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SMALL INORGANIC MOLECULES ON Os(001) AND Ru(001)

K.L. Shanahan
(Ph.D. Thesis)

April 1984

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THE SURFACE CHEMISTRY OF LARGE HYDROCARBON AND SMALL
INORGANIC MOLECULES ON Os(001) AND Ru(001)

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April 1984

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The Surface Chemistry of Large Hydrocarbon and
Small Inorganic Molecules on Os(001) and Ru(001)

Kirk Leo Shanahan

Abstract

The surface chemistry of five general classes of compounds has been investigated on the flat, hexagonally close-packed Os(001) and Ru(001) surfaces. The five classes were: (1) small inorganic molecules, (2) benzene and its derivatives, (3) heteroaromatics, (4) inorganic and organic cyanides, and (5) oxygen-containing hydrocarbons. Studies were conducted both at room and low temperature with thermal desorption mass spectrometry, low energy electron diffraction, and Auger electron spectroscopy. In general, the chemistry displayed on these surfaces after adsorption at room temperature was quantitative decomposition, except for the small inorganic molecules, and hydrogen cyanide, cyanogen, and trifluoroacetonitrile. Adsorption at low temperature often led to the appearance of new but weak molecular desorptions, however, the major process observed was still decomposition. Aspects of the decomposition processes of certain molecules have been elucidated by utilizing isotopic labelling and by comparing the decomposition of series of homologous compounds.

DEDICATION

To Earl Muettert, whose unique approach to surface science stimulated my imagination, and whose understanding and guidance allowed me to grow as a scientist and a person.

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CHAPTER ONE. INTRODUCTION

Recently the Committee to Survey Opportunities in Chemical Sciences, a committee of the National Academy of Sciences/ National Research Council, has concluded a survey of the forefront areas in chemistry(1). One of the areas pointed out by the Committee as an area of fundamental importance was catalysis. The Committee posed several questions regarding this area which are crucial to understanding catalytic processes and technology, but which have not yet been substantially answered. Two of these questions were: (1) Why are transition metals the best catalysts?, and (2) Can we identify and characterize active sites in heterogeneous catalysis?.

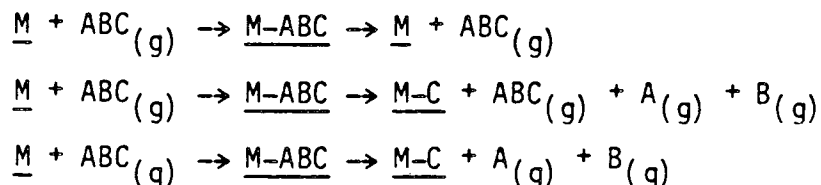
The surface science studies conducted in this laboratory are directed at dissecting the adsorption/desorption chemistry of hydrocarbon molecules on Group VIII transition metal surfaces into its fundamental steps. It is hoped that in so doing, the fundamental questions posed above can be addressed. Because of the complexity of this task, we utilize ultra-high vacuum conditions and well-defined single crystal surfaces. In ultra-high vacuum we are able to employ the advanced tools of surface physics as well as classical chemical techniques, and through this combination new information regarding hydrocarbon surface chemistry can be extracted.

With this general goal in mind, this thesis presents a survey of hydrocarbon chemistry on the basal planes of the hexagonally close packed metals ruthenium and osmium, Ru(001) and Os(001). A representation of this surface is shown in Figure 1. The geometric arrangement

of atoms in this surface is the same as that for the (111) surfaces of face centered cubic metals such as the nickel group metals, rhodium, and iridium (if only the first two layers are taken into account), and the intent is to compare and contrast the chemistry observed on Ru and Os with the analogous surfaces of other Group VIII metals. The techniques utilized in this survey can be divided into two conceptual regimes; the physical techniques, which include thermal desorption spectroscopy (TDS), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES), and the chemical techniques, which include the chemical displacement reaction, isotopic labelling, and the use of homologous series of molecules.

The major physical technique utilized in these studies is thermal desorption spectrometry. The thermal desorption experiment consists of the adsorption of a gaseous molecule ABC on a surface M to form a surface complex M-ABC. This complex is then heated, usually in a linear fashion, and the gaseous desorption products are monitored by mass spectrometry. A schematic representation of the chemical reactions often observed in these type of experiments is illustrated in Scheme 1.

SCHEME 1



The first reaction represents the ideal case of totally reversible chemisorption, where the heating of the adsorbate covered surface leads to an unchanged surface and an unaltered molecule ABC appearing in the gas phase. The second reaction represents a commonly observed result for adsorption of large molecules on Ni group metals, where competitive decomposition and desorption are observed as evidenced by the appearance of both the intact molecule ABC and decomposition products A and B in the gas phase. For the Fe group metals Ru and Os, the third reaction typifies the observed chemistry, where total decomposition is the rule.

By monitoring the gas phase we can obtain the time profile of the rate of appearance of the gaseous products. Since the heating rate is known as a function of time, the time axis of that profile can be converted to a temperature axis. This produces the thermal desorption spectrum. As these spectra reflect the rate of production of the gaseous products, in principle they can be analyzed under the assumption of Arrhenius kinetics in order to obtain the kinetic parameters which govern the rates. There are several equally valid methods for extracting these parameters from thermal desorption spectra(2), however, there is one crucial assumption implicit in all these analyses.

Specifically, all current methods assume that the mechanism and the rate-limiting step in that mechanism are known, and that this rate-limiting step is desorption of the gaseous products. For simple adsorbate systems such as CO or H₂ on clean surfaces, this can be a

reasonable assumption. In this case, Arrhenius kinetics for first or second order desorption processes give well defined peak characteristics and coverage dependences. When the observed data fits either of those models, values of the activation energy and frequency factor derived by mathematical analysis of the desorption spectra can be directly related to surface-molecule bond characteristics. However even in simple cases complications arise.

One common complication is to see desorption spectra that show characteristics of both first and second order kinetics. This is observed as a desorption whose maximum rate (peak maximum in the TD spectrum) occurs earlier during the heating as coverage is increased (a characteristic of a second order process) while maintaining a peak shape characteristic of a first order process. In the more extreme cases, a shoulder on the main desorption peak will develop at higher coverages.

King (2d) has shown that the appearance of a shoulder on a desorption peak, as well as a simple broadening, can arise from lateral interactions between adsorbed molecules. To analyze the resulting desorption spectrum, a "combination" method is used where a first order expression of the kinetics is employed but with a variable, coverage dependent activation energy. On the other hand, a new peak or the appearance of shoulder can also indicate a completely new chemical state on the surface (bridge-bonded verses on-top CO, for example) and in fact thermal desorption spectroscopy alone can not differentiate

between these two cases. In more subtle circumstances, slight changes in the peak shape cause the kinetic parameters derived from fitting the first half of the desorption curve to be different from those obtained from the second (5).

Therefore, even in the case of simple diatomic adsorbates, interpretation of the derived kinetic parameters becomes a nontrivial task. When one moves up the scale of molecular complexity to large hydrocarbon molecules these problems are magnified substantially. Coverage dependences and overlapping peaks become a common occurrence and King (2d) and Solar and Garcia (6) have shown that the extraction of kinetic parameters is no longer an unambiguous process. In fact, the original assumption regarding the reaction mechanism and rate-limiting step becomes suspect.

The thermal desorption spectra provided in this thesis reflect most of the problems described in the foregoing paragraphs. Therefore, this thesis will concentrate on elucidating fundamental concepts in the surface chemistry of hydrocarbon materials. In so doing, the classical chemical techniques of isotopic labelling and alteration of substituents will be used extensively to probe the stereochemical and electronic requirements of the reactions. By studying a large number of related compounds, trends which point out definitive chemical features will become apparent. Where applicable, other techniques (LEED, chemical displacements, AES, etc.) will be employed to support interpretations of thermal desorption spectra and to correlate this work with that of others.

A wide variety of compounds was examined on both the Ru(001) and Os(001) surface. They can be classified into five general categories: (1) aromatic hydrocarbons, (2) heteroaromatic hydrocarbons, (3) inorganic and organic cyanide compounds, (4) oxygen containing compounds, and (5) small inorganic molecules. In general the investigation of small inorganic molecules was conducted for comparison purposes, but certain aspects of their chemistry were expanded and clarified. When possible, comparisons to the chemistry of other Group VIII metal surfaces will be given.

Previous work on the Os(001) surface has been limited to one study of CO chemistry (7a) and a comparable study of CO chemistry on Os films also exists (7b). The available data on Ru(001) surface chemistry is much more extensive but is limited mainly to diatomics (8) and small inorganic molecules(9). A smaller number of studies of saturated hydrocarbons(10) and unsaturated hydrocarbons and hydrocarbon derivatives(11) has been published. In general, diatomics and small inorganic molecules dissociate on Ru(001) at room temperature. Thus usually only decomposition products are detected in thermal desorption experiments, but in some cases molecular species are detected on the surface with spectroscopic techniques. If the adsorption temperature is lowered to less than -100°C , new molecular states are observed by both thermal desorption experiments and spectroscopic techniques.

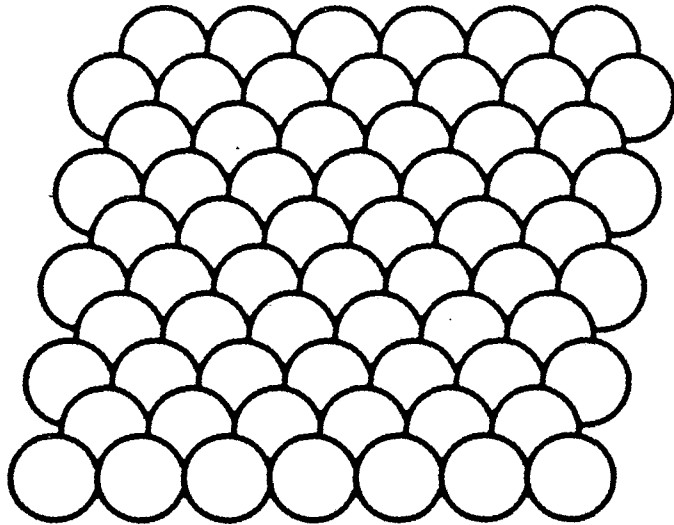
With larger molecules a divergence in behavior is noted. Molecules such as saturated hydrocarbons adsorb and desorb in a

reversible fashion(23). Trifluorophosphine, PF_3 , also shows extensive reversibility(21) although we have detected a small amount of decomposition. However hydrocarbons with unsaturated centers or heteroatoms still decompose extensively. Therefore in relation to the general chemistry of the Ni group metals where competitive desorption and decomposition is common, the chemistry of hydrocarbons adsorbed on Ru and Os is less reversible. The data presented in this thesis will support this general statement.

As a preview of the upcoming chapters, we have noted a general similarity between Ru and Os chemistry and, with certain exceptions, all molecules studied displayed extensive, if not complete, decomposition on the clean surface. Some surface contaminants were observed to have significant effects on thermal desorption spectra. As was observed previously for Ru(001), lowering the adsorption temperature induced new but weak molecular desorptions on both surfaces. Exceptions exist to all of these generalizations and thus the chemistry of Ru(001) and Os(001) offers an interesting variation which we hope to document in the following pages.

We will first present a detailed description of the experimental apparatus and protocols. Next we will detail our results on the Ru(001) surface, followed by our results on the Os(001) surface. Finally we will attempt to compare and contrast the chemistries displayed by Ru(001) and Os(001) and relate them to the chemistry displayed by other Group VIII transition metals. (Portions of this thesis have been or will be published(31).)

Figure 1. The (001) surface of the hexagonally close packed metals ruthenium and osmium (shown above) is hexagonally close packed. This geometry is also the same as the (111) surface of face centered cubic metals such as nickel, palladium, platinum, rhodium, and iridium.



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CHAPTER TWO. EXPERIMENTAL

EQUIPMENT

The equipment utilized in the experiments described herein consisted of the following: a Varian FC12E pumping system, a Varian four-grid low energy electron diffraction system, a Varian glancing incidence electron gun and single pass cylindrical mirror analyzer Auger electron spectroscopy system, and a Uthe Technology, Ltd. (UTI) 100C quadrupole mass spectrometer (1-300 amu range) and programmable peak selector thermal desorption system. Exposures were effected with needle dosers and were measured with an uncalibrated Varian nude ionization gauge. Thus all exposures reported are for comparison purposes only.

Temperatures were measured either with a chromel-alumel or a tungsten/5% rhenium-tungsten/26% rhenium thermocouple spotwelded to the crystal. The thermocouples were referenced to 0°C by an Omega electronic ice point compensator. The crystal was heated by electron bombardment and cooled via a thin copper plate attached to the crystal mount and a liquid nitrogen reservoir. The crystal, heater, and reservoir were mounted on a Varian 2 1/2" offset manipulator in a standard Varian UHV workchamber.

The Varian FC12E pumping system consisted of a 200 l/sec ion pump array, a titanium sublimation pump, and a liquid nitrogen cooled cryoplate. Typical base pressures achieved were in the $1-3 \times 10^{-10}$ torr range. Many of the compounds employed in these studies

showed extremely poor pumping characteristics and this led to difficulties in determining the exposures of these compounds. (None of the compounds that showed molecular desorptions displayed distortions of the thermal desorption spectra due to poor pumping speeds.) Nevertheless we will report exposures in Langmuirs for comparison purposes ($1\text{L} = 1 \times 10^{-6}$ torr-sec).

LEED experiments were generally conducted at 80-130 eV with beam currents on the order of 1-5 microamps (as measured by the associated Varian electronics). Several compounds utilized in these studies showed evidence of electron beam damage, and this will be indicated where appropriate. The AES system typically utilized .5 microamps beam current at 2000 eV, with modulation voltages ≤ 1 volt. All thermal desorption results reported here will be for unirradiated samples as in all cases LEED and AES experiments were conducted separately.

The UTI mass spectrometer was equipped with a mass analyzer optimized for a 1-300 amu mass detection range. However (due to the severe loss in sensitivity at higher masses), it was rarely used to record masses above 125 amu. Searches for ruthenium fluorides and osmium oxides were conducted by increasing the gain and degrading the resolution of the mass spectrometer for maximum sensitivity at high masses. Nominal operating parameters produced a gain of approximately 1000 at mass 28.

The UTI programmable peak selector is a dedicated minicomputer with the capability of recording the intensity versus time profiles of up to ten masses simultaneously. It was rarely used to record more than four at a time due to the resulting loss in resolution in the time axis suffered during thermal desorption experiments. The peak selector operates by setting the DC voltage on the rods to the point nominally specified by the mass selected, delaying for a specified period of time, and then stepping the voltage in fixed units for a number of steps specified by the operator. Also specified by the operator is the length of time spent measuring ion intensity for the given mass during each step. The peak selector then stores the maximum intensity measured during the steps before moving on to the next mass. A typical program consists of four channels (four masses) on a sensitivity setting of 10^{-9} amps, ten steps of one millisecond, and a time delay between channels of 5 milliseconds.

For the ruthenium studies a chromel-alumel thermocouple was used, while this was replaced by a tungsten/5% rhenium-tungsten/26% rhenium thermocouple for Os(001). In both cases the thermocouples were connected to a feedthrough purchased from Ceramaseal, Inc. The crystals were quite thick (.1 to .125") and the thermocouples were spotwelded directly to the side of the crystals near the front face. Calibration curves for the thermocouples supplied by Omega Engineering, Inc. were used where possible. When measuring temperatures below 0°C with the tungsten-rhenium thermocouple the calibration curve of Sandstrom et al. (32) was used.

Heating was accomplished by permanently grounding the crystal and biasing a tungsten filament suspended behind the crystal with 500-1300 eV. A power supply then passed up to 7 amps of current through the filament which produced electron emission. Linear heating rates could be obtained over a 300-400 degree range at rates of 10-100°/sec but some falloff at the upper end of the heating curve was typical. The electrons were not collected completely by the sample and some escaped into the vacuum. This led to an increase in the level of background gases in the mass spectrometer, probably due either to increased ionization in the region of the mass spectrometer, electron stimulated desorption from the supports, or both. However this increase was constant while the heater was on and thus could easily be recognized in thermal desorption experiments. In addition, desorption from the filament itself was noted but easily recognized and discounted.

Cooling to -140 - -160°C was achieved by mounting the crystal with a tantalum plate which was connected to a copper plate. The copper plate was connected directly to a reservoir cooled to low temperatures by liquified air flowing through 1/8" stainless steel tubes. The air was liquified by passing dried air through copper coils immersed in liquid nitrogen external to the vacuum system and fed into the UHV chamber through a welded feedthrough which also served to ground the crystal. By placing baths other than liquid nitrogen in the heat exchanger, different adsorption temperatures could be obtained. Cooling was continuous while experiments were being conducted.

Gases were stored in stainless steel lines and admitted to the work chamber through stainless steel needles of 1/8" diameter connected to Varian bakeable leak valves. Evacuation on the gas handling manifold was accomplished with a 20 l/sec ion pump and two sorption pumps (which were also used to rough out the main chamber) except in the case of hydrogen or argon where a liquid nitrogen trapped mechanical pump was used.

The vacuum system was also equipped with a Varian ion bombardment gun, but it was rarely used as cleaning of the samples did not require ion bombardment.

MATERIALS

Two ruthenium crystals were used interchangeably in the studies. They and the single osmium crystal were kindly supplied by Professor Thor Rhodin of Cornell University and were prepared for him by the Cornell Materials Science Center. They were polished to 1/4 micron flatness by standard procedures and their flatness and orientation were checked with LEED and found to be excellent.

All chemicals were reagent grade. Commercial sources were: Aldrich Chemical Co. (benzene, toluene, hexafluorobenzene, ortho, meta, and para xylene, $p\text{-(CD}_3)_2\text{C}_6\text{H}_4$, thiophene, pivalonitrile, acrylonitrile, acetaldehyde, and d_4 -methanol), Mallinckrodt, Inc. (pyridine, acetonitrile, methanol, acetone, and acetic acid), Merck and Co., Inc. (d_3 -acetonitrile, d_5 -pyridine, C^{18}O , $\text{CD}_3\text{C}_6\text{H}_5$, and $\text{CH}_3\text{C}_6\text{D}_5$), Pfaltz and Bauer, Inc. (CF_3CN), Ozark-Mahoning (trifluorophosphine),

Matheson Gas Products (H_2S , cyanogen and carbon monoxide), Fumico, Inc. (HCN), Biorad Laboratories (^{13}CO), and Eastman Chemical Products, Inc. (methyl acetate). Trimethylphosphine was prepared and purified as described previously (33). 2,5- d_2 -thiophene was prepared by literature methods (34) and graciously supplied by Mr. Robert Lum.

Purity of all gases was insured by careful degassing with freeze-thaw cycles and by careful examination of the vapor phase via mass spectrometry. Examination of the AES spectrum of the surface after a thermal desorption experiment to check the chemical content of the residues also insured no impurities were present.

METHODS

The Os(001) crystal was cleaned by heating at 1000–1100°C in 4×10^{-8} torr oxygen for four minutes followed by a four minute anneal at approximately 1700°C. This treatment resulted in a surface whose Auger spectrum showed no traces of oxygen or carbon. During the first few weeks of use, a low level of oxygen remained on the surface after this treatment. This could be removed by adsorbing a source of carbon, i.e. benzene, and flashing to 1000–1100°C, but this often left traces of carbon on the surface instead. Eventually this problem disappeared, but as is the case with ruthenium, a low level of oxygen which is not detectable with Auger electron spectroscopy may be present on the surface.

Oxygen and carbon coverages were quantified by using Auger peak-to-peak heights of the 517 and 272 eV transitions respectively,

and are expressed as ratios to the peak-to-peak height of the Os 221 eV transition. These ratios are defined as R_O and R_C , respectively.

The sulfur AES transition falls on the low energy side of the main osmium transition and as such could complicate the use of this peak as a reference for quantifying contaminant coverages. However the actual sulfur peak-to-peak height could easily be determined, so a simple peak height ratio to the 221 eV Os peak was utilized in this case also. It should be noted that some distortion of the sulfur peak height is to be expected, especially at low coverages, and thus the values of this number are not necessarily linear in coverage. This peak height ratio is defined as R_S .

For Ru(001) the same basic treatment was utilized for cleaning except that the oxygen treatment was conducted at 900–1000°C and the anneal was conducted at 1000–1100°C for a minimum of three minutes. Weinberg et al. (35) have shown that oxygen can be a substantial contaminant if the crystal is not annealed at high temperature for sufficient time periods. The three minute anneal was judged to be sufficient to remove surface oxygen, however a problem with oxygen did develop with time. Specifically, when surfaces that were contaminated with a source of carbon (any organic molecule) were rapidly heated, the formation of CO was noted in the 500–700°C region.

Diffusion of oxygen atoms to the ruthenium surface from the bulk is an established thermal process(13) and it is felt that the observed

CO arose from the recombination of surface carbon and bulk oxygen. When oxygen was present on the surface as detected by AES and an organic molecule was adsorbed on at surface, rapid heating produced CO desorption in the 250–350°C region in addition to the high temperature region. It should be noted that Hrbek et al. (30) have noted the same desorptions and attribute them to different forms of carbon rather than oxygen. In particular, they feel that the carbon undergoes a transition from "carbide" to "graphitic" around 400–450°C. However, we have noted that we could adsorb an organic molecule and not obtain the low temperature CO desorptions while observing the high temperature ones and thus we feel that the difference lies in the nature of the oxygen, not in the nature of the carbon.

The important point regarding this minor difference of opinion is at the high temperature CO desorption usually occurred at the same place as nitrogen desorptions arising from the decomposition of nitrogen containing compounds. However, the combination of mass spectrometric analysis and Auger analysis (to monitor loss of nitrogen from the surface) removed the ambiguity as to whether nitrogen or carbon monoxide was desorbing.

Carbon and sulfur Auger transitions (272 and 152 eV respectively) overlap with ruthenium transitions. To quantify the sulfur coverage, we employed the method of Keleman and Fischer (19), where the peak height ratio of the sulfur transition to the Ru 231 eV transition of the clean surface was obtained and subtracted from the same value of

the sulfur contaminated surface. This value is defined as R_s . Carbon was especially difficult to detect at low coverages as its AES transition occurs at the same place as the strongest ruthenium transition. The methods outlined by Goodman and White (36) to measure the level of carbon contamination were adopted. In this method two values are calculated as numerical measures of carbon coverage. The first was the peak height ratio of the 272 eV transition to the 231 eV transition and is defined as R_c . The second was the ratio of the negative portion of the 272 eV transition to the positive portion, and was defined as γ . Oxygen coverage was quantified by ratioing the peak height of the 517 eV transition to the 231 eV Ru transition, giving a quantity defined as R_o .

All of the numerical values used to quantify contaminant coverages on either ruthenium or osmium are susceptible to the Auger system's tuning parameters (such as crystal position) which affected resolution and peak shape. The observed values of peak height ratios could vary due to tuning differences more than due to actual variation of contaminant levels. Thus, the reported values of the peak height ratios should be used for comparison only.

When the adsorption temperatures were less than room temperature all Auger spectra were recorded at $\leq 25^\circ\text{C}$. For room temperature adsorption, Auger spectra were taken with the crystal at $< 150^\circ\text{C}$.

In the ruthenium studies adsorption was conducted at both 25°C and at -160°C for all molecules studied, but for the osmium studies, this

duality was not as complete. In several instances only adsorption at -140°C was conducted (37) and this will be noted where appropriate. In all cases where comparative data exist, no thermal desorption maxima were detected after adsorption at room temperature which were not present after adsorption at low temperature.

LEED experiments were conducted independently of thermal desorption experiments as several of the compounds examined showed evidence of electron beam damage, especially those molecules that contained fluorine. Usually, independent thermal desorption experiments were conducted after LEED studies to assess the extent of the beam induced damage, and these results will be included where important. In general, only high and intermediate coverages were investigated by LEED, so any ordered patterns appearing only at very low coverages would have been missed. Annealing of adsorbate layers was often employed in attempts to induce ordering, with limited success, and residues from thermal desorption experiments were also examined for ordering. No ordered patterns from residues were ever found with the exception of the thiophenes.

LEED results were recorded photographically only when new or complex patterns were observed. A Polaroid camera using 3000 ISO speed film was used and exposure times of 2-4 minutes at f4.7 or f8 were employed.

In a few instances, AES experiments were conducted in an attempt to determine if actual desorption from the crystal was occurring (as

differentiated from desorption from the supports). Spectra were run before and after the flash and compared with the TDS results. Chemical effects in the AES spectra often made the interpretation difficult, but in all cases where questionable desorptions were observed, the AES studies confirmed at the desorptions arose from the supports since the Auger did not change significantly before and after the flash. In all cases, these TDS results were duplicated without exposure to the electron beam.

Exposures were conducted with the crystal facing the dosing needles in most cases, but occasionally adsorption from the ambient was utilized also. During exposures the main pump was partially valved off from the main chamber for the duration of the exposure. This procedure would increase the background pressure into the low 10^{-9} torr range. Typically, pressures in the mid to high 10^{-8} range were used for exposures and the duration of those exposures was 30 seconds to 2 minutes on average.

Prior to conducting a thermal desorption experiment the crystal was cleaned as described previously and then cooled to the adsorption temperature. Since high temperatures were used in the cleaning process, the cooling usually required 15-20 minutes. During this period adsorption of background CO and H₂ occurred and therefore when the adsorption temperature was reached, the crystal was heated to 500-600°C to remove these gases and recooled to the adsorption temperature. This cooling required only 3-5 minutes and during this

period only trace amounts of CO adsorbed (less than 1 percent of a monolayer based on peak areas). As hydrogen was a major constituent of the background, some H_2 was usually present on the surface at very low levels (1-5%). This is especially important with regards to the interpretation of results using deuterium labelled molecules. At this point the crystal was exposed to the vapor of the compound being studied as described above and the crystal was flashed while recording the preselected mass-time traces with the TDS system.

Several background problems were noted and identified, some of which have already been mentioned (desorption from the filament and the increase in the background level of ambient gases due to the heater). Two other problems should be discussed. First, whenever CO desorbed in appreciable quantities a concomitant H_2 signal was noted which displayed the same peak shape and position as the CO desorption, although at approximately 10-20 percent of the CO intensity. As the CO and H_2 peak positions are normally quite different this was easily recognized and discounted. Whenever this did create a problem due to overlap, the appropriate perdeutero compound was employed, solving the problem.

Second, for the cases where adsorption was conducted at room temperature, whenever the exposures of the compound being studied were "heavy" (sometimes as low as 1-2L), a weak molecular peak was observed in the initial stages of the thermal desorption. This peak always had the same general characteristics, broad and relatively weak with a

maximum at 60–80°C, for all molecules studied. Experiments with a 10 mil Ta plate in place of the crystal showed that the source of this peak was the Ta supports as experiments with benzene, pyridine, acetonitrile, ethylene, and cyclohexene (which produced benzene) all produced the same peaks at the same position (60–80°C) in the molecular desorption spectra (except cyclohexene). This Ta plate was heavily sulfided and oxidized and even showed H-D exchange in mixtures of perdeutero- and perprotiobenzene. While this chemistry was interesting it was not the goal of this research to study Ta/S/O chemistry. As these peaks were weak and as they always occurred in the same place we ignored desorptions on a sensitivity scale of less than $\times 10$ of full scale, especially when they occurred in the 60–80°C region. With nitriles this adsorption was often especially strong, requiring the previously mentioned AES experiments to verify the origin of the desorptions.

When the adsorption temperature was lowered to -140 – -160°C, this desorption broadened out slightly but was still present. In addition, physisorption peaks were observed to appear near the beginning of the desorption profile (around -120 – -140°C) and is led to a confusion as to the exact origin of the multilayer peaks when they were observed. Therefore multilayer desorption temperatures will only be reported when they were unambiguously separated from the support desorptions (usually at temperature greater than -110°C).

The general procedure for recording the thermal desorption data was to record the heating curve in real time while the peak programmer

recorded the mass-time profiles. Then after the flash, these profiles were recorded on paper. This method was felt to be superior for two reasons. First by interpolation on the time axes of the heating curve and mass-time profiles any point could be directly related to a temperature with good accuracy. Second, periodically the heater settings would be incorrect or the heater would malfunction and this could be detected immediately if the heating curve was recorded. In that situation only a single experiment needed to be repeated. If the heating curves were only periodically recorded, a malfunction of this type would not be easily detected, necessitating the repetition of several experiments to identify the ones with the different heating curve.

Thermal desorption spectra presented in this thesis and associated publications are direct tracings of the real data with manual smoothing of the noise levels. In general, the figures will be on the same sensitivity scale (except CO spectra, which are usually on less sensitive scales) and different scales will be noted where appropriate. These differences in peak intensities result from two factors; (1) the differences in sensitivity of the mass spectrometer as a function of mass, and (2) changes in the general sensitivity of the mass spectrometer over periods of time (days). This last factor is especially important when the mass spectrometer was retuned or operating parameters were altered (as in the searches for ruthenium fluorides or osmium oxides). Therefore comparisons of spectra of the

same molecule (H_2 for example) resulting from different adsorbates should be made only with great care.

On the nickel group metals the chemical displacement reaction is highly successful in addressing the question of whether or not a molecule has been adsorbed in a nondissociated state (38). Unfortunately on the Ru(001) and Os(001) surfaces, chemical displacement reactions did not occur. Therefore for a complete description of the protocol of displacement experiments the reader is referred to earlier publications (38). The attempts at displacements will be mentioned in the text where appropriate. It should be noted that negative results in displacement reactions say nothing regarding the dissociative or nondissociative character of adsorption, as the actual mechanism of the displacement reaction is not understood.

CHAPTER THREE. Ru(001) STUDIES

INTRODUCTION

In this chapter, results of studies on the surface chemistry of Ru(001) will be presented. They will be divided into five general sections which include: (1) a comparison of CO and PF₃ chemistry with some additional isotopic scrambling experiments and a comment on attempted displacement reactions, and a study of the effect of surface carbon on CO thermal desorption; (2) a study of benzene, toluene, and hexafluorobenzene chemistry; (3) a study of the surface chemistry of some heteroaromatic compounds; (4) a study of inorganic and organic cyanide compounds; and (5) a study of a series of oxygen containing compounds (related by the fact they all decompose to form CO and H₂).

Thermal desorption and LEED studies were conducted on all of these compounds at both room temperature and approximately -160°C, but no significant changes were noted for the different adsorption temperatures. The only major difference was the appearance of new, weak molecular desorptions in the low temperature regions which in some cases showed slight coverage dependences. In certain instances this generalization does not hold and these cases will be pointed out in the text. Multilayer desorptions will be reported only when they could be unambiguously resolved from support desorptions. Searches were always conducted for all possible fragmentation, hydrogenation, or cyclization products but no products other than simple molecules

such as hydrogen, nitrogen, hydrogen cyanide, and carbon monoxide (and CO_2 from acetic acid) were ever detected.

CARBON MONOXIDE and SMALL INORGANIC MOLECULES

Our results with CO were in agreement with previous work(15). There were two thermal desorption maxima, one at 135–140°C and the second at 185–195°C. Carbon and oxygen were not detectably present on the surface after the desorption experiment, which is consistent with a fully reversible chemisorption process. To further distinguish between associative and reversible–dissociative processes, the thermal desorption from $\text{Ru}(001)\text{-}^{13}\text{C}^{16}\text{O}\text{-}^{12}\text{C}^{18}\text{O}$ was examined. There was no detectable increases in the scrambled products, $^{13}\text{C}^{18}\text{O}$ or $^{12}\text{C}^{16}\text{O}$, above the levels already present in the original samples. Hence, within experimental detection limits, the carbon monoxide chemisorption process on $\text{Ru}(001)$ is fully associative (molecular) in character.

