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Dynamical studies of the dissociative adsorption of some primary alkanes on Pt(111)

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Abstract

The initial dissociative sticking coefficients, S_0^{diss}, of ethane (C_2H_6) and neopentane ($C(CH_3)_4$) on a Pt(111) surface at 550 K have been investigated as a function of the translational and vibrational energy content of the incident molecules using supersonic molecular beam methods. In the case of ethane, the new data are consistent with previously published data. In addition two new thresholds are observed at translational energies of *ca.* 35 and 60 kJ mol^{-1}. With neopentane, a threshold is observed at around 90 kJ mol^{-1}.

Keywords: Alkanes; dissociactive adsorption; molecular bean, Pt(111).

Estudios dinámicos de la adsorción disociativa de algunos alcansos primarios sobre Pt(111)

Resumen

Los coeficientes iniciales de la adsorción disociactiva, S_0^{diss}, de estano (C_2H_6) y neopentano ($C(CH_3)_4$) sobre una superficies de Pt(111) a 550 K se investigaron con la técnica de haces moleculares supersónicos, en función de la energia trasnacional, y de la energía vibracional de las moléculas incidentes. En el caso de etano, la nueva data es consistente con data previamente publicada. Adicionalmente se observaron dos nuevos umbrales a ca. 35 y 60 kJ mol^{-1}. Con neopetano el umbral se observó aproximadamente a 90 kJ mol^{-1}.

Palabras clave: Alcanos; adsorción disociativa, haz molecular, Pt (111).

Introduction

In most catalytic processes involving primary alkanes (*i.e.* alkanes with only primary C-H entities) dissociative adsorption of the alkane at the catalyst surface is the rate-limiting step in the catalytic reaction sequence. It comes as no surprise therefore that with the marriage of supersonic molecular beam technology and surface science in the late 1980's that studies of the nuclear dynamics of the dissociation of primary C-H bonds would become crucial to our understanding of this deceptively simple process. Such studies seek to address a simple question. Is the dissociation dynamical in nature, *i.e.* does the nature of the potential energy surface play a key role? Or is this simple reaction governed by the simple rules of statistical chemical reactivity as exemplified by transition state theory.

At least with methane (CH_4), the combination of experiment and theory has gone a

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long way to answering this question. Studies of the dissociative adsorption of CH_4 on flat, single crystal surfaces abound (1). However, these studies have only relatively recently turned to addressing the issue of vibrational promotion. Using back-seeding methods with heated supersonic beams, it is possible to deconvolute the translational promotion of dissociative adsorption from any vibrational promotion as we ourselves have demonstrated (2). However, it is only with the coupling of laser-based vibrational mode specific infrared-pumping methods that it has truly been possible to make detailed measurements on the vibrational promotion of C-H dissociation in CH_4 (3). Such measurements now leave little doubt that the dissociation of CH_4 is a dynamical process.

However, the doorway remains open for the heavier primary alkanes, ethane (C_2H_6) and neopentane ($C(CH_3)_4$). There are, in contrast, only a limited number of studies of the dissociative adsorption of the heavier primary alkanes. Some of these studies show no evidence for any vibrational promotion of the dissociative adsorption of C_2H_6 (1c, 4). While our own work (2, 5) clearly indicates that vibrational promotion of the dissociative adsorption of C_2H_6 does occur. In this short communication, we revisit our previous study of the dissociative adsorption of C_2H_6 to confirm our observations of vibrational promotion using an alternative methodology for the detection of accumulated surface carbon resulting from the dehydrogenation of the primary reaction products. We also report for the first time, new observations on the heaviest of the primary alkanes, $C(CH_3)_4$, which build on our earlier study of this system (6) and report here to the observation of vibrational enhancement.

