JOURNAL OF CATALYSIS **143**, 138–148 (1993)

Infrared Spectroscopic Study of the Adsorption and Dissociation of Methyl Halides on Silica-Supported Pd

J. RASKÓ, J. BONTOVICS, AND F. SOLYMOSI

Institute of Solid State and Radiochemistry, A. József University, and Reaction Kinetics Research Group of the Hungarian Academy of Sciences,[1] *P.O. Box 168, H-6701 Szeged, Hungary*

Received October 15, 1992; revised February 10, 1993

The adsorption and dissociation of CH_3Cl and CH_3I have been investigated by means of infrared spectroscopy at 193–573 K. Both compounds adsorb molecularly on Pd/SiO_2 at 193 K and interact strongly with the OH groups of silica to form H-bridge-bonded alkyl halides. This was exhibited by a significant attenuation of the absorption band at 3744 cm^{-1} and by the development of a broad spectral feature at 3607 cm^{-1}. The absorption band due to adsorbed CH_3 species, indicating the dissociation of CH_3Cl, was detected first at 263 K and was eliminated above 373 K. Preadsorbed CO and O exerted no observable influence on the adsorption and dissociation CH_3Cl. However, potassium additive promoted the dissociation and somewhat stabilized the CH_3 group on the surface. The dissociation of CH_3I occurred at lower temperature and to a greater extent than that of CH_3Cl. © 1993 Academic Press, Inc.

1. INTRODUCTION

Two reasons motivated the present study of the adsorption and dissociation of alkyl halides on solid surfaces. First, halogenated organic compounds are hazardous materials, the destruction of which is an important project for catalysis (*1*). Second, alkyl halides, particularly CH_3I, are suitable compounds for the generation of adsorbed CH_3 species on solid surfaces (*2*). This permits determination of the bonding, structure and reactivity of such species, which may play important roles in the methanol and Fischer–Tropsch syntheses, and in the oxidative dimerization of methane.

As silica-supported Pd is an effective catalyst in methanol synthesis, we concentrated first on this material. In the case of a Pd(100) single-crystal, we found that CH_3Cl adsorbs molecularly on the clean surface, and desorbs below 300 K without detectable dissociation (*3, 4*). Potassium adatoms, however, greatly promote the dissociation, to give CH_3 and Cl (*3, 5*). Illumination with the full spectrum of a mercury lamp induces CH_3Cl dissociation on clean Pd and enhances the extent of its dissociation on K-promoted Pd(100) (*6, 7*). CH_3I was found to be much more reactive than CH_3Cl on Pd(100): at low coverage it dissociates thermally to adsorbed CH_3 and I (*7*).

In the present work, the above studies are extended to silica-supported Pd and to higher pressure. We apply infrared spectroscopy, which, as far as we are aware, has not been used so far to follow the adsorption and dissociation of alkyl halides on supported metals.

2. EXPERIMENTAL

Pd/SiO_2 samples were prepared by incipient wetting of silica (Cabosil) with an aqueous solution of palladium chloride (Ventron). For preparation triply distilled water was used. The Pd content was 10 wt%. The Pd + K/SiO_2 sample was prepared by coimpregnation of SiO_2 in an aqueous solution of palladium chloride and potassium nitrite (Reanal). The K weight percentage was 2.5%. All materials used were of analytical grade. The purity of Cabosil SiO_2 was checked by Inductively Coupled Plasma

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[1] These laboratories are part of the Center for Catalysis, Surface, and Materials Science at the University of Szeged.

0021-9517/93 $5.00

(ICP) spectroscopy. The following elements were detected: Zn, 0.00128%; Ni, 0.00076%; Fe, 0.00053%; and Co, 0.00002%. Tests for Mg, Al, Ca, Cr, Ba, Ti, Na, K, Li, Cu, and Cd were negative. After impregnation, the samples were dried in air at 373 K. For IR studies, the dried Pd/SiO_2 powder was pressed into self-supporting wafers (30 × 10 mm, 10 mg/cm^2). The pretreatment of samples was performed in a vacuum IR cell: the samples were (a) heated (20 K/min) to 673 K under continuous evacuation, (b) oxidized with 100 Torr (13.3 kPa) of O_2 for 30 min at 673 K, (c) evacuated for 15 min, and (d) reduced in 100 Torr of H_2 for 60 min at 673 K. This temperature is sufficient to achieve a complete reduction (*8*). This was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment.

CH_3Cl (Merck) and CH_3I (Merck) were purified by fractional distillation and stored in a glass bulb. CH_3I was protected against light.

Infrared spectra were recorded with a Biorad (Digilab. Div.) Fourier transform IR spectrometer (FTS 7) with a wavenumber accuracy of ±2 cm^{-1}. Typically 16 scans were registered. All subtractions of the spectra were taken without the use of a scaling factor (f = 1.0000). Mass spectrometric analyses were performed with the help of an MS 10 (AEI) mass spectrometer.