The two thermal desorption maxima for $\text{Ru}(001)$ may reflect the presence of two stereochemically differentiable chemisorption states(39). To assess this possibility, the surface was exposed to enough $^{12}\text{C}^{16}\text{O}$ to fill the high temperature peak and then to enough $^{13}\text{C}^{16}\text{O}$ to saturate the surface. In the subsequent thermal desorption the ratio of the two molecules in the two peaks was identical within experimental error. The permissible conclusion from this is that either there is only one chemical state of chemisorbed CO or that there are two or more states and diffusion between these states is rapid and complete.

Phosphorous trifluoride is formally analogous to carbon monoxide in its bonding capability: both molecules are poor sigma donors and good pi acceptors. Ertl and coworkers(21) have conducted extensive photoelectron studies on the chemistry of PF_3 on several surfaces and have estimated a thermal desorption maximum of 245°C for desorption from $\text{Ru}(001)$. In addition, they did not detect any decomposition. We confirmed the PF_3 desorption maximum, but did detect a slight amount of decomposition. Due to chemical effects in the AES spectra, it is only possible to estimate the extent of decomposition as being less than 5 percent. The PF_3 thermal desorption spectrum often showed a weak low temperature shoulder, especially at high coverages. A $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ LEED pattern was observed for $\text{Ru}(001)\text{-PF}_3$ at 25°C ; which is the same pattern observed for $\text{Ru}(001)\text{-CO}$ at moderate coverages.

Chemical displacement of CO from $\text{Ru}(001)\text{-CO}$ (1/2 to full monolayer coverage) did not occur with displacing agents like PF_3 or $\text{P}(\text{CH}_3)_3$, but the thermal desorption of CO was affected by those agents. Trimethylphosphine caused the two CO desorption peaks to merge into a single sharp peak. The effect however was probably not from molecular $\text{P}(\text{CH}_3)_3$; this molecule decomposes on $\text{Ru}(001)$ and its decomposition products of C and P were the species that affected the CO desorption spectrum. CO and PF_3 coadsorbed during the attempted displacement reaction. The resulting thermal desorption spectra of both CO and PF_3 were complex and show effects of interactions between the two molecules. A detailed study of this phenomenon was not attempted.

Surface carbon substantially affected the chemisorption behavior of CO on Ru(001). The carbon surface impurities decreased the CO saturation coverage but the most significant effect was on the relative intensities of the two CO desorption peaks from a saturated layer. With increasing carbon coverage, the intensity of the high temperature peak was decreased relative to that of the low temperature peak and eventually at high carbon coverages, the desorption spectrum consisted of one broad assymetric peak with a maximum at 105-110°C, a shift of approximately 25°C from the maximum of the low temperature peak for the clean surface (Figure 1). Analogous effects on the CO desorption behavior were observed with carbon derived from either benzene or acetaldehyde decomposition at 500°C. In addition, the desorption maxima from CO coverages of approximately one half monolayer (based on peak areas compared to desorption from the clean surface) were shifted down by 25-50°C, depending on the coverage of the surface carbon.

BENZENE AND BENZENE DERIVATIVES

The thermal reactivity of benzene on Ru(001) is very high and only hydrogen (or deuterium) molecules were detected in thermal desorption experiments with Ru(001)-C₆H₆ (or C₆D₆) formed at 25°C or -160°C except for benzene desorption from multilayers at -110°C after adsorption at -160°C. At low coverages the H₂ desorption comprised a relatively sharp peak at 180°C that "tailed" and dropped to baseline levels at approximately 450°C. With increased benzene coverages, the H₂ maximum broadened and shifted to 150°C and the details of the

high temperature region altered (see Figure 2). These desorption profiles are substantially different from the desorption profile of H_2 adsorbed in the clean surfaces (12). No benzene was detectably displaced from $Ru(001)-C_6H_6$ at $25^\circ C$ or below by either PF_3 or $P(CH_3)_3$. On heating $Ru(001)-C_6H_6-P(CH_3)_3$ formed at $25^\circ C$, there was no evidence of benzene molecular desorption, but when heating a similar layer formed at $-160^\circ C$ a small molecular benzene desorption was noted at $20^\circ C$, indicating that at least some benzene must be adsorbed in a molecular fashion at $-160^\circ C$.

Benzene chemisorbed on $Ru(001)$ at $25^\circ C$ formed an ordered $p(3 \times 3)$ overlayer at all coverages. This unit cell just envelops the van der Waals extension for benzene, and would allow close packing of benzene molecules in a plane parallel to the surface basal plane of ruthenium.

Hexafluorobenzene also irreversibly adsorbed on $Ru(001)$ at $25^\circ C$. Although nothing detectably desorbed during the thermal desorption experiment, fluorine (but not carbon) disappeared from the surface at approximately $700^\circ C$ as judged by AES. A search was made for desorbing ruthenium fluorides but none were detected. Adsorption at $-160^\circ C$ produced multilayer desorption at $-110^\circ C$ and another very weak molecular desorption peak which appeared at $-60^\circ C$ at low coverages (this peak was obscured by the multilayer peak at high coverages). No evidence of ordering was noted by LEED but an ordered state could have been missed because of the sensitivity of fluorinated compounds to electron beam damage.

Toluene chemisorption on Ru(001) was irreversible and resembled that of benzene. As shown in Figure 3, the hydrogen desorption from toluene decomposition on Ru(001) was complex and very sensitive to initial toluene coverage. Most notably, the desorption spectra did not simply reflect the two different types of C-H bonds in the molecule in that a simple spectrum consisting of two peaks with an intensity ratio of 3:5 was not observed. Nevertheless, to probe the issue of regioselectivity more sensitively, the thermal decomposition of $\text{CD}_3\text{C}_6\text{H}_5$ and $\text{CH}_3\text{C}_6\text{D}_5$ was studied. There was only slight indications of site-selective bond breaking in that the low- and high-temperature desorption regions for Ru(001)- d_3 -toluene contained proportionately more deuterium and hydrogen, respectively. The d_5 -toluene experiments yielded complimentary results and the desorption spectra from different initial coverages can be seen in Figures 4a, b, and c for layers formed at 25°C. Adsorption at -160°C did not alter these results except for the appearance of a multilayer desorption at -65°C. A poorly ordered $p(3 \times 3)$ LEED pattern was observed for Ru(001)-toluene surfaces formed at 25°C and also for surfaces formed by annealing at 0°C after initial adsorption at -160°C.

Readsorption of both benzene and toluene on Ru(001)-C produced by the decomposition of those molecules in general produced a desorption spectrum that resembled one obtained from higher coverages, but at a much reduced intensity. Eventually after several cycles like this, no adsorption would take place.

HETEROAROMATIC MOLECULES

Pyridine chemistry on Ru(001) was likewise characterized by irreversibility with the decomposition products produced being hydrogen, hydrogen cyanide, and nitrogen. For example, Ru(001)-NC₅D₅, formed at 25°C with a .3 Langmuir exposure, yielded a broad D₂ desorption with maxima at 110°C and 400°C, DCN desorption at 400°C (confirmed as DCN by experiments with the perprotio molecule, which gave HCN), and N₂ above 500°C. The character of the desorption spectra was dependent upon the adsorption temperature in that the hydrogen desorption spectra broadened out and initiated at lower temperatures when adsorption was conducted at -160°C. No new products were detected after adsorption at low temperature except for multilayer pyridine desorption at -100°C. A thermal desorption study of Ru(001)-2,6-d₂-NC₅H₃D₂ indicated a very slight degree of regioselectivity, namely scission of the alpha C-H bond, in the earliest stages of the decomposition. No ordered LEED patterns were detected for pyridine adsorbed at 25 or -160°C.

Furan irreversibly chemisorbed on Ru(001) and displayed no evidence of regiospecificity in the C-H bond breaking process. It behaved like all other oxygen containing hydrocarbon molecules by decomposing to surface carbon, H₂, and CO. The CO and H₂ desorptions resembled the desorptions arising from adsorbing those molecules on the clean surface (desorption limited), and for CO desorption the peak maximum shifted as expected for CO desorbing from

Ru(001)-C. Adsorption at -160°C produced a weak molecular peak at -50°C in addition to multilayer desorption at lower temperatures. No ordered LEED patterns were observed upon adsorption of furan, either at 25°C or -160°C . However, upon heating of the adsorbate to $100\text{--}150^{\circ}\text{C}$, faint $(\sqrt{3} \times \sqrt{3}) \text{R}30^{\circ}$ patterns could be detected.

Thiophene also irreversibly adsorbed on Ru(001) both at -160°C and 25°C . For adsorption at room temperature only a broad H_2 desorption appearing at approximately $280\text{--}290^{\circ}\text{C}$ was observed, and then only at high exposure. Readsorption of thiophene on its own residue in general produced results analogous to those observed with benzene and toluene. If 2,5- d_2 -thiophene was used no deuterium appeared in the hydrogen desorption spectrum from the clean surface. When adsorption was conducted at -160°C on the clean surface, a new hydrogen desorption peak arose which showed a strong coverage dependence. At low coverages, a single broad hydrogen desorption was observed with a maximum at approximately 220°C . As the coverage increased, this peak separated into two peaks. One moved up in temperature to approximately 300°C and the other lowered to -30°C at the highest coverages. In addition, at the highest coverages a third peak appeared at approximately 100°C . This is illustrated in Figure 5.

Studies with 2,5- d_2 -thiophene adsorbed in intermediate coverages (only two peaks) in the TD spectrum on the clean surface at -160°C showed complete regioselective bond breaking in that the lower temperature H_2 desorption contained all the deuterium and none was

found in the high temperature peak. This is illustrated for two different coverages in Figures 6 and 7. However, if one quarter of a monolayer of sulfur was coadsorbed with the labelled thiophene, extensive but not complete loss of regioselectivity was noted in that the high temperature peak now had substantial deuterium content and the low temperature peak had substantial hydrogen content, both in the form of HD. For adsorption at room temperature, HD was also noted in the single hydrogen desorption.

The sulfur was deposited on the surface by selectively cleaning thiophene residues of carbon (carbon was removed first in the normal cleaning procedure), and produced sharp $p(2 \times 2)$ patterns because of the high temperatures used in the cleaning treatments. Considering previous studies of sulfur adsorption arising from hydrogen sulfide decomposition(19), it is estimated based on AES and LEED that the levels of sulfur studied here represent approximately one quarter of a monolayer of sulfur. Higher levels were extremely difficult to obtain due to the desorption of sulfur(19), but in one case a mixed $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3}) R30^\circ$ LEED pattern was obtained, indicating a slightly higher sulfur coverage.

Sulfur also caused the appearance of a weak molecular peak at -60°C for low thiophene exposures. This peak was later obscured by the multilayer desorption, which occurred at -105°C . Finally, in one instance where the sulfur coverage was probably greater than one quarter monolayer (the LEED pattern from the Ru(001)-S surface showed

both $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})$ spots of approximately equal intensity) a change in the structure of the hydrogen desorption was noted for what normally would have been intermediate levels of thiophene coverage. Specifically, the 300°C peak was suppressed and a new peak at 155°C arose.

No ordered LEED patterns were ever observed after adsorption of thiophene on the clean surface, but after a thermal desorption experiment fuzzy $(\sqrt{3} \times \sqrt{3})$ $R30^\circ$ patterns could be observed. By raising the temperature to 1000°C these patterns could be made to sharpen up. Removing the carbon then produced the $p(2 \times 2)$ patterns mentioned above. Adsorption of either more thiophene or benzene on $\text{Ru}(001)\text{-S}$ followed by heating to $500\text{--}600^\circ\text{C}$ caused the $p(2 \times 2)$ pattern to change to the $(\sqrt{3} \times \sqrt{3})$ $R30^\circ$ pattern.

INORGANIC AND ORGANIC CYANIDE COMPOUNDS

For studies of the surface chemistry of cyanides on $\text{Ru}(001)$, two inorganic compounds, HCN and cyanogen, and four organic compounds, acetonitrile, trifluoroacetonitrile, pivalonitrile (t-butyl cyanide), and acrylonitrile (vinyl cyanide) were used. These compounds also showed extensive decomposition, but HCN, cyanogen, and trifluoroacetonitrile did produce some molecular desorptions after adsorption at room temperature. Readsorption of the nitriles on their residues did not induce any significant changes in desorption behavior, except for CF_3CN . The only effect noted was an apparent drop in the sticking coefficient.

The thermal desorption experiments for Ru(001)-HCN showed complex molecular HCN desorption behavior, including a coverage dependence. As illustrated in Figure 8, the molecular desorption spectra showed maxima at 110°C and 155°C with significant intensity out to approximately 400°C. In addition, a 28 amu peak was observed at 450-500°C that was due to N₂ (decomposition) as judged by AES measurements of the surface, and an H₂ peak appeared at 115°C. Even though molecular desorption was noted, decomposition was still the major process occurring on the clean surface. Adsorption at -160°C did not alter these results. HCN adsorption at 25°C or at -160°C followed by annealing to approximately 0°C produced sharp ($\sqrt{3} \times \sqrt{3}$) R30° LEED patterns.

Cyanogen chemisorption on Ru(001) was also partially reversible and only cyanogen and nitrogen (T_{max} of 470°C) were detected in the thermal desorption experiment. The molecular desorption spectra were dependent both on coverage and adsorption temperature as shown in Figures 9 and 10. If background amounts of hydrogen were present on the surface, HCN was observed to desorb at 120°C and 320°C. No ordered LEED patterns could be detected for Ru(001)-C₂N₂, either after adsorption at room temperature or adsorption at low temperature followed by annealing to 25°C (40).

Acetonitrile formed on Ru(001) at 25°C an ordered chemisorption state of p(2 x 2) form but no molecular desorption was detected. Decomposition products were hydrogen, nitrogen, and hydrogen cyanide

($T_{\max}$ of 110°C, 530°C, and 350°C, respectively) and the hydrogen desorption resembled the desorption of H_2 from the clean surface. After adsorption of CH_3CN at -160°C, the thermal desorption yielded a sharp molecular desorption at 50°C in addition to the decomposition products. The character of the hydrogen desorption also changed to mimic the molecular desorption in that the peak maximum and shape of the H_2 desorption became similar to that of the molecular desorption as illustrated in Figure 11. Heating a mixed layer of CH_3CN and CD_3CN produced only CH_3CN and CD_3CN in the 50°C molecular desorption, indicating that no significant reversible C-H bond breaking had occurred.

Pivalonitrile behaved analogously to acetonitrile although it did not yield LEED evidence of an ordered state. After pivalonitrile adsorption at -160°C, the thermal desorption experiment yielded a weak molecular desorption at 35°C as well as multilayer desorption at -100°C. Hydrogen, hydrogen cyanide, and nitrogen also formed ($T_{\max}$ of 110°C, 345°C, and 550°C, respectively).

Acrylonitrile adsorbed at 25°C also gave no LEED evidence of ordered chemisorption states and the adsorption was totally irreversible, both at 25°C and -160°C, except for multilayer desorptions at -100°C. Hydrogen, hydrogen cyanide ($T_{\max}$ of 270°C), and nitrogen ($T_{\max}$ of 570°C) were thermal decomposition products as with other nitriles. The hydrogen desorption was coverage and temperature dependent since for adsorption at -160°C, the desorption

began at approximately 25°C for low coverages and shifted down to approximately 0°C for high coverages. With adsorption at 25°C, the H₂ desorption initiated directly at the start of the flash. In both cases the desorption maximized early and continued out to approximately 450–500°C.

Trifluoroacetonitrile chemisorption behavior on Ru(001) was complex and substantially different from the behavior of the alkyl cyanides discussed above. The thermal desorption spectra for Ru(001)-NCCF₃ formed at 25°C are illustrated in Figure 12, and a saturation desorption spectrum arising from adsorption at -160°C is shown in Figure 13. Although adsorption was partially reversible, decomposition was still the major process occurring on the clean surface. Decomposition products included nitrogen (T_{max} of 600°C) and small amounts of FCN appearing at approximately 400°C (the point where the N₂ desorption initiated). Fluorine was present on the surface to approximately 600°C and was fully lost by 900°C as judged by AES measurements. No evidence of ordered arrays was detected by LEED, but the high sensitivity of fluorinated compounds to electron beam damage could have easily led to the destruction of ordered arrays. In fact, recording the AES spectrum of a layer of CF₃CN completely suppressed all molecular desorption, and irradiation by the Auger electron gun for 15–20 minutes removed all fluorine from the surface.

The complexity of the molecular desorption spectra of CF_3CN suggests multiple types of chemisorbed molecules, and studies on readsorption of CF_3CN on the residues of trifluoroacetonitrile, acetonitrile, cyanogen, and on $\text{Ru}(001)\text{-C,O}$, or F support this contention. If an amount of CF_3CN sufficient to saturate the 350°C desorption peak was adsorbed on the clean $\text{Ru}(001)$ surface and then flashed to less than 500°C (stopping before significant amounts of nitrogen had desorbed), readsorption of CF_3CN on this residue-covered surface became totally reversible. As long as the temperatures reached in the thermal desorption experiment were kept low enough to prevent nitrogen desorption, the adsorption/desorption cycle could be repeated indefinitely.

The molecular desorptions from the CF_3CN residue covered $\text{Ru}(001)$ surface showed desorptions which did not appear from the clean surface, as well as a coverage dependence. The spectra resulting from different initial coverages are shown in Figure 14. Decomposition of the residue, as signalled by N_2 desorption, produced a surface layer containing C and F, and readsorption on this surface then produced molecular CF_3CN desorption characteristics identical to those from the clean surface.

Attempts were made to identify the species which allowed this reversibility by exposing CF_3CN to $\text{Ru}(001)$ surfaces covered with the residues of several different molecules (cyanogen, acetonitrile, oxygen, nitrogen trifluoride, and trifluoroacetonitrile). These

molecules (except NF_3) were adsorbed and then warmed to 400–500°C (before significant nitrogen desorption occurred from the nitriles), and finally cooled to the adsorption temperature desired. NF_3 did not adsorb at all at 25°C or above, but adsorption did occur at -160°C. The Ru(001)- NF_3 layer was then flashed to approximately 700°C to decompose it. At 700°C both nitrogen and fluorine disappeared from the surface, but at different enough rates to preferentially remove the N and leave some F behind. (An attempt was made to use xenon difluoride as a source of surface F, but failed due to the reaction of XeF_2 with the gas handling lines to form xenon gas and HF.)

The reversibility displayed by the CF_3CN residue was never totally duplicated by the residues of these other molecules. In Figure 15 is presented a compilation of several thermal desorption spectra for a constant 2.4L exposure of CF_3CN to "dirty" Ru(001) surfaces. Spectrum (a) represents the desorption from mildly heated CF_3CN . Spectrum (b) and (c) represents the desorption from a cyanogen and acetonitrile residue, respectively, while spectrum (d) is the desorption arising from one Ru(001)-O surface. Fluorine alone, derived from nitrogen trifluoride, had no effect and the CF_3CN desorption was no different than desorption from the clean surface.

The molecular CF_3CN desorption from oxygen covered Ru(001) showed both a dependence on the oxygen coverage and an oxygen clean-off reaction. The oxygen coverage dependence is illustrated in Figure 16. For the higher oxygen coverages, no nitrogen or fluorine

remained on the surface after heating to 400–500°C, while for lower oxygen coverages, some did remain after the thermal desorption experiment. As would be expected more N and F remained if the initial oxygen coverage was lower. The R_0 values in the figure represent the oxygen coverage before the heating. The surfaces which produced spectra (a) and (b) both had residual N and F after the TDS experiment, while those producing (c) and (d) did not. The exposures required to obtain the indicated initial R_0 values were .3, 1, 1.8, and 55L of O_2 respectively.

OXYGEN CONTAINING COMPOUNDS

All oxygen-based hydrocarbon derivatives underwent largely thermal decomposition on the clean Ru(001) surface; and explicably, hydrogen and carbon monoxide were the common decomposition products. The molecules studied were methanol, acetaldehyde, acetone, acetic acid, methyl acetate, furan, and tetrahydrofuran. (The results of furan chemisorption are described in the previous section on heteroaromatic molecules.) With the exception of acetic acid, the thermal desorption spectra of the decomposition products (CO and H_2) were remarkably similar, as illustrated for acetaldehyde and acetone in Figure 17. The desorption spectra of CO and H_2 resembled those obtained from the adsorption of molecular CO or H_2 on the clean or carbon covered surface. Differences between the spectra from different molecules could be attributed to variations in sticking coefficients of the oxygen-containing molecules and in the resultant carbon coverage

produced during the decomposition. Readsorption experiments with oxygen containing compounds did not show any significant changes in thermal desorption behavior (except for acetic acid). Drops in sticking coefficients and the expected changes in CO desorption maxima were the only effects noted.

Methanol adsorbed on Ru(001) at -160°C produced a molecular methanol desorption peak at approximately -60°C . Carbon monoxide and hydrogen were the only decomposition products detected with maxima at 215°C and 105°C , respectively, and no carbon or oxygen was detected on the surface after the experiment. (Hrbek and coworkers(30) have completed a more extensive study of methanol chemistry on Ru(001) and have come to slightly different conclusions.)

Acetaldehyde decomposed quantitatively on Ru(001) to form CO at 205°C , H_2 at 110°C , and Ru(001)-C. Acetone also decomposed quantitatively to form CO, H_2 , (T_{max} of 205°C and 90°C , respectively), and Ru(001)-C (Figure 17). Adsorption at -160°C only produced multilayers of acetaldehyde and acetone, which both desorbed at approximately -120°C . Methyl acetate also decomposed to produce CO and H_2 at 205°C and 100°C , but an additional molecular desorption, which shifted from 0°C to -90°C (where it merged with the multilayer peak at approximately -110°C), was noted. Shown in Figure 18 is the coverage dependence of the molecular thermal desorption spectra of methyl acetate.

One curious feature of methyl acetate chemisorption behavior was a conspicuous lack of surface carbon remaining after the desorption. Repeated adsorption/desorption cycles failed to produce any surface carbon. Since all the other oxygen-containing hydrocarbon molecules produced surface carbon during the desorption, it is unreasonable to presume that for methyl acetate, carbon diffused into the bulk. Therefore desorption of some carbon-containing molecule that would not adsorb on Ru(001) at -160°C must have occurred during adsorption. A likely candidate for this molecule is methane. The mass spectrum of the acetate did show a manifold of peaks in the 12-16 amu region during exposure, but so did all the other oxygen-containing compounds that contained methyl groups, so this piece of data is inconclusive and a resolution of this problem is not forthcoming from these studies.

Tetrahydrofuran adsorbed on Ru(001) at 25°C also decomposed quantitatively to CO, H_2 (T_{max} of $170\text{--}220^{\circ}\text{C}$ and $70\text{--}90^{\circ}\text{C}$, respectively), and surface carbon. Adsorption at -160°C produced a coverage dependent molecular desorption that ranged from 5°C for low coverages to -80°C for high coverages (then merged with the multilayer peak). No ordered LEED patterns were observed upon adsorption at 25°C or -160°C .

As carbon monoxide was a common decomposition product of these molecules and as CO forms an ordered ($\sqrt{3} \times \sqrt{3}$) $\text{R}30^{\circ}$ LEED pattern at the coverages represented by the observed desorptions, LEED was used

to sense at what temperature decomposition was extensive and an ordered CO pattern was produced. Very faint $\sqrt{3}$ patterns were observed for methanol at 25°C and for all the other chemisorbed molecules (except acetic acid) upon warming to 100–150°C.

Acetic acid decomposition displayed some coverage dependences. At low coverages, acetic acid decomposition yielded H₂ and CO desorption maxima at 220°C and a small CO₂ maximum at 180°C. Higher coverages shifted the CO and H₂ maxima down to 180°C and the CO₂ maximum up to 220°C. Additional CO desorption were observed in the 250–350°C region which were most likely due to recombination of surface carbon and oxygen, also produced in the decomposition. The coverage dependence of the CO and CO₂ desorptions are illustrated in Figure 19 and 20. Readsorption of acetic acid on the carbon and oxygen contaminated Ru(001) surface resulted in CO, H₂, and CO₂ thermal desorption spectra which all peaked at 205–210°C with analogous peak shapes. Multilayer desorption was noted at –80°C for adsorption at –160°C.

No ordered LEED patterns were observed upon adsorption of acetic acid at 25°C or –160°C. However, faint p(2 x 2) patterns could occasionally be observed after warming Ru(001)–CH₃COOH to 150°C.

Figure 1. Carbon monoxide thermal desorption spectra were sensitive to surface carbon contamination. By adsorbing either benzene or acetaldehyde on the surface and heating to 400-500°C, carbon was deposited on the surface. Illustrated here are the CO desorption spectra for Ru(001)-C-CO prepared by sequential doses of .5, 2.5, and 2.5L of benzene (spectra (b)-(d), respectively), then thermolysis at 500°C, and finally CO (3L) adsorption at 25°C. Spectrum (a) is for the clean surface. The sensitivity scale on this figure is one-fifth that of all other figures.

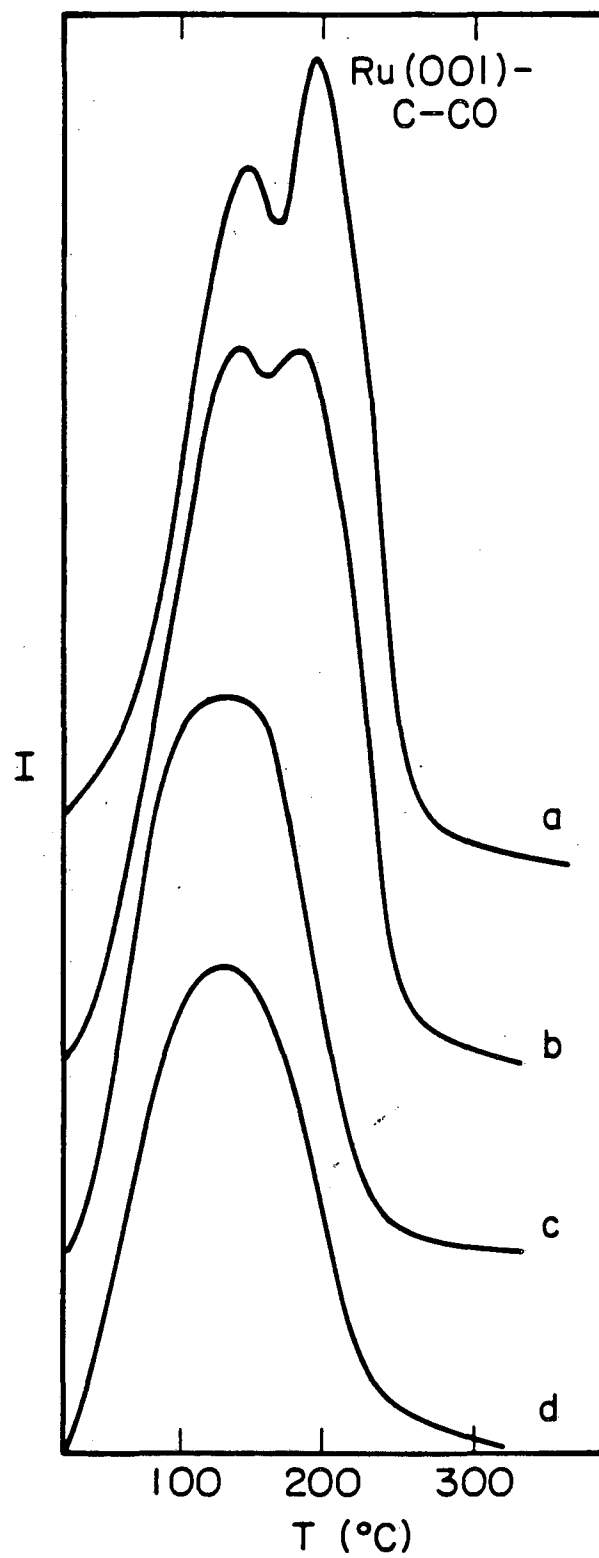


Figure 2. Benzene decomposes quantitatively on Ru(001) to give hydrogen gas and surface carbon. The character of the hydrogen desorption peaks is affected by the initial surface coverage of benzene. This is illustrated above for deuterium desorption from Ru(001)-C₆D₆ decomposition for initial exposures of .2, .5, and 4L to the clean Ru(001) surface at 25°C in spectra (a)-(c), respectively.

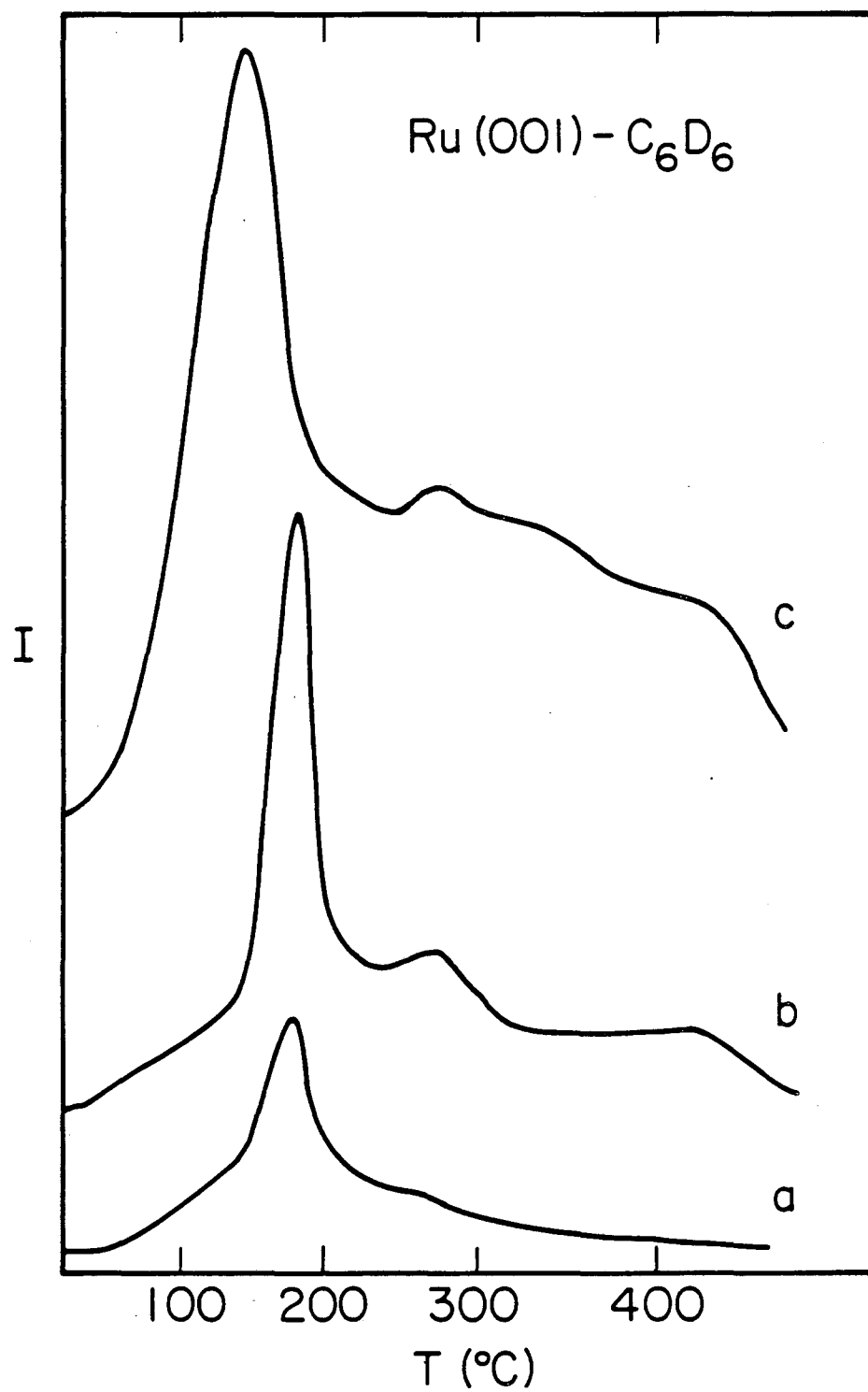


Figure 3. Like benzene, toluene decomposes quantitatively to hydrogen and surface carbon when adsorbed on the clean Ru(001) surface and then heated. Illustrated here is the coverage dependence of the deuterium desorption (amu 4) from perdeuterotoluene decomposition. Spectra (a)-(e) represent desorption from exposures of .1, .5, .8, 1.5, and 2.5L, respectively, at 25°C.

