter observation should be confirmed in a subsequent study as the analyzer of the MS was not in line during the irradiation.)

At a lower Cl coverage, $\Theta_{Cl} = 0.3$, when a submonolayer of CH₃Cl could be produced ($T_p = 115$ K), the photodissociation of CH₃Cl occurred, as indicated by the postirradiation TPD. However, the amount of methane formed

relative to that of adsorbed CH₃Cl was smaller than for the clean surface.

C. Effects of a potassium adlayer

Potassium adatoms markedly influenced the adsorption of CH₃Cl on the Pd(100) surface and induced its thermal dissociation to produce adsorbed Cl and CH₄, C₂H₆, and C₂H₄ (desorbed products at elevated temperature).^{15,25} Detailed measurements concerning the illumination were carried out at a coverage of $\Theta_K = 0.5$ which corresponds to the monolayer.

1. TPD measurements

In Fig. 5 we present the molecular desorption of CH₃Cl. For the unirradiated sample, CH₃Cl desorbs in one state with $T_p = 142$ K. As a result of the illumination, the amount of CH₃Cl desorbed decreased by about 60%. The amount of methane formed following irradiation increased by a factor of 2 at monolayer of CH₃Cl. Interestingly, the peak of methane formation was shifted to lower temperature from 293 to 247 K. The formation of ethane and ethylene was also detected. Ethylene was formed in a wide temperature range, between 190 and 270 K. The amount of ethane was higher by 25% as compared to the unirradiated surface.

Similarly as for the clean surface, the wavelength dependence of the irradiation was examined on K-promoted Pd(100) at monolayer CH₃Cl coverage. The results are displayed in Fig. 6 and some characteristic data are given in

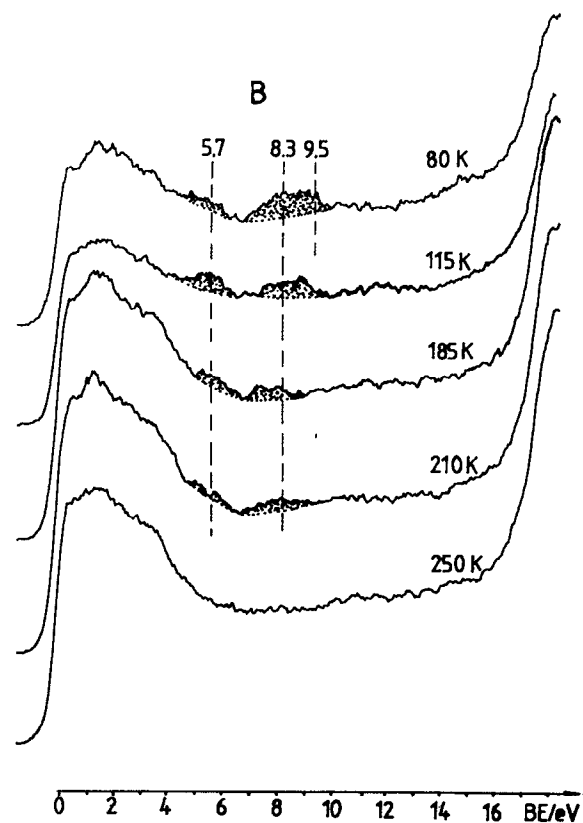
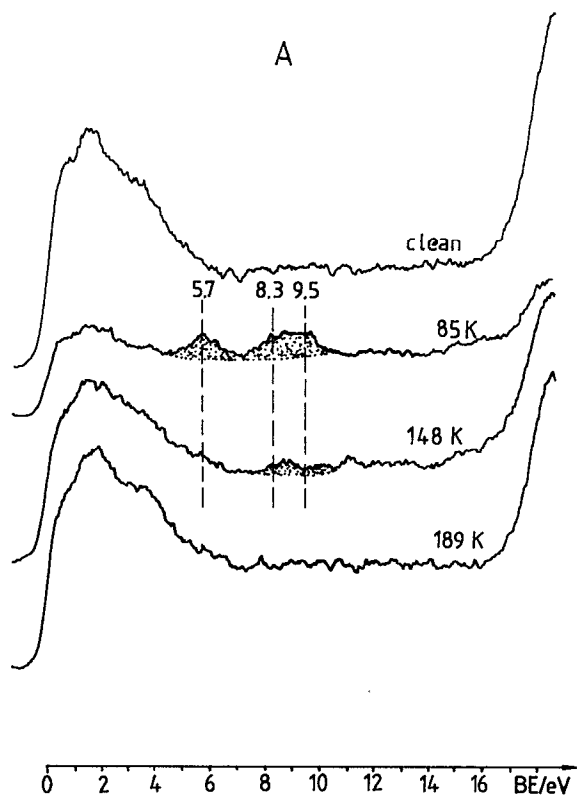


FIG. 4. Effects of irradiation on ultraviolet photoelectron spectra of adsorbed CH_3Cl at monolayer on clean Pd(100) surface. (A) no illumination, (B) illumination. Illumination time was 60 min and full arc was used.