3. RESULTS

3.1. Adsorption of CH_3Cl

Figure 1 shows the infrared spectrum of gaseous CH_3Cl (10 Torr). Absorption bands are listed in Table 1. The spectrum is consistent with the literature data (*9*).

The spectrum obtained in the presence of 10% Pd/SiO_2 at 193 K showed the same characteristic bands, with the difference of a new band at 2962 cm^{-1}. Small shifts in the positions of the other bands also occurred (Fig. 1). In response to CH_3Cl adsorption, the intensity of the OH band of SiO_2 at 3744 cm^{-1} decreased and a broad band centered at 3612 cm^{-1} developed. All these new bands disappeared or were greatly attenuated after evacuation at 193 K: very weak bands remained at 3607 and 2954 cm^{-1}.

Heating of the sample in vacuum to 243 K caused the complete elimination of these absorption bands, too (Fig. 2). Surprisingly, however, further heating of the sample under continuous evacuation to and above

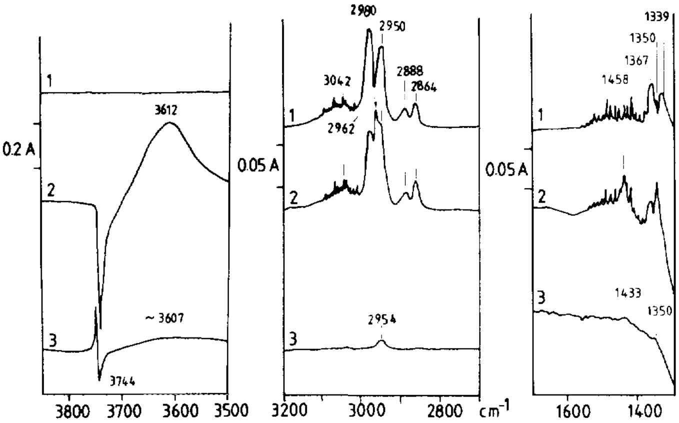


FIG. 1. Infrared spectra of Pd/SiO_2 following the adsorption of CH_3Cl at 10 Torr and 193 K and subsequent evacuation. For comparison the gas-phase spectrum of CH_3Cl is also shown. (1) CH_3Cl gas at 300 K, (2) CH_3Cl adsorbed at 193 K, and (3) evacuation at 193 K after (2). The minimum at 3744 cm^{-1} is indicative of consumption, while the maximum centered at 3612 cm^{-1} indicates the production of OH groups.

TABLE I

Comparison of the Fundamental Vibrational Frequencies (in cm^{-1}) for CH_3Cl and CH_3I in the Gas Phase and Physically Adsorbed on Pd/SiO_2

Assignments	CH_3Cl (*9*) gas	CH_3Cl[a] gas	CH_3Cl[a] adsorbed	Assignments	CH_3I (*23*) gas	CH_3I[a] gas	CH_3I[a] adsorbed
			3612				~3609
$\nu_{as}(CH_3)$	3042	3042	3042	$\nu_{as}(CH_3)$	3060	3064	3064
$\nu_s(CH_3)$	2966	2980	2980	$\nu_s(CH_3)$	2933	2958	2963
$\delta_{as}(CH_3)$	1455	1458	1433	$\delta_{as}(CH_3)$	1436	1438	1431
$\delta_s(CH_3)$	1355	1350	1350	$\delta_s(CH_3)$	1252	1252	—
δ(C–Cl)	1015	1019	—				
				$\rho(CH_3)$	882	916	—
ν(C–Cl)	732	—	—				
				ν(C–I)	533	—	—

[a] This work. Several weak bands shown in the spectra for gaseous compounds have been observed before, but were not assigned to particular vibrations (*9*, *23*).

263–283 K caused the reappearance of a group of bands in the interval 2856–2954 cm^{-1}, with the dominant feature at 2920 cm^{-1} (Fig. 2). Maximum intensity was measured at 293 K, and these bands were detected up to 373 K. Mass-spectrometric analysis of the gas phase during heating of the adsorbed layer formed by the adsorption and degassing of CH_3Cl at 193 K showed a well-detectable desorption of CH_3Cl from 250 K (Fig. 3).