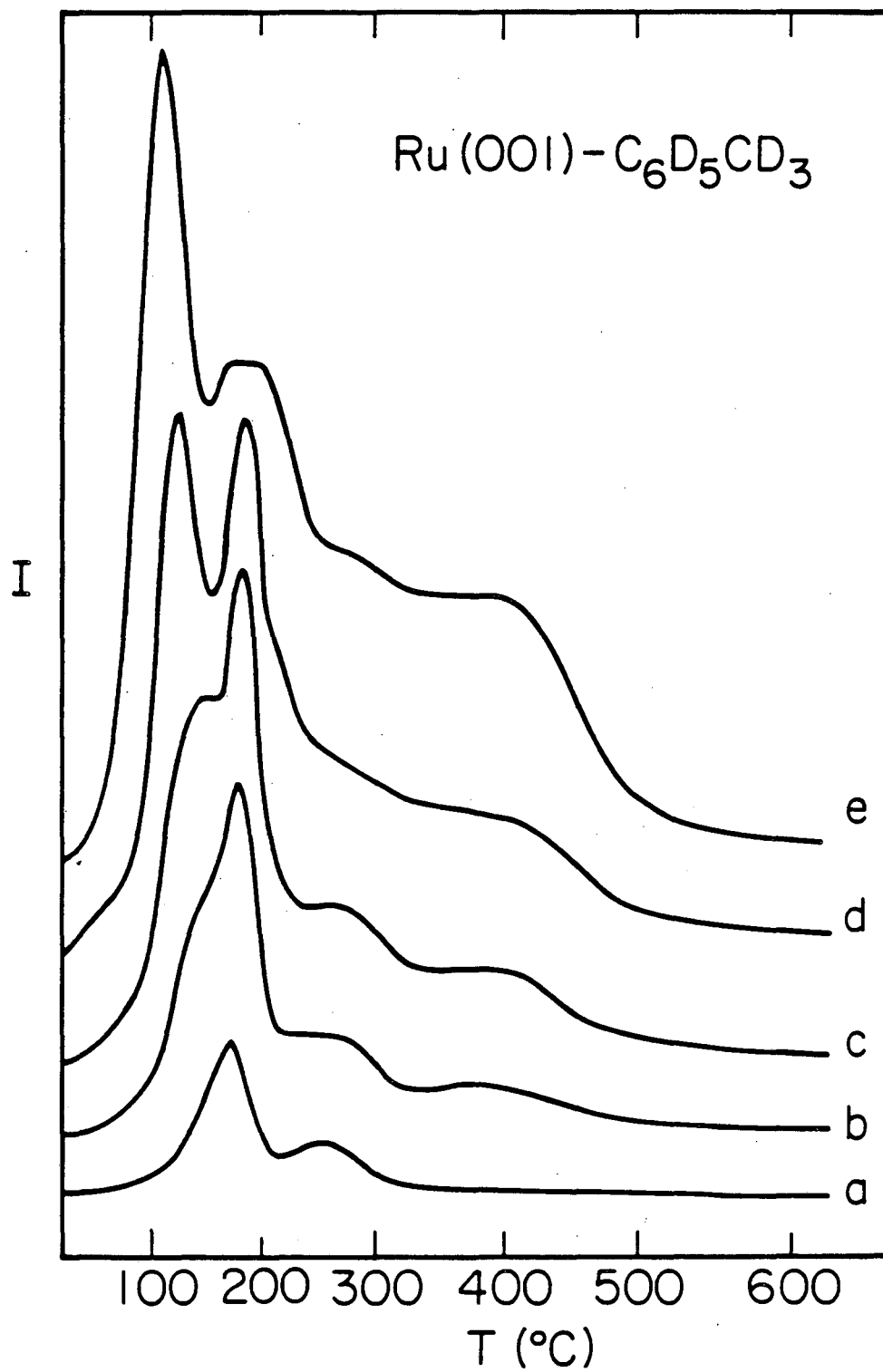
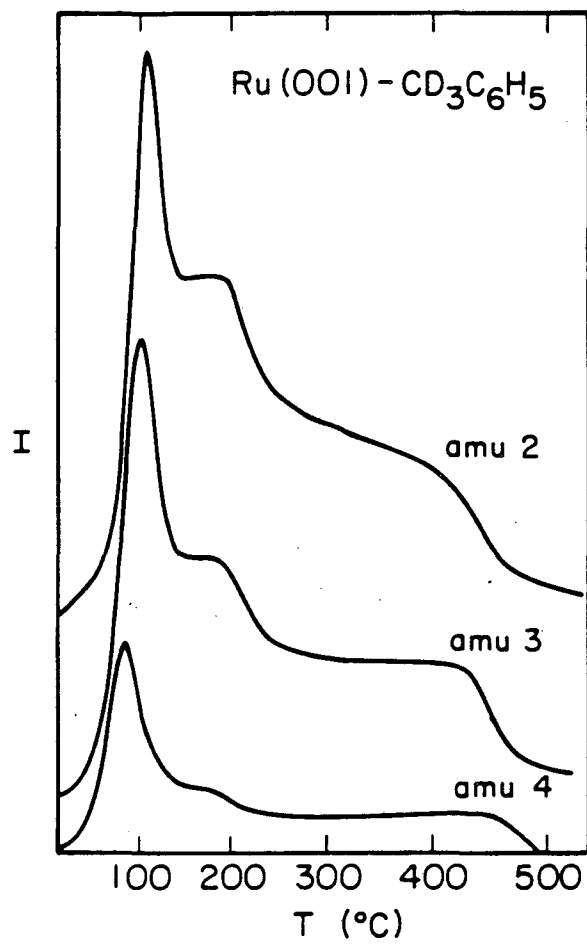
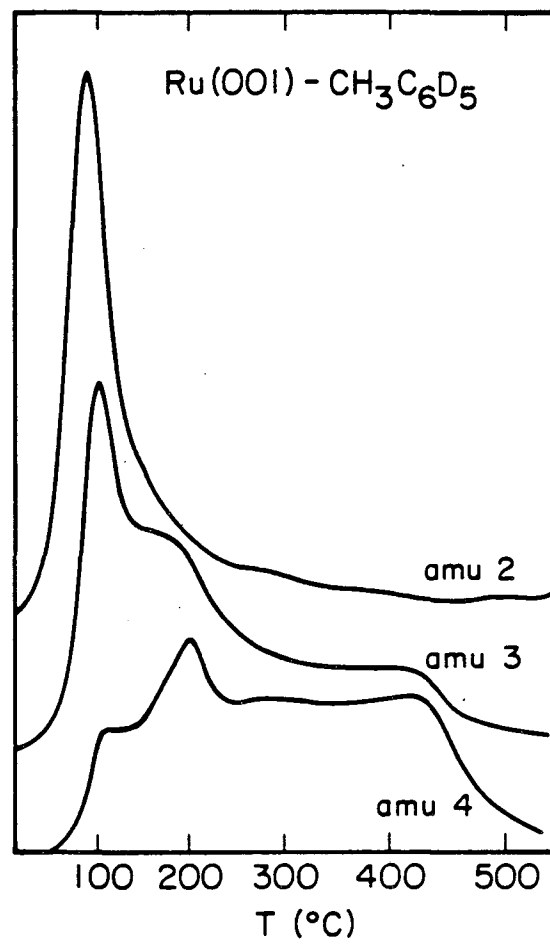


Figure 4. When toluene decomposes on Ru(001), aliphatic C-H bonds appear to cleave first. This regiospecificity was established in thermal decomposition experiments of $\text{CD}_3\text{C}_6\text{H}_5$ and $\text{CH}_3\text{C}_6\text{D}_5$ adsorbed on Ru(001). The H_2 , HD, and D_2 desorption spectra are presented in Figures 4(a)-(c) for initial toluene exposures of 2.5, 1.5, and .2L, respectively, to Ru(001) at 25°C.

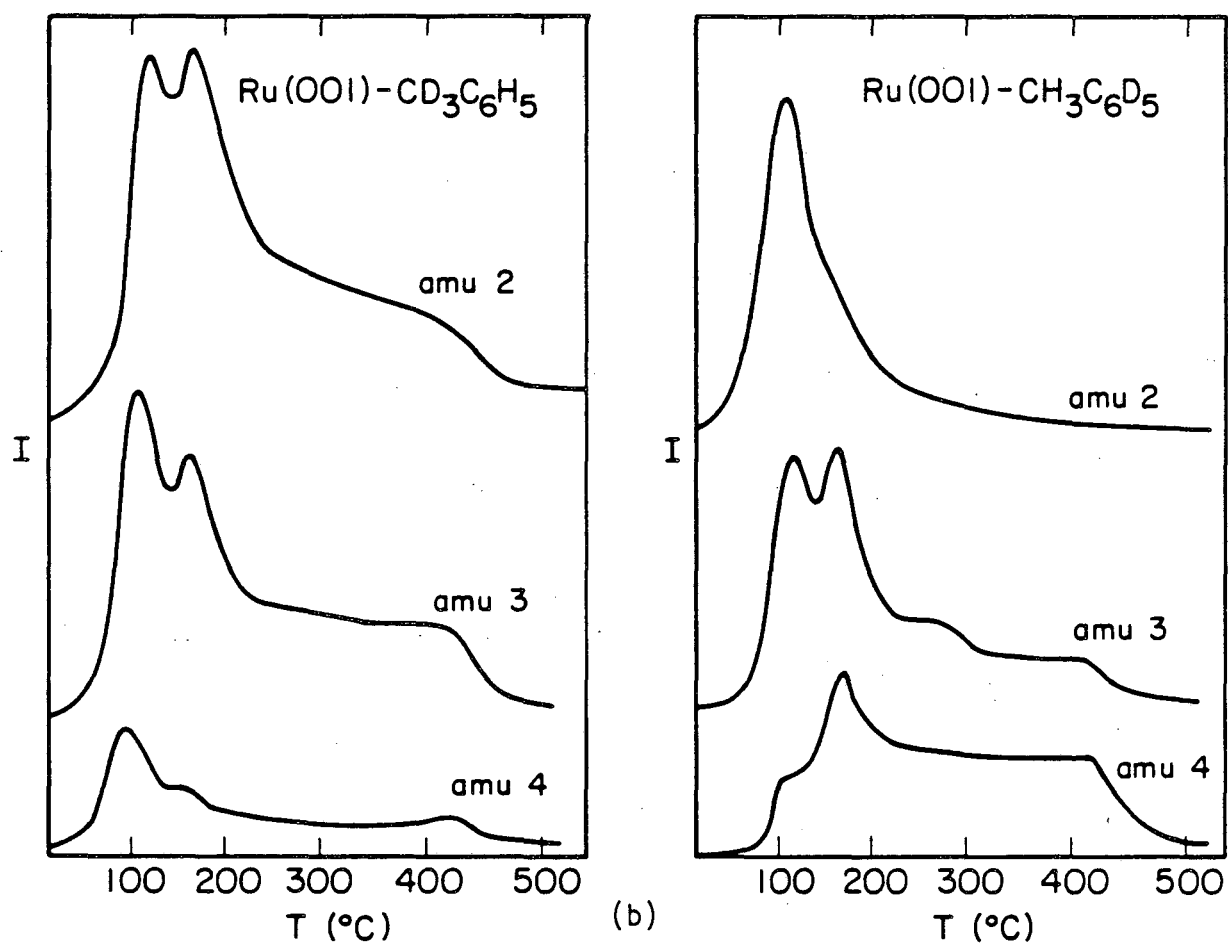
51a



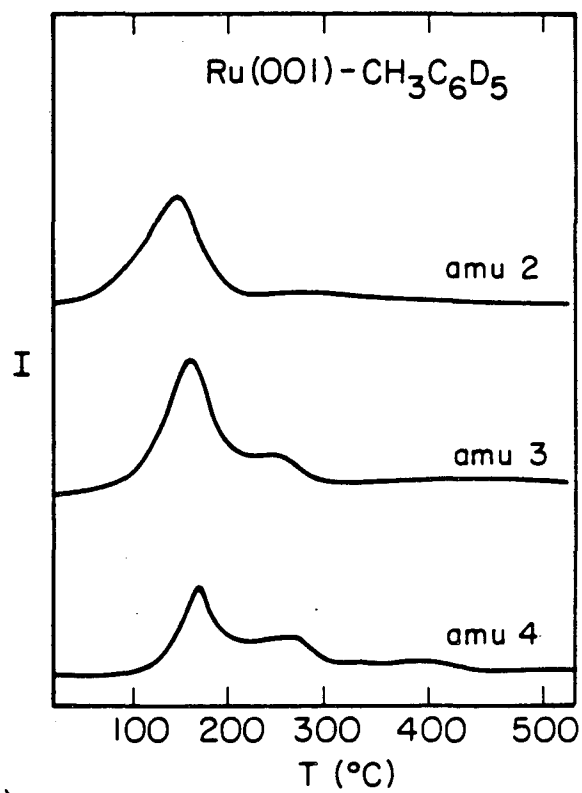
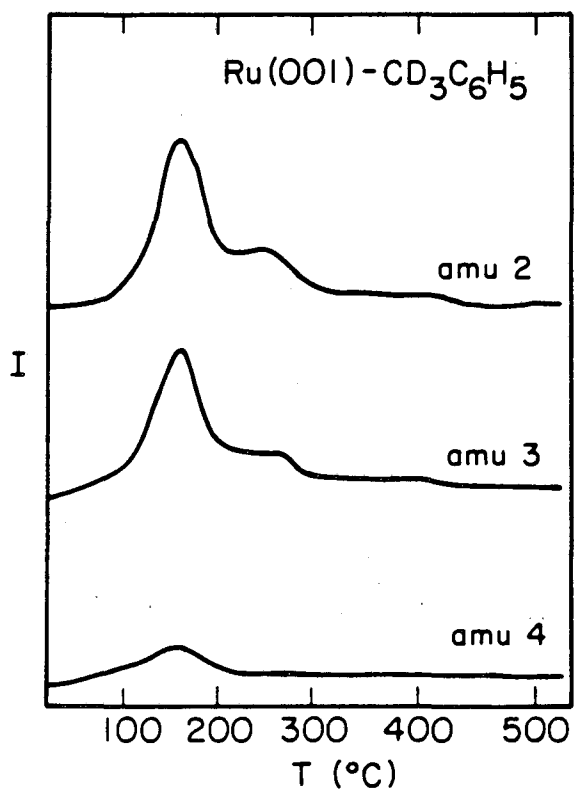
(a)



XBL 843-1253



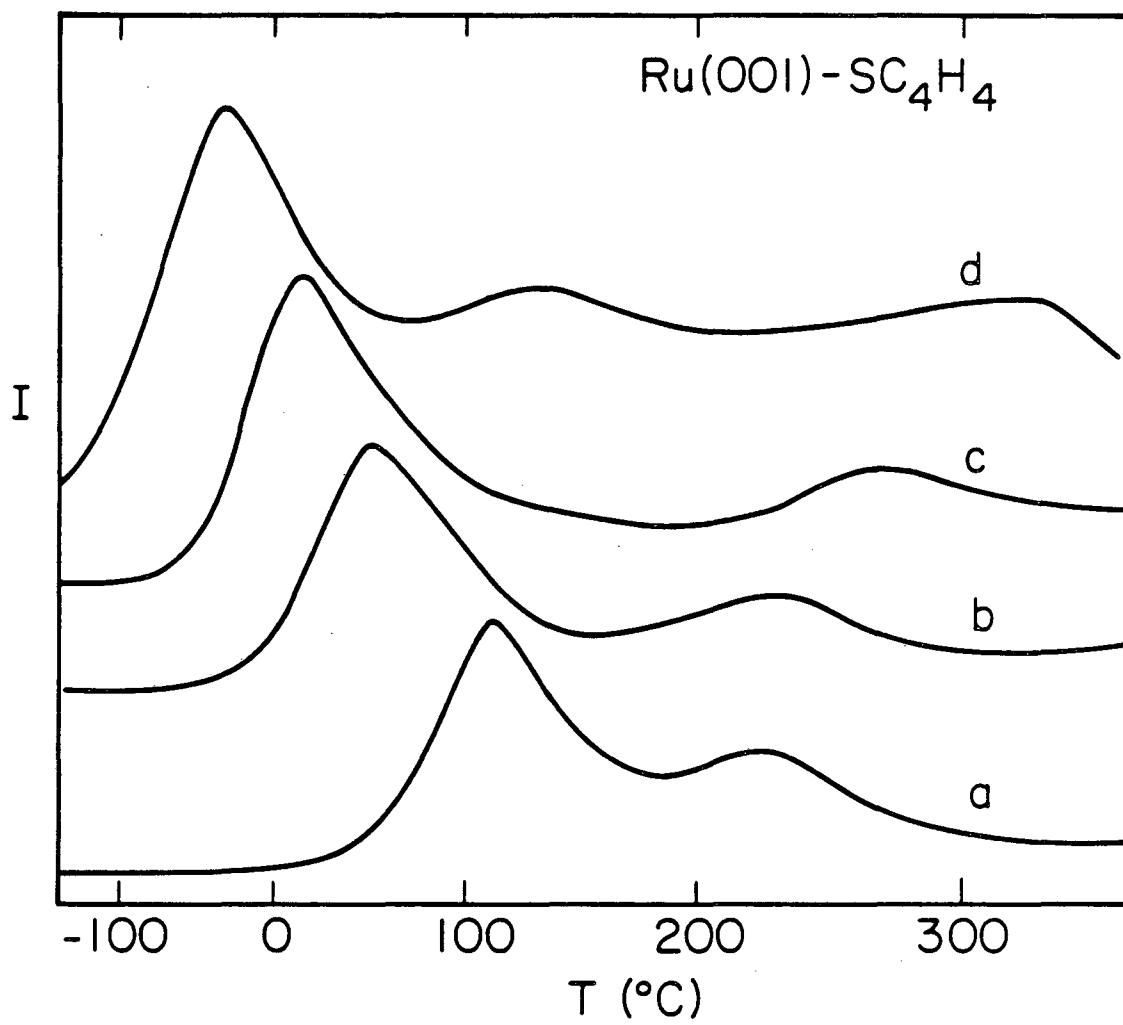
51c



(c)

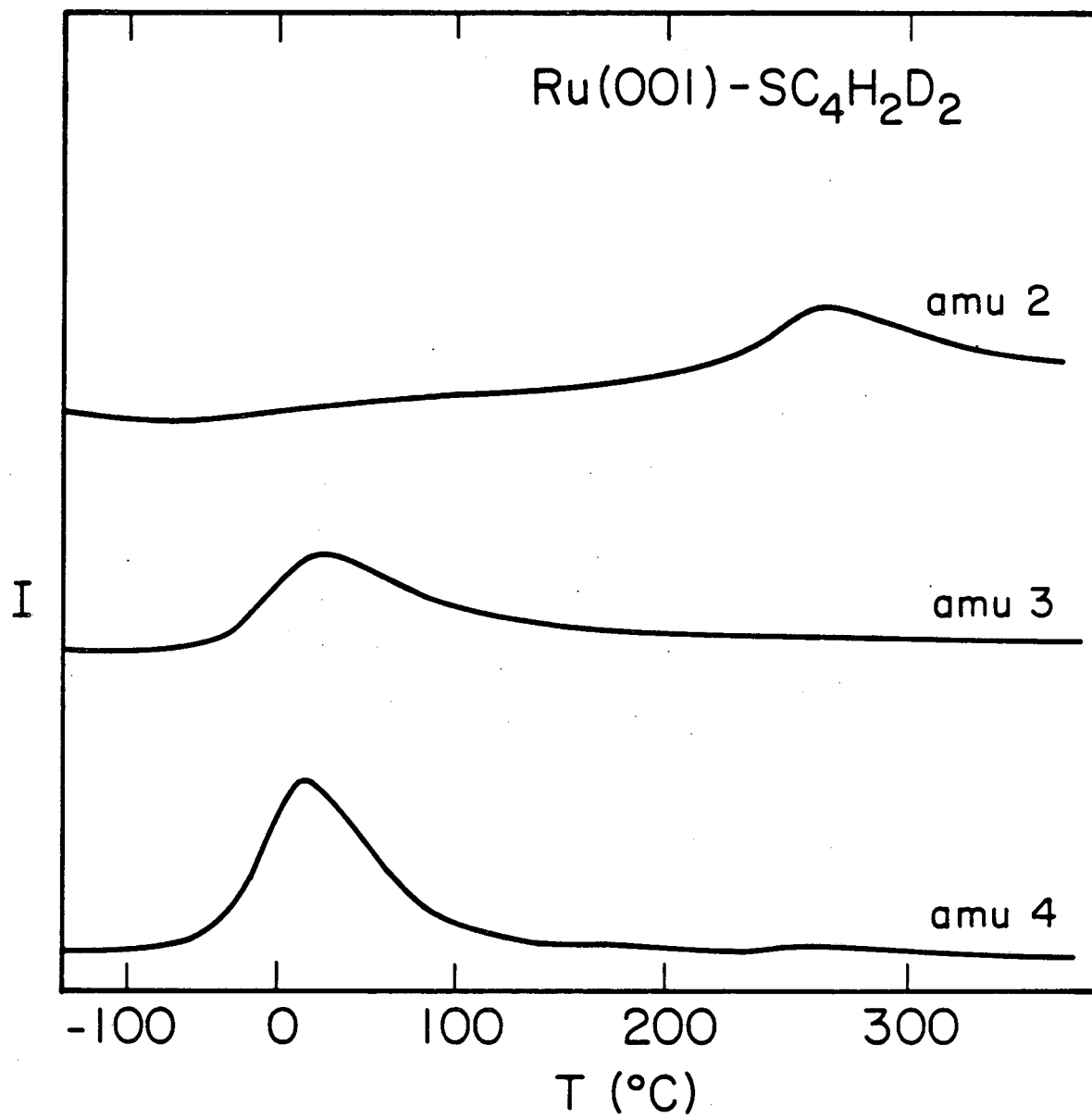
XBL 843-1255

Figure 5. The heteroaromatic molecule thiophene also decomposes quantitatively to hydrogen and surface C and S when adsorbed on the clean Ru(001) surface. The resultant hydrogen desorptions vary with initial thiophene coverage, as illustrated in this figure. Exposures were .1, .2, .3, and .5L, respectively, and spectrum (d) represents the desorption arising from saturation coverage.



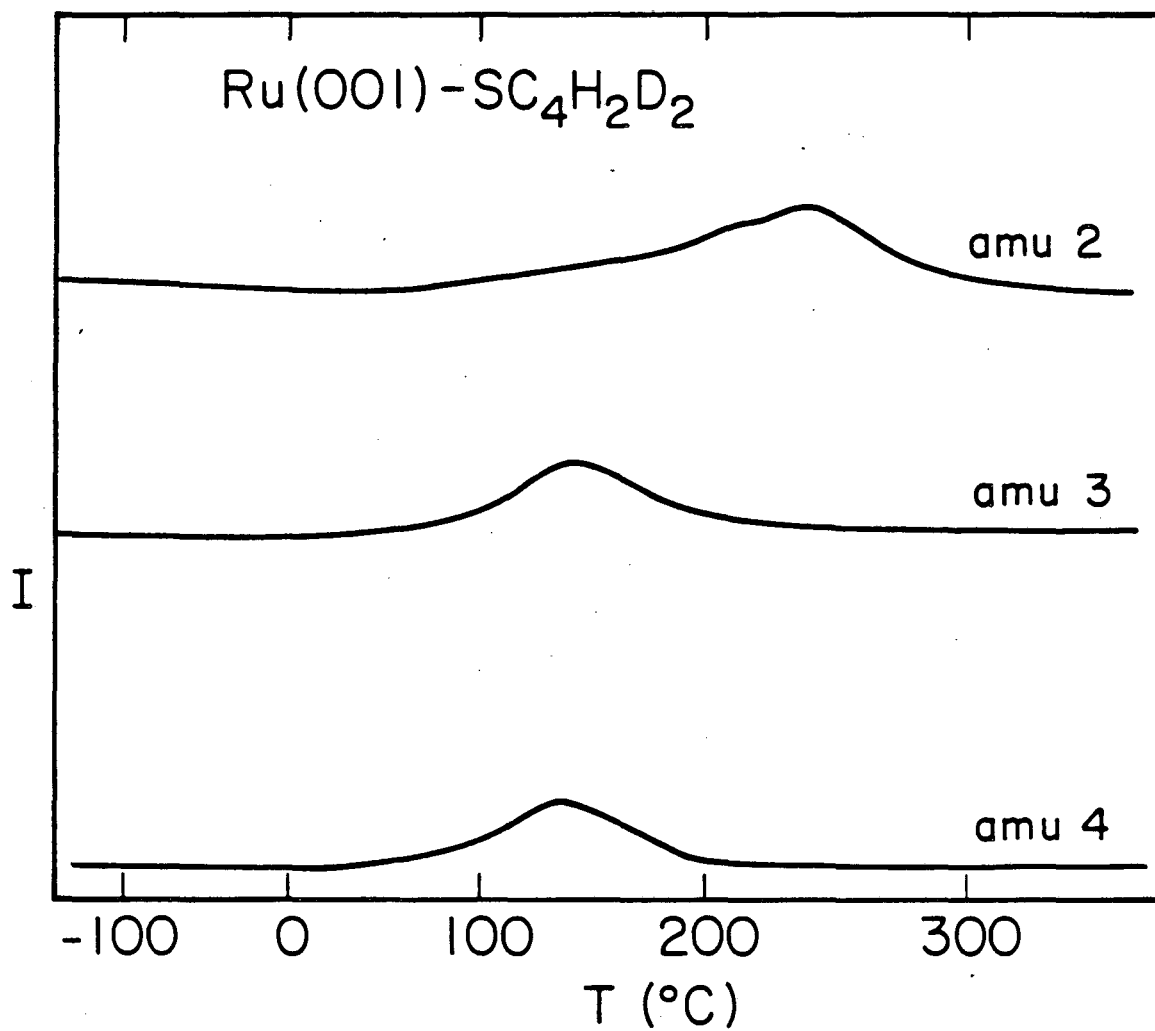
XBL 843-1269

Figure 6. Thiophene decomposition showed a high degree of specificity in its decomposition. When 2,5-d₂-thiophene was adsorbed on the clean Ru(001) surface, the resulting hydrogen desorptions had all deuterium atoms appearing in the low temperature desorption peak. This figure illustrates the H₂, HD, and D₂ resulting from a .3L exposure of the labelled thiophene molecule to the clean Ru(001) surface at -160°C. (This corresponds to spectrum (c) of Figure 5.)



XBL 843-1270

Figure 7. The regiospecificity of thiophene decomposition was maintained even at low coverages where the desorption peaks overlapped. Shown here are the H_2 , HD, and D_2 desorption profiles for a .1L exposure of the labelled thiophene molecule to the clean Ru(001) surface at -160°C . (This corresponds to spectrum (a) of Figure 5.)



XBL 843-1271

Figure 8. Hydrogen cyanide underwent partial reversible desorption after adsorption at either 25°C or -160°C. Hydrogen cyanide thermal desorption profiles from Ru(001)-HCN formed by exposures of .5, 1, and 3L (spectra (a)-(c), respectively) at 25°C on clean Ru(001) are presented above to illustrate the coverage dependence of the molecular desorption.