Experimental

All experiments were performed in a stainless steel UHV chamber (Leisk Engineering) coupled to a triply differentially-pumped molecular beam system. The UHV chamber is equipped with a liquid nitrogen trapped 9" oil diffusion pump (Edwards E09), a 250 mm liquid nitrogen trapped titanium sublimation pump and a 6" oil diffusion pump in the differential chamber separated from the main chamber by a 4 mm collimating orifice, which in unison provide sufficient pumping capacity to achieve a base pressure of 1×10^{-10} mbar and routine operating pressure with the continuous molecular beam operating in the mid 10^{-9} mbar range. The main chamber consists of two operating levels. The upper level is equipped with a hemispherical electron energy analyser (CLAM100, VG Microtech) and electron gun for Auger electron spectroscopy (AES), and an ion-sputter gun (AG21, VG Microtech) for sample cleaning. The lower section houses the rear-view LEED optics (RVL640, VG Microtech), the infrared optics for reflection absorption infrared spectroscopy RAIRS and quadrupole mass spectrometer (QMS, Micromass PC300D, VG Microtech) on a rotary table for temperature programmed desorption (TPD) experiments. Molecular beams formed from a variable temperature supersonic nozzle source enter the main chamber at this level through the 4 mm orifice described above.

The Pt(111), thickness 2 mm and diameter of 10 mm, crystal was mounted on a rotatable XYZ sample manipulator and could be resistively heated to above 1300 K and cooled to 90 K with liquid nitrogen. The surface temperature of the Pt(111) crystal was measured by a chromel-alumel thermocouple inserted into a small hole spark eroded into its edge and secured with ceramic adhesive (Aremco 516). Cleaning was afforded by cycles of argon-ion bombardment followed by annealing to 1000 K. On occasion, the Pt(111) surface was heated in an oxygen environment to remove any accumulative build up of surface and sub-surface carbon. AES and RAIR spectra of adsorbed CO monitored surface cleanness. The latter is extremely sensitive to small levels of contamination.

Ethane (BOC 99.9% minimum stated purity) and neopentane (Aldrich, 99% minimum stated purity) hyperthermal molecular beams were formed from a variable temperature alumina nozzle source having an orifice of *ca.* 40 µm diameter. Nozzle temperatures of between 300 and 1200 K can be achieved by resistively heating a length of tungsten wire coiled around the alumina tube and coated with a temperature-resistant ceramic adhesive (Aremco 552) to reduce any heat loss and tungsten evaporation. The temperature is carefully monitored by a chromel-alumel thermocouple inserted into the ceramic adhesive. The maximum nozzle temperature is restricted by the onset of hydrocarbon pyrolysis, which is monitored by the appearance of the known thermolysis products of C_2H_6 and $C(CH_3)_4$ in the QMS. A conical nickel skimmer (Beam Dynamics Inc.) skims the free-jet expansion from this source and the resultant molecular beam is directed through two stages of differential pumping before finally emerging into the main chamber through the 4 mm collimating orifice. Exposure times can be accurately controlled by a movable tantalum flag placed in front of the crystal face or *via* the gate valve placed between the main chamber and the beam source. Beam flux measurements were performed using a modified mass spectrometer employed as a stagnation gauge and from knowledge of the pumping speed and volume of the UHV chamber.

The average translational energy of the hydrocarbon molecules incident on the surface from the molecular beam has been determined by the TOF technique using a fixed QMS (Q7, VG Microtech) housed inside the UHV chamber in the direct flight path of the beam. At source stagnation pressures of between 1000 and 1800 mbar, the TOF measurements indicate substantial acceleration of the hydrocarbon molecules and the resultant gaussian-like velocity distributions are characterised by velocity spreads ($\Delta v/v$) of the order 15 to 30 %. Equation 1 can be used to calculate the average velocity of the hydrocarbon molecules in admixture with light carrier gases,

$$(v_t)_l = (v_t)_h = \left[\frac{2k\bar{\gamma}T}{(\bar{\gamma}-1)\,\overline{m}}\right]^{1/2}$$

where $(v_t)_l$ and $(v_t)_h$ are the terminal velocities of the light (He) and heavy (C_2H_6 or $C(CH_3)_4$) particles respectively, $\bar{\gamma}$ is the mean specific heat ratio and is the mean molecular mass. Table 1 gives a comparison of the measured translational energies for C_2H_6 in admixture with He at a ratio of 5:95 with calculations based on Equation 1. As can be seen, and in contrast to our earlier studies on CH_4 (1h, 2), there is significant disagreement between the experimental and calculated translational energies indicative of substantial velocity slip in the expansion. This clearly reflects the importance of empirical determination of the translational energy of the components in the supersonic beam rather than assuming purely theoretical expansion behaviour.

