between 0.05 (water/N12,Bz,1,1/chlorobenzene in Figure 3) and 0.24 (water/N14,Bz,1,1/chlorobenzene in Figure 2) can be found for the percolation threshold, depending on the nature of the system. The results indicate that the value of the percolation threshold is decreased as the strength of the attractive interdroplet interactions increases, as predicted by recent theoretical calculations.[21,22] Indeed, the virial coefficient for the droplet translational diffusion coefficient determined by quasielastic light scattering has been found to become increasingly negative, indicating increasingly attractive interactions as the surfactant chain length decreases for the water/chlorobenzene/Nm,Bz,1,1 microemulsions[20] and as the oil chain length increases for the water/AOT/*n*-alkane microemulsions.[5,23] From the above it is also clear that a strong correlation exists between the variations of k_e and interdroplet interactions with surfactant and oil chain lengths.

Mechanism of Electrical Conductivity above Percolation Threshold in w/o Microemulsions. Various mechanisms have been proposed to explain the percolative conduction observed with some w/o microemulsions, the most accepted one being associated with surfactant ions hopping from one droplet to the neighboring ones in the clusters of droplets then present in the microemulsion above percolation threshold. Such a mechanism, however, does not easily explain why percolation occurs only when the rate constant for droplet collisions with exchange of material becomes larger than (1-2) × 10^9 M^{-1} s^{-1}. In fact this feature suggests that the electrical conductivity is mainly due to the motion of counterions in the narrow water tubes or channels created within the clusters of droplets present above the percolation threshold upon opening of the surfactant layers separating water cores of contiguous droplets. The length and number of these transient tubes and in turn the conductivity would increase rapidly above the percolation threshold.

Conclusions

We have shown that the rate constant k_e for droplet collision with exchange of material must reach a value of a least (1-2) × 10^9 M^{-1} s^{-1} for percolative conduction to occur in a number of w/o microemulsions, irrespective of the parameter which is varied to induce percolation and the nature of the w/o microemulsion. We have also shown that the increase of k_e and the occurrence of electrical percolation correlate with an increase of attractive interactions between droplets. We are currently undertaking experiments on more complex w/o microemulsions to check the degree of generality of these conclusions.

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Adsorption and Dissociation of CH_3Cl on Clean and Potassium-Promoted Pd(100) Surfaces

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CH_3Cl adsorbs molecularly on a clean Pd(100) surface at 100 K and desorbs intact without a detectable dissociation. Preadsorbed potassium dramatically influences these processes: it induces the cleavage of C-Cl bond to yield adsorbed CH_3 and Cl even at 135 K which then react further to give CH_4, C_2H_6, C_s, and H_2.

Introduction

The study of the adsorption and dissociation of alkyl halides on metal surfaces has a strong relevance to the better understanding of C_1 chemistry, particularly the synthesis of methane and methanol from CO and CO_2 as well as the partial oxidation of methane. The adsorption and thermal dissociation of CH_3Cl has so far been investigated on Fe(100),[1] Ni(100),[2] Pt(111),[3] Al(111),[4] and Ag(111)[5] single-crystal surfaces. The adsorption was weak and molecular; CH_3Cl dissociated only on Fe(100).

Recently, we found that the potassium adatom is an excellent activator for CO_2 on Pd(100) and Rh(111) surfaces.[6-8] It induced a change in the structure and bonding of CO_2 and led to its dissociation. The key compound in the interaction is the CO_2^- anion. Potassium was also an effective promotor for other compounds, such as CO,[9] CH_3OH,[10] and HCOOH,[11] playing an important role in C_1 reactions.

In this work we present the first study of the effect of an alkali-metal overlayer on the adsorption and reaction of CH_3Cl on a transition-metal surface. It is demonstrated that potassium as an electron donor strongly influences the stability of CH_3Cl molecule, which desorbs practically intact from most of the transition metals.