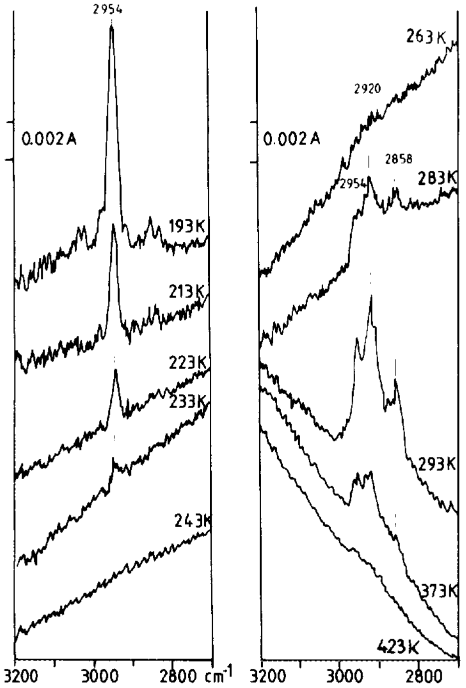


FIG. 2. Spectral changes observed upon heating the adsorbed layer on Pd/SiO_2 under continuous evacuation. CH_3Cl (10 Torr) was adsorbed at 193 K.

In the subsequent measurements, the Pd sample was heated in the presence of CH_3Cl vapor from 193 to 300 K and the spectra were recorded at the adsorption temperatures. The spectra obtained were identical with that of gaseous CH_3Cl. A significant change occurred in the OH frequency range: with the increase of temperature, the new band at 3609–3649 cm^{-1} gradually attenuated and at the same time the OH band of SiO_2 at 3744 cm^{-1} gained in intensity. This is illustrated in Fig. 4.

On subtraction of the spectrum of gaseous CH_3Cl from each spectrum, weak absorption bands were registered at 2964, 2864, 1440, and 1349 cm^{-1} (Fig. 5), which can be attributed by physisorbed CH_3Cl.

When the sample was kept in CH_3Cl vapor at high temperature (300–573 K) for 10 min and the spectra were then recorded in the presence of CH_3Cl at 300 K, no spectral features different from those attributed to gaseous CH_3Cl were observed. However, after degassing the sample at 300 K, weak absorption bands were detected at 2960,

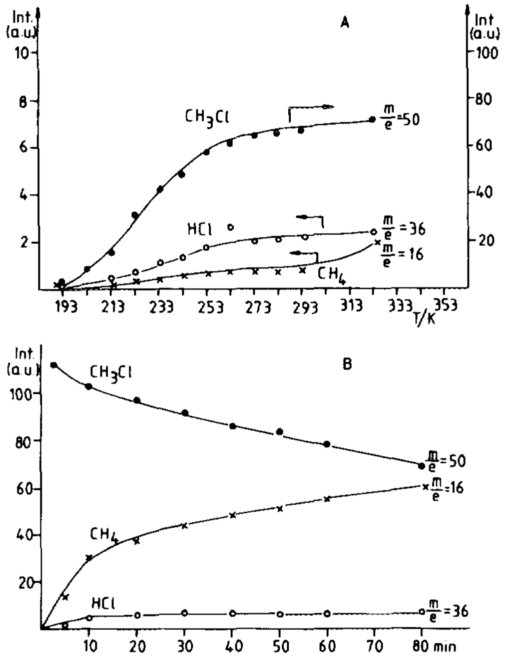


FIG. 3. Mass spectrometric analysis of the gas phase: (A) during heating the adsorbed CH_3Cl (CH_3Cl was adsorbed at 193 K and evacuated at the same temperature) and (B) during the decomposition of CH_3Cl (10 Torr) on Pd/SiO_2 at 473 K.

2920, and 2852 cm^{-1}. The most intense one was that at 2920 cm^{-1}. Their intensities were maximum when the catalyst sample was treated with CH_3Cl at 373 K, and decreased to very low values at adsorption temperatures of 573 K and above. No bands were seen in the frequency range 1300–1700 cm^{-1}.

Mass-spectrometric analysis of the gas phase during high-temperature adsorption of CH_3Cl on Pd/SiO_2 at 473 K showed that decomposition results in the formation of CH_4 and HCl (Fig. 3).

Similar measurements were performed with the silica support alone. Weakly adsorbed CH_3Cl was eliminated by evacuation at 213 K. It is important that the absorption bands that appeared in the spectra of Pd/SiO_2 degassed at 283–373 K were not observed for pure SiO_2. In contrast with Pd/SiO_2, no spectral features were found after high-temperature (300–573 K) treatment with CH_3Cl.

