ACTIVATED CHEMISORPTION OF MOLECULES

CHARLES N. STEWART
GERT EHRlich

UNIVERSITY OF ILLINOIS – URBANA, ILLINOIS

"THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC RELEASE AND SALE; ITS DISTRIBUTION IS UNLIMITED."
ACTIVATED CHEMISORPTION OF MOLECULES

by

Charles N. Stewart and Gert Ehrlich

This work was supported by the Air Force Office of Scientific Research (AFSC), USAF, under Grant AFOSR 69-1671 and 72-2210.

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.
Chemisorption of molecular gases on metals is generally rapid, occurring at a rate comparable to the rate of molecular collisions with the crystal. The chemisorption of simple hydrocarbons, however, has long been recognized as a slow process, which accelerates at higher temperatures. In earlier days such activated chemisorption was the subject of considerable speculation, and a variety of limiting steps has been proposed: excitation of phonons, interband transitions, or plasmons in the solid, as well as excitation of electronic, translational, vibrational, or rotational states of the gas molecule. However, there has never been a clear cut experiment to probe the nature of the barrier to dissociative chemisorption on a clean metal. We wish to report a series of experiments which establish activated adsorption of molecules on a clean metal surface and for the first time provide a clue to the mechanism of activation.

A fundamental problem in activated adsorption is to locate the site of the activation. To this end we have adopted molecular beam techniques. These permit independent control over the temperature of the reacting gas as well as of the crystal surface. The reaction chosen for study is the adsorption of methane on rhodium. For chemisorption of methane on nickel, Kemball some time ago found a sizeable activation

*Supported by the Air Force Office of Scientific Research (AFSC), USAF, under Grant AFOSR 69-1671 and 72-2210.
energy, 11 kcal/mole. More recently Frennet and Lienard\textsuperscript{2} have reported a more rapid, but still activated chemisorption on rhodium. Rhodium was selected in preference to nickel in view of the difficulty of cleaning the latter.

Our molecular beam system is shown schematically in Fig. 1. The beam, formed by a multi-channel source, impinges directly on a rhodium crystal mounted as the emitter in a field emission microscope. This arrangement makes it possible to visually establish the cleanliness of the crystal under ultra-high vacuum conditions and to sample the amount of gas on the surface after exposure to the beam, using the work function change as an indicator of coverage. During adsorption no fields are applied to the microscope; this is operated only after the beam has been interrupted and ultra-high vacuum conditions have been restored. A liquid hydrogen coldfinger keeps the background during operation of the beam below $10^{-7}$ mm and lowers the pressure rapidly after the gas source is shut off. With the exception of the crystal, its supports, and a few electrical connections, the system is made entirely out of glass to minimize the chance decomposition of the methane.

The initial purity of the gas is also a major consideration in any study of activated adsorption. For a process with an activation energy of 10 kcal/mole less than one in $10^4$ molecules can be expected to react even at $700^\circ$K (the upper limit of our equipment). The level of impurities must be kept substantially below this, to ensure that they cannot mask reaction of the beam. In our system this is accomplished by a series of selective getters.
Fig. 1 Schematic diagram of molecular beam field emission microscope with liquid hydrogen coldfinger.
The ability to detect adsorption on the field emitter has been established by allowing a (low pressure) beam of methane at 79°K to impinge on the rhodium crystal at the same temperature. A layer of physically adsorbed methane is clearly visible in the emission pattern, and at saturation the work function of the surface is found to diminish by 0.5 eV. On heating the rhodium to room temperature with the beam interrupted, the work function of the surface was restored to the value prior to gas exposure, 4.9 eV, and a clean emission pattern was obtained. Evidently the physically adsorbed gas was not converted into a chemisorbed layer, rather it was evaporated into the gas. That the physically adsorbed layer was deposited directly from the beam and not from the ambient was proven in separate experiments. The rhodium crystal was cooled to liquid hydrogen temperature to halt surface diffusion of the physisorbed gas. The area of crystal surface that had been shadowed by the beam was then clearly visible.

With the molecular beam at 300°K and the crystal at 245°K it is apparent from Fig. 2 that no significant changes occur in the work function (or the appearance of the emission pattern), even after the rhodium crystal has been struck by $10^{18}$ molecules/cm$^2$. Raising the crystal temperature to 400°K brings no change here. Clearly there is no reaction with the methane, and impurities have been successfully eliminated.

A vastly different behavior is apparent when the methane is brought to 680°K. The work function of the surface, still at 245°K, now changes appreciably. As indicated in Fig. 2, the increase at saturation amounts to 0.4 eV or more. That this change in the emission properties is due to a chemisorbed layer of methane, and not to impurities evolved
Fig. 2 Change in work function of rhodium crystal as a function of exposure to the molecular beam at two beam temperatures.
from the hot beam source, was established in blank runs. In these the beam source was kept at 680°K for comparable periods without admitting methane. No significant changes were detected on the surface.

When the rhodium was maintained at a much lower temperature, at 145°K, essentially the same behavior was documented. Again adsorption could be initiated merely by heating the beam to 500°K or higher. These measurements therefore establish for the first time that excitation of the gas is sufficient to bring about dissociative chemisorption of the methane, even on a cold surface.

The detailed mechanism by which the methane molecule overcomes the barrier to chemisorption does not yet emerge unequivocally from these experiments. However, assuming a saturation concentration of $1.4 \times 10^{14}$ methane molecules on rhodium, the rate of work function change observed in our experiments leads to a barrier on the order of 10 kcal/mole. This eliminates electronically excited states as intermediaries in the reaction—the lowest excited level lies 8.5 eV above the ground state. Rotational excitation of the molecule also does not appear important as the level spacing, $5 \times 10^{-3}$ eV, is much too small. Only the translational or vibrational modes of the molecule are therefore likely to be directly involved in surmounting the barrier. A decision about their relative contribution must await the results of quantitative rate measurements now underway.
References


### ACTIVATED CHEMISORPTION OF MOLECULES

#### Abstract

Dissociative chemisorption of polyatomic gases on crystal surfaces has long been reported as a slow process. Using molecular beam techniques, we have investigated the adsorption of methane on clean rhodium surfaces and provided a clue to the mechanism of activation.
<table>
<thead>
<tr>
<th>KEY WORDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemisorption</td>
</tr>
<tr>
<td>Surface chemistry</td>
</tr>
<tr>
<td>Activated adsorption</td>
</tr>
</tbody>
</table>