Experimental Section

Experiments were performed in a standard UHV chamber equipped with facilities for AES, EELS (in the electronic range), TDS, and work function measurements. Sample preparation, cleaning, and potassium deposition have been described in our previous paper.[12]

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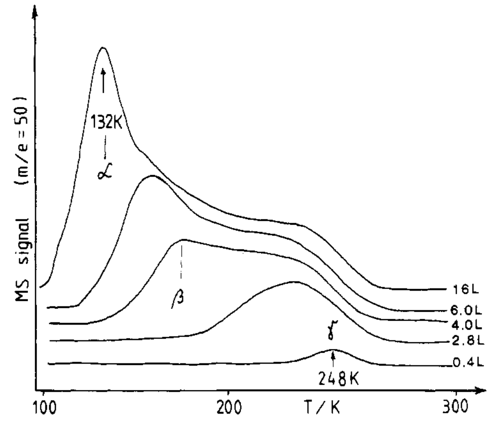

Figure 1. Thermal desorption spectra of CH_3Cl following CH_3Cl adsorption on clean Pd(100) surface at 100 K.

Results and Discussion

Figure 1 shows selected thermal desorption spectra for adsorbed CH_3Cl on a clean Pd(100) surface at 100 K. Low exposures produced only a single peak (γ) with a peak temperature, T_p = 248 K, which shifted to lower temperatures with increasing exposures. A new state (β) developed at 2 langmuirs (T_p = 200 K) and grew in parallel with the exposure. Its peak temperature also shifted when the exposure was increased. At 8-langmuir exposure, an intense peak appeared at 132 K (α) which showed no variance with the exposure. Upon heating the adsorbed layer to about 900 K, no other desorbing products were identified. Accordingly, we may conclude that CH_3Cl adsorbs molecularly on a clean Pd(100) surface at 100 K and desorbs below 270 K without any detectable dissociation.

From plotting the area of TPD curves against exposure, it appears that the surface becomes saturated by CH_3Cl at 20–24 langmuirs. A similar curve was obtained when the Auger signal of chlorine relative to Pd was plotted against the exposure. From the slope of these curves, the relative sticking probability of CH_3Cl adsorption was calculated to be 0.2. From the measured intensity of Cl Auger signal at saturation, using the method applied in our previous paper,[12] the approximate surface concentration of adsorbed CH_3Cl was calculated to be 0.7×10^{15} CH_3Cl molecules/cm^2. This value approaches well half of the number of Pd atoms on this face, which may suggest that every second Pd atom bonds one CH_3Cl molecule. Taking into account the vibrational spectrum of adsorbed CH_3Cl on other surfaces,[2-4] we assume that CH_3Cl is bonded to Pd through chlorine.

Following the adsorption of CH_3Cl at 100 K, new loss features developed at 17.7 and 13.1 eV in the EEL spectrum. Their intensity increased with increasing CH_3Cl exposure and decayed on exposure to the electron beam. These losses were eliminated around 260 K, when the EEL spectrum characteristic for a clean Pd(100) surface was restored. This is in harmony with thermal desorption data. No other loss features developed during gradual heating of the adsorbed layer to this temperature, and AES did not indicate the presence of any adsorbed species.

Different behaviors were observed when CH_3Cl was adsorbed on potassium-dosed Pd (Figure 2). The more strongly bonded state was missing both at low and high potassium coverages. The amount of CH_3Cl desorbed in the α state significantly decreased at low K coverage, θ_K = 0.05–0.20, whereas it increased in the β state. At high potassium coverage, θ_K = 0.4–0.5 (monolayer); a strong α peak was noticed, but no adsorption occurred in the β state. While no decomposition products were found for clean Pd, hydrogen and methane evolution was observed for potassium-dosed surfaces at all K coverages (Figure 2). At θ_K = 0.2 the peak temperatures of hydrogen and methane were at 393 and 216 K, respectively. At monolayer coverage of potassium, hydrogen evolution occurred at much higher temperatures, between 680 and 950 K. Methane also desorbed in a broad peak between 230 and 340 K, T_p = 270 K. In addition, ethane formed at low temperature, T_p = 135 K. The amount of decomposition products as a function of K coverage is plotted in Figure 3.