3.2. *Effect of Preoxidation of Pd/SiO₂*

A Pd/SiO_2 sample reduced at 673 K was treated with 10 Torr of O_2 for 30 min. After degassing at 300 K, the sample was cooled to 190–200 K and 10 Torr of CH_3Cl was introduced. In the presence of CH_3Cl, the same spectral features were observed as for the reduced sample. After evacuation at 193 K, absorption bands could be detected at 2952 and 2865 cm^{-1}. Elevation of the evacuation temperature to 213 K eliminated both bands. Between 223 and 263 K, there were no apparent signs of these bands in

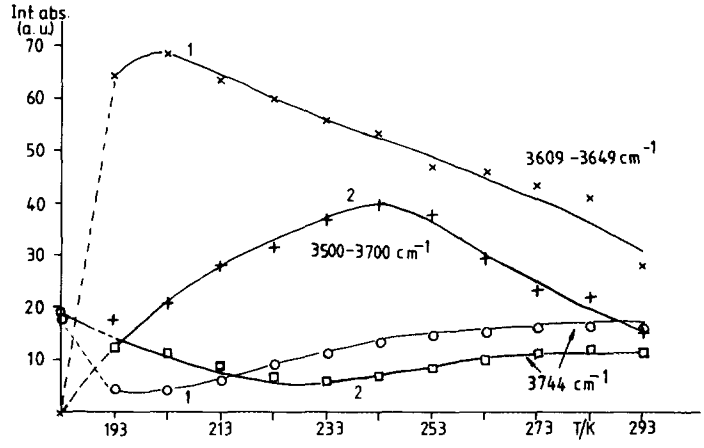


FIG. 4. Changes in the integrated absorbances of the bands observed in the OH region of Pd/SiO_2 spectra during (1) CH_3Cl adsorption and (2) CH_3I adsorption as a function of temperature.

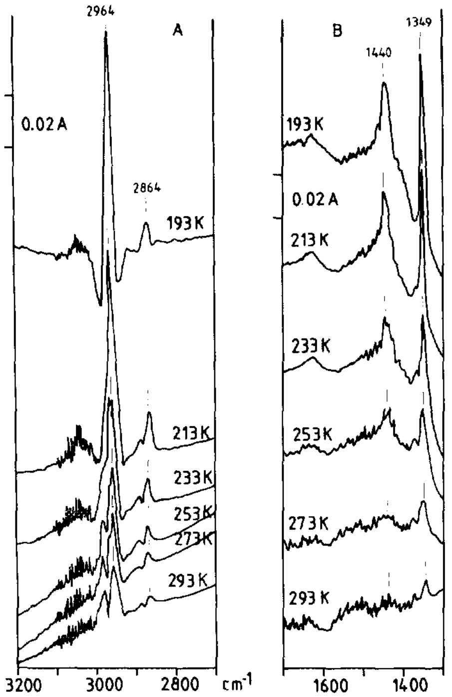


FIG. 5. Effects of the adsorption temperature of CH_3Cl (10 Torr) on the infrared spectra of Pd/SiO_2. The spectrum for gaseous CH_3Cl has been subtracted form each spectrum. (A) CH stretching region and (B) CH deformation region.

the spectra. At 273 K, however, they appeared again at 2956 and 2855 cm^{-1}, with very low intensities. At and above 283 K, a band developed at 2921 cm^{-1}, which became dominant at 283–373 K. All bands disappeared at 423 K.

3.3. Effect of Preadsorbed CO

The presence of preadsorbed CO (adsorption of CO at 10 Torr and degassing at 300 K before CH_3Cl admission) did not affect the spectral features characteristic of physisorbed CH_3Cl and the development and stability of the 2922-cm^{-1} band, under the same experimental conditions as in Section 3.1.

3.4. Effect of Potassium

Since potassium adatoms markedly changed the chemistry of CH_3Cl on Pd single-crystal surfaces under UHV conditions (5), it seemed worthwhile to investigate the effects of potassium in the case of the Pd/SiO_2 catalyst at much higher pressure.

Following the adsorption of CH_3Cl on 10% Pd + 2.5% K/SiO_2 at 193 K and degassing at the same temperature, absorption bands were detected at 2962 and 2858 cm^{-1} (in the absence of potassium, only the 2954-cm^{-1} band remained in the spectrum under similar conditions). The most striking feature observed during heating of the layer adsorbed on Pd + K/SiO_2 was the appearance of the small 2923-cm^{-1} band (with concomitant decrease of the 2962-cm^{-1} band) at as low as 213 K, a somewhat lower temperature than on potassium-free Pd/SiO_2 (at 263 K). The 2923-cm^{-1} band (at higher temperatures at 2918 cm^{-1}) was stable against