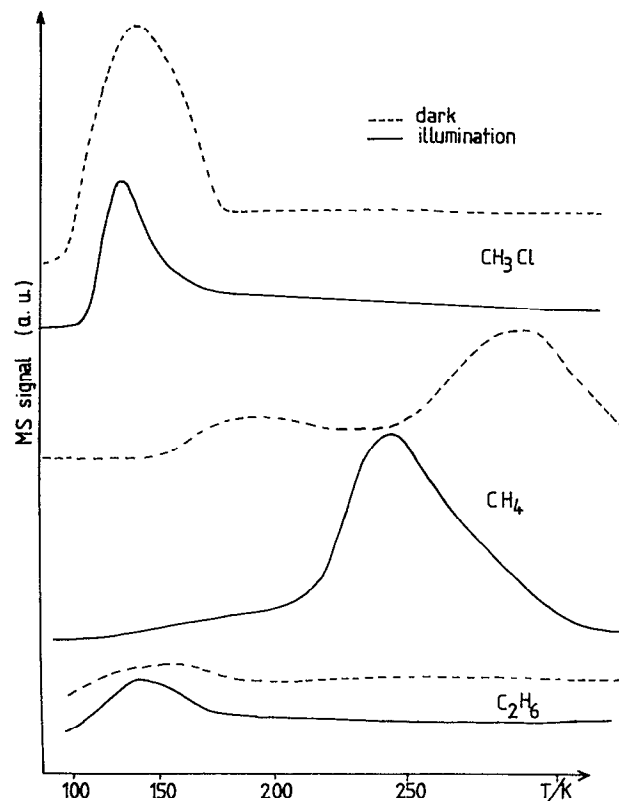


FIG. 5. Effects of irradiation on the desorption of CH_3Cl , CH_4 , and C_2H_6 at monolayer coverage of CH_3Cl on K-dosed Pd(100) at $\Theta_K = 0.5$. Irradiation time was 60 min and full arc was used. Dashed line shows the blank experiments: no irradiation, but held in vacuum for 60 min.

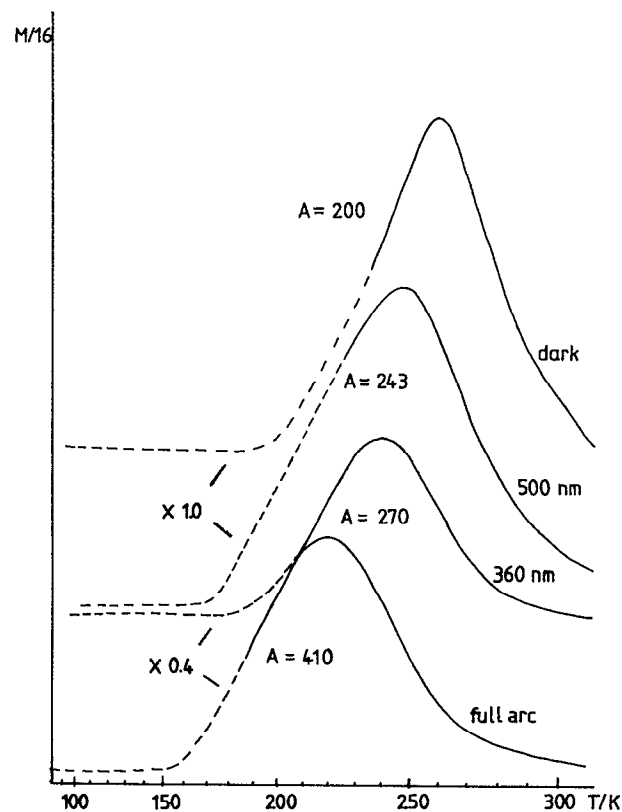


FIG. 6. Same as for Fig. 2, but on K-promoted surface at $\Theta_K = 0.5$.

Table I. With a 280 nm cutoff filter, the amount of methane only slightly decreased, and only a little additional methane formation was observed when a 500 nm cutoff filter was applied. Analogous features were experienced for ethane and ethylene. These results clearly indicate that the wavelength dependence of the irradiation is different between clean and K-dosed Pd surfaces.