A consequence of achieving the range of E_k by increasing the nozzle temperature is to increase the amount of energy contained within the internal degrees of freedom. However, many spectroscopic studies have shown that the supersonic expansion results in a significant cooling of the low energy rotational degrees of freedom Typically, in such studies, it is found that the rotational temperature is of the order of 10% of nozzle temperature. In contrast, the larger separations between vibrational energy levels mean that the extent of vibrational cooling is considered to be insignificant and it therefore assumed that the vibrational temperature of the molecules issuing from the nozzle is in accord with the nozzle temperature. In the case of simple hydrocarbons, the cooling of rotational populations and the sudden freezing of vibrational populations following free-jet expansion from hot nozzles has been confirmed by infrared laser ab-

Table 1
A comparison of the variation of experimental translational energy with nozzle temperature for mixtures of 5% ethane in helium with calculations based on the simple model presented by Equation 1 in the text.

Nozzle Temperature / K	Observed Translational Energy / kJ mol^{-1}	Calculated Translational Energy / kJ mol^{-1}
650	28.1	80.1
750	32.8	92.4
843	34.4	103.8

sorption measurements (7). There is an obvious exception to this, however, in vibrational degrees of freedom possessing low (typically <500 cm^{-1}) vibrational frequencies such as unrestricted torsions. Such lower frequency vibrations are expected to cool to a similar extent to the external rotations of the molecule.

The initial dissociative sticking coefficients, S_0^{diss}, of C_2H_6 and $C(CH_3)_4$ were determined by exposing the Pt(111) crystal surface at a temperature of 550 K to the hydrocarbon containing supersonic beam for a measured time and then determining the build-up of atomic carbon on the metal surface. In contrast to our previous studies of C_2H_6 (1h, 2, 5), where we utilised calibrated AES measurements of the surface concentration of atomic carbon, and of $C(CH_3)_4$ (6), where we used the well-known King and Wells method (8), the measurements reported herein have adopted the oxygen titration method of Valden *et al.* (9). In this technique, the hydrocarbon beam exposed crystal is rapidly heated to 650 K and then exposed to a molecular beam of pure oxygen. The atomic carbon on the surface is oxidised producing gaseous carbon monoxide (CO) and carbon dioxide (CO_2), which can be detected mass spectrometrically. Figure 1 shows a typical set of CO and CO_2 traces obtained from exposure of the Pt(111) crystal to ethene at a surface temperature of 320 K. Ethene is known to adsorb on the Pt(111) substrate at this temperature as the ethylidyne (CCH_3) moiety with a saturation coverage of 0.25 monolayers (10) and it has been previously well established that no carbon containing species are lost from the surface during dehydrogenation (11) as the layer is heated to 650 K yielding a carbon overlayer with a coverage of 0.5 monolayers. As such, ethene is an ideal calibrant for surface carbon coverage. However, it is clear from Figure 1 that, at low carbon exposures, both CO and CO_2 signals may be useful for carbon quantification. However, as the carbon coverage increases, the CO signal broadens and is increasingly lost in a large background CO signal arising from partial oxidation of carbon on other hot surfaces in the sample holder assembly *cf.* Figure 1(c). The CO_2 signal is therefore likely to be the most reliable measure of carbon coverage and was therefore used in these measurements.

The values of S_0^{diss} for C_2H_6 and $C(CH_3)_4$ could then be readily determined from the initial gradient of plots of calibrated carbon uptake *versus* the calibrated flux of C_2H_6 and $C(CH_3)_4$ to which the surface was exposed as in Figure 2. For each point in this figure at least four measurements of carbon coverage were made following independent beam exposures and we are confident that the resulting coverages, and hence the values of S_0^{diss}, are accurate to at least ± 10%.