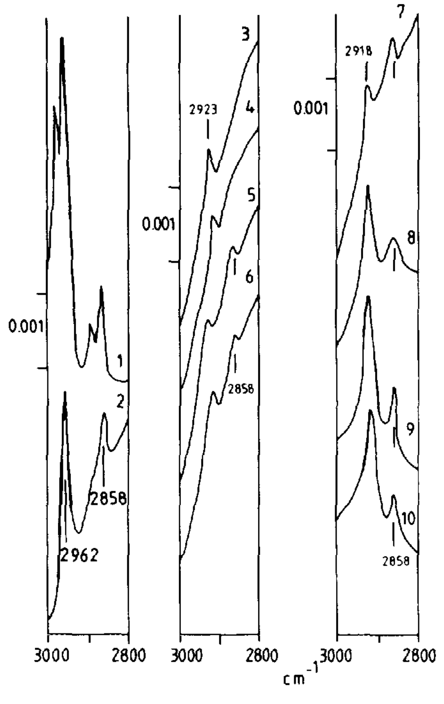


FIG. 6. Spectral changes observed on heating the adsorbed layer on 10% Pd + 2.5% K/SiO_2 under continuous evacuation: (1) CH_3Cl (10 Torr) adsorbed at 193 K and evacuation at (2) 193 K, (3) 213 K, (4) 223 K, (5) 233 K, (6) 243 K, (7) 263 K, (8) 283 K, (9) 293 K, and (10) 373 K.

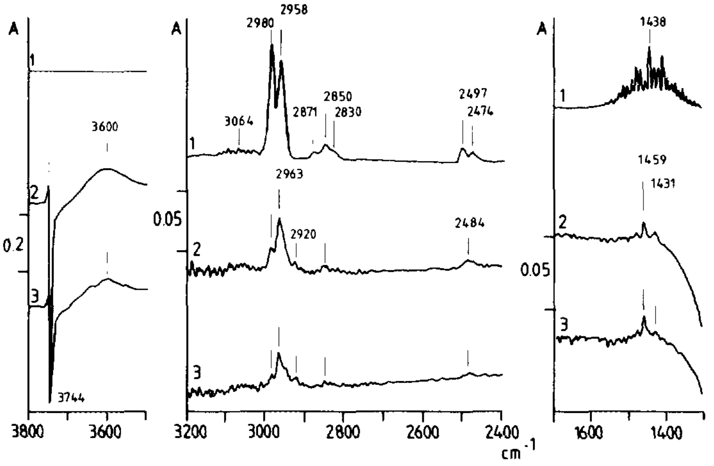


FIG. 7. Infrared spectra of Pd/SiO$_2$ following the adsorption of CH$_3$I at 10 Torr and 213 K and subsequent evacuation. For comparison the gas phase spectrum of CH$_3$I is also shown. (1) CH$_3$I gas at 300 K, (2) CH$_3$I adsorbed at 213 K, and (3) evacuation at 213 K after (2).

evacuation up to 423 K. Spectra are displayed in Fig. 6.

Although the presence of potassium resulted in the earlier appearance of the 2923–2918 cm^{-1} band, its intensity was lower than on potassium-free Pd/SiO$_2$. This points to the smaller adsorptive capacity of the Pd + K/SiO$_2$ surface.

3.5. Adsorption of CH$_3$I

Infrared spectra of gaseous CH$_3$I and CH$_3$I adsorbed on Pd/SiO$_2$ are depicted in Fig. 7. Characteristic absorption bands are listed in Table 1. In the case of adsorbed CH$_3$I, absorption bands different from those observed for gaseous CH$_3$I were measured at 2920 and 1459 cm^{-1}, and the gaseous band at 1438 cm^{-1} shifted appreciably to 1431 cm^{-1}. An intense new band at 3552–3609 cm^{-1} was also recorded here. Degassing of the sample at 213 K caused only a loss in intensity of absorption bands.

On heating the adsorbed layer to 223 K, the 3600-cm^{-1} band was not further seen, while in the C–H stretching region absorption bands were detected at 2963, 2945, 2920, and 2850 cm^{-1} (Fig. 8). These were

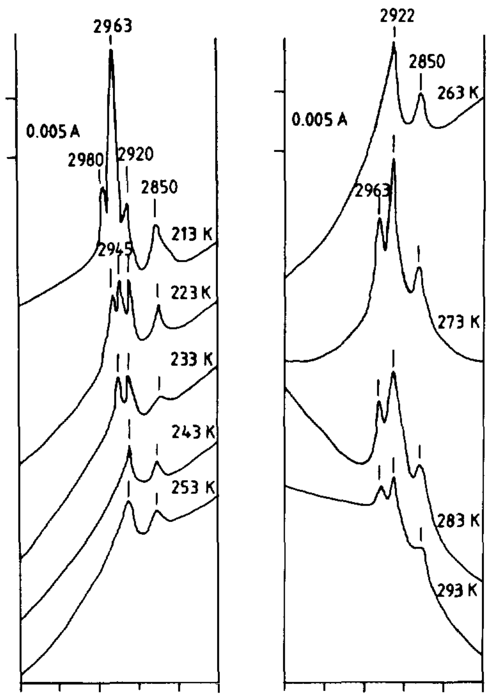


FIG. 8. Spectral changes observed on heating the adsorbed layer on Pd/SiO$_2$ under continuous evacuation. CH$_3$I (10 Torr) was adsorbed at 213 K.

stable up to 293 K, except for the bands at 2963 and 2945 cm^{-1}, which could be detected only up to 233 K. In the low-frequency region (in the range of deformation modes of CH$_3$), only the band at 1431 cm^{-1} remained in the spectra after degassing of the sample at 213 K. With the increase of temperature, this band split into bands at 1456 and 1420 cm^{-1} (at 223–233 K) and bands at 1457 and 1394 cm^{-1} could be detected up to 293 K.