2. AES, UPS, and EELS measurements

The results of AES measurements are plotted in Fig. 7. The procedure followed was the same as for the K-free sample. The effect of illumination is clearly seen for the K-dosed surface, too. While the K-induced dissociation was about 40% on the unirradiated sample at monolayer CH₃Cl coverage (Fig. 7), this value increased to almost 70% following irradiation for 60 min, otherwise under the same experimental conditions.

The quantitative time dependence of irradiation revealed different behavior from that experienced for the K-free surface. The chlorine signal increased more sharply than on the clean surface and reached saturation after irradiation for only 60 min. A good correlation was again obtained between the amount of chlorine atoms formed and the amount of undecomposed CH₃Cl as a function of the irradiation time.

As the work function of Pd(100) surface sensitively varies with the amounts of potassium, this provided a possibility to perform more detailed studies concerning the wavelength dependence and the effects of photoelectrons on the dissociation process. In order to obtain comparable data, the work function changes (following potassium deposition and after CH₃Cl adsorption) have been determined for all samples and the data obtained are plotted in Fig. 8. The calculated energy required for excitation of photoelectrons, and characteristic data for photodissociation, measured after irradiation using different cutoff filters, are listed in Table I.

It appears that the extent of photodriven dissociation increases with the increase of the potassium coverage and the wavelength dependence of the photolysis varies with the work function of the coadsorbed system. In the case of $\Theta_K = 0.5$ the insertion of a 280 nm cutoff filter caused only a slight decrease in the photodissociation of adsorbed CH₃Cl

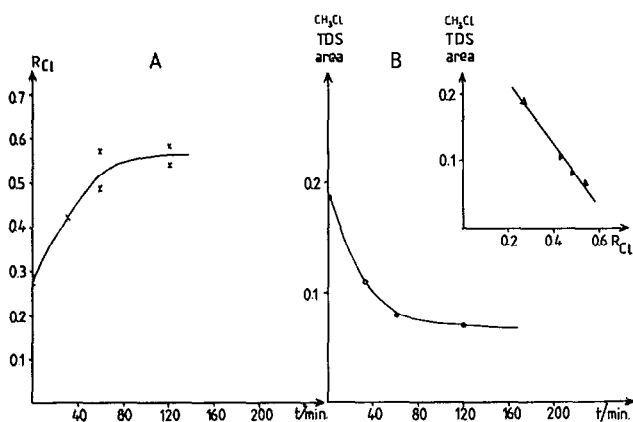


FIG. 7. Same as for Fig. 3, but on K-promoted surface at $\Theta_K = 0.5$.

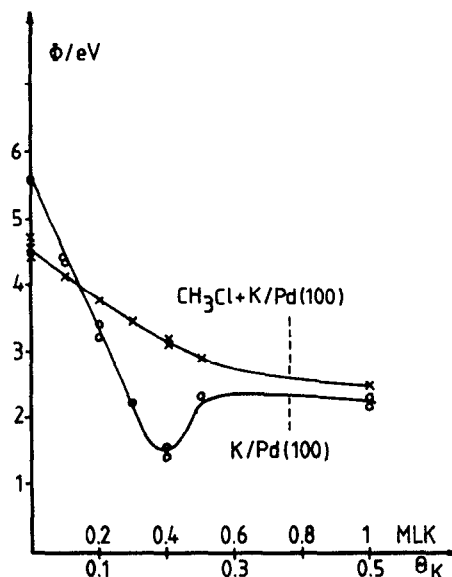


FIG. 8. Work function of K + Pd(100) and CH₃Cl + K/Pd(100) systems as a function of potassium coverage.

compared to the value obtained with the full arc. With a 500 nm cutoff filter, the extent of the dissociation approached well the value measured for the unirradiated surface.

The drastic change on irradiation of the CH₃Cl-K coadsorbed layer with the full arc at 85 K is demonstrated by the photoelectron spectrum. After irradiation for 60 min with full arc, we found only very weak signals due to molecularly adsorbed CH₃Cl: the dominant photoemission peak appeared at 9.2 eV, and weaker ones at 12.8, 6.5, and 4.7–5.0 eV [Fig. 9(B)]. The intensity of the 12.8 and 6.5 eV emissions slightly increased up to 136–150 K. Both peaks disappeared above 190 K. The 9.2 eV peak vanished when the adsorbed layer was heated to above 325 K. The emission at 4.7–5.0 eV shifted to 5.2 eV at higher temperatures, and was eliminated at above 600 K [Fig. 9(B)].