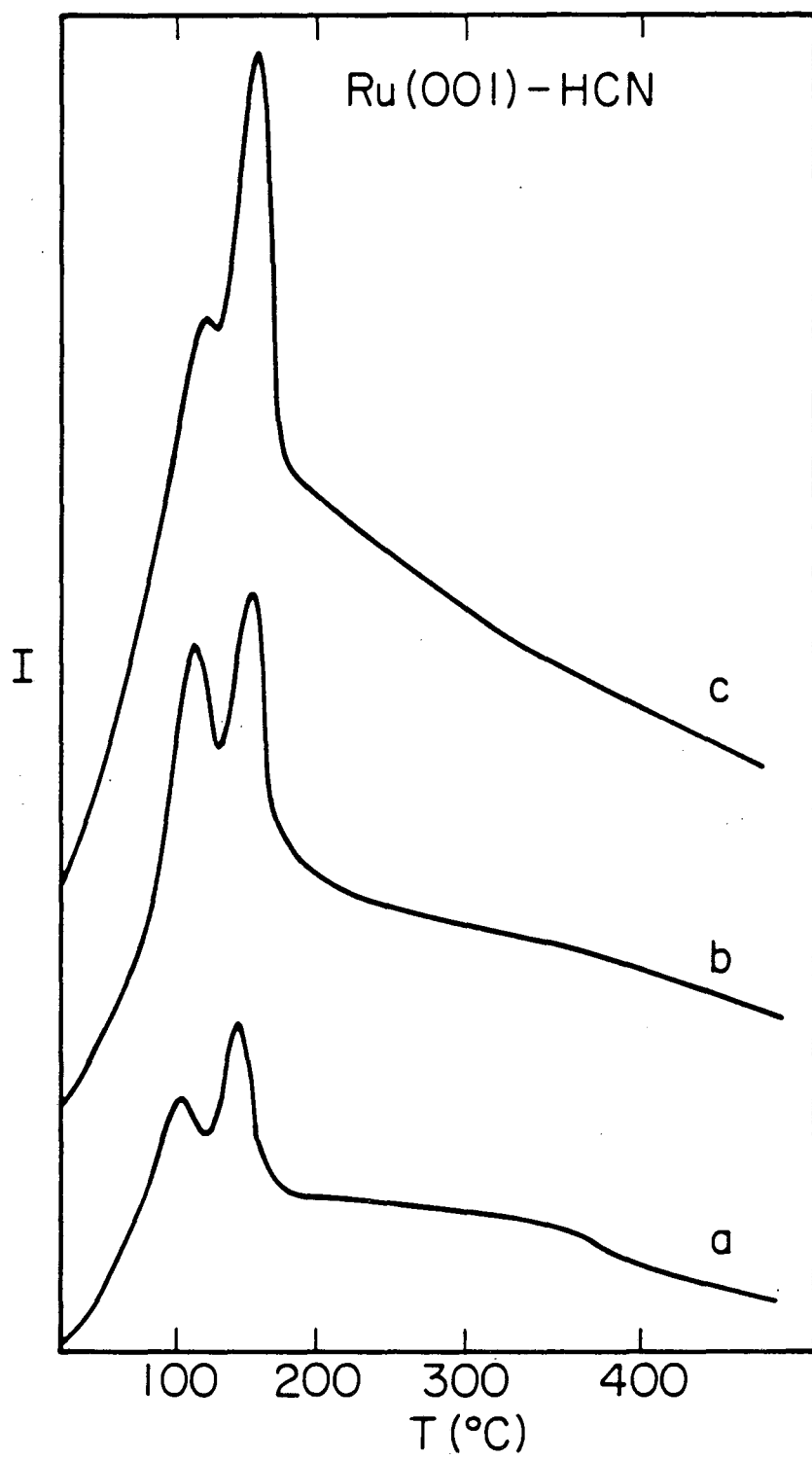
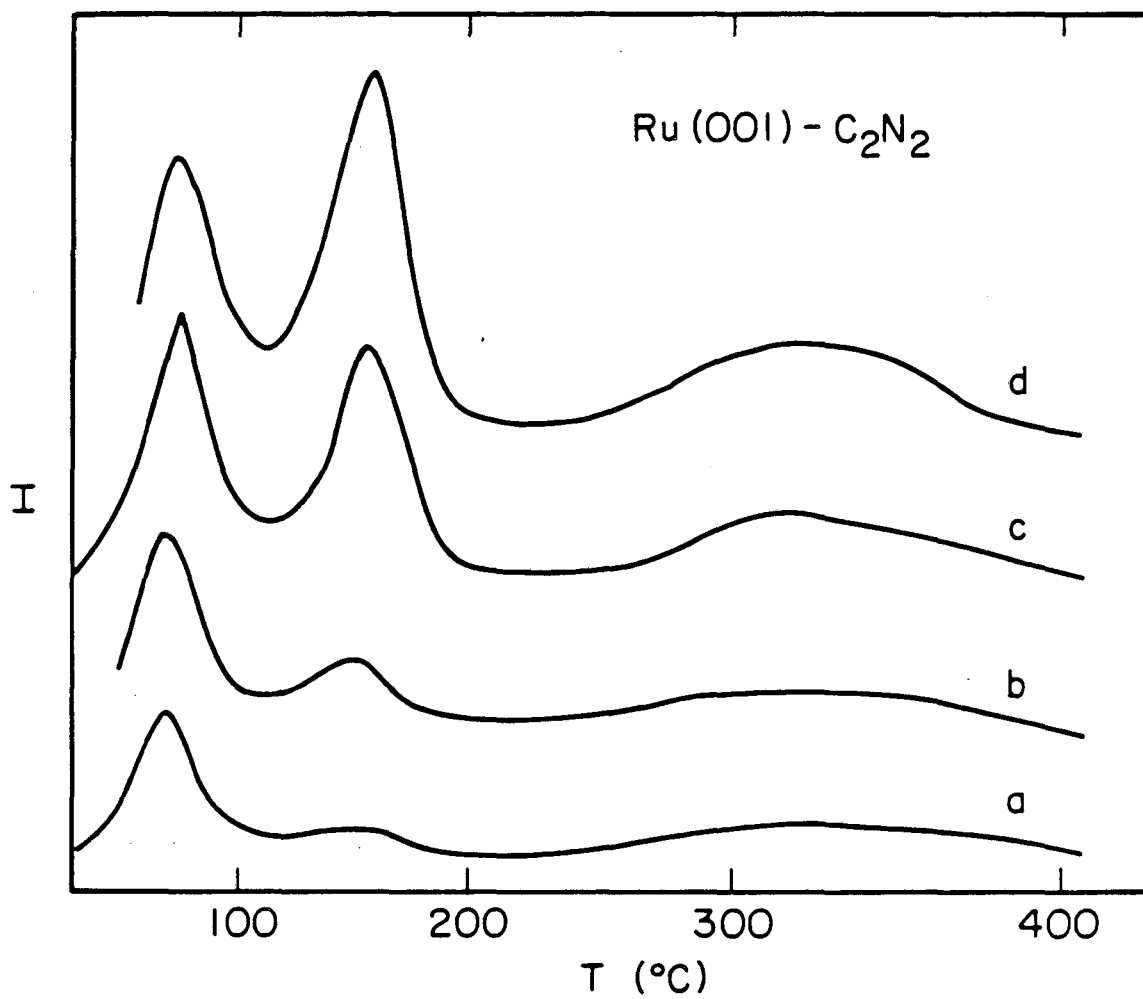


Figure 9. Cyanogen was one of the few molecules studied that exhibited molecular desorption after adsorption at room temperature. The cyanogen desorption was coverage dependent as shown above in the molecular desorption spectra for cyanogen adsorbed on Ru(001) at 25°C for exposures of 2.5, 5, 20, and 40L (spectra (a)-(d), respectively).



XBL 843-1263

Figure 10. The character of the cyanogen desorption from Ru(001) was significantly affected by the temperature of adsorption. The surface coverage and the percentage of reversible cyanogen desorption increased with a decrease in adsorption temperature. Spectra (a) and (b) above are representative of thermal desorption from Ru(001)-C₂N₂ formed initially at -160°C and at exposures of .3 and .6L, respectively. Spectrum (b) represents the new saturation spectrum. Desorption from multilayers is not shown due to interference from crystal support desorptions.

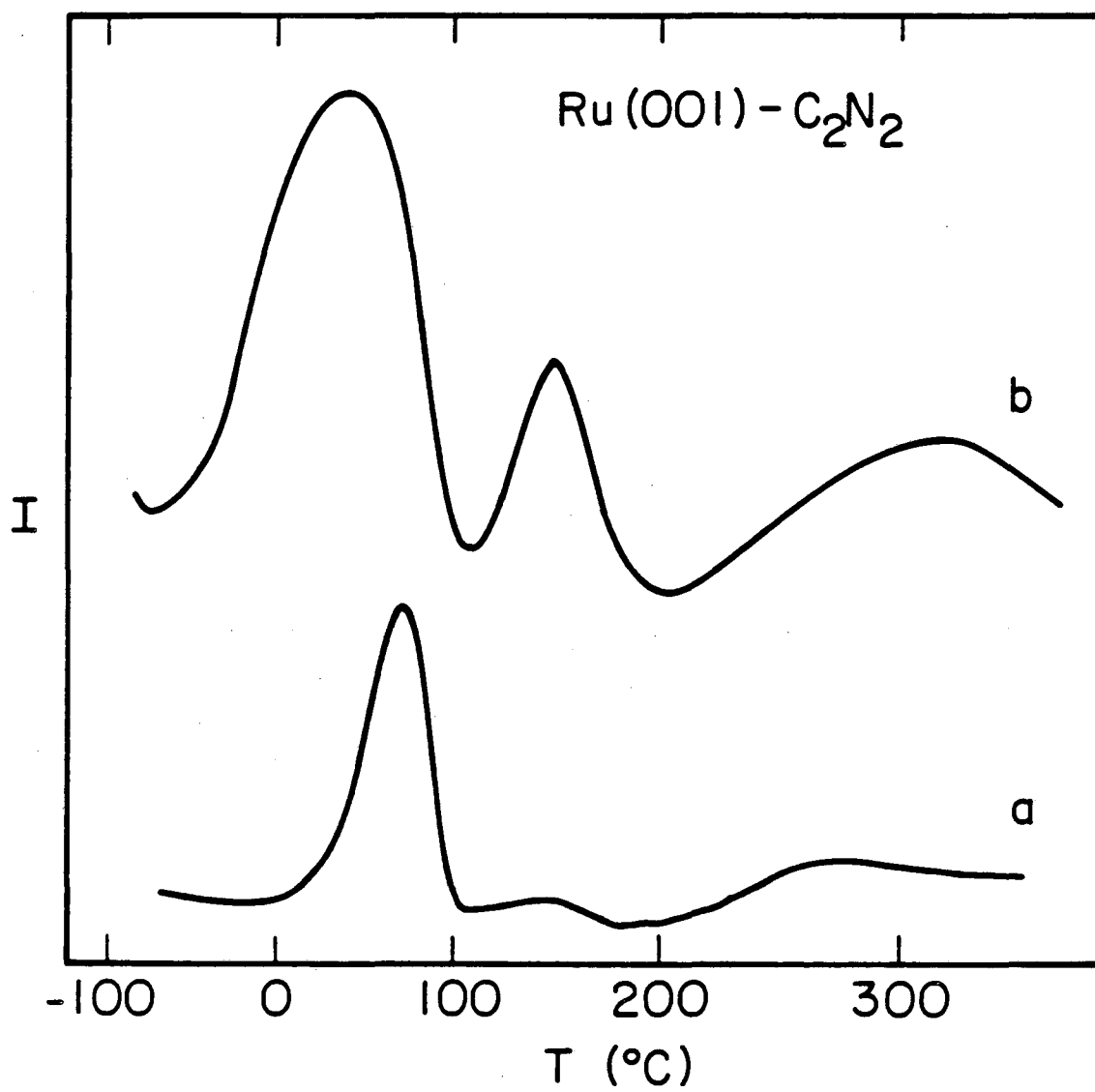


Figure 11. Acetonitrile adsorbed on clean Ru(001) at -160°C underwent both desorption and decomposition in the thermal desorption experiment. This is illustrated above for CD_3CN on Ru(001) for states formed at -160°C with initial exposures of .05 and .1L (spectra (a) and (b), respectively). Atomic mass units 44 and 4 represent CD_3CN and D_2 , respectively. Desorption from multilayers is not shown due to interference from crystal support desorptions.

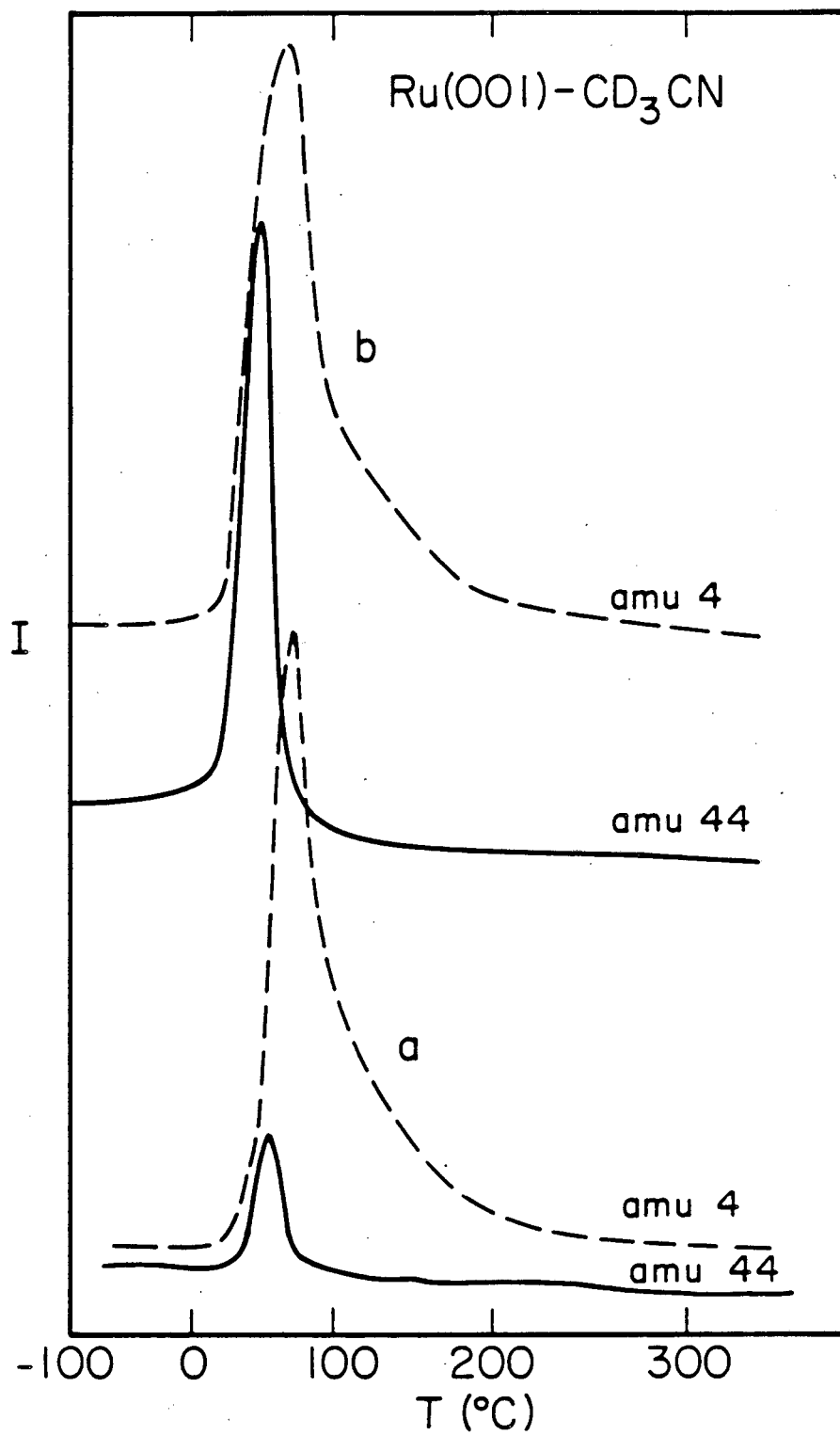


Figure 12. The chemisorption of trifluoroacetonitrile on Ru(001) was partially reversible. Shown here is the coverage dependence of the molecular desorption (amu 69) from Ru(001)-CF₃CN formed at 25°C (the molecular peak (amu 95) showed the same profile but at reduced intensity). Spectra (a)-(e) are for initial exposures of 1.5, 2, 2.5, 5, and 11L, respectively.

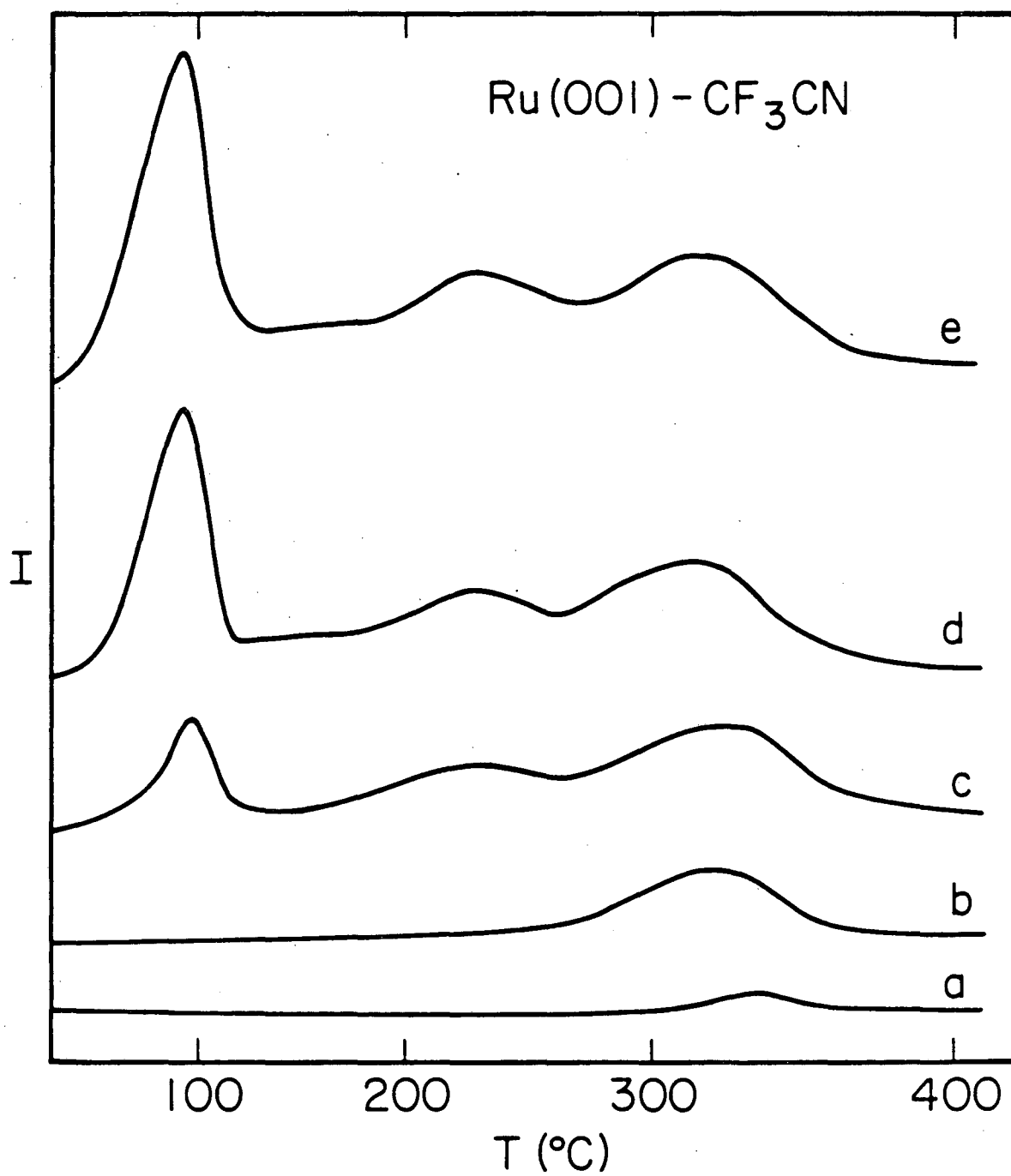
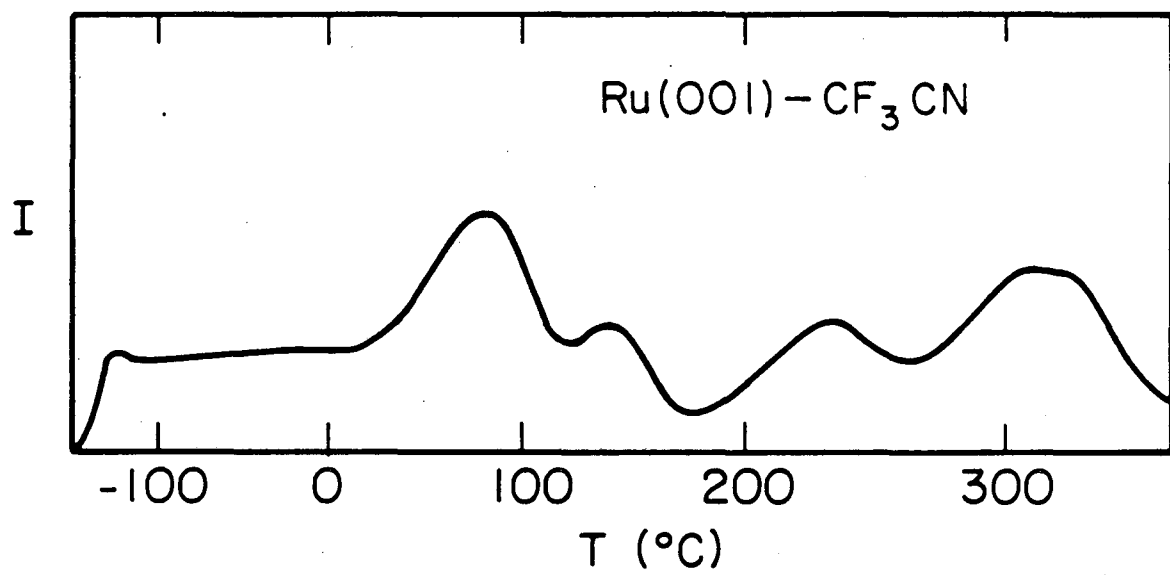
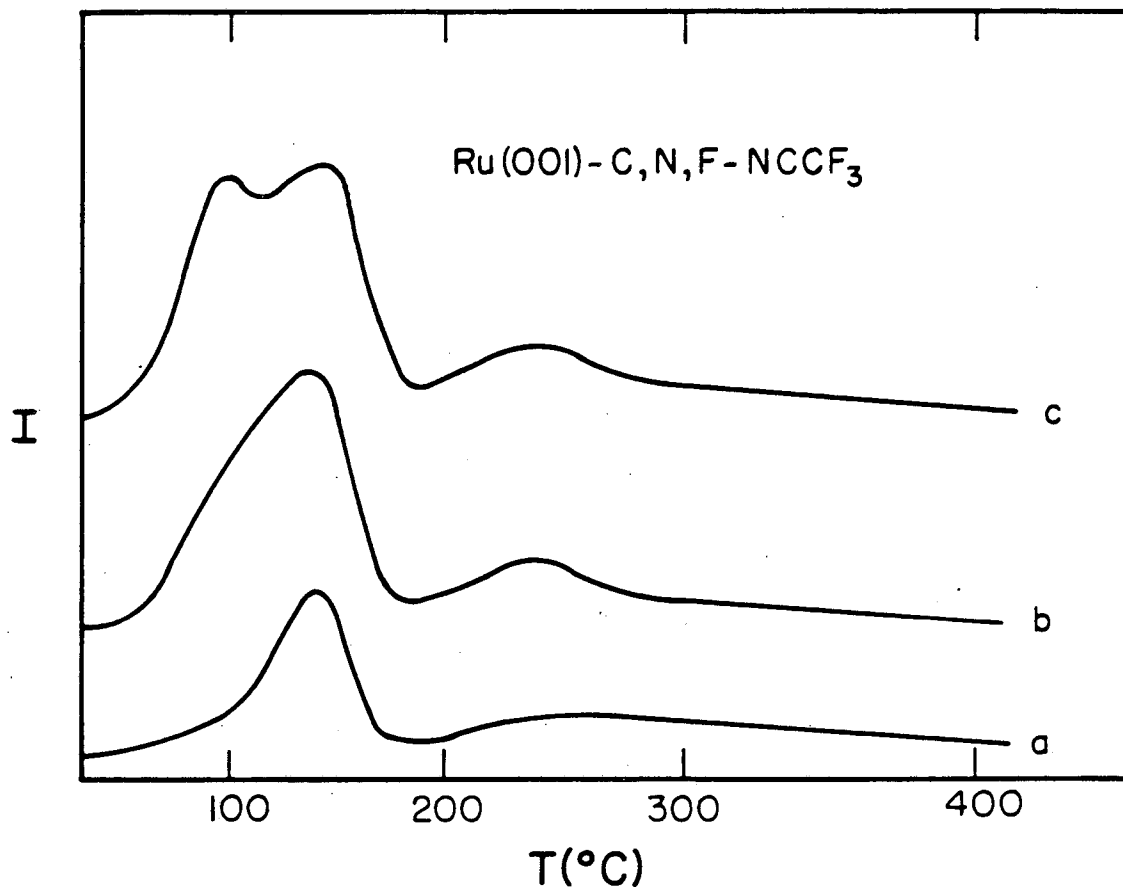


Figure 13. For adsorption at -160°C , CF_3CN on $\text{Ru}(001)$ displayed an additional peak in the molecular desorption spectrum. Shown here is the desorption profile for CF_3CN (amu 69) for saturation coverage (the molecular peak, amu 95, showed the same profile at reduced intensity). Multilayer desorptions are not shown due to interfering desorptions.



XBL 843-1262

Figure 14. Readsorption of CF_3CN on its own decomposition residue produced fully reversible chemisorption as long as heating did not exceed approximately 500°C where significant nitrogen production would begin to occur. Shown above is the coverage dependence of the molecular CF_3CN desorption (amu 69) for exposures of .4, 1.2, and 2.4L (spectra (a)–(c), respectively) at 25°C to the $\text{Ru}(001)$ surface covered with CF_3CN residue.



XBL 844-1272

Figure 15. In an attempt to define the characteristics of the CF_3CN residue which allowed the reversibility illustrated in Figure 14, several other adsorbates were used to cover the surface before adsorbing CF_3CN . A constant 2.4L exposure of CF_3CN was adsorbed on the residue of a 2.4L exposure of CF_3CN , on the residue of a saturation dose of cyanogen, on the residue of a saturation dose of acetonitrile, and on a 1L dose of oxygen at 25°C . The resulting molecular CF_3CN desorptions (amu 69) are shown above in spectra (a)-(d), respectively. (Note that desorption from $\text{Ru}(001)\text{-O}$ showed a dependence on the O coverage, see Figure 16.)

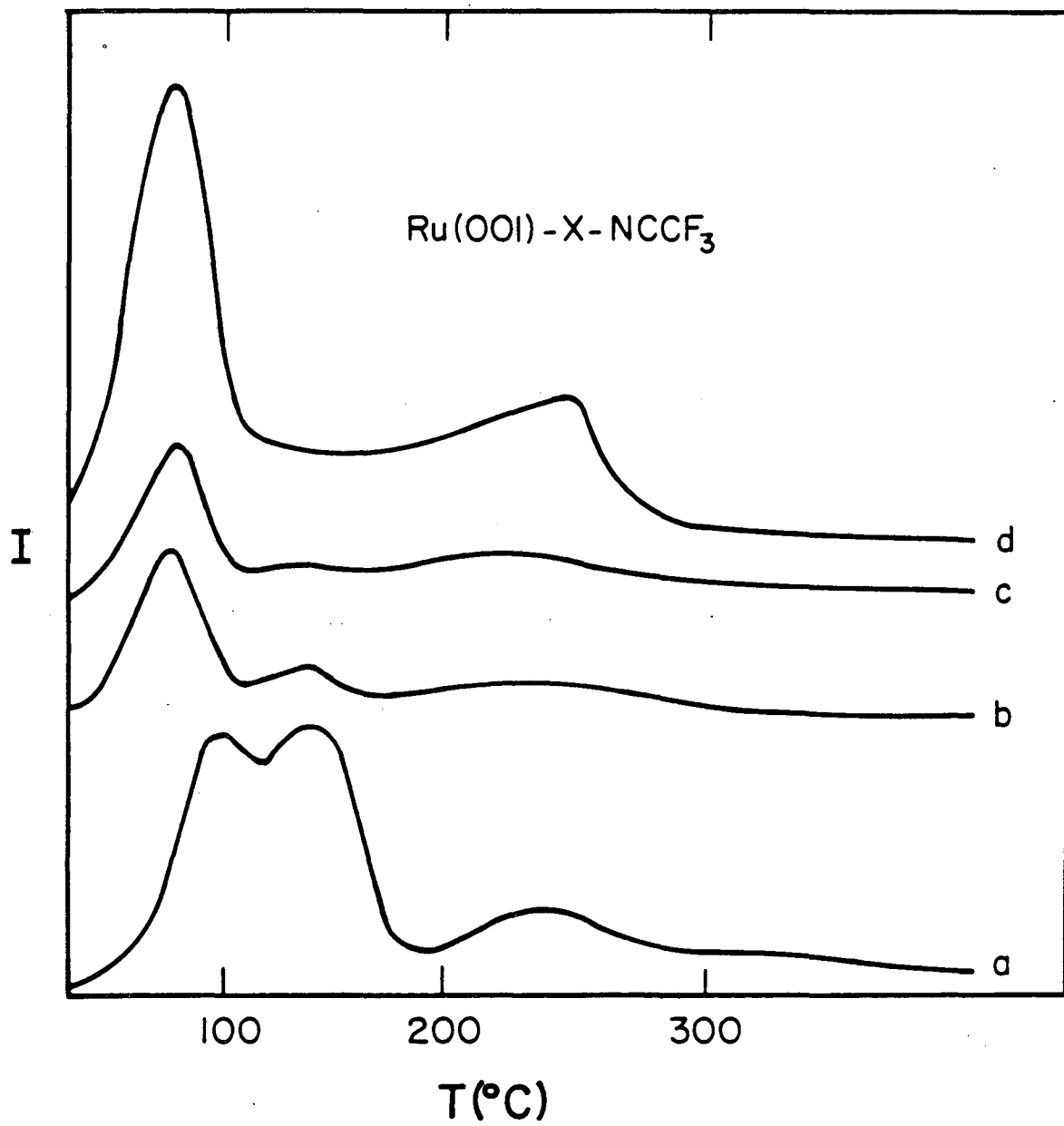


Figure 16. Desorption of CF_3CN from $\text{Ru}(001)\text{-O-CF}_3\text{CN}$ showed a dependence upon the amount of O on the surface. Shown above is the molecular CF_3CN (amu 69) desorption for a constant 2.4L exposure of CF_3CN from various $\text{Ru}(001)\text{-O}$ surfaces. Oxygen coverage is indicated by Auger peak height ratios R_{O} , and represent exposures of .3, 1, 2, and 55L of O_2 at 25°C , respectively.

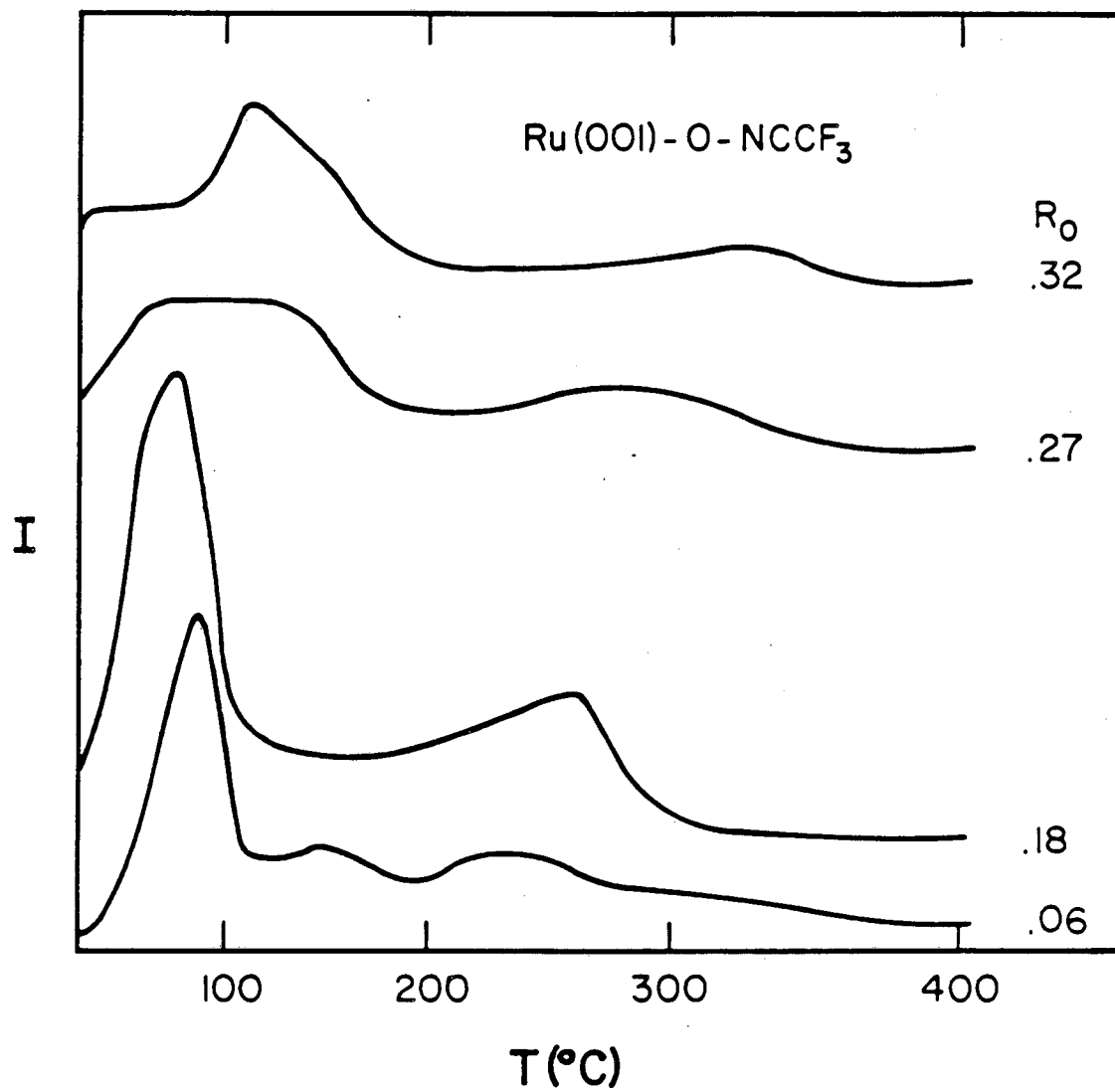


Figure 17. Acetaldehyde and acetone adsorbed on Ru(001) at 25°C decomposed quantitatively to yield CO, H₂, and surface carbon in the thermal desorption experiment. Illustrated above are the H₂ (amu 2) and CO (amu 28) thermal desorption spectra for 1.2L exposures of acetaldehyde (a) and acetone (b) on clean Ru(001) at 25°C. The CO desorption spectra in this figure are on a 2.5 times lower sensitivity scale than all other figures.