Subtraction of the gas-phase spectrum of CH$_3$I from those registered after CH$_3$I adsorption at different temperatures led to the appearance of small bands at 2964, 2481, and 1430 cm^{-1}. At higher temperatures, bands at 2978 and 2849 cm^{-1} have also developed, with a concomitant shift of the 2964 cm^{-1} band to 2960 cm^{-1}. The 2964–2960 cm^{-1} band had maximum intensity at 243–253 K. Besides the band at 3744 cm^{-1}, characteristic of OH groups on the silica surface, a broad band centered at around 3600 cm^{-1} was also observed during heating of the sample in CH$_3$I. The integrated absorption of this broad band showed a maximum at 243 K, and the 3744 cm^{-1} band passed through a minimum at 233 K (Fig. 4). All these bands can be assigned to CH$_3$I physisorbed on the Pd/SiO$_2$ surface.

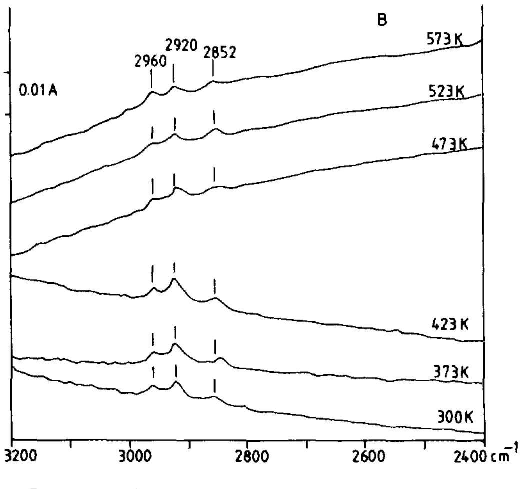


FIG. 9. Infrared spectra of Pd/SiO$_2$ treated with CH$_3$I (10 Torr) at different temperatures and after degassing at 300 K. All spectra were recorded at 300 K.

Figure 9 shows IR spectra recorded at 300 K following CH$_3$I adsorption at 300–573 K with degassing of the sample always at 300 K. After evacuation of the sample, weak absorption bands were identified at 2960, 2920, and 2852 cm^{-1}. Their intensities decreased with increase of the temperature.

For comparison we performed the same kind of experiments on the pure silica support. After the evacuation of gaseous CH$_3$I, we could identify very weak absorption bands at 2960, 2920, and 2850 cm^{-1} up to 223 K, but the absorbance of these bands was less than a factor of 5 compared to those registered for Pd/SiO$_2$.

4. DISCUSSION

4.1. Characteristics of Alkyl Halides on Single-Crystal Surfaces

Although efforts to destroy halogenated hydrocarbons have recently increased, very little is known of their adsorption behavior on oxide and supported metal catalysts. A notable exception is the IR study of the adsorption of CH$_3$Cl on an alumina surface (*10, 11*). In contrast, several thorough studies have been performed on the adsorption and dissociation of these compounds on metal single-crystal surfaces, using the modern tools of surface science (*2–7, 12–20*). Their surface photochemistry has also been the subject of detailed studies; the formation of a strong bond between metal and halogen atoms greatly facilitates the completion of the photoinduced dissociation of the C–halogen bond (*2*).

A general feature of the adsorption of alkyl halides on metal single-crystal surfaces is a significant decrease in the work function of the metal, indicating that adsorbed methyl halides have positive outward dipole moments. This is consistent with the bonding of molecular methyl halides through the halogen atoms, as these molecules all have permanent dipoles with the methyl group positive. The binding energy of methyl halides adsorbed on metals, and the tendency of the C–halogen bonds to undergo cleavage generally, increase in the sequence CH_3Cl–CH_3Br–CH_3I.

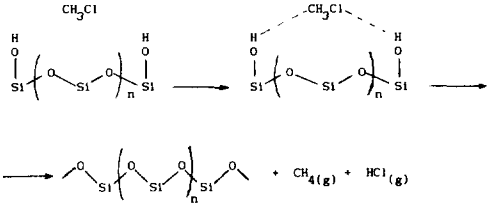
CH_3Cl adsorbs relatively weakly on most of the Pt metals, and desorbs below 300 K without detectable dissociation. This was the case for the Pd(100) surface (*3*, *4*), and the occurrence of dissociation required the presence of electron-donating promoters, or illumination of the adsorbed layer (*5–7*).