Some EELS measurements in the electronic range were also carried out. In harmony with the UPS data, following the irradiation with full arc, the intensities of all the losses characteristic for molecularly adsorbed CH₃Cl drastically diminished. However, no new losses attributable to the CH₃ species were detected, very likely due to its sensitivity to the electron beam.

IV. DISCUSSION

The illumination of adsorbed CH₃Cl with the full arc of mercury on clean and K-promoted Pd(100) surfaces at 85–90 K caused a drastic change in the coadsorbed layer. As the features are different on the two surfaces, it seems best to discuss the results separately.

A. Clean surface

1. General features

Methyl chloride adsorbs molecularly on a clean Pd(100) surface at 80–100 K and desorbs completely below 270 K without any detectable dissociation.^{15,16} Illumination

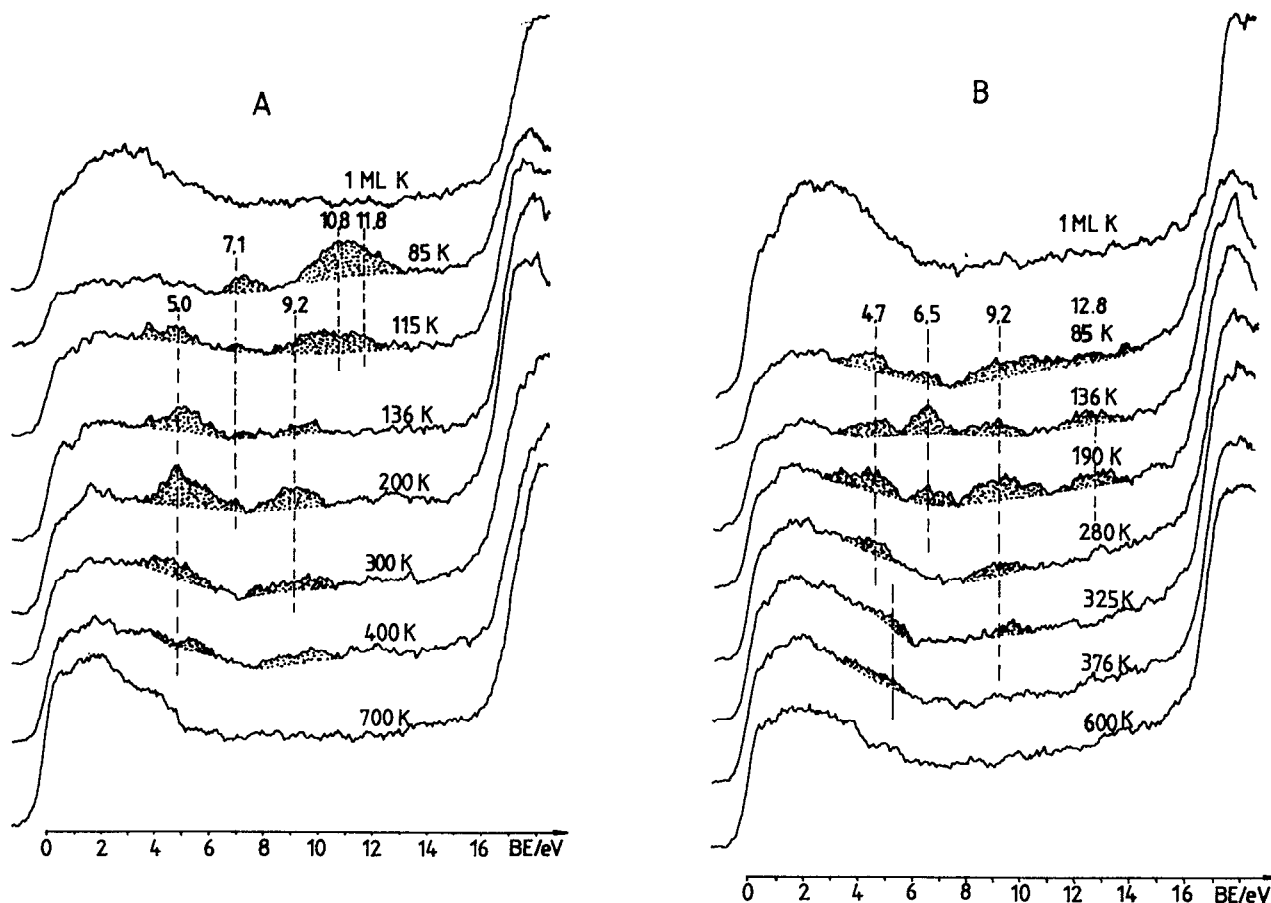


FIG. 9. Effects of irradiation on ultraviolet photoelectron spectra of adsorbed CH₃Cl at monolayer on K-dosed Pd(100) at $\Theta_K = 0.5$. (A) No illumination; (B) Illumination. Irradiation time was 60 min and full Hg arc was used.