Results and Discussion

Dissociative Adsorption of Ethane

We have previously reported vibrational enhancement of the dissociative adsorp-

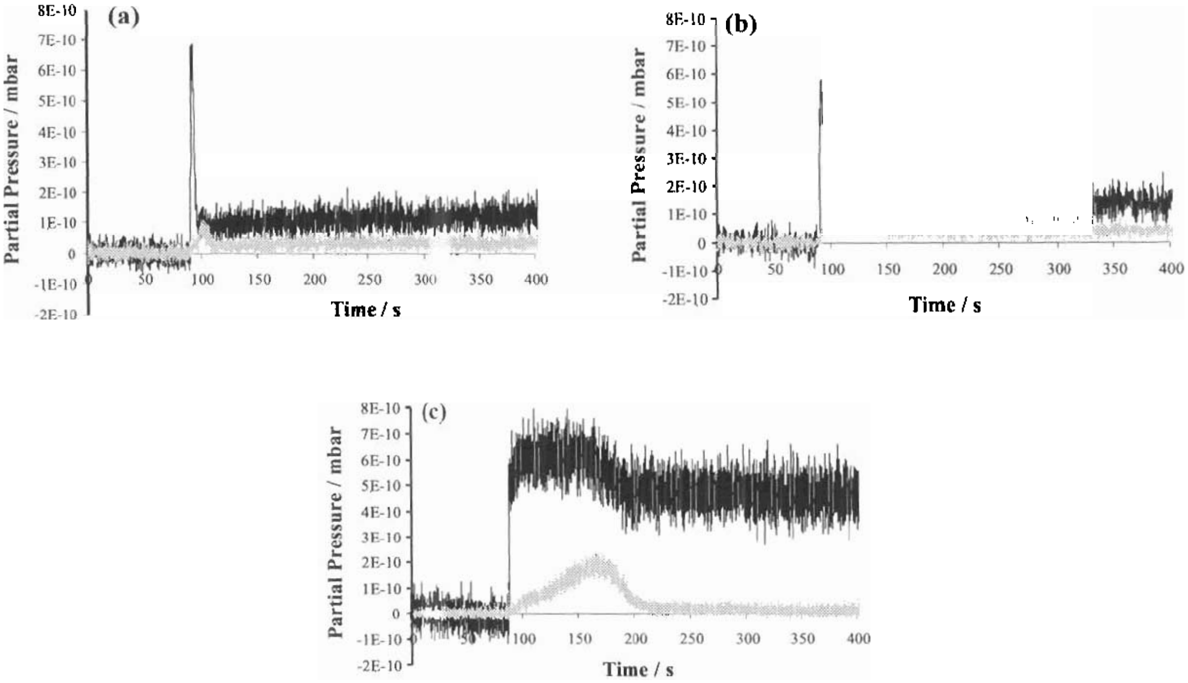

Figure 1. CO (black) and CO₂ (grey) traces from oxygen titration of the Pt(111) surface at a surface temperature of 650 K as exposed to (a) 0.02 L, (b) 0.2 L and (c) a saturation exposure of ethene at 320 K.

tion of C_2H_6 on Pt(111) based on AES measurements of carbon uptake (2,5). Figure 3 presents the results from our current measurements using the oxygen titration method and compares them with those previous results. The comparison between the measurements made at a fixed nozzle temperature of 823 K and utilising back seeding to control the translational energy of the C_2H_6 is remarkable. The reproduction of the behaviour of S_0^{diss} with C_2H_6 translational energy using independent approaches to the analysis of surface carbon accumulation gives confidence to the contention presented in our previous work that the dissociative sticking of C_2H_6 is significantly enhanced for C_2H_6 molecules which are vibrationally excited. Indeed, further analysis of that data, as previously presented (2, 5), would support the contention that C_2H_6 molecules possessing multiple quanta of vibrational energy in deformation modes of the CH_3 group play a significant role in the dissociative adsorption of C_2H_6 (2, 5).