4.2. Characteristics of Adsorption of CH_3Cl on Pd/SiO$_2$

Comparison of the spectra of adsorbed CH_3Cl with the gas-phase spectrum of CH_3Cl indicates that the adsorption on Pd/SiO_2 (or on SiO_2) causes the absorption bands of CH_3Cl to shift in frequency to lower wavenumber, with a reduction in intensity of the band at 3744 cm^{-1}. The bands observed for adsorbed CH_3Cl were assigned as in Table 1. The absorption bands of adsorbed CH_3Cl underwent peculiar changes as a function of temperature; they decreased from 193 to 243 K and appeared again above 263 K. They were detected up to 373 K. At the moment we cannot propose a proper explanation of this behaviour. We may speculate that the structure of CH_3Cl in the adsorbed layer altered above 260 K.

The changes observed in the OH region in the spectra of both Pd/SiO_2 and SiO_2 samples show the important role of surface OH groups (silanol groups) in the processes of CH_3Cl adsorption. After the pretreatment used in this study, a sharp band at 3744 cm^{-1} was detected in the spectra, which is characteristic of free OH groups on a silica surface. In response to CH_3Cl adsorption, a long tail appeared on the low-wavenumber side of this band, indicating the presence of H-bridge-bonded surface species. In parallel with this phenomenon, the intensity of the band of free silanol groups was reduced.

After elimination of the broad absorption on the low-wavenumber side of the 3744-cm^{-1} band (by evacuation at low temperatures, for instance), the intensity of the 3744-cm^{-1} band never reached its original value. All of these phenomena indicate that (i) silanol groups are involved in the development of H-bridge-bonded CH_3Cl surface species, and (ii) surface OH groups of silica are consumed in the formation of the desorption products. We assume the following scheme for the above processes:



In harmony with this picture we detected the formation of HCl and CH_4 by mass-spectrometry when adsorbed CH_3Cl was heated. However, the amounts of HCl and CH_4 evolved were small. Accordingly, the consumption of silanol groups in these processes should be very limited, a view which was supported by the small difference between the intensities of the silanol group bands before and after CH_3Cl treatment.

Another reason for the disappearance of the broad absorption in the OH region may be the desorption of CH_3Cl molecules (also detected by MS). This process may contribute to a relatively high extent to elimination of the broad spectral feature, but it does not explain the formation of HCl and CH_4 and the consumption of silanol groups, respectively.

It is to be noted that similar phenomena were observed in the CH_3Cl/Al_2O_3 system by Beebe *et al.* (*11*). The broad absorption centered at ~3500 cm^{-1} was interpreted as a result of "the production of hydroxy groups having these rather low frequencies." The consumption of "free" hydroxy groups of alumina (3732 and 3691 cm^{-1}) has been connected with the formation of surface methoxy species (clearly demonstrated by the bands at 2960, 2849, 1475, and 1055 cm^{-1} at and above 430 K).

In the present case we have no evidence for the formation of methoxy species on silica and silica-supported Pd in the adsorption of CH_3Cl: the spectral features observed in the detectable region (above 1300 cm^{-1}) do not fit the spectroscopic criteria for a convincing assignment of $CH_3O(a)$.

4.3. Dissociation of CH_3Cl on Pd/SiO_2

Let us deal now with the question of the dissociation of CH_3Cl on Pd/SiO_2. In this respect, the HREEL (high-resolution electron energy loss) spectra following the adsorption of alkyl halides on single-crystal surfaces are of great help. In the case of Pt(111) and Ru(001) surfaces, White and coworkers (*12, 17*) observed the dissociation of CH_3I even at 100–150 K. The dissociation was accompanied by a shift in the C–H stretching frequency from 3060–3025 cm^{-1} to 2910–2925 cm^{-1}. Another diagnostic for CH_3I dissociation is a decrease in the C–H bending frequencies, particularly the asymmetric C–H bending mode, by about 100 cm^{-1}, from 1430 to 1320 cm^{-1}. Photolysis of molecular CH_3Br to produce a CH_3 group adsorbed on Pt(111) and Cu/Ru(001) also caused a 45–65 cm^{-1} decrease in the C–H stretching frequency: losses appeared at 2940 cm^{-1}, $\nu_{as}(CH_3)$, and 1360 cm^{-1}, $\delta_{as}(CH_3)$ (*21*). These absorption bands attributed to $CH_3(a)$ species are very close to those registered for adsorbed CH_3 on Ni(111) from the activated dissociation of CH_4 (*22*).