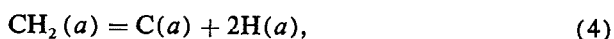
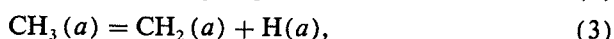
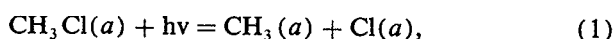
with the full arc of mercury, however, induces cleavage of the C–Cl bond even at 85 K. This conclusion is primarily based on the identification of adsorbed Cl by AES after desorption of the undecomposed CH₃Cl. Without irradiation no Cl AES signal is seen, even with sensitive AES measurements. We can rule out thermal effects as being responsible for production of the Cl AES signal, first because the temperature increase during irradiation never exceeded 5–10 K, which is far too low to cause any effect on the adsorbed CH₃Cl, and secondly because the adsorption of CH₃Cl on the Pd(100) surface, even at higher temperatures, 100–300 K, under UHV conditions produced no AES signal due to atomic Cl.

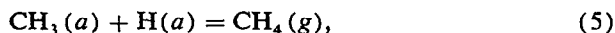
Further evidence for rupture of the C–Cl bond is the appearance of a new photoemission peak at 8.2 eV in the UPS after the desorption of CH₃Cl at 180–200 K. This signal was never observed following the adsorption of CH₃Cl on the clean Pd(100) surface and subsequent heating of the adsorbed layer to the above temperature. On the basis of previous UPS measurements,¹⁶ we attribute this signal to adsorbed CH₃ species, i.e., to the 1e orbital of the CH₃ group. We observed the same emission following CH₃I adsorption on the Pd(100) surface at 100–150 K; methyl iodide dissociates almost completely on the Pd surface in this temperature range, to give adsorbed CH₃ and I.²⁷ In accord

with the TPD results, the 8.2 eV peak was eliminated only above 210 K [Fig. 4(B)], when its hydrogenation to methane occurred.

In addition to the 8.2 eV signal, a somewhat weaker emission can also be seen at 5.5 eV in the UPS after desorption of the remaining CH₃Cl. This peak is eliminated together with the 8.2 eV emission at 250 K. As the Cl Auger signal attenuated only at above 650 K, this makes it unlikely that the 5.5 eV peak is due to adsorbed Cl, which gives an emission near this energy, at 4.5 eV.²⁸ Control measurements showed that UPS is less sensitive to Cl than AES, and such a small amount of adsorbed Cl can escape detection under the experimental conditions used for Fig. 4. A more probable explanation is that the 5.5 eV UPS signal is associated with the partially dehydrogenated CH₃ species, which may decompose further or be hydrogenated to methane above 210 K.

As regards the product formation channels we assume the occurrence of following reactions:





The results obtained clearly suggest that the cleavage of C–Cl bond, the reaction 1, is purely a photoinduced process. The other reactions are very likely thermal processes and occur during post irradiated heating of adsorbed layer. To confirm this, experiments are being conducted with adsorbed CH₃I which dissociates thermally on Pd surface to give adsorbed CH₃ and I. In this case the photolysis of CH₃(a) can be studied separately from the photodriven dissociation process.

2. Effect of coverage

The photolysis yield depends in general on the surface concentration of the adsorbed layer.^{6–8} In the present work, we examined the photolysis of a submonolayer, a monolayer and a monolayer covered by a condensed phase. Dissociation of the C–Cl bond occurred in all three cases (Fig. 1). The extent of the dissociation relative to the amount of adsorbed CH₃Cl decreased in the order submonolayer, monolayer, and condensed layer. Accordingly, a much larger fraction of the initially adsorbed CH₃Cl is desorbed or reacted in a given photolysis time when the initial coverage is small. This indicates that there is a coverage dependence as concerns the extent of photolysis, i.e., the various adsorbed molecules do not participate equally in the photolysis. Since irradiation with the full arc can lead to dissociation of the C–Cl bond, it is not surprising that under similar conditions the condensed layer is also completely removed. As the condensed layer desorbs at 105 K, we cannot completely exclude the possibility that a local, undetected thermal effect during the irradiation also contributes to its desorption. Furthermore, it appears that the condensed layer could not prevent the photolysis of the adsorbed CH₃Cl and its photoinduced dissociation even in this case. However, this protection is only apparent, as removal of the condensed layer occurs within 15–20 min, and thus photolysis of the adsorbed layer could proceed.