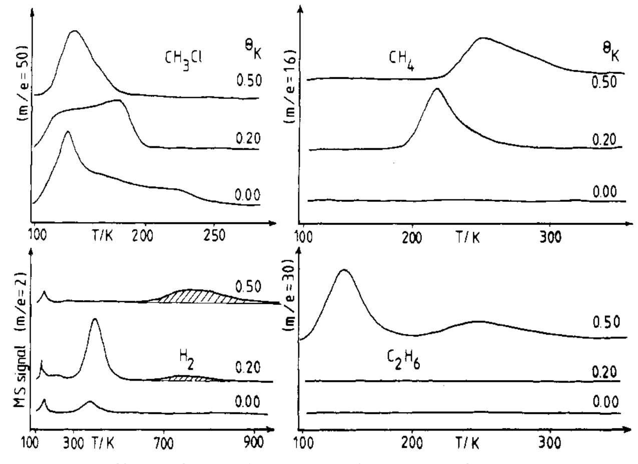

Figure 2. Effects of potassium on the desorption of CH_3Cl and on the formation of H_2, CH_4, and C_2H_6. The adsorption temperature was 100 K, and the CH_3Cl exposure was 20 langmuirs.

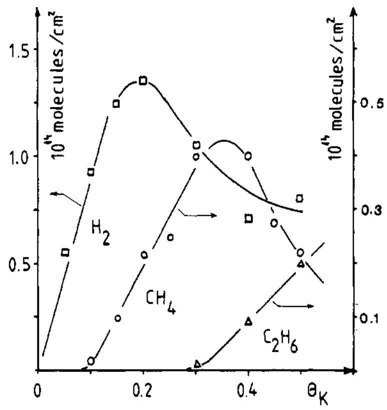

Figure 3. Amounts of decomposition products of CH_3Cl as a function of potassium coverage. The adsorption temperature was 100 K, and the CH_3Cl exposure was 20 langmuirs.

Taking into account the adsorption and desorption behaviors of methane and ethane on K-dosed Pd,[13] we can conclude that in the present case the evolution of both compounds is reaction-limited. In contrast, the formation of hydrogen is a desorption-limited process, as the same features of hydrogen desorption were observed from H + K coadsorbed layer on Pd(100).[13] (The effect of potassium on the adsorption and desorption of hydrogen on Pd(100) is very complex. We may count with a more significant penetration of hydrogen in the bulk, the study of which is in progress in our laboratory.)

During the heating of the adsorbed layer, the Cl Auger signal underwent a decrease (about 21% for θ_K = 0.5) in intensity at 100–200 K, remained constant at 200–500 K, and then gradually decreased to zero at 730 K. An important observation is that even after desorption of carbon-containing compounds, AES indicated the presence of surface carbon.

Adsorption of CH_3Cl on a potassium-dosed surface dramatically changed the desorption of potassium, particularly around monolayer coverage. As was shown before,[12] potassium desorbs from Pd(100) in a broad peak starting at 300 K; maxima were observed at 346, 427, and 530 K. Following the adsorption of CH_3Cl on a K-dosed surface, potassium desorbed in a narrow peak with T_p = 691 K, indicating a significant increase in the binding energy of potassium to the Pd. In a search for other desorption products in this temperature range, we detected Cl and KCl; their peak temperatures were also 691 K, which strongly suggests that potassium reacted with chlorine and thus was stabilized in the form of K–Cl on the Pd surface.

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In conclusion we can state that, as on Pt(111), Al(111), Ni(110), and Ag(111) surfaces,[1-5] CH_3Cl does not dissociate on clean Pd(100). It appears that the interaction energy with these metals is not sufficient to cause C–Cl cleavage in this molecule, the dissociation energy of which is 349 kJ/mol. However, the presence of potassium adatoms induces the rupture of this bond to yield $CH_{3(a)}$ and $Cl_{(a)}$. This effect can be very likely attributed to the electron-donating character of the potassium and to the formation of stable K–Cl. The effects of potassium and the details of the surface reactions depend on the state of potassium. We may assume that at low K coverage, when K exhibits mainly ionic character, (maximum decrease in the work function of Pd was observed at $\theta_K = 0.2$[12]), electron donation occurs through Pd metal:

$$CH_3Cl_{(a)} + e^- = CH_{3(a)} + Cl_{(a)}^{\delta-}$$

As a result of this the C–Cl bond is weakened and ruptured even around 216 K. At monolayer coverage, when K exhibits mainly metallic character,[12] we propose a direct interaction between K and CH_3Cl:

$$CH_3Cl_{(a)} + K_{(a)} = CH_{3(a)} + K^{\delta+}\text{–}Cl^{\delta-}{}_{(a)}$$

In subsequent reactions the dehydrogenation, the hydrogenation, and the dimerization of adsorbed CH_3 radical occur. The formation of ethane at low temperature, $T_p = 135$ K, indicates that the CH_3Cl bond is activated to such a great extent that dissociation on this surface occurs even at or below this temperature. The fact that methane formation for $\theta_K = 0.5$ proceeded at higher temperature than for $\theta_K = 0.2$ may indicate that a fraction of the adsorbed CH_3 is stabilized on this surface and decomposes only at 230–340 K.