Some of the above spectral features were clearly observed following the adsorption of CH_3Cl on Pd/SiO_2 (Fig. 2). Relatively intense absorption bands were detected at 2922 cm^{-1} after degassing of the sample at 300 K. The same, but much weaker bands were also noted when the adsorbed layer was heated from 193 to above 283 K. The appearance of the 2922 cm^{-1} band in our case suggests that the dissociation of CH_3Cl may occur on the Pd/SiO_2 surface:

$$CH_3Cl(a) = CH_3(a) + Cl\ (a).$$

The extent of the dissociation is very low and only the very sensitive FTIR spectroscopy permitted detection of the absorption band of adsorbed CH_3 species. Attempts to determine the pathways of reactions of adsorbed CH_3 species were not successful, very probably due to the low concentration. In the case of the Pd(100) surface we established three reactions of CH_3 groups: self-hydrogenation to methane, recombination to ethane, and complete decomposition to surface carbon (*6, 7*).

4.4. Effects of Coadsorbed Species

As concerns the coadsorbed species (O(a), CO(a), or K), we could detect an appreciable effect on CH_3Cl adsorption only in the presence of potassium. Its effect was manifested in a promotion of the CH_3Cl dissociation and in a greater stability of the 2922-cm^{-1} band (due to $CH_3(a)$). The intensity of this band (and consequently its surface concentration), however, was smaller than on potassium-free Pd/SiO_2. The latter phenomenon can be interpreted as a consequence of the relatively high coverage of Pd by potassium, which reduces the number of surface sites available for CH_3Cl adsorption.

Similar features were observed for CH_3Cl + K/Pd(100) system, where the effect of potassium was attributed to its electron-donating character, which leads to an enhanced electron transfer from the Pd to the CH_3Cl antibonding orbital (*5*). It was assumed that the formation of partially negatively charged species facilitates the dissociation of the C–Cl bond. In the present case the situation is more complicated as potassium is present as K^+ ion. Surprisingly, however, no significant difference was experienced in the promoting effect of potassium when it was deposited in metallic form or in the form of K^+–OH^- on transition metal surfaces (*24*). The electron donation can be ascribed to the simultaneous effect of K^+ and O^{2-} taking into account that K^+ alone would hardly release electrons. The electron donating character of potassium and oxygen overlayers has been considered by others as well (*24–28*). Alternatively, we can assume that the strong electric field exerted by K^+ ion influences the reactivity of adsorbed CH_3Cl. Several recent papers demonstrated that electric fields could significantly affect surface reactions (*29–31*). Further work in this area is clearly required.

The findings that adsorbed oxygen and carbon monoxide do not alter the processes of CH_3Cl adsorption can be connected with the special adsorptive behavior of palladium. In this respect, we detected only multiple-bonded CO (bridge, or hollow-site adsorbed CO) during CO adsorption. These adsorbed CO forms leave the on-top positions free, and thus the adsorption of CH_3Cl on these sites is possible.

4.5. Adsorption and Dissociation of CH_3I on Pd/SiO_2

In the study of the adsorption of CH_3I on Pd/SiO_2 we observed features that were in many respects similar to those in the case of the adsorption of CH_3Cl. Shifts in the characteristic absorption bands of CH_3I to lower wavenumbers were experienced following its adsorption (Table 1). Changes in the intensities of the absorption in the OH region clearly demonstrate that the surface OH groups are involved in the bonding of CH_3I on the surface. An important finding is that *the absorption band at around 2920 cm^{-1}, attributed to the $CH_3(a)$ stretching frequency, appeared at much higher intensities* than in the case of CH_3Cl adsorption, and it was detected at as low a temperature as 213–223 K. On the basis of this result, we can conclude that the extent of dissociation of CH_3I is greater than that of CH_3Cl. The higher reactivity of CH_3I to form surface CH_3 is in harmony with the literature findings (*12*), and is interpreted on the basis of the different bond strengths in CH_3–I and CH_3–Cl. In this case we also identified very weak absorption bands at 2945, 2850, and 1394 cm^{-1}, which may be assigned to the stretching and deformation modes of C–H in CH_3O species. As silica absorbs IR radiation below 1300 cm^{-1}, the band due to the C–O vibration in CH_3O could not be detected. Accordingly, the formation of CH_3O in the reaction of the OH groups of the support with CH_3I may also occur in this case.

The high reactivity of CH_3I is reflected by the fact that all these absorption bands were seen, although in much lower intensities following the adsorption of CH_3I on the Pd-free silica surface.

5. CONCLUSIONS

1. Methyl chloride and iodide interacted with OH groups of silica to form H-bridge-bonded surface species.
2. The dissociation of both CH_3Cl and CH_3I was observed on Pd/SiO_2 at as low as 263 K for CH_3Cl and 213 K for CH_3I, as indicated by the appearance of a new band at 2920–2922 cm^{-1} attributed to the vibration of adsorbed CH_3 species.
3. Methyl groups were detectable on Pd/SiO_2 up to 373 K.
4. Preadsorbed potassium promoted the dissociation of CH_3Cl and extended the stability region of adsorbed CH_3 up to 423 K.

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