The photolysis of the condensed layer was also studied separately from the presence of adsorbed CH₃Cl. This was achieved by saturation of the Pd(100) surface with Cl₂, which interacts strongly with the surface Pd atoms to form a PdCl₂ layer.^{26,29} While the adsorption of CH₃Cl was completely prevented on this modified surface, the formation of a condensed layer was facilitated.¹⁶ A significant photoinduced desorption of the condensed CH₃Cl was observed in this case, too, without any indication of dissociation of the CH₃Cl molecule and its transformation into more strongly adsorbed species. This conclusion is mainly based on the postirradiation TPD and surface analysis. The question is still open as whether a fraction of the condensed CH₃Cl molecules underwent dissociation (which would resemble gas-phase photolysis), but neither of the products could remain adsorbed on the surface due to the lack of empty adsorption sites.

Photoinduced dissociation in the condensed multilayer was recently observed by Yates *et al.*³⁰ in the illumination of azomethane on the Pd(111) surface. The photolysis broke the C–N bond even at 87 K.

3. Time and wavelength dependences

The extent of the dissociation estimated from the amount of adsorbed Cl formed increased with the increase of the illumination time (Fig. 3); at 240 min it reached almost 32%. It is very likely that even higher values can be produced, as no saturation for Cl AES signal was attained under our experimental conditions. As regards the wavelength dependence, we can say that photolysis occurs at photon energies higher than 4.44 eV.

4. Mechanism of excitation

The mechanism of the excitation process is the central point in photoinduced chemical reactions. Several assumptions have been proposed for this process.^{6–8,31,32} In a study of the photolysis of CH₃Br on the Pt(111) surface, White *et al.*³¹ divided the possible mechanisms by which the C–Br bond is broken into three classes: (i) direct optical excitation of the adsorbate–substrate complex, (ii) optical excitation of the substrate to produce photoelectrons above the vacuum level, and (iii) optical excitation of the substrate to produce hot electrons below the vacuum level. From a detailed discussion of these possibilities, it was concluded that at shorter wavelengths (250 nm) the first two excitation models are consistent with the data.

Differentiation between these possibilities in the present case is not easy, but a knowledge of the work functions of Pd(100) and CH₃Cl/Pd(100) may give a clue. The work function of clean Pd(100) is 5.65 eV, this value decreased on average by 1.1 eV at a monolayer of adsorbed CH₃Cl (Fig. 8). If we assume that photoelectrons and their attachment to adsorbed CH₃Cl play important roles in the photolysis, then photolysis should be minimal below a photonenergy of 4.55 eV. In harmony with this, the photolysis of adsorbed CH₃Cl underwent a strong decline, when photon energies higher than 4.44 eV were filtered out (with the use of a 280 nm cutoff filter) (Table I). With regard to the energy spectrum of the Hg lamp, the line at 254 nm (4.88 eV) is probably responsible for the photodissociation of the C–Cl bond. *This result strongly supports the idea that the photoelectrons play a dominant role in the photodissociation of CH₃–Cl, and the effect of hot electrons is not significant. The photo electron may attach to an adsorbed CH₃Cl to form a partially negatively charged species that dissociates more easily.*

The role of photoelectrons in the photolysis of CH₃Cl on Pd may be supported by the observations that the bombardment of adsorbed CH₃Cl with electrons facilitates C–Cl bond breaking,^{16,33} and that an additive (K) with an electron-donating character also promotes the dissociation of CH₃Cl.^{15,25} The photodissociation of CH₃Cl on Ni(111) surface has been successfully described with a model of substrate excitation and the generation of photoelectrons.²¹

B. Potassium-promoted surface

1. General characteristics

The presence of potassium additive greatly increased the efficiency of photolysis of coadsorbed CH₃Cl, or in other words the illumination enhanced the influence of potassium. These features are clearly demonstrated by the data plotted in Figs. 5–7 and 9. The most important result is that the extent of the dissociation of adsorbed CH₃Cl (established from the intensity of the Cl AES signal) increased from 40% to 70% at monolayer coverage.