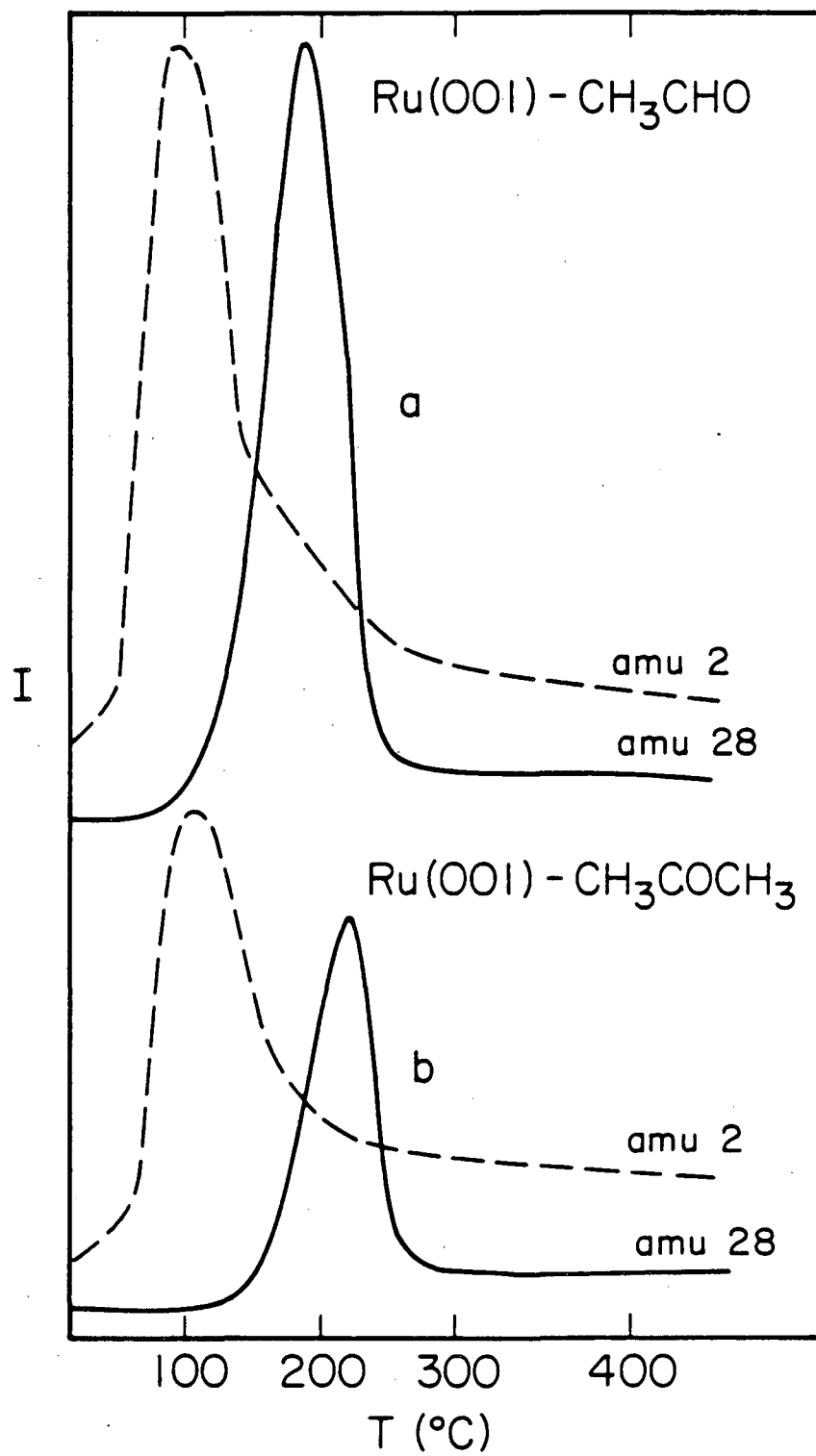


Figure 18. Methyl acetate showed extensive molecular desorption from Ru(001) after adsorption at -160°C . The coverage dependence of the molecular desorption (amu 43) is illustrated here (the molecular peak, amu 74, showed the same profile at reduced sensitivity). Spectrum (a) is the thermal desorption spectrum resulting from an exposure of approximately 1L to the clean surface with spectra (b)-(d) representing sequentially lower exposures. Exposures of $>1\text{L}$ resulted in further broadening and increase in intensity, and lowering of the peak maximum until it merged with the multilayer desorption at -90°C .

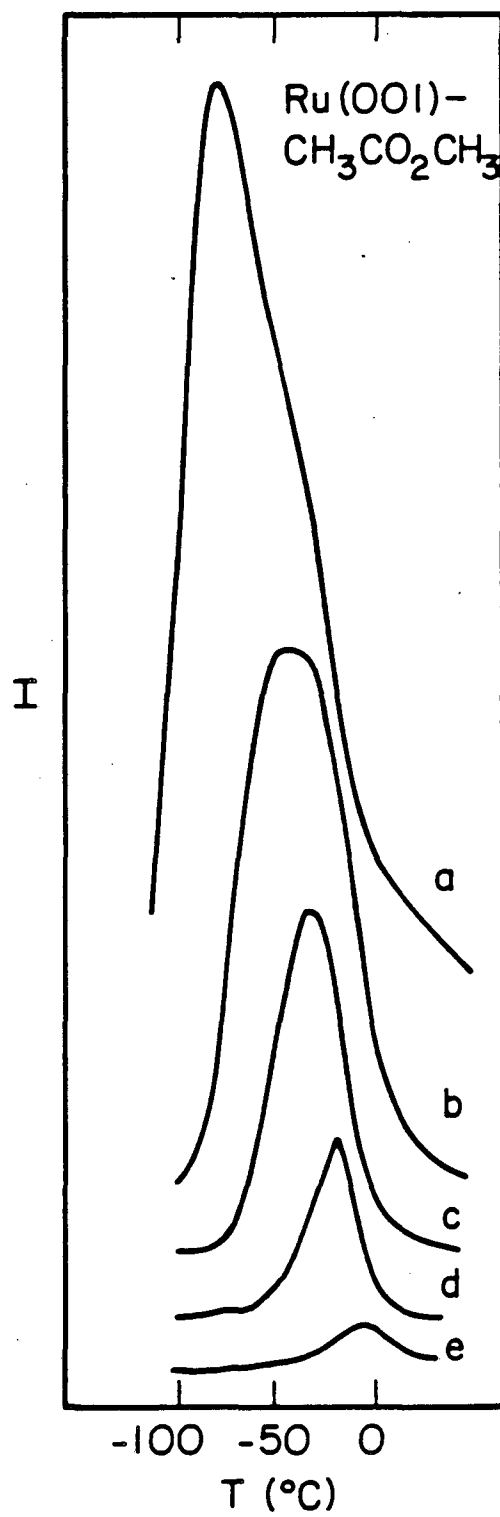


Figure 19. Acetic acid adsorbed on Ru(001) decomposed to produce CO, H₂, CO₂, and surface carbon and oxygen. Shown here are the CO desorption profiles (amu 28) for exposures of .05, .3, and 1L of acetic acid on clean Ru(001) at 25°C (spectra (a)-(c), respectively). The peak in spectrum (c) at 220°C is due to a fragment of CO₂ (see Figure 20). The sensitivity scale used in this figure is 5 times less than in all other Figures. See Figure 20 for the CO₂ desorption profiles from these three experiments.

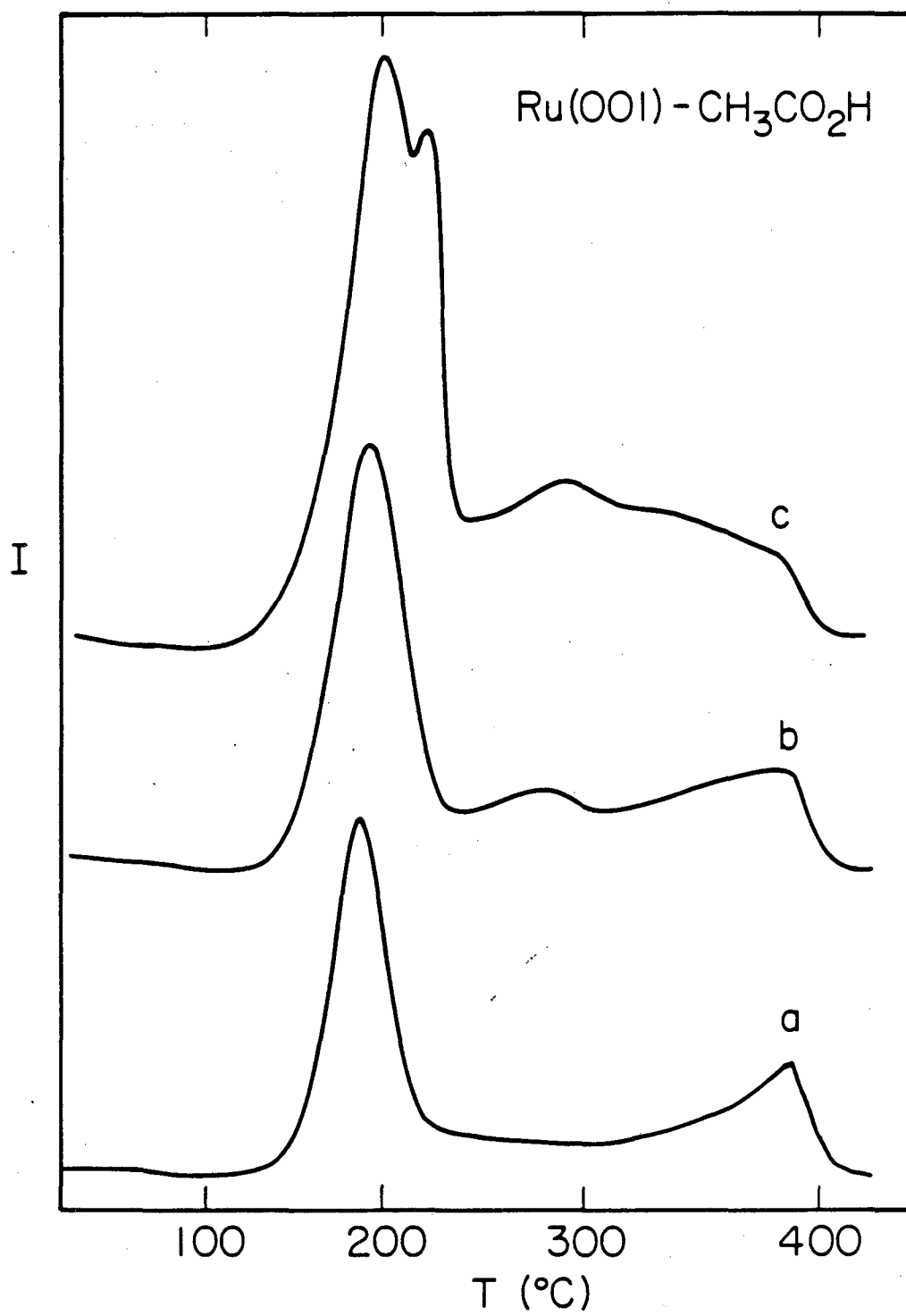
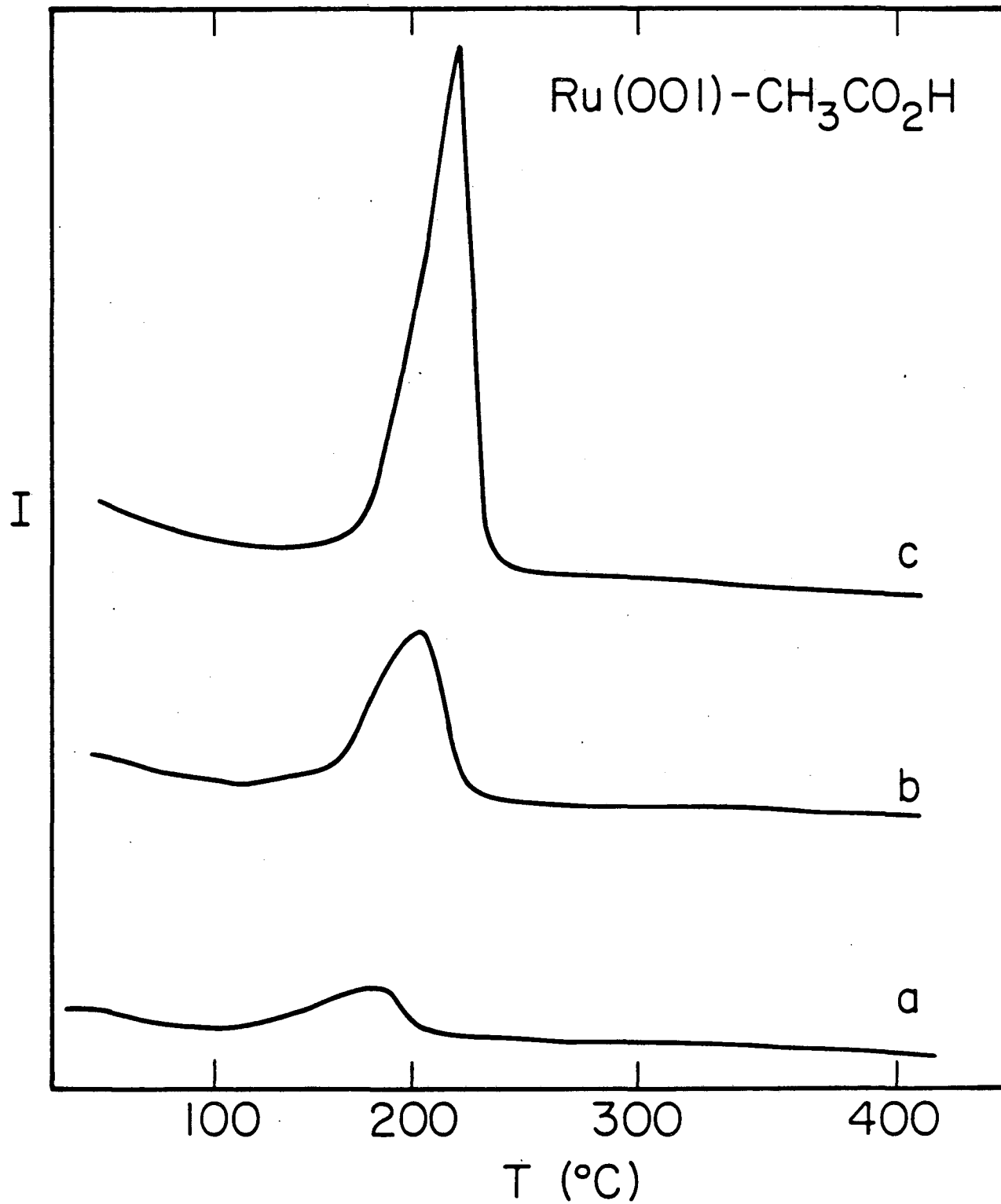


Figure 20. This set of CO_2 desorption profiles from the decomposition of acetic acid on $\text{Ru}(001)$ are from the same three experiments illustrated in Figure 19 with CO desorption from acetic acid decomposition. The peak maximum shifts up in temperature with increasing coverage (exposures and sensitivity scales are the same as in Figure 19).



CHAPTER FOUR. Os(001) STUDIES

INTRODUCTION

In this chapter the results of examinations of Os(001) surface chemistry will be detailed. The same outline will be used as was employed in Chapter 3. The surface chemistry of Os(001) was found to be similar to that of Ru(001) and because of this, different directions were taken in some instances. In addition, because of the lack of significant change with adsorption temperature noted in the Ru(001) studies, many of the results presented in this chapter will be for only one adsorption temperature. As before when low temperature adsorption (-140°C in this case) was employed, multilayer desorptions will be reported only when their origin is certain. As with Ru, only small molecules were observed in TDS experiments; no fragmentation, hydrogenation, or cyclization products were detected.

CARBON MONOXIDE AND SMALL INORGANIC MOLECULES

Previous workers(7) have studied the chemisorption of CO on clean Os(001) at low temperatures and found that its thermal desorption spectrum is quite similar to that of CO adsorbed on Ru(001)(15). For low coverages of CO on Os(001), one peak is observed and its maximum decreases to approximately 240°C as the coverage is increased, whereupon a second peak begins to develop as a low temperature shoulder. At saturation the desorption spectrum consists of two partially resolved peaks of comparable intensity located at 177°C and 232°C (as compared to 135°C and 185°C for Ru(001)). The low energy electron

diffraction results are likewise similar in that for the coverages where only one thermal desorption peak is present a $(\sqrt{3} \times \sqrt{3})$ $R30^\circ$ pattern is observed and when the coverage is increased, a compression pattern develops. However a $(2\sqrt{3} \times 2\sqrt{3})$ $R30^\circ$ pattern appears on Ru(001) which is not observed on Os(001). In the previous Chapter we have detailed results illustrating that CO chemisorbed on Ru(001) is not chemically distinguishable, even though two thermal desorption peaks exist, and that it is non-dissociatively adsorbed. We report here a similar series of studies on CO chemisorbed on Os(001).

Specifically, we have investigated the possibility of dissociative adsorption by coadsorbing ^{13}CO and C^{18}O . In the subsequent thermal desorption no crosslabelled molecules, $^{13}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}$, were detected above levels already present in the original samples. In addition, to assess the possibility that the two thermal desorption peaks represent two stereochemically differentiable states, the clean Os(001) surface was exposed to an amount of ^{12}CO sufficient to fill the first peak and then to enough ^{13}CO to saturate the surface. In the subsequent thermal desorption the ratios of the two molecules in the two peaks were identical within experimental error. The permissible conclusions from these experiments are (1) either there is only one chemisorption state on the surface or there are two or more states and diffusion between these states is rapid and complete, and (2) CO adsorbs on Os(001) in a fully molecular (associative) fashion. We have also attempted to displace CO with trimethylphosphine, a strongly

electron donating molecule, and trifluorophosphine, a strongly electron accepting molecule, but as was the case on Ru(001), no displacement was observed in either case at room temperature.

Carbon was shown to have significant effects on CO thermal desorption from Ru(001) and we have duplicated these studies on Os(001)(42) as well as adding studies on the effect of coadsorbed oxygen. Carbon was deposited by adsorbing benzene, heating to approximately 500°C to fully remove all hydrogen, and cooling to the adsorption temperature. Oxygen was treated in a similar fashion.

Oxygen and carbon coverages were quantified by using Auger peak-to-peak heights of the 517 and 272 eV transitions respectively, and are expressed as ratios to the peak-to-peak height of the Os 221 eV transition. These ratios are defined as R_O and R_C , respectively.

In the case of carbon this procedure introduces a certain amount of ambiguity as changes in the carbon peak shapes were noted when comparing spectra from high and low carbon coverages. Specifically, at low coverages a small Auger peak was observed at approximately 250 eV in addition to the main 272 eV peak. However at high coverages this small transition at 250 eV was replaced by a reasonably strong positive excursion and only a slight inflection remained at the point where the maximum of the 272 eV transition had been located in the low coverage spectra. Thus at high coverages, the location of this inflection point was used as the most positive point on the 272 eV transition for peak height determination. This is illustrated in Figure 1. No ordered

arrays of C were ever detected by LEED to aid in an interpretation of these effects.

In addition a change in the oxygen peak shape was noted for low oxygen coverages after heating to 500–600°C several times (Fig. 1). However, no change in the thermal desorption spectra from the coadsorption states was noted and no CO₂ or water(43) desorbed. As the temperatures reached in the thermal desorption experiments with CO and D₂ were lower than those required to desorb oxygen or osmium oxides, the values reported for the peak height ratios reflect the Auger spectra taken immediately before adsorption of CO or D₂. No similar change in the carbon Auger spectra was noted after the thermal desorption experiments. Oxygen produced p(2 x 2) LEED patterns in all cases.

Presented in Figure 2 are thermal desorption spectra obtained from a constant 10L exposure of CO (resulting in approximately monolayer coverage) to the Os(001) surface covered with varying amounts of carbon. A 1/2L benzene exposure treated as described resulted in an R_C value of .5. A cumulative exposure of roughly 1L produced R_C = .8, and a total exposure of approximately 2L (approximately the saturation benzene coverage) gave R_C = 1.5. The major effect observed is a loss in intensity, predominantly from the high temperature peak, combined with a slight downward shift in temperature of the maximum. A downwards shift of 20–30°C in the peak maximum of the desorption from intermediate levels of CO coverage was also observed. The results

illustrated here are for room temperature adsorption, but adsorption at -140°C did not affect the results.

The effect of surface oxygen on the CO thermal desorption spectra from Os(001) was also investigated. Presented in Figure 3 are the results for a constant 10L exposure of CO to the Os(001) surface covered with varying amounts of oxygen at room temperature. The R_0 value of .3 was obtained from a .5L O_2 exposure. Increasing the total exposure to 2L produced a value of .8 and the highest value of 1.2 arose from a 12L O_2 exposure. The oxygen Auger signal arising from a dose of 4-6L was only slightly less than that arising from a 16L dose, indicating that saturation was being approached at 4L. In this case the major effect appears to be the opposite of that observed with carbon covered surfaces in that the major loss of intensity in the thermal desorption spectrum of CO occurs in the lower temperature peak. However a slight decrease in the maximum of the remaining peak is also noted. No CO_2 was ever detected in these experiments.

Thermal desorption studies of oxygen were also attempted but these results are not reported in detail here because of the high degree of nonlinearity in the heating curve at the oxygen desorption temperatures. Briefly, oxygen was observed to start desorbing at approximately 1000°C and to reach its maximum rate of desorption at roughly 1200°C . A faint $p(2 \times 2)$ low energy electron diffraction pattern was observed for all exposures greater than .5-1L for adsorption at $25-35^{\circ}\text{C}$. Heating the Os(001)-O surface to $125-150^{\circ}\text{C}$ caused the oxygen to order so that

the $p(2 \times 2)$ spots became very sharp. Sharp thermal desorption peaks for masses 192, 208, 224, and 240, (Os , OsO , OsO_2 , and OsO_3 , respectively) were observed at approximately $1000^\circ C$, concomitant with the onset of oxygen desorption. Mass 256, OsO_4 , was not detected.

Adsorption of hydrogen, in the form of D_2 , on the clean, carbonized, and oxidized $Os(001)$ surface was also investigated. In Figure 4, we present the thermal desorption spectra arising from varying exposures of deuterium to the clean $Os(001)$ surface at $-140^\circ C$. Spectrum (a) represents an exposure of approximately .1L, while spectrum (h) arises from an exposure of 40L, the maximum exposure investigated. The peak maximum shifts from approximately $160^\circ C$ for the lowest coverages to roughly $50-60^\circ C$ for the highest coverage. Of note is the weak shoulder which develops between 5-10L, which then apparently merges with the main peak at the highest coverage and produces a slight broadening of the desorption profile. (In three different studies of H_2 chemisorption on $Ru(001)$ (46,47,48), the appearance of two states is indicated in only two cases(46,48) and the relative intensities of those two peaks are different in those cases.)

The effects of surface C and O were also investigated for deuterium chemisorption. Figures 5 and 6 present the D_2 thermal desorption spectra from carbon covered $Os(001)$ for constant exposures of 5 and .5L respectively. In the same style as was done for the CO studies, the R_c values represent cumulative benzene exposures of .5, 1,

and 2L respectively. Also shown is a spectrum of the desorption from the clean surface for comparison. For the .5L D_2 exposures a noticeable broadening accompanied by a slight upwards shift in peak maximum is observed. This effect is also apparent in the spectra arising from the 5L exposure in the increased "tailing" of the peak, but also observed is a slight downwards shift in the peak maximum. For D_2 adsorption on the oxygen covered Os(001) surface, a similar but much more dramatic downwards shift is also observed. In this case similar effects were observed for the .5L D_2 exposure to Os(001)-O; thus only the results for the higher exposure are presented in Figure 7. Again, the peak height ratio R_0 indicates the relative oxygen coverage. No D_2O was ever detected in the thermal desorption experiments.

Hydrogen sulfide was used as a source of surface sulfur for studies with thiophene and its derivatives. A limited study of the surface chemistry of H_2S was made and will be described briefly. Shown in Figure 8 is the hydrogen desorption spectra resulting from the decomposition of two different initial coverages of hydrogen sulfide. A strong coverage effect is indicated by the changes in the desorption spectra but this was not thoroughly investigated. In addition, very complex LEED patterns could be obtained by annealing at different temperatures. Annealing at $1000^\circ C$ however, produced a sharp and strong $(\sqrt{3} \times \sqrt{3}) R30^\circ$ pattern for the limited number of coverages examined (although saturation coverage was one of the coverages examined). No S or S_2 was detected in the thermal desorption and heating to $1000^\circ C$ had little effect on the AES spectra.

BENZENE AND BENZENE DERIVATIVES

Benzene chemisorbed on Os(001) behaved essentially as it did on Ru(001) in that it decomposed quantitatively, with hydrogen being the only detected gaseous decomposition product. Shown in Figure 9 is a deuterium desorption spectrum arising from a saturation exposure (approximately 4L) of perdeuterobenzene to the clean Os(001) surface. The low temperature peak showed the same type of coverage dependence as the low temperature peak observed in the coverage dependence of the decomposition of toluene on Ru(001). Specifically, at low coverages it was not detected, while it increased in intensity with increasing coverage from intermediate exposures and up. Exposure of benzene to the clean Os(001) surface at room temperature produced ($2\sqrt{3} \times 2\sqrt{3}$) R30° LEED patterns for all coverages.

Toluene also mimicked its behavior on Ru(001) when adsorbed on Os(001) in that it again quantitatively decomposed to surface carbon and hydrogen gas. In Figure 10 the coverage dependence of the deuterium thermal desorption spectra is shown for adsorption at room temperature. A LEED pattern similar to that observed on Ru(001) was also detected. Diffuse rings formed around the Os substrate spots which were of the same diameter as the $2\sqrt{3}$ pattern observed for benzene, but which did not show clear concentration of intensity at the $2\sqrt{3}$ spot positions as had been observed for the (3 x 3) spots in the Ru(001)-toluene case.

The adsorption of the specifically labelled toluene molecules was also examined on Os(001) as had been done for Ru(001), but again no clear case for regiospecific decomposition could be made. Shown in Figure 11 are the H_2 , HD, and D_2 desorption spectra for the decomposition of two coverages of d_5 -toluene, with the left half of the Figure representing desorption from an exposure equivalent to the exposure used to produce spectrum (e) of Figure 10 and the right half representing the exposure equivalent to spectrum (d) of Figure 10. Figure 12 presents the complimentary data for d_3 -toluene decomposition. About the most that can be said is that a very slight degree of regio-specificity can be seen in that there is a slight preponderance of desorption originating from the methyl protons at low temperatures.

On Os(001) the homologous series started with benzene and toluene was extended to the three isomeric xylene molecules. Shown in Figures 13, 14, and 15 are the hydrogen or deuterium desorptions arising from different initial coverages of perdeutero-ortho-xylene, perprotio-meta-xylene, and perdeutero-para-xylene, respectively, adsorbed at -140°C . No ordered LEED patterns were detected for any of these molecules chemisorbed on Os(001), even after warming to room temperature.

The decomposition of para-xylene was probed by using the specifically labelled compound $(CD_3)_2C_6H_4$. Figure 16 presents the H_2 , HD and D_2 desorptions resulting from a .3L exposure of the labelled xylene adsorbed at -140°C . Again, only limited regioselectivity is indicated.

A few brief thermal desorption experiments were conducted with cycloheptatriene adsorbed on the clean Os(001) surface at room temperature. Again only hydrogen was observed to desorb but in this case the desorption profile was quite different from that observed for the benzene, toluene, and xylenes series. Two broad and featureless maxima were observed at approximately 130°C and 440°C for high exposures (approximately 10L). These peaks seemed to shift up and down, respectively, in temperature as the exposure was decreased. No LEED studies were attempted with this molecule.

HETEROAROMATIC MOLECULES

In contrast to the studies conducted on Ru(001) with heteroaromatic molecules, no studies of pyridine or furan chemistry were attempted. Instead, a homologous series of substituted thiophenes, consisting of thiophene, 3-methylthiophene, and 2,5-dimethylthiophene, was examined.

In Figure 17 is presented a hydrogen thermal desorption spectrum from a saturated layer of thiophene on the clean Os(001) surface. As with Ru(001), three peaks are observed and the one which occurs at the lowest temperature displays a coverage dependence similar to that observed for the low temperature peak observed from Ru(001)-thiophene. However, on Os(001) the intermediate temperature peak at approximately 225°C was present throughout the entire coverage range studied, while it was only apparent at high coverages on Ru(001). No other desorption products were observed. No ordered LEED patterns were detected upon adsorption of thiophene, but after heating to approximately 500°C, faint and diffuse ($\sqrt{3} \times \sqrt{3}$) R30° patterns were observed.

Examination of the decomposition of the specifically labelled compound 2,5-d₂-thiophene showed a different regioselectivity than was seen on Ru(001). As shown in Figure 18(a), (b), and (c) the second peak (225°C) shows substantial deuterium content at all coverages, and the third, high temperature peak also shows deuterium content at the highest coverages. Coadsorbed sulfur, at levels similar to those obtained from a saturated layer of thiophene, had no effect on the desorption spectra.

3-methylthiophene and 2,5-dimethylthiophene also decomposed quantitatively to surface carbon and sulfur and gaseous hydrogen. The thermal desorption spectra of the hydrogen produced from different initial coverages of the thiophenes are shown in Figures 19 and 20. No ordered LEED patterns were detected upon adsorption, but as with thiophene, heating to approximately 500°C produced ($\sqrt{3} \times \sqrt{3}$) R30° patterns. Coadsorbed sulfur also had no effect on the desorption spectra.

The coadsorbed sulfur used in these studies was derived from the decomposition of H₂S and always showed ($\sqrt{3} \times \sqrt{3}$) R30° LEED patterns (because the sulfur layer was annealed at 1000°C). AES analysis indicated that in all cases less than one quarter of the amount of sulfur derived from a saturation layer of H₂S had been deposited, and the S AES signal from this amount was approximately equal to that arising from a saturation dose of any thiophene.

ACETONITRILE

The only member of the cyanide compounds studied on Ru(001) which was studied on Os(001) was acetonitrile. Because the behavior of acetonitrile on Ru(001) depended on the adsorption temperature, adsorption at both 25°C and -140°C was investigated on Os(001). Perprotio- and perdeuteroacetonitrile were used interchangeably in these studies and, where appropriate, this will be indicated in the figures.

For adsorption at room temperature on the clean surface no molecular desorption was noted. Decomposition was indicated by the production of hydrogen, hydrogen cyanide, and nitrogen. The hydrogen cyanide desorption spectrum arising from CH₃CN adsorbed either at low or room temperature consisted of two peaks at high coverages, one at 230°C and the other at 415°C. The peak at 230°C did not appear at low coverages. Nitrogen was observed to desorb in a very broad peak centered at 650°C.

The hydrogen desorption spectra were complex and depended on the adsorption temperature. As illustrated in Figure 21 for saturation coverages, adsorption at -140°C induced substantial shifts in the peak positions and produced a new desorption at low temperature. In addition, the peak which appears at approximately 110°C now shows a coverage dependence in that it is not present at low coverages, and grows in as the coverage is increased.