The data in Figure 3 also reveal strong evidence for two new energetic thresholds in the dissociative adsorption of C_2H_6 that we have previously not observed. As the translation energy is increased at a fixed nozzle temperature of 294 K (filled circles) steps in the variation of S_0^{diss} are clearly observed at around 35 kJ mol^{-1} and 60 kJ mol^{-1}. Back seeding measurements made at other fixed nozzle temperatures (650 K, 750 K and 800 K), but not reproduced here, also show evidence for these thresholds. These thresholds correspond to vibrational energies of *ca.* 2930 and 5030 cm^{-1} and may represent enhancement of the dissociative sticking of C_2H_6 through population of the C-H stretch and combinations of the stretch with multi-

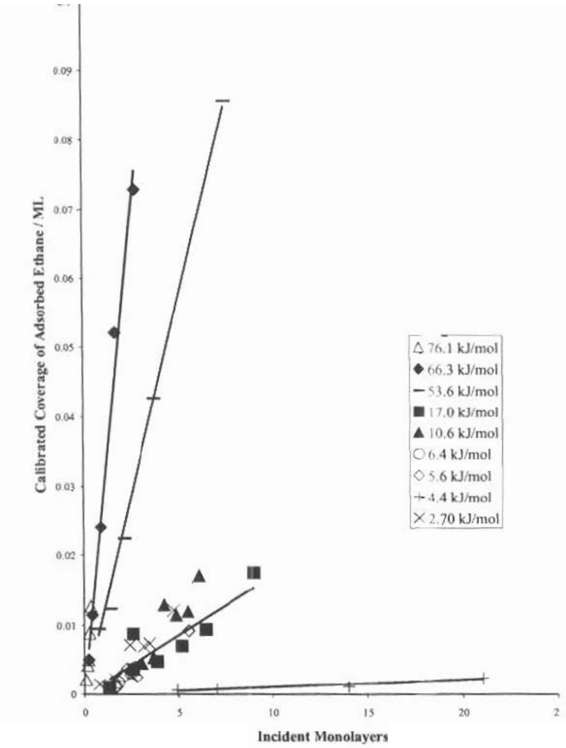

Figure 2. Typical uptake curves for C_2H_6 seeded in mixtures of hydrogen, helium, argon and krypton expanded through a nozzle at a temperature of 294 K and incident on a Pt(111) surface at 550 K. The figure legend presents the experimentally determined translational energy of the C_2H_6 moieties in the molecular beam. For clarity only some of the data sets have the initial gradients (*i.e.* S_0^{diss}) plotted.

ple quanta of vibrational energy in the deformation modes.

Dissociative adsorption of neopentane

The results for an investigation of the effect of vibrational and translational energy on the dissociative adsorption of $C(CH_3)_4$ are shown in Figure 4. The sticking

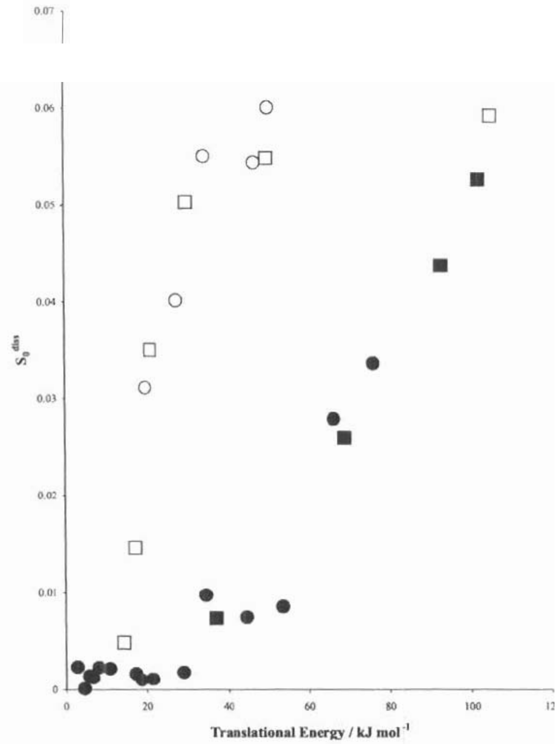

Figure 3. Comparison of the variation of S_0^{diss} with C_2H_6 translational energy obtained in the present experiments for nozzle temperatures of 823 and 294 K, respectively (open and filled circles) with those obtained previously and reported in the references 2 and 5 (open and filled squares). Only the data set represented by the open squares can be directly compared as these were obtained using identical back-seeding methods to those employed herein at fixed nozzle temperature. The data set presented by the filled squares used a fixed beam composition and nozzle temperature variation to achieve the variation in C_2H_6 translational energy.