For identification of the other product of the initial step of CH₃Cl dissociation, adsorbed CH₃, the photoelectron spectroscopy was used. In the case of the unirradiated K-dosed surface, the photoemission signal of the adsorbed CH₃ group appeared at somewhat higher energy, 9.2 eV, than on the clean Pd surface, and exhibited a much higher stability.²⁵

Following illumination of the coadsorbed CH₃Cl + K layer at 85 K with the full arc, the photoemission signal at 9.2 eV, together with an emission at 4.7 eV, appeared at 85 K (Fig. 9). This supports the view that the photoinduced dissociation of CH₃Cl on K-dosed Pd occurs even at such a low temperature. The intensity of the 9.2 eV signal was higher than on the unirradiated surface, indicating that the CH₃ group was produced in a greater quantity in this case. In addition, two new signals at 6, 5, and 12.8 eV were also detected at 85 K, which were not seen in the case of unirradiated surface. These signals are attributed to adsorbed CH₂ and/or C₂H₄ species.

On heating of the coadsorbed system after irradiation, the 9.2 eV signal was present up to 325 K and disappeared at somewhat lower temperature than in the case of unirradiated surface (Fig. 9). The emissions at 6.5 and 12.8 eV intensified up to 136–150 K and were eliminated above 190 K. The appearance of 4.7–5.0 eV signal, together with the 9.2 eV signal, and its high thermal stability [Fig. 9(B)] suggest that it is mainly due to adsorbed Cl formed in a greater quantity in the photoinduced dissociation of CH₃Cl. By means of TPD measurements, we identified CH₄, C₂H₄, and C₂H₆. These products were also formed in the case of the unirradiated K/Pd(100) surface, but their concentrations were lower than in the present case. Their formation can be described by the same processes as found for the clean surface. We point out that the desorption of CH₄, C₂H₆, and C₂H₄ occurred at somewhat lower temperatures than those corresponding to the elimination of new photoemission signals attributed to adsorbed CH₃ and CH₂. This may indicate that a certain fraction of adsorbed CH₃ and CH₂ species are not hydrogenated and recombined, but decompose at higher temperatures.

2. Time and wavelength dependences

With increase of the irradiation time, the extent of the dissociation, as determined by the increase in the Cl AES signal, increased more sharply and reached a constant value at an irradiation time of around 60 min. This differs from the behavior for the K-free sample, when no saturation was attained even after 240 min. The intensity of the Cl AES signal

increases linearly with decrease in the amount of undecomposed CH₃Cl, which may suggest that no significant photoinduced desorption occurred from this surface either.

It is an interesting characteristic of the potassium-dosed surfaces that the wavelength dependence is completely different from that found for the clean Pd surface (Table I). We believe that this feature is of importance as concerns establishment of the mechanism of the photoexcitation process.

As demonstrated in Fig. 8, the deposition of potassium on Pd(100) surface decreases the work function of Pd, which is increased following the adsorption of a monolayer of CH₃Cl. As a result, the work function of the CH₃Cl + K/Pd(100) system is lower than that of K-free system and varies with the K coverage. If the same excitation mechanism and electron attachment described for a clean Pd surface is valid for this system, then the photolysis should occur at much less photonenergy than in the case of a clean Pd surface. Data collected in Table I support this consideration, as significant photolysis occurred on K-dosed surface (above $\Theta_K = 0.1$) even when wavelengths below 360 nm were removed. At monolayer K coverage, photodissociation only ceased when a 500 nm cutoff filter was used. These features suggest that the mechanism of the photostimulated decomposition of adsorbed CH₃Cl on K-promoted sample is the same as proposed for the clean Pd. Photoelectrons generated by illumination are responsible for the photodissociation of CH₃Cl and the preadsorbed potassium greatly facilitates this process.

V. CONCLUSIONS

(1) Illumination of adsorbed CH₃Cl on a clean Pd(100) surface at 85 K with Hg arc lamp induced the cleavage of C–Cl bond. The relative extent of the dissociation increased in the order submonolayer, monolayer, and condensed phase.

(2) The primary products of the photoinduced dissociation are Cl and CH₃ species; the latter decomposes to give CH₄, H₂, C₂H₆, and C₂H₄.

(3) The rate of photodissociation is negligible at wavelength longer than 280 nm. The estimated cross section for photodissociation of adsorbed CH₃Cl at monolayer at 254 nm was found to be 2.05×10^{-20} cm².

(4) Preadsorbed potassium markedly enhanced the effect of illumination, while preadsorbed Cl decreased it. The cross section of photodissociation at 254 nm for $\Theta_K = 0.5$ (monolayer) was calculated to be 3.23×10^{-20} cm².

(5) The study of the effect of the work function of coadsorbed layers and that of wavelength dependence suggested that the photoelectrons generated in the photoexcitation process play a dominant role in the photolysis of CH₃Cl on both clean and K-promoted Pd(100) surfaces.