Three molecular desorptions were also noted when adsorption was conducted at -140°C . Two were of low intensity and appeared at -15 to 10°C and at 250 – 275°C . These two peaks had small coverage dependences, with the lower temperature one shifting down and the higher one shifting up with increasing coverage. The third peak appeared at 155°C with a very low intensity and showed no shifts in peak maximum with changing coverage. The molecular desorption at approximately 260°C , the hydrogen cyanide desorption at 230°C , and the hydrogen desorption at approximately 245°C all initiated at the same point suggesting competitive desorption and decomposition as observed commonly in nickel group surface chemistry. Unlike $\text{Ru}(001)\text{-CH}_3\text{CN}$, no ordered LEED patterns were observed for acetonitrile adsorbed on $\text{Os}(001)$ at low temperature, even if the $\text{Os}(001)\text{-CH}_3\text{CN}$ formed at -140°C was annealed at room temperature.

METHANOL

Of the series of oxygen containing compounds studied on $\text{Ru}(001)$, only methanol was studied on $\text{Os}(001)$. Both CH_3OH and CD_3OD were used in these studies. Molecular desorption and decomposition were observed after adsorption on the clean $\text{Os}(001)$ surface at -140°C . Carbon monoxide, hydrogen, and surface oxygen were detected. Presumably surface carbon also formed but in amounts lower than AES detection limits. Hydrogen appeared at 70°C and CO at 250 – 280°C and both desorptions resembled desorption limited peaks.

The molecular desorptions observed showed complex behavior. At low exposures a peak appeared at -5°C . This peak lowered to approximately -30°C as exposures increased. A second peak then began to develop as a low temperature shoulder on the first desorption. At certain coverages, this peak could be resolved and its maximum was at -55°C . Further exposure produced multilayer desorption at -115°C . This multilayer peak often obscured the -55°C desorption so the the region between the -115°C and -30°C peaks showed only a flat, featureless profile.

When using CD_3OD , extremely weak amu 20 signals could be detected at the temperature where molecular desorptions occur. By using perprotiomethanol, it was shown that these peaks were not methane, and thus the 20 signal must be due to water. It is unclear however if the water was being produced on the surface or in the mass spectrometer.

No ordered LEED patterns were detected upon adsorption of methanol on $\text{Os}(001)$ at -140°C , but warming to room temperature produced faint $(\sqrt{3} \times \sqrt{3}) \text{ R}30^{\circ}$ patterns.

Figure 1. Chemical effects were noted in the Auger spectra of many molecules and atoms chemisorbed on Os(001) and shown here are two examples of this. Spectrum (a) is from the clean surface. Spectrum (b) shows the carbon signal obtained after exposing the crystal to .5L of benzene and decomposing it by heating to 500-600°C. Spectrum (c) shows the carbon signal for a total benzene exposure of 2L similarly decomposed. Spectrum (d) shows the oxygen signal for a 2L exposure of O_2 that has been heated to 500-600°C. Spectrum (e) is the same oxygen signal after two thermal desorption experiments had been conducted with the oxygen covered surface.

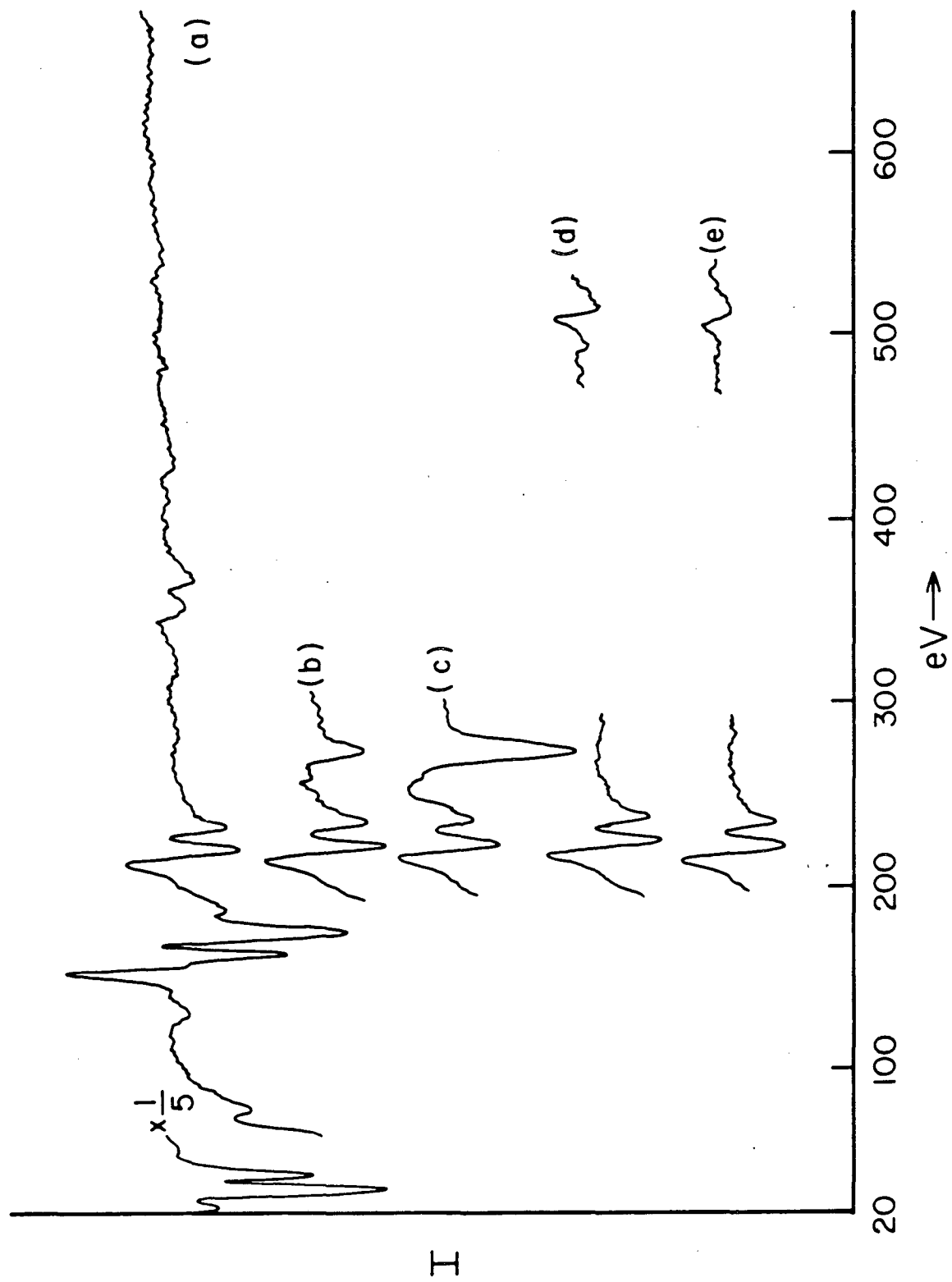


Figure 2. Carbon monoxide thermal desorption spectra from Os(001) are significantly affected by coadsorbed carbon. The data presented above illustrate this for surface carbon obtained by decomposing benzene on the clean or carbon-covered Os(001) surface. The spectra presented represent the desorption arising from a constant 10L CO exposure at 25°C. Carbon coverage is measured by Auger peak-to-peak height ratios, R_c , and values of .5, .8, and 1.5 represent cumulative benzene exposures of .5, 1, and 2L, respectively. The sensitivity scale used in this figure is 2 1/2 times less than that of other figures.

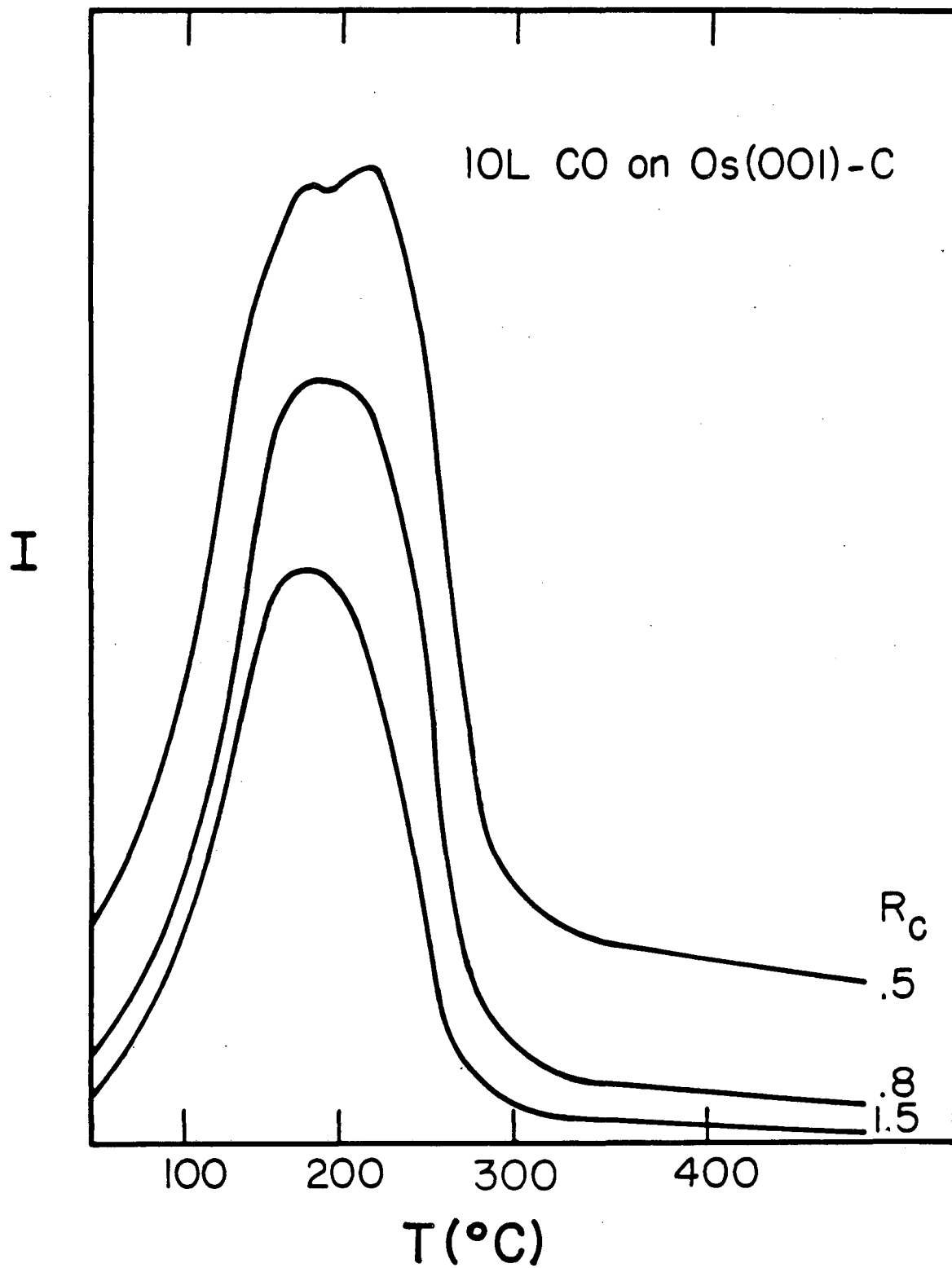


Figure 3. Coadsorbed oxygen also dramatically alters the CO desorption profile from the Os(001) surface. Shown are CO thermal desorption spectra from 10L exposures of CO at room temperature to surfaces previously exposed to 1, 2, and 12L of oxygen resulting in R_O values of .3, .8, and 1.2, respectively. The sensitivity scale used in this figure is 2 1/2 times less than all other figures.

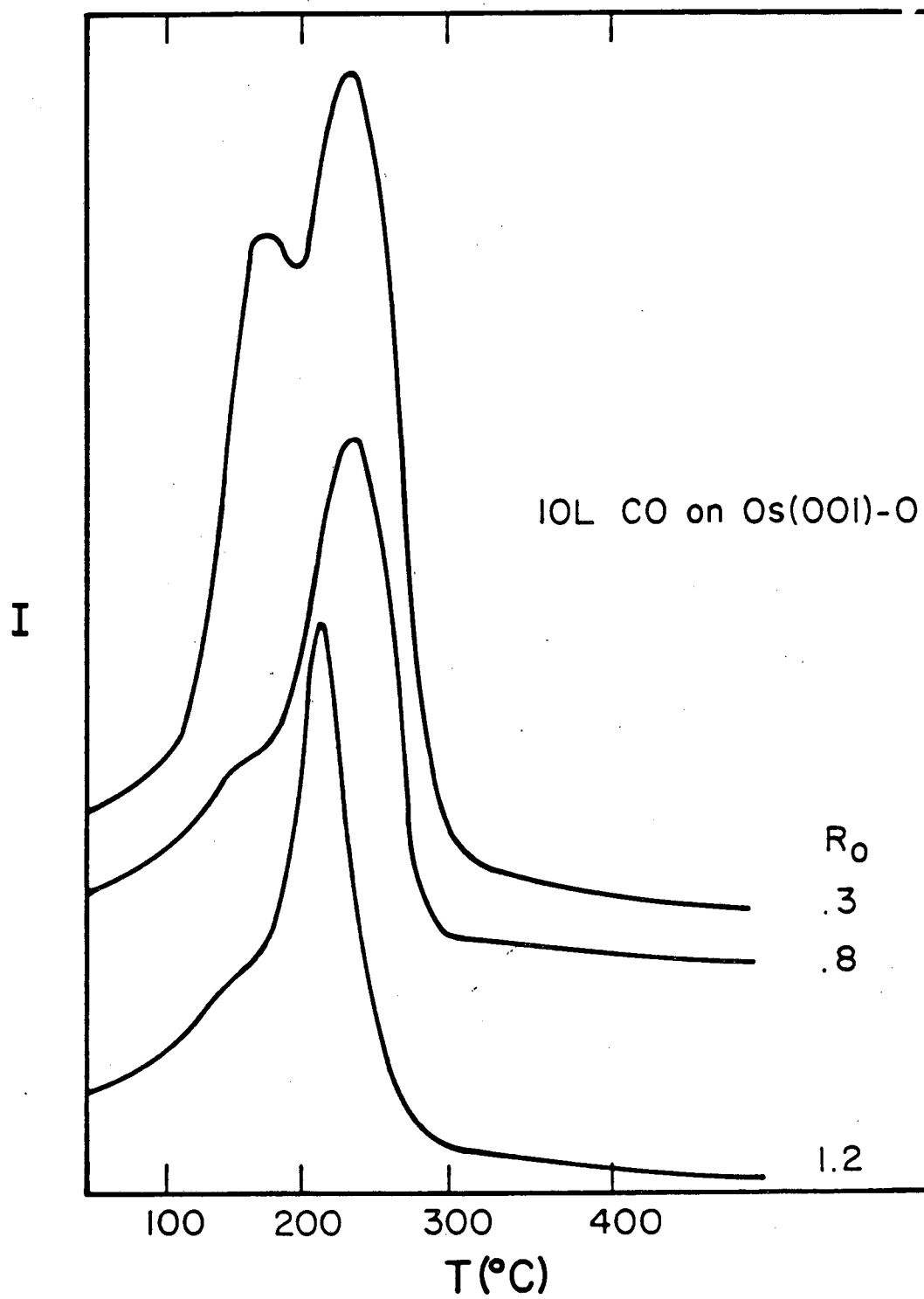


Figure 4. The thermal desorption spectra of deuterium adsorbed on the clean Os(001) surface at -140°C shows a strong coverage dependence. The deuterium desorption spectra presented here are for exposures of .1, .25, .5, 1, 5, 10, 20, and 40L, respectively.

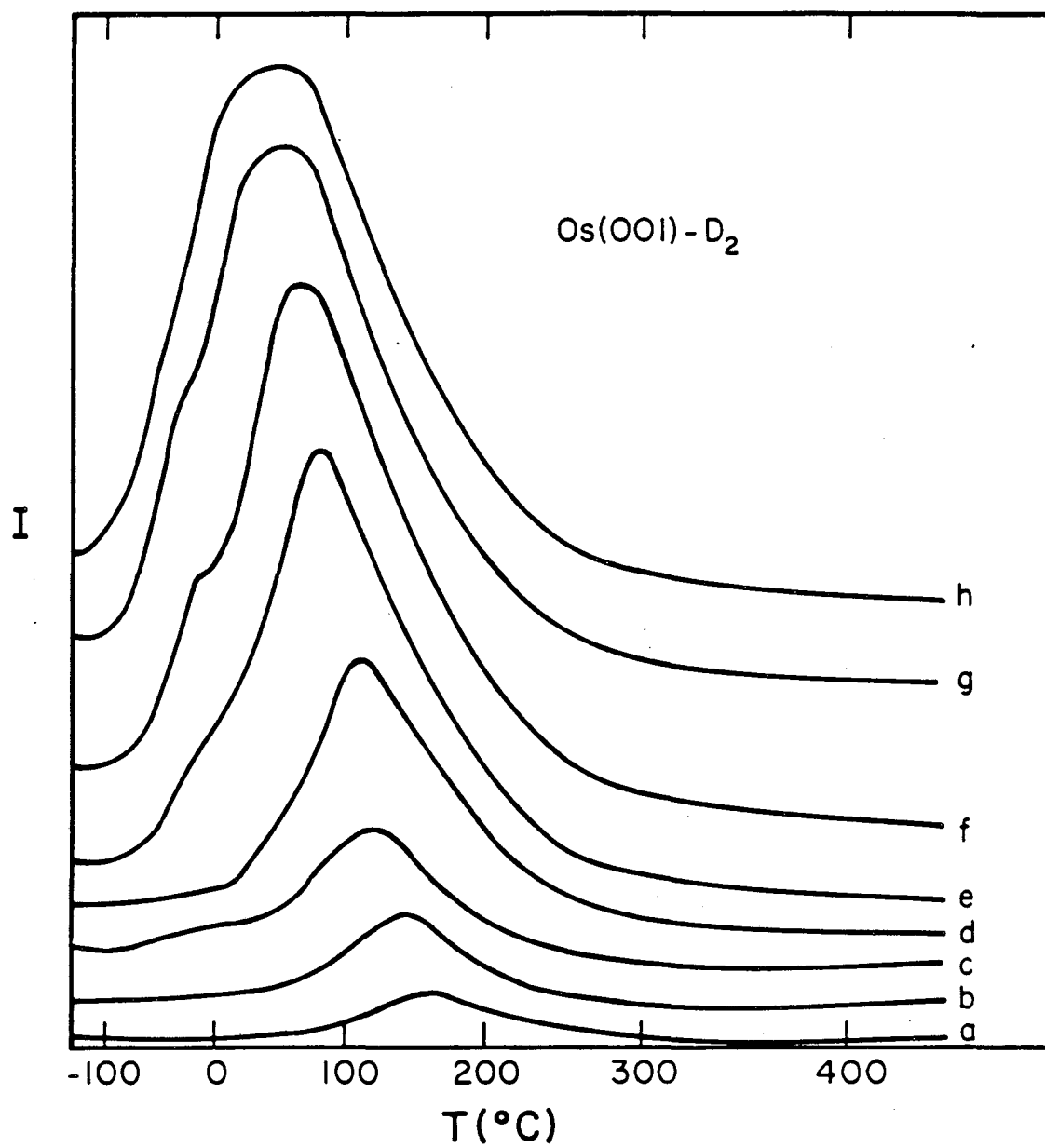


Figure 5. As was observed for CO chemisorbed on carbon covered Os(001) (and Ru(001)), adsorption of D_2 on carbon covered Os(001) also shows evidence of strong interactions. The top spectrum represents the D_2 thermal desorption spectrum resulting from an exposure of 5L to the clean Os(001) surface ($R_c = 0.0$) at -140°C . As in Figure 2, the remaining spectra are the desorptions from carbon covered surfaces produced by .5, 1, and 2L exposures with benzene.

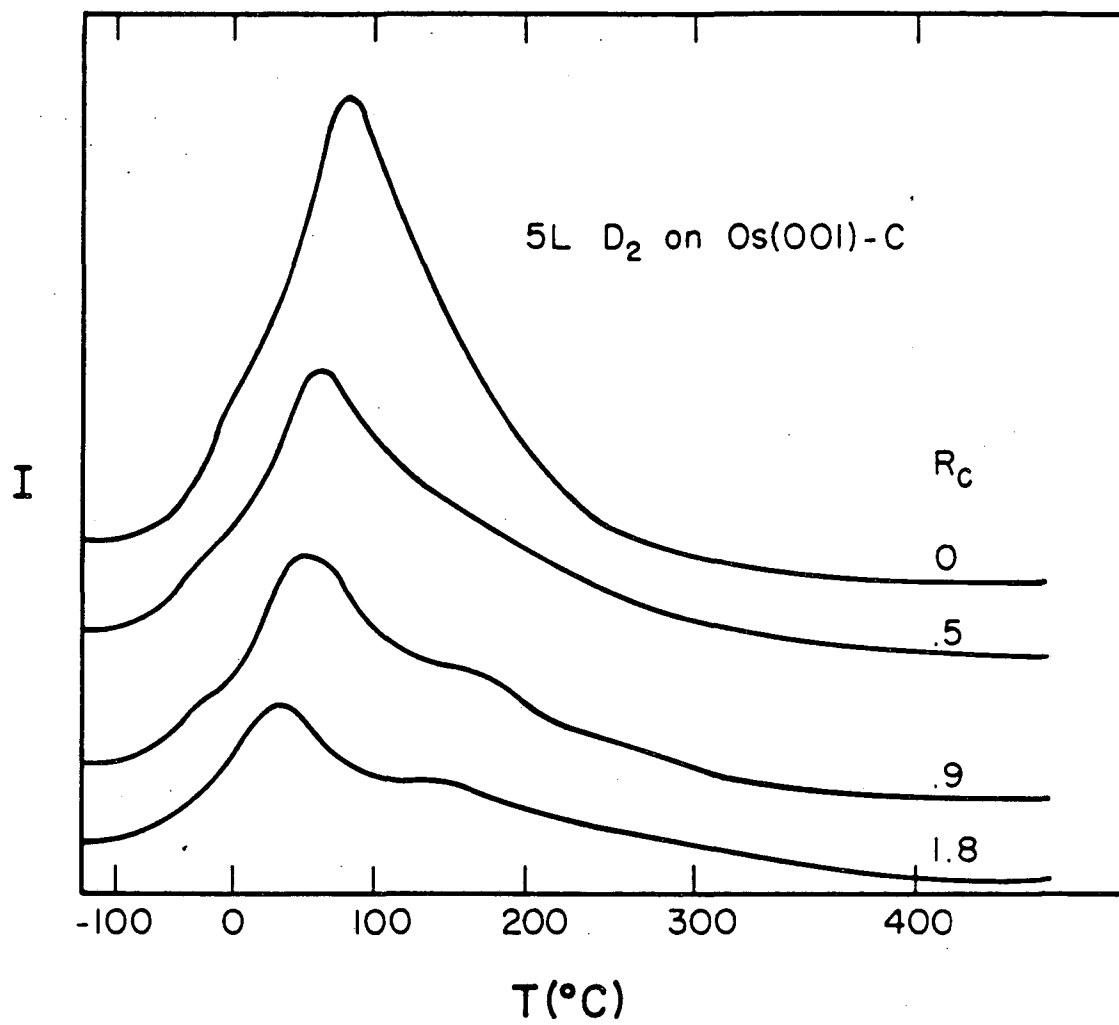
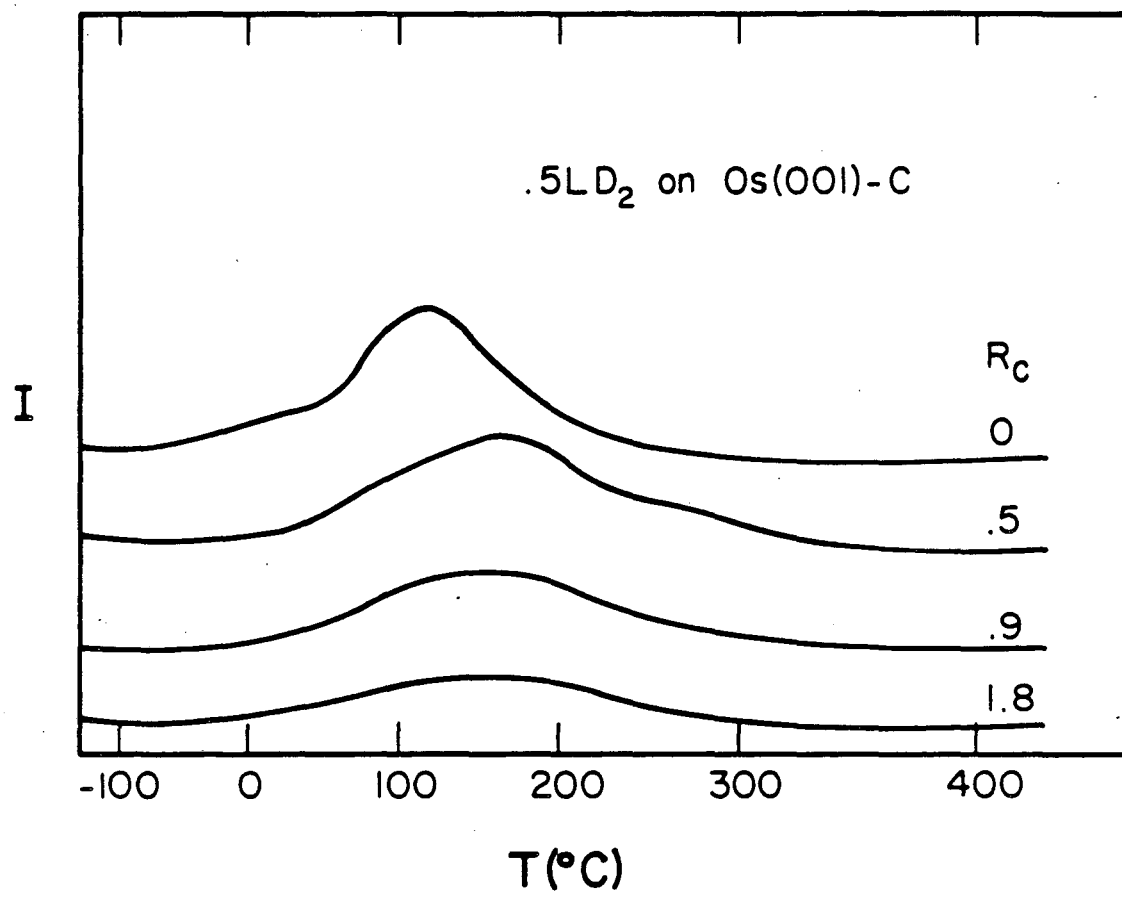


Figure 6. Low coverages of D_2 on carbon covered Os(001) seemed to show a slight upwards shift of the thermal desorption maximum along with a broadening of the peak in contrast to the downward shift observed for higher coverages of D_2 . This figure presents the thermal desorption spectra from .5L exposures of D_2 to the clean ($R_c = 0.0$) and carbon covered ($R_c = .5, .9, 1.8$) Os(001) surface at -140°C . The benzene exposures used to produce the surface carbon are identical to those of Figure 5.



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Figure 7. Unlike the results for adsorption on Os(001)-C, deuterium adsorption on oxygen covered surfaces produced a much more dramatic downwards shift in the thermal desorption maxima, and no significant differences were observed between high and low exposures. The desorptions shown above are from 5L exposures to the clean ($R_0 = 0.0$) and oxygen covered ($R_0 = .2, .4, 1.3$) Os(001) surface at -140°C . The R_0 values represent desorption from oxygen coverages obtained from 1, 2, and 4L exposures of O_2 , respectively.

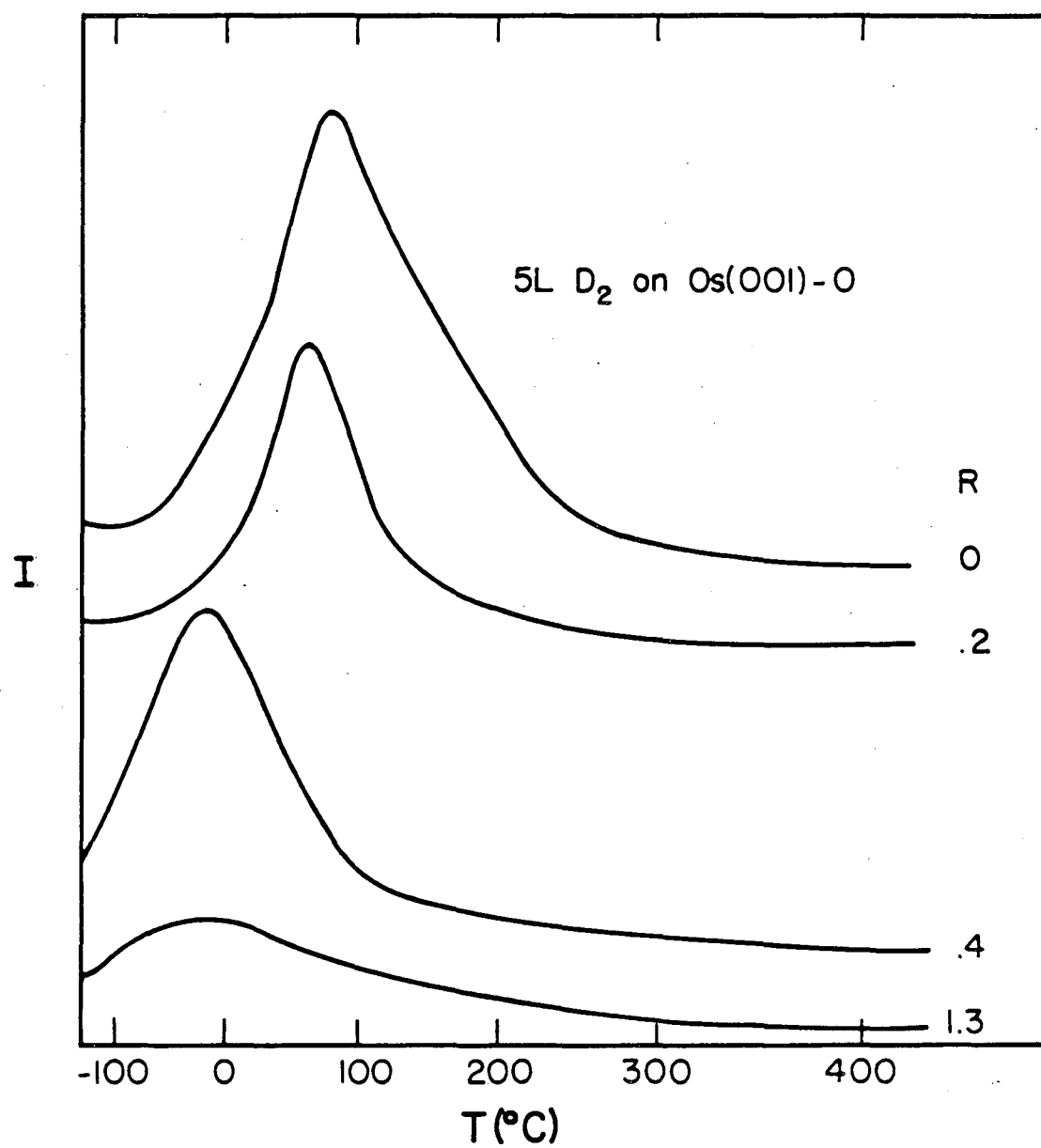


Figure 8. Hydrogen sulfide chemisorbed irreversibly on Os(001) at -140°C . The decomposition was complex and showed a strong coverage dependence. Shown are the hydrogen desorption spectra from H_2S exposures of .2 and .5L (spectra (a) and (b), respectively).