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Preparation and Luminescence Properties of the *J* Aggregate of Cyanine Dyes at the Phospholipid Vesicle Surface

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J aggregate of several cyanine dyes without long alkyl chains was prepared by adsorbing dye molecules at the vesicle surface composed of L-α-dimyristoylphosphatidylcholine and dicetyl phosphate from aqueous phase. Two *J*-bands were observed in aqueous solutions of the vesicles whose surfaces were coadsorbed by two kinds of cyanine dyes. First experimental evidence of quenching of the resonance fluorescence of one dye aggregate by another dye aggregate at the same vesicle surface was noticed. A Stern–Volmer-type plot consisted of the combination of two straight lines with different slopes.

Some cyanine dyes could form the *J* aggregates in aqueous solutions in the presence or absence of certain electrolytes.[1] Several cyanine dyes with long alkyl chains could form monolayers containing the *J* aggregates at the air-water interface.[2] We have recently proposed tractable methods to prepare the *J* aggregates of some cyanine dyes without long alkyl chains by means of the Langmuir–Blodgett technique.[3] The *J* aggregate was prepared by cospreading both the cyanine dye and arachidic acid on a water surface and compressing the layer (spreading method). It was also prepared by the adsorption of cyanine dye molecules onto the arachidic acid monolayer from the subphase composed of dye solutions (adsorption method). Recently, Kinnunen and coworkers confirmed the requirement for the presence of the acidic phospholipid in the membrane for the binding of cytochrome *c* to the vesicle.[4] In this context, it is expected that cationic cyanine dyes are incorporated in the form of the *J* aggregate into acidic phospholipid containing vesicles.

The present paper reports that *J* aggregates of several cyanine dyes without long alkyl chains are really formed at the vesicle surface by adsorbing the dye molecules from the solution. Further, the first experimental evidence of quenching of the resonance fluorescence of one dye aggregate by another dye aggregate at the same vesicle surface is noticed.

Structural formulas of phospholipids and cyanine dyes used in this work are summarized in Figure 1. The phospholipids were L-α-dimyristoylphosphatidylcholine (DMPC, Sigma) as a neutral phospholipid and dicetyl phosphate (DCP, Nacalai Tesque Co.) for giving the negative charge to the vesicle. The cyanine dyes were 1,1′-diethyl-2,2′-cyanine chloride (dye I) and 5,5′-dichloro-3,3′-diethyl-9-phenylthiacarbocyanine chloride (dye II). Cyanine dyes were from Nippon Kanko Shikiso Co.

The 20 mL of the chloroform solution of DMPC and DCP (molar mixing ratio was 1:0–2:3; total amount of lipids (DMPC + DCP) 8.0×10^{-5} mol) in a round-bottom flask was slowly evaporated with an aid of a rotary evaporator on a water bath at 40–70 °C to remove the solvent. Thin films of phospholipids at the flask surface were hydrated with ca. 20 mL of the singly distilled water at 40–70 °C and the mixture was shaken vigorously. To obtain small unilamellar vesicles (SUV), the dispersions were sonicated at 40–70 °C under a stream of nitrogen by use of a Nissei US-300 sonifier equipped with a 26ϕ probe (Nippon Seiki Seisakusho Co.) at 300-W output for 30–60 min. After sonication, the solution became transparent at the visible region whose wavelength λ was longer than 380 nm. The pH of the solution was adjusted to 6.0 with 0.1 M NaOH (1 M = 1 mol·dm^{-3}), and the solution was then diluted to 50 mL with water. Final total concentration of the lipids was 1.6×10^{-3} M. Although the actual size of the vesicle was not determined, an average diameter of the SUV prepared in this manner was estimated to be 30–40 nm.[5]

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