¹ F. Solymosi and T. Bánsági, *J. Phys. Chem.* **83**, 552 (1979). F. Solymosi, L. Völgyesi, and J. Raskó, *Z. Phys. Chem. N.F.* **120**, 79 (1980), and references therein.

² F. Solymosi and J. Kiss, *Surf. Sci.* **135**, 243 (1983).

³ F. Solymosi and L. Bugyi, *Surf. Sci.* **177**, 685 (1984).

⁴ F. Solymosi, J. Kiss, and I. Kovács, *Surf. Sci.* **192**, 47 (1987).

⁵ F. Solymosi, A. Berkó, and T. I. Tarnóczy, *J. Phys. Chem.* **88**, 6170 (1984), and references therein.

⁶ T. J. Chuang, *Surf. Sci. Rep.* **1**, 3 (1983).

- ⁷W. Ho, Surface Photochemistry, in *Desorption Induced by Electronic Transition Springer Series in Surface Sciences*, edited by G. Betz and P. Varga, Vol. 19, 1990, p. 48.
- ⁸X. L. Zhou and J. M. White, *J. Phys. Chem.* **94**, 2643 (1990).
- ⁹F. Solymosi, J. Kiss, and K. Révész, *J. Phys. Chem.* **94**, 2224 (1990).
- ¹⁰Z. C. Ying and W. Ho, *Phys. Rev. Lett.* **65**, 741 (1990).
- ¹¹A. Berkó and F. Solymosi, *Surf. Sci.* **187**, 359 (1987).
- ¹²J. B. Benzinger and R. J. Madix, *J. Catalysis* **65**, 49 (1980).
- ¹³M. A. Henderson, G. E. Mitchell, and J. M. White, *Surf. Sci.* **184**, L325 (1987).
- ¹⁴X.-L. Zhou and J. M. White, *Chem. Phys. Lett.* **142**, 376 (1987).
- ¹⁵A. Berkó and F. Solymosi, *J. Phys. Chem.* **93**, 12 (1989).
- ¹⁶F. Solymosi, A. Berkó, and K. Révész, *Surf. Sci.* **240**, 50 (1990).
- ¹⁷J. G. Chen, T. P. Beebe, Jr., J. E. Crowell, and J. T. Yates, Jr., *J. Am. Chem. Soc.* **108**, 2881 (1986).
- ¹⁸X.-L. Zhou, F. Solymosi, P. M. Blass, K. C. Cannon, and J. M. White, *Surf. Sci.* **219**, 294 (1989).
- ¹⁹X.-L. Zhou, C. Yoon, and J. M. White, *Surf. Sci.* **206**, 379 (1988).
- ²⁰F. Steinbach, J. Kiss, and R. Kral, *Surf. Sci.* **157**, 401 (1985).
- ²¹E. P. Marsh, T. L. Gilton, W. Meir, M. P. Schneider, and J. P. Cowin, *Phys. Rev. Lett.* **61**, 2725 (1988).
- ²²E. P. Marsh, F. L. Tabares, M. R. Schneider, and J. P. Cowin, *Vac. Sci. Technol. A* **5**, 519 (1987).
- ²³S. K. Jo and J. M. White, *J. Phys. Chem.* **94**, 6852 (1990).
- ²⁴B. Roop, K. G. Lloyd, S. A. Costello, A. Campion, and J. M. White, *J. Chem. Phys.* **91**, 5103 (1989).
- ²⁵J. Kiss, A. Berkó, K. Révész, and F. Solymosi, *Surf. Sci.* **240**, 59 (1990).
- ²⁶F. Solymosi and A. Berkó, *J. Chem. Phys.* **90**, 2492 (1989).
- ²⁷F. Solymosi and K. Révész, *J. Am. Chem. Soc.* (in press).
- ²⁸D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley Interscience, New York, 1970).
- ²⁹W. T. Tysoe and R. M. Lambert, *Surf. Sci.* **1**, 199 (1987).
- ³⁰L. Hanley, X. Guo, and J. T. Yates, Jr., *Surf. Sci.* (in press).
- ³¹Z. M. Liu, S. A. Costello, B. Roop, S. R. Coon, S. Akhter, and J. M. White, *J. Phys. Chem.* **93**, 1681 (1989).
- ³²St. J. Dixon-Warren, K. Leggett, M. S. Matyjaszczyk, J. C. Polanyi, and P. A. Young, *J. Chem. Phys.* **88**, 4092 (1988).
- ³³X. L. Zhou and J. M. White, personal communication.

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