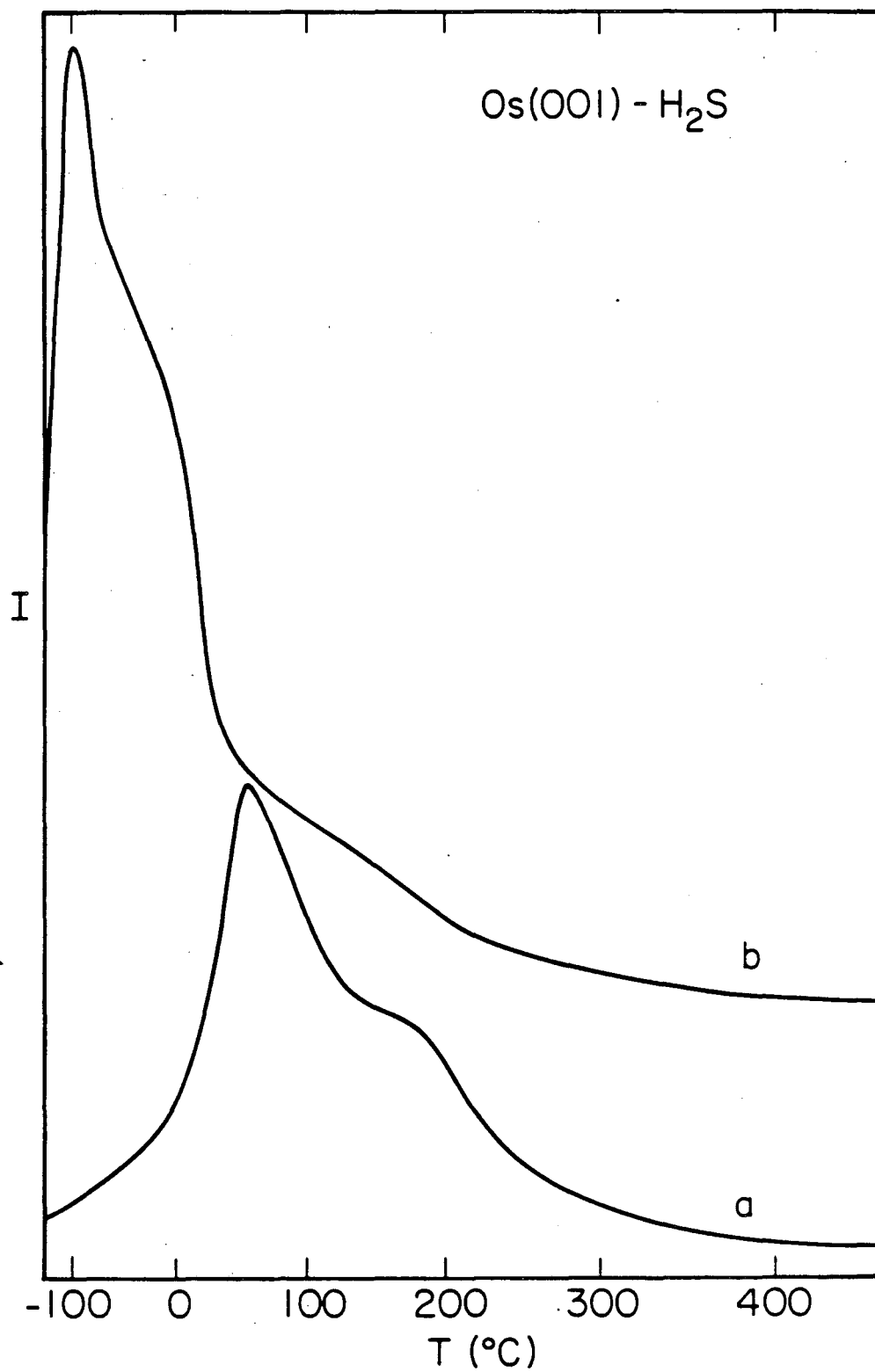
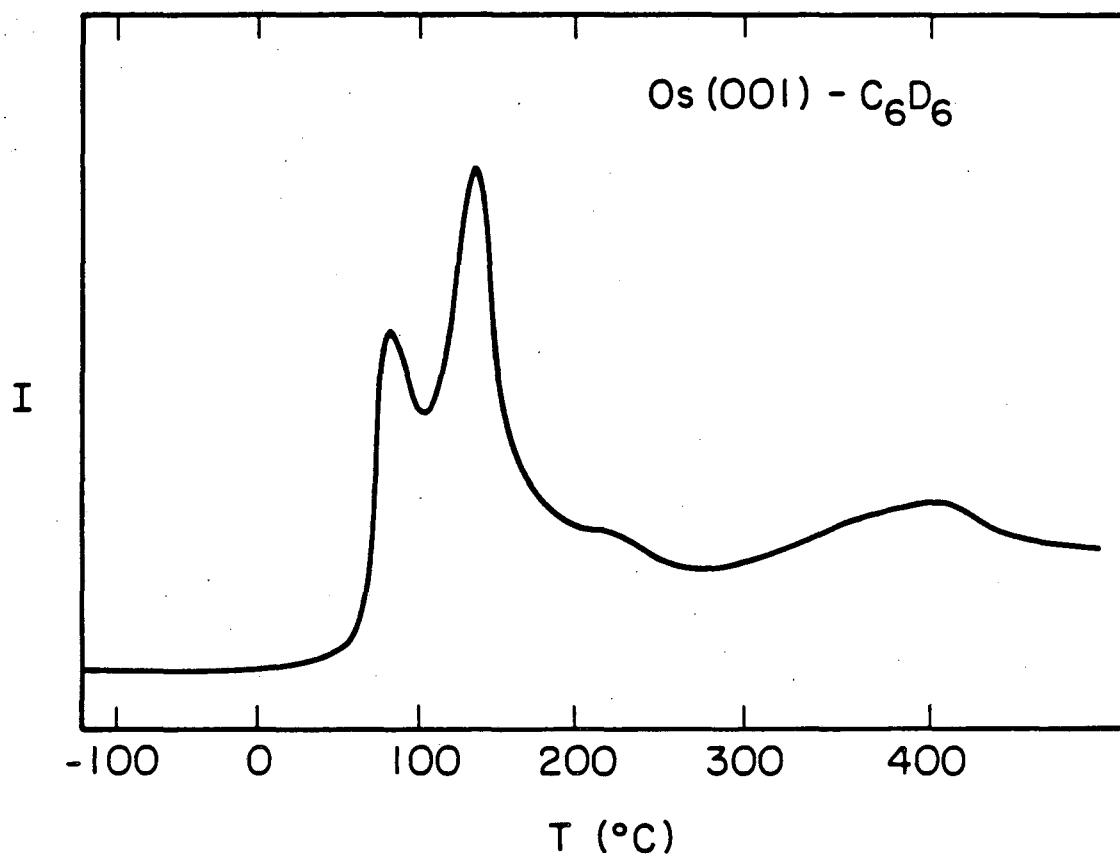


Figure 9. As was observed for Ru(001), benzene decomposed quantitatively on Os(001). Shown is the deuterium desorption spectrum arising from a saturation exposure (2L) of benzene to the clean Os(001) surface at -140°C .



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Figure 10. Toluene chemisorption on Os(001) was also characterized by total irreversibility. The hydrogen thermal desorption spectra shown above bear a striking similarity to hydrogen desorption from adsorption of benzene and toluene on Ru(001) and benzene on Os(001). Spectra (a)-(e) represent initial toluene exposures of .25, .5, 1, 2, and 4L, respectively, to clean Os(001) at 25°C.

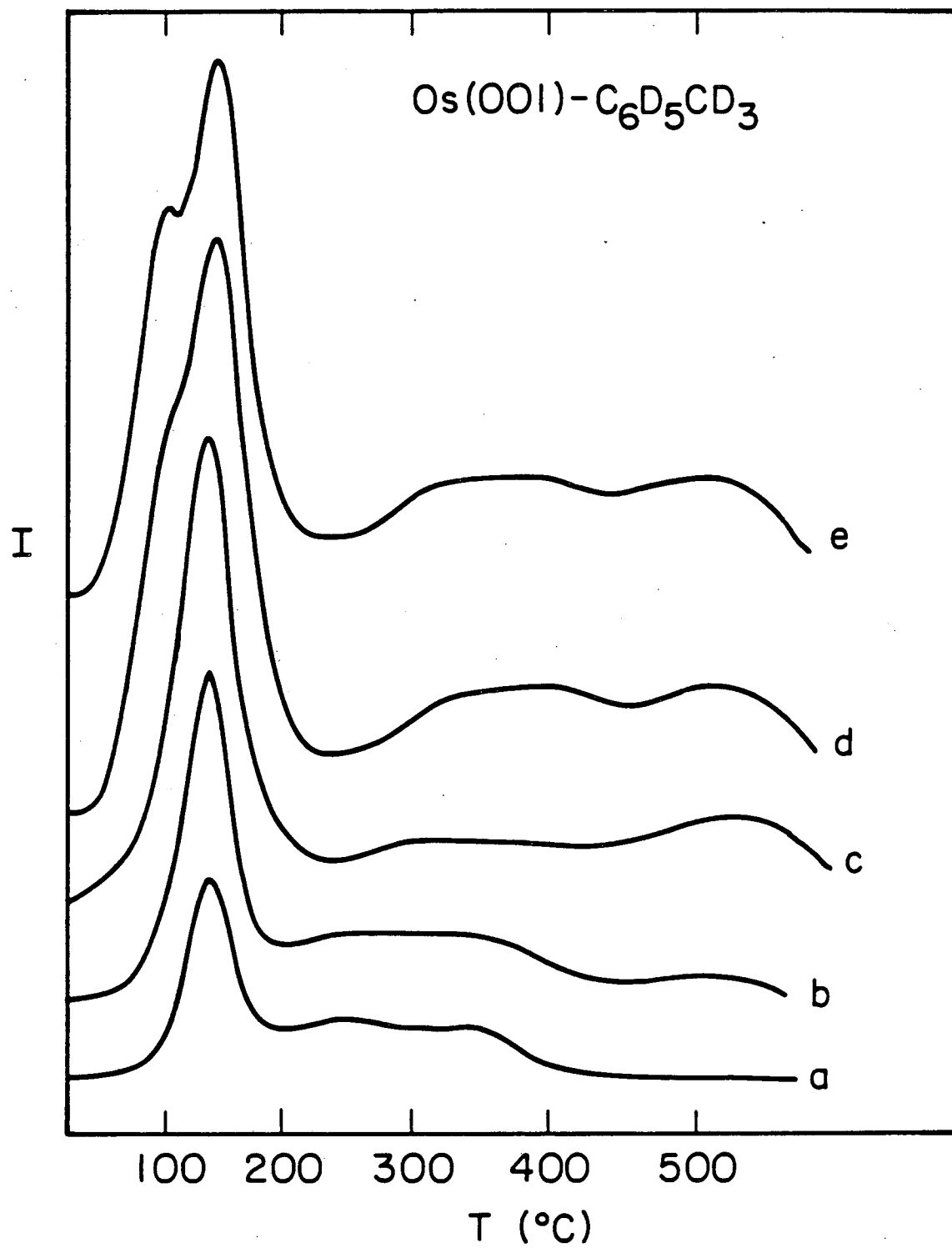


Figure 11. The regioselective nature of toluene decomposition on Os(001) was investigated with the specifically labelled compound $\text{CH}_3\text{C}_6\text{D}_5$. Shown are the H_2 , HD, and D_2 thermal desorption spectra arising from two different exposures of d_5 -toluene to Os(001) at 25°C . The left panel is for an exposure of 4L and the right is for 1L.

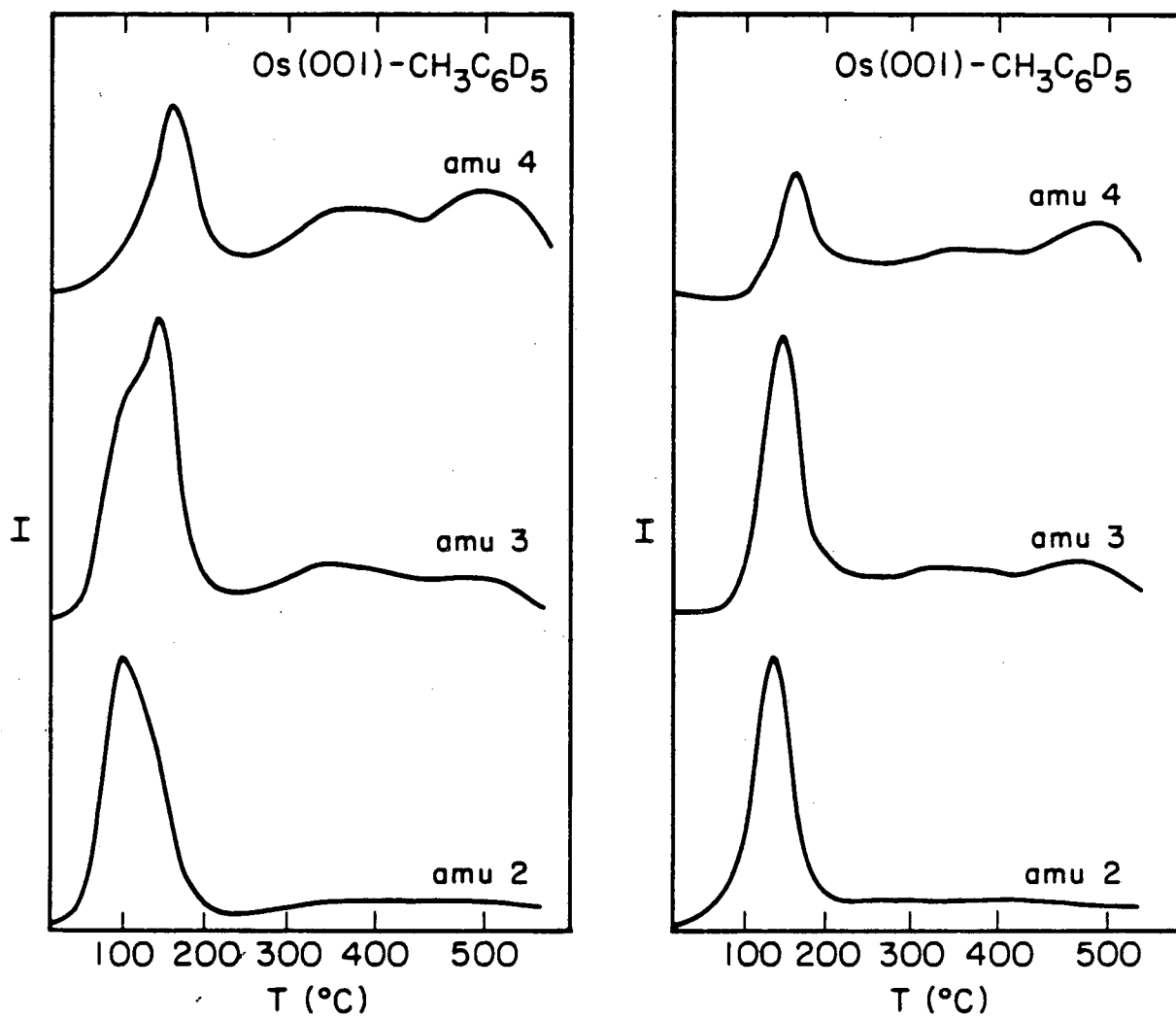


Figure 12. Studies complimentary to those illustrated in Figure 11 were conducted with d_3 -toluene and the results are presented here. Again, the left panel is for a 4L exposure to the clean Os(001) surface at 25°C, while the right panel represents the hydrogen desorptions arising from a 1L exposure.

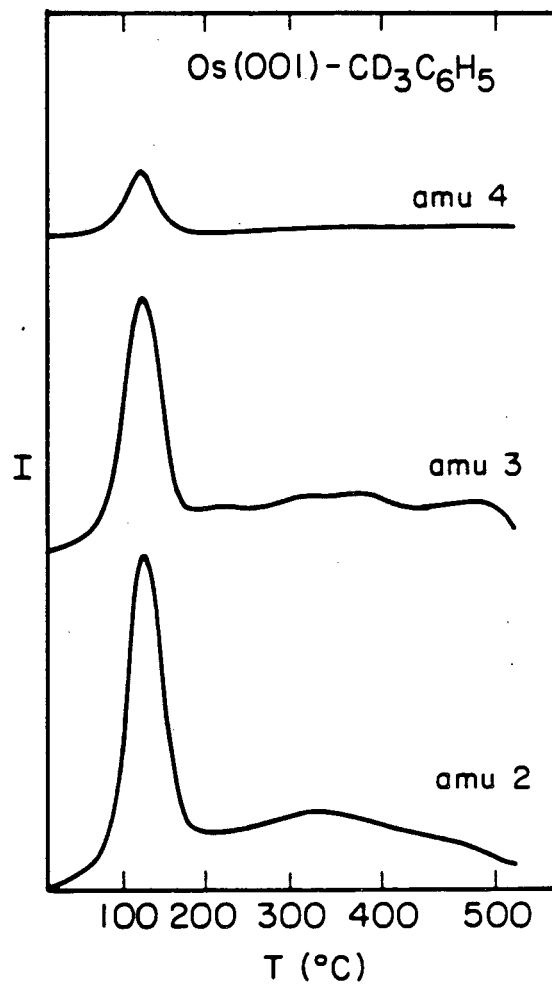
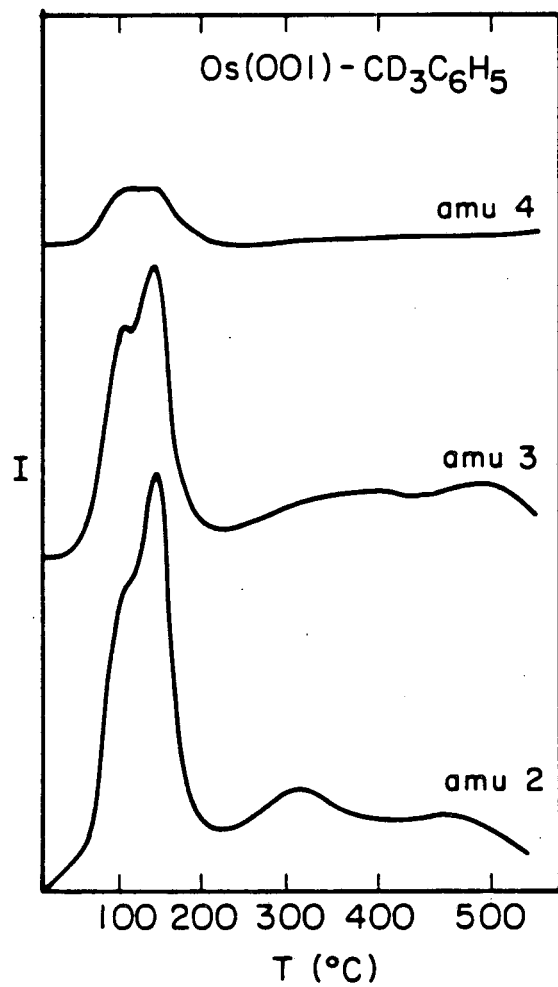


Figure 13. The coverage dependence of the decomposition on Os(001) of ortho-xylene was not as strong as that of toluene and benzene. Deuterium desorption spectra for three different coverages of perdeutero-ortho-xylene on the clean surface at -140°C are presented. Exposures were .1, .5, and 2L, respectively, and spectrum (c) represents desorption from a saturated layer.

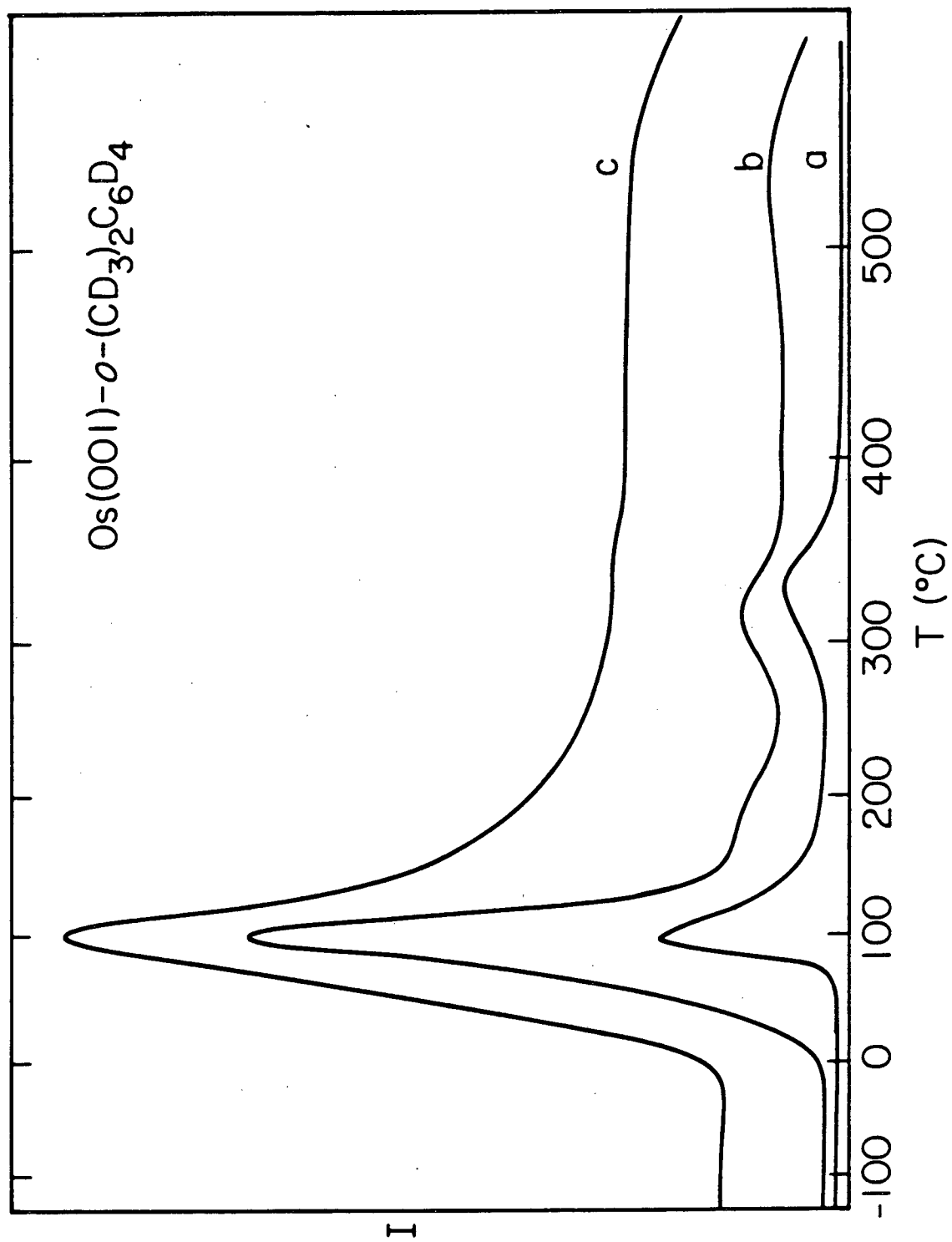


Figure 14. The coverage dependence of the decomposition of meta-xylene on Os(001) was more pronounced than that of ortho-xylene. Shown above are the H₂ thermal desorption spectra arising from exposures of .02, .04, .2, and .4L of m-xylene to the clean surface at -140°C (spectra (a)-(d), respectively).

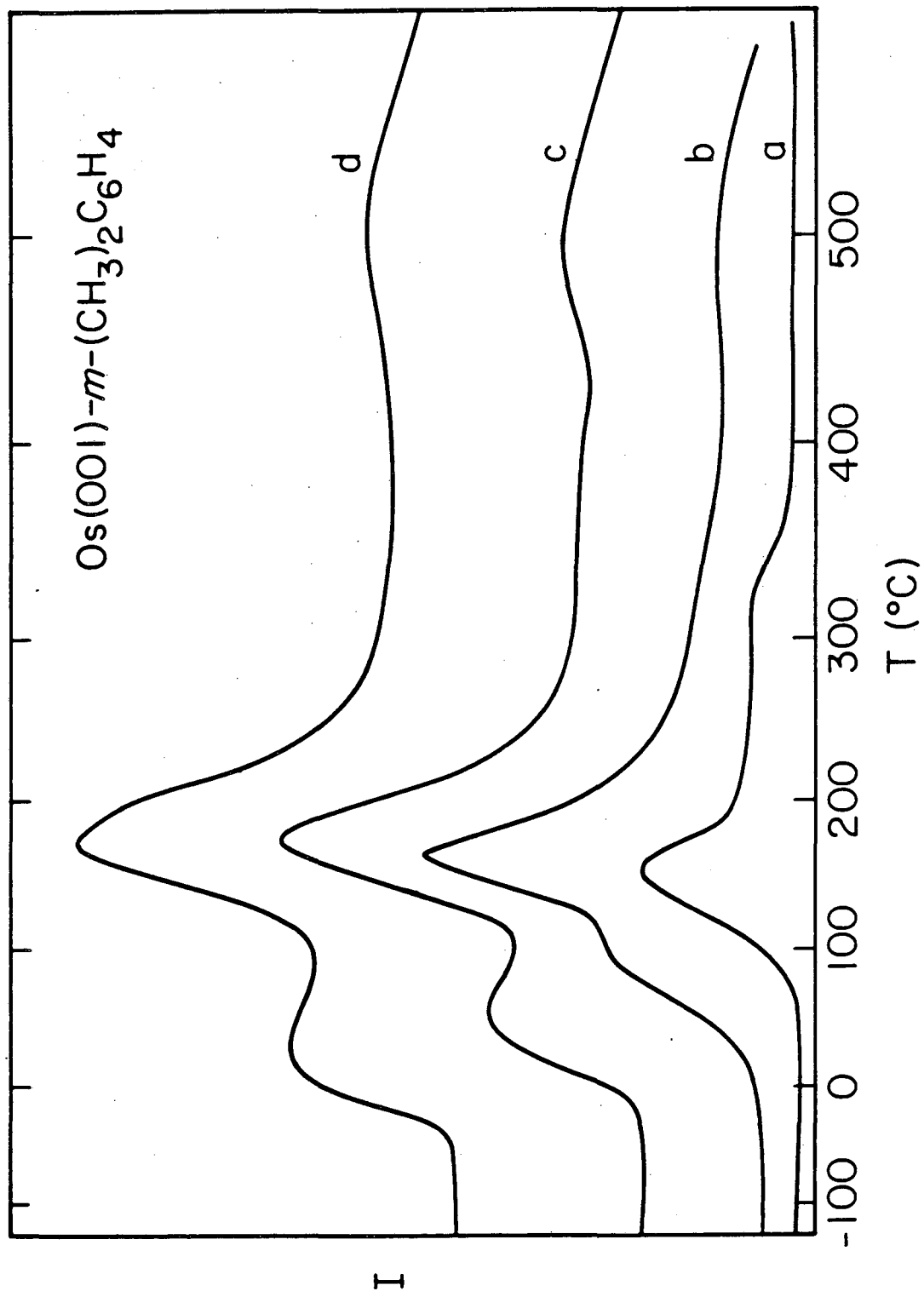


Figure 15. Para-xylene adsorbed on clean Os(001) produced hydrogen desorption spectra which resembled those produced by o-xylene.

Spectra (a)-(c) represent the deuterium desorptions from surfaces prepared by exposing the clean Os(001) surface to .01, .02, and .3L of perdeutero- para-xylene at -140°C . A slightly stronger coverage dependence is indicated when compared to o-xylene decomposition (Figure 13).

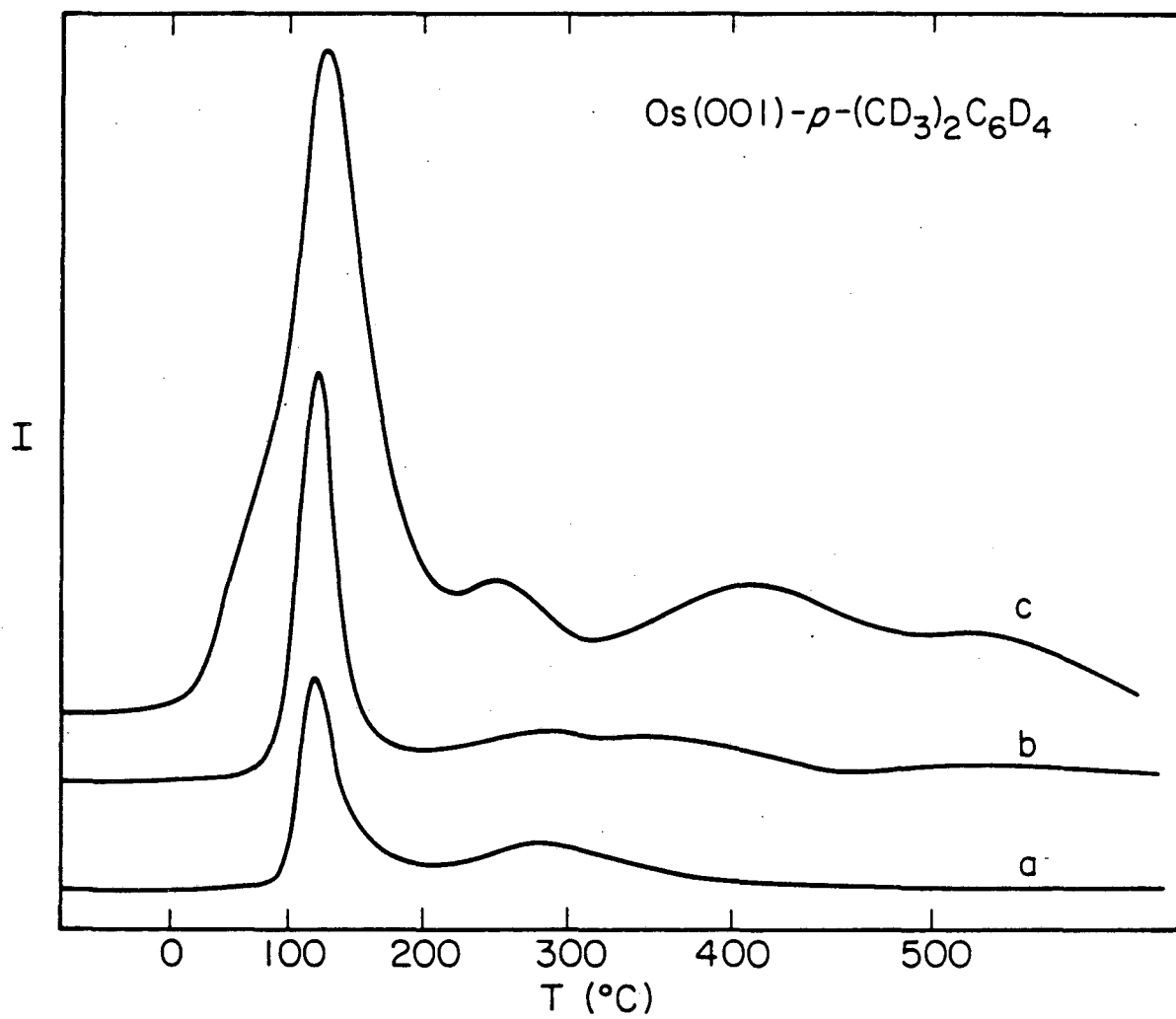


Figure 16. The decomposition of para-xylene was studied by using the specifically labelled compound $(\text{CD}_3)_2\text{C}_6\text{H}_4$. Shown are the H_2 , HD, and D_2 desorptions from a saturated layer of the para-xylene adsorbed on Os(001) at -140°C (corresponding to Figure 15, spectrum (c)).