probabilities obtained in this study for high translational energies (*e.g.* S_0^{diss} = 0.12 at 113 kJ mol^{-1}) are similar to those obtained using the King and Wells technique and reported in our previous communication (6). The agreement is not quite as good as was found when comparing the present data for C_2H_6 with that obtained previously using AES to measure carbon build up on the Pt(111) surface discussed above. This probably reflects the limitation of the King and Wells method in determining sticking coefficients around 0.1 and lower.

For each nozzle temperature, S_0^{diss} remains fairly constant, until a threshold is reached, at which point the sticking probability increases significantly for a small increase in translational energy. The sticking probability then begins to plateau out. The threshold energies for the two different nozzle temperatures are at 100 - 110 kJ mol^{-1} for the 294 K nozzle, and 70 - 80 kJ mol^{-1} for the 673 K nozzle. For translational energies between these two threshold energies there is clearly an enhancement of the sticking probability due to vibrational excitement of the neopentane molecules. The energy range where this vibrational enhancement can be seen (80 - 100 kJ mol^{-1}) is below the lowest energies probed in previous studies of the dissociative adsorption of $C(CH_3)_4$ [12,13]. Energetically, this threshold (*ca.* 7500 cm^{-1}) may well correspond to at least double excitation of the C-H stretching modes and multiple excitation of the bending modes.

Conclusions

New data are presented for the dissociative adsorption of ethane and neopentane on a Pt(111) surface at 550 K. There is clear evidence in the variation of initial dissociative sticking coefficient, S_0^{diss}, with the translational and vibrational energy content of the molecules for vibrational promotion of dissociative adsorption. Clear threshold are observed in these variation in both molecules that may point to the participation of both C-H stretching modes and combinations of CH_3 deformation modes in enhancing the rate of dissociative adsorption of these simple primary alkanes. We leave further interpretation of the origin of these thresholds until more extensive data sets are available.

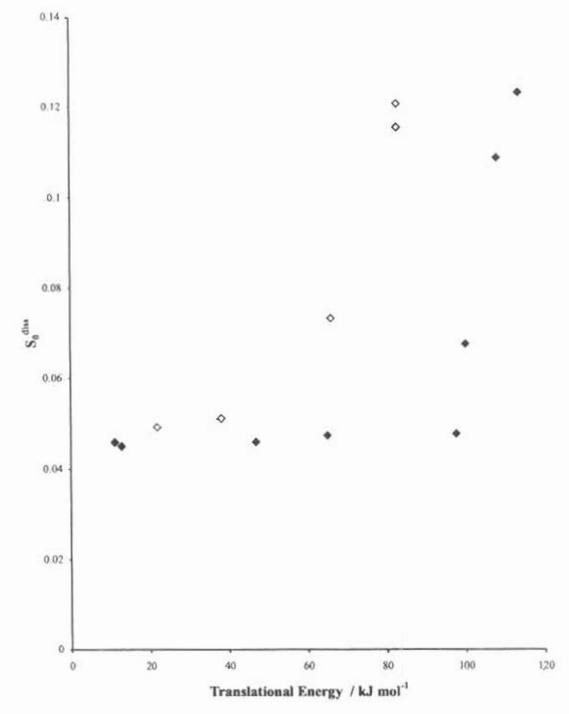

Figure 4. Variation of S_0^{diss} with $C(CH_3)_4$ translational energy obtained in the present experiments for nozzle temperatures of 673 K (open symbols) and 294 K (filled symbols), respectively.

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