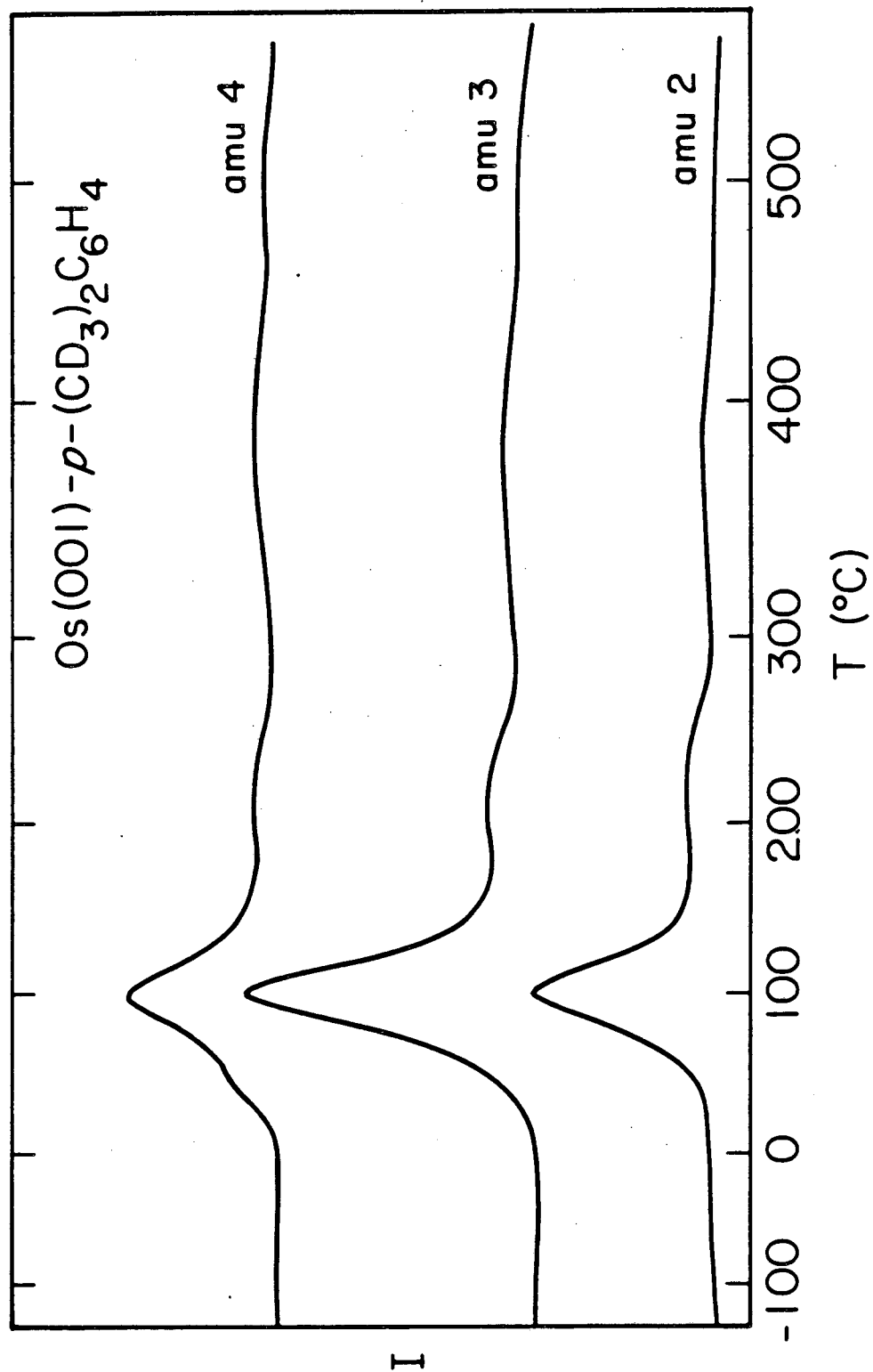
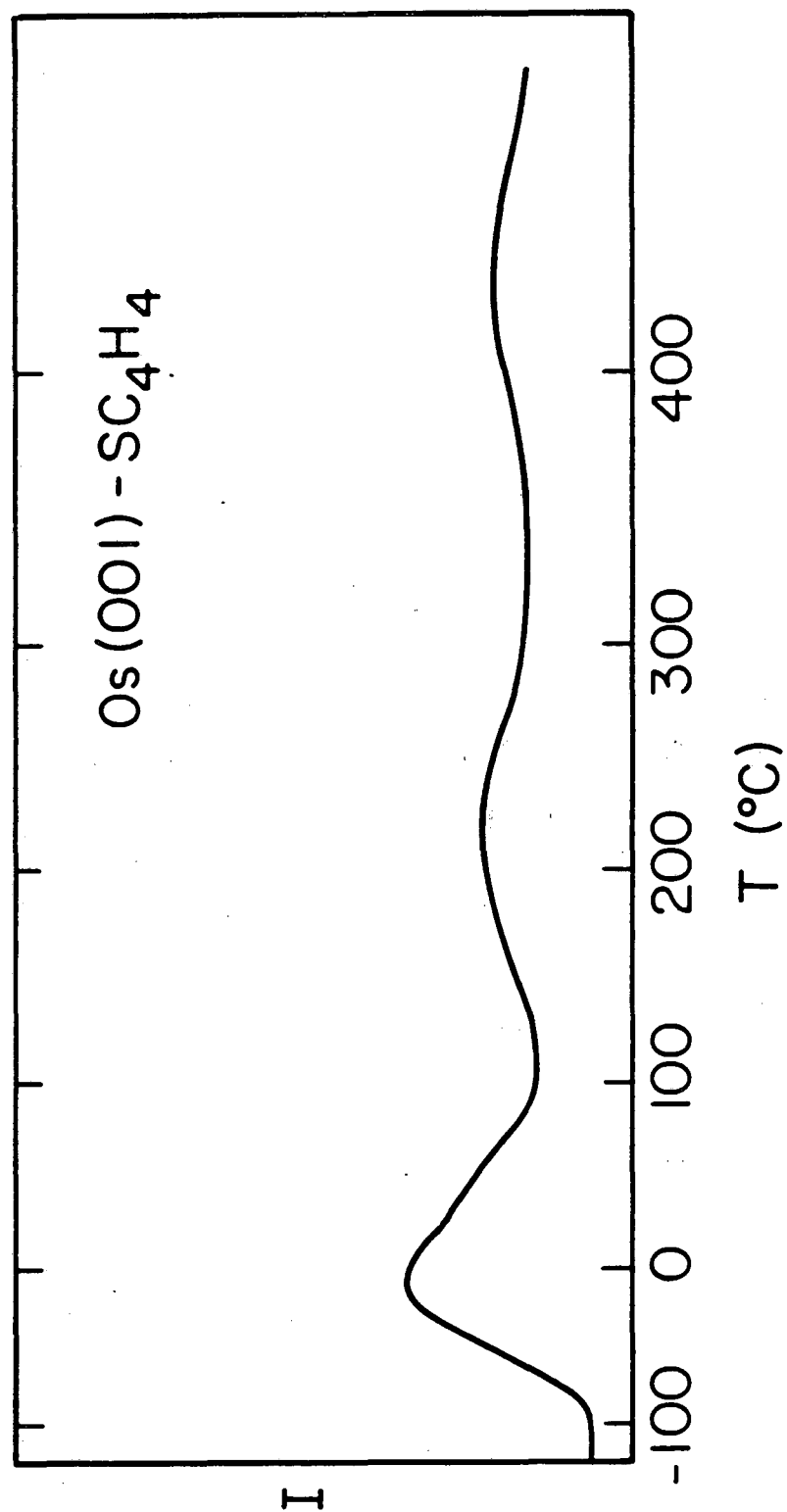
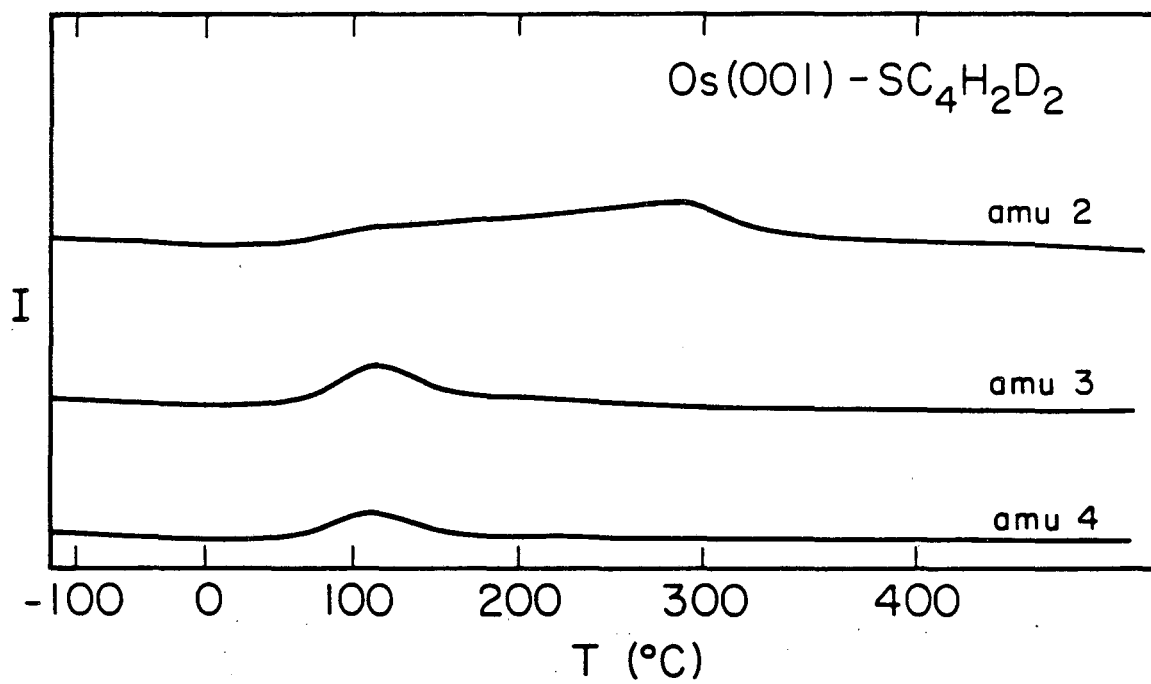


Figure 17. Thiophene chemisorption on Os(001) was completely irreversible, but it showed less of a coverage dependence than thiophene chemisorbed on Ru(001) (see text for details, compare to Chapter 3, Figure 5). The hydrogen desorption from a saturated layer (.5L exposure) of thiophene adsorbed on clean Os(001) at -140°C is shown above.



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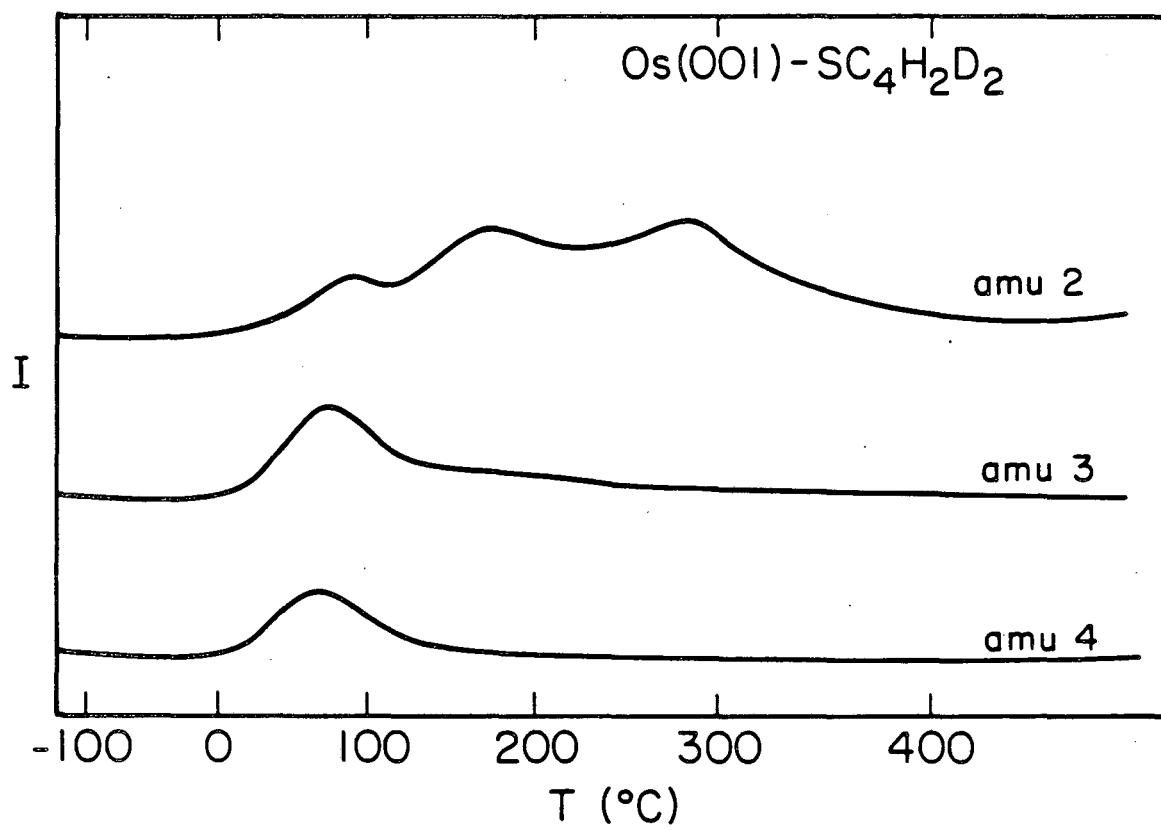
Figure 18. The regioselectivity of thiophene decomposition was also less extensive on Os(001) when compared to Ru(001) (compare to Chapter 3, Figures 6 and 7). Figures (a), (b), and (c) represent the H_2 , HD, and D_2 thermal desorption spectra arising from exposures of .04, .2, and .5L, respectively, of 2,5- d_2 -thiophene to the clean Os(001) surface at $-140^\circ C$.



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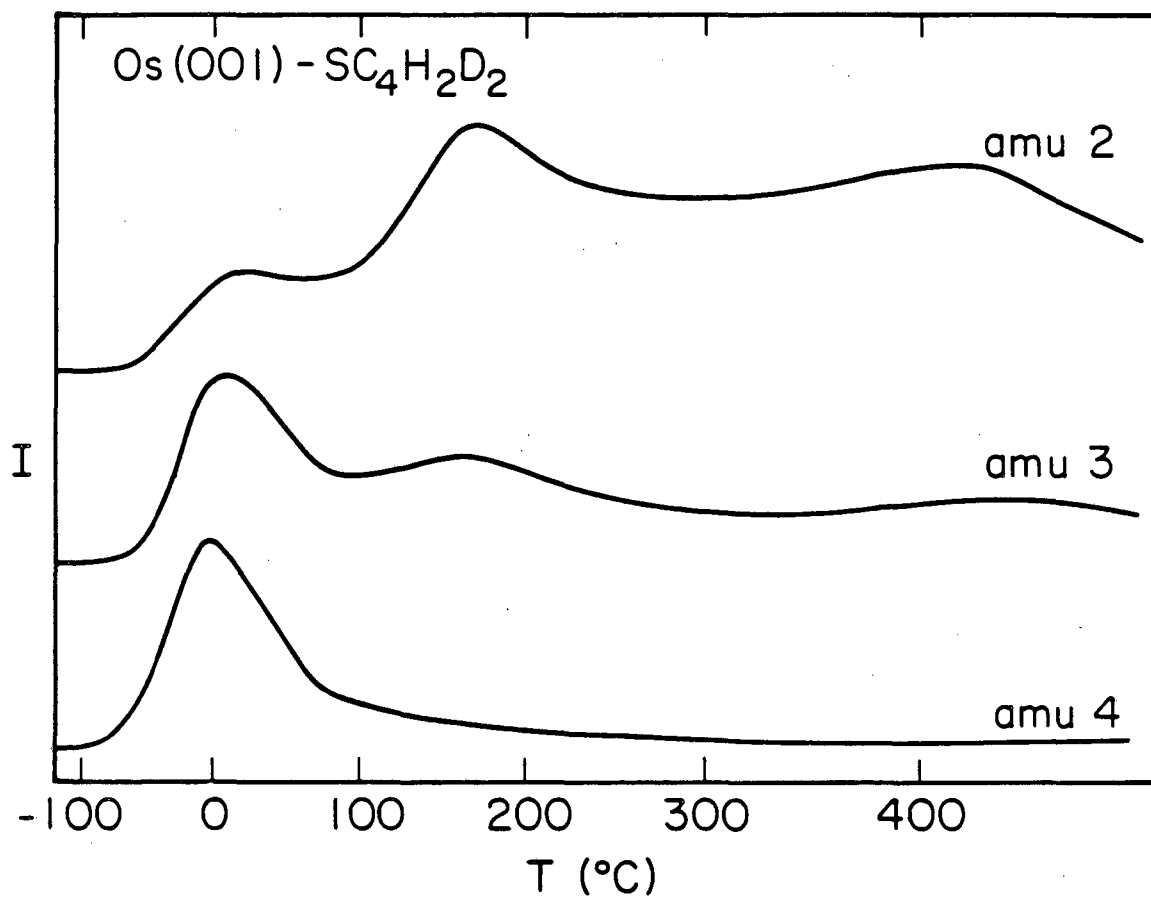
(a)

133b



(b)

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(c)

XBL 843-1248

Figure 19. The decomposition of 3-methylthiophene was quantitative and coverage dependent. This is illustrated for exposures of .1, .2, .5, and 1L (spectra (a)-(d), respectively) of 3-methylthiophene to clean Os(001) at -140°C .

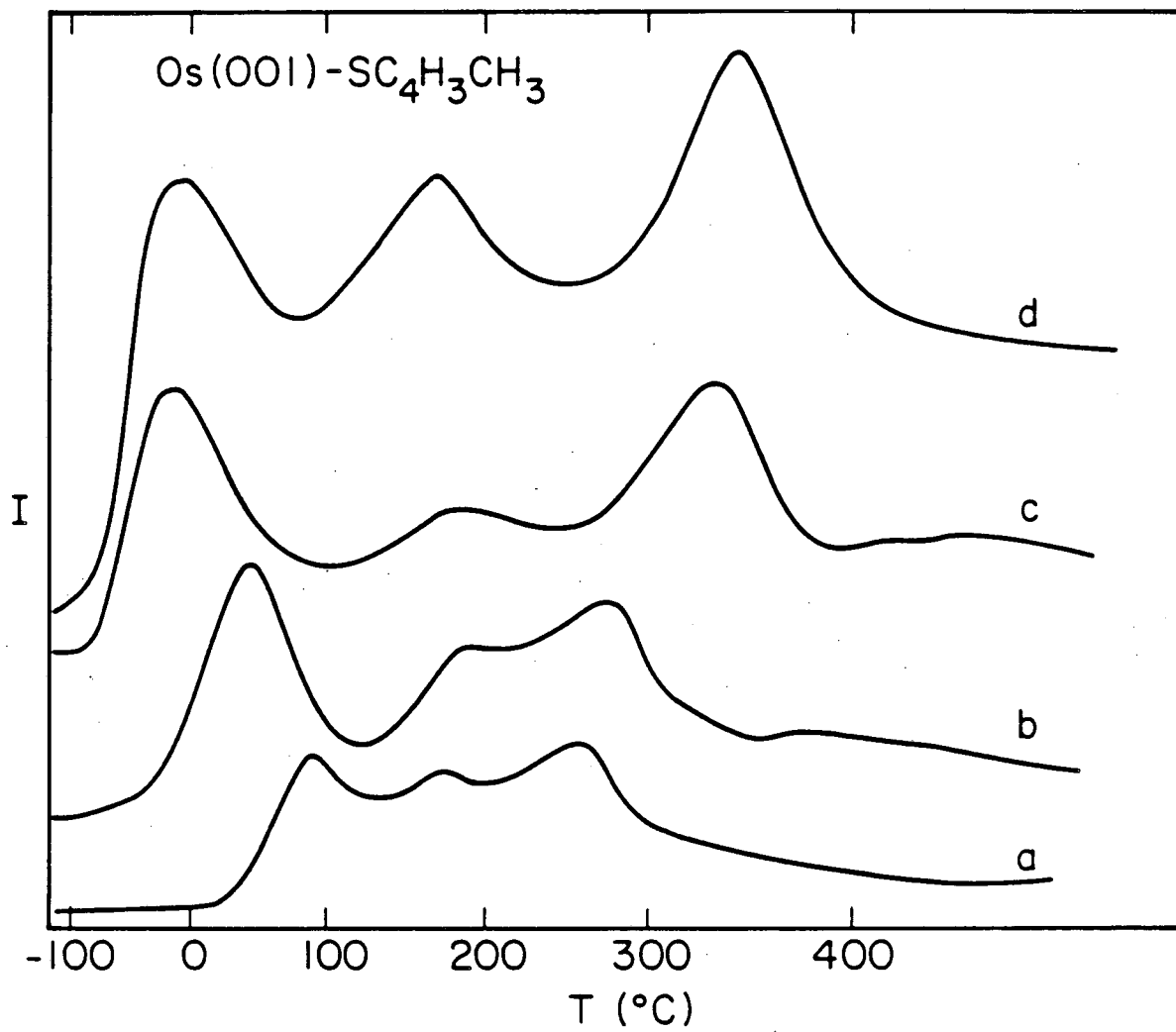


Figure 20. 2,5-dimethylthiophene also decomposed quantitatively and showed a strong coverage dependence as well. Spectra (a)-(e) are hydrogen desorption profiles arising from exposures of .05, .1, .3, .5, and 1L, respectively, to the clean surface at -140°C .

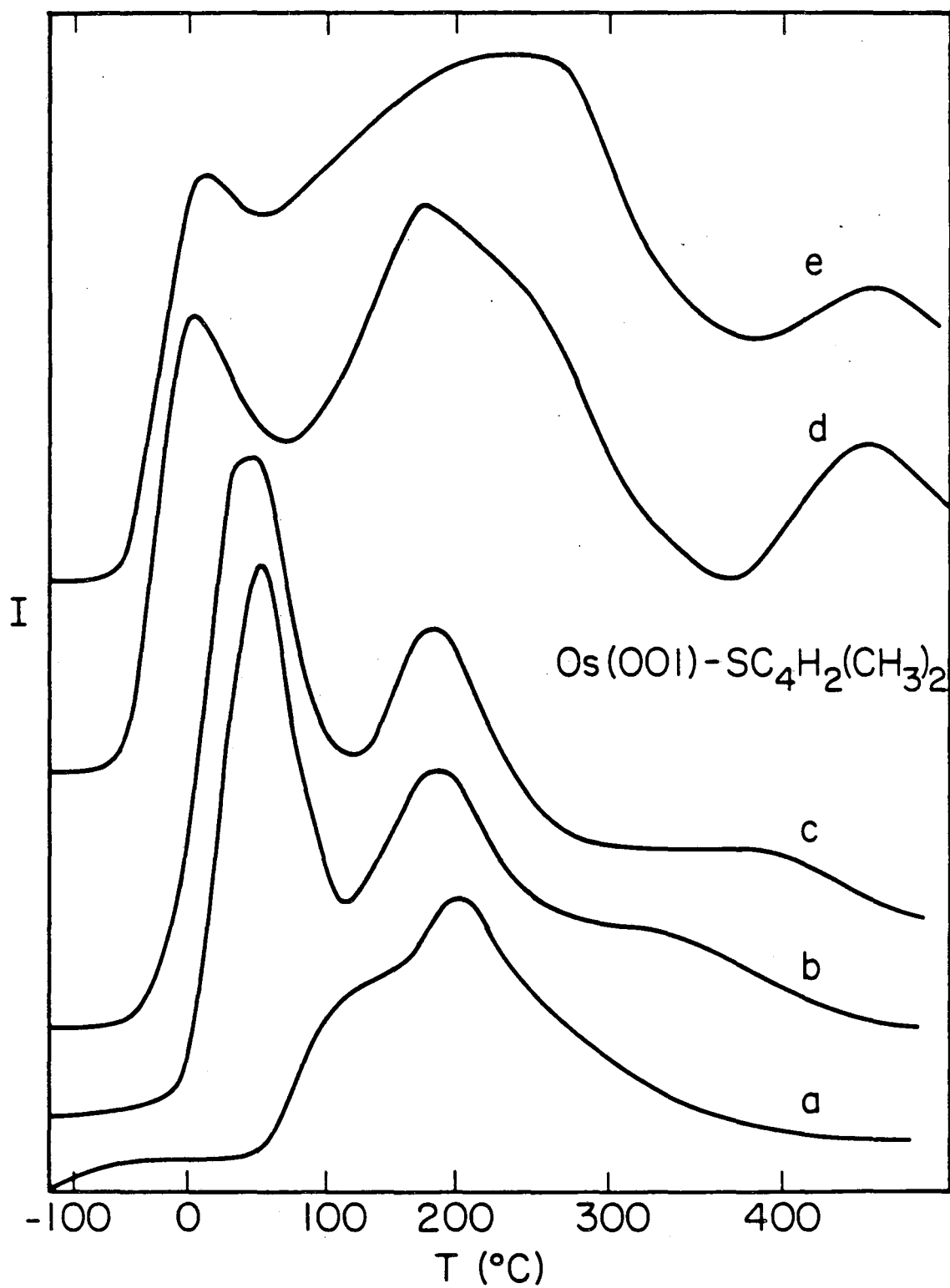
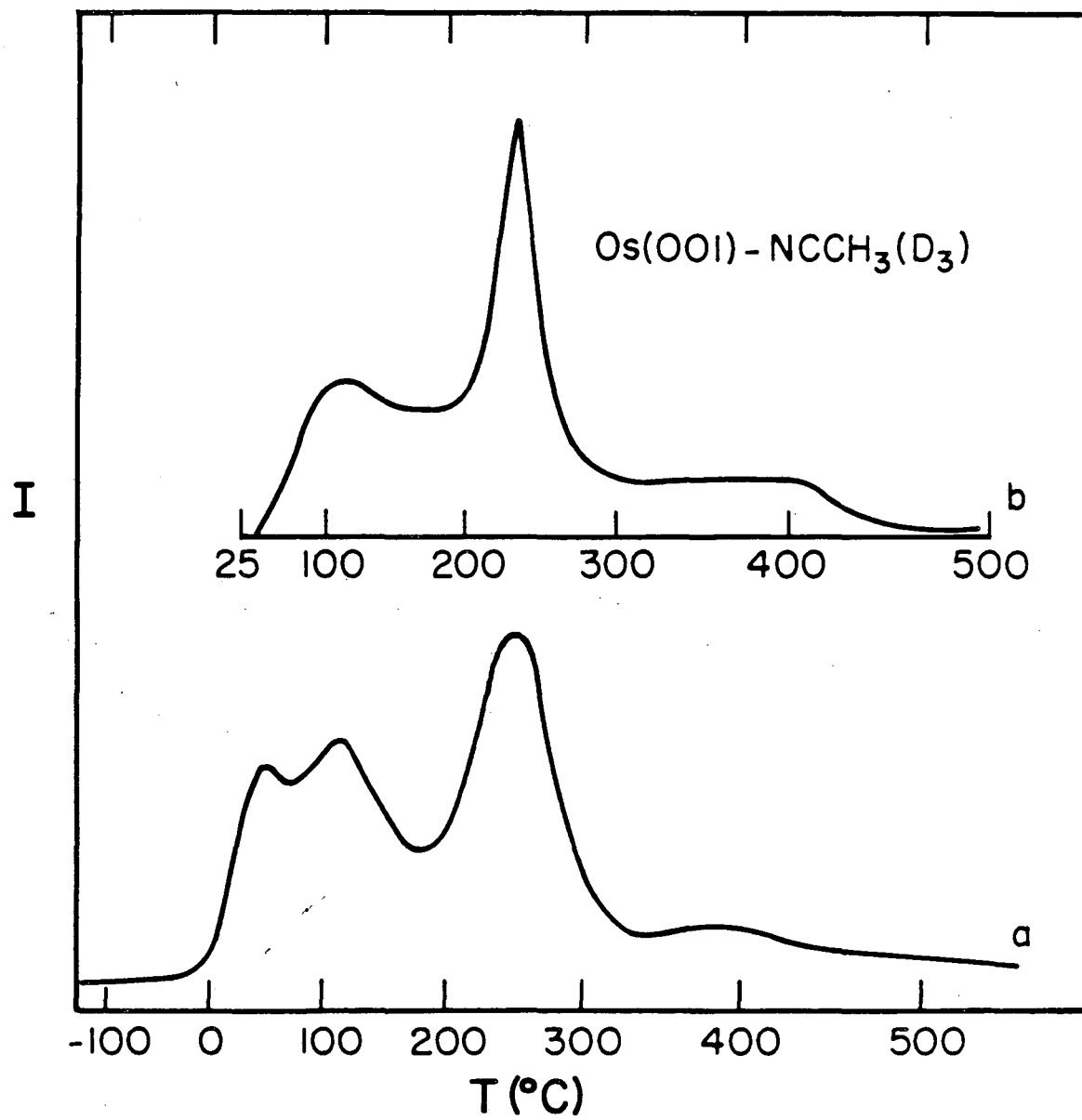


Figure 21. Acetonitrile decomposition showed a dependence on adsorption temperature in that molecular desorptions were observed when adsorption was conducted at -140°C . Also the hydrogen desorption spectra were dependent upon the adsorption temperature. Shown are two hydrogen desorption profiles from 1L exposures of acetonitrile to the clean Os(001) surface at -140°C and 25°C (spectra (a) and (b), respectively). (Spectrum (a) is actually D_2 arising from adsorption of perdeuteroacetonitrile.)



CHAPTER FIVE. COMPARISONS AND CONCLUSIONS

INTRODUCTION

In this Chapter, comparisons and conclusions will be drawn from the studies reported in this thesis. In particular, an attempt will be made to relate these studies to other work on Group VIII transition metal surfaces. First, each general class of compounds, as presented in Chapters 3 and 4, will be discussed and then overall conclusions will be made. In addition, areas where future work would be helpful will be pointed out.

CARBON MONOXIDE and SMALL INORGANIC MOLECULES

Previous workers have completed extensive studies of CO adsorption and desorption on Ru(001)(15) and Os(001)(7), and several authors have concluded the adsorption is associative based on spectroscopic evidence. Our studies with the labelled CO molecules have clearly shown that the process is associative and thus are in agreement with those authors. More importantly, the studies on carbon and oxygen covered surfaces have shown that surface contaminants can have a profound effect on the thermal desorption spectra of CO.

Previous authors(49,50,51,52) have interpreted the thermal desorption behavior of CO on Ru(001) on the basis of repulsive lateral interactions. The general similarity of CO thermal desorption from Ru(001) and Os(001) suggest that the same type of interactions are present on both surfaces. Our results with labelled CO molecules suggest only one type of chemically distinct CO on the surfaces.

Lateral interactions can alter the activation energy required for desorption and in the case of simple adsorbate systems such as carbon monoxide or hydrogen on clean surfaces, discussions based on these type of interactions are highly appropriate. Nevertheless for the complex systems probed in this work it is also possible to affect the preexponential factor by altering the entropy of the desorption process. For example, the adsorbed C or O could easily affect the collision frequency of coadsorbed H atoms. An effect of this type would be expected to depend on the detailed structure of the adsorbed C or O. Finally, it is often not possible to rule out a change in the chemical nature of the adsorbates caused either by changes in the electronic structure of the metal itself or by steric strains present in the adsorbate layer.

White and coworkers(45) have shown that hydrogen reacts to form water with co-chemisorbed oxygen on Ru(001) and that this reaction is highly sensitive to structural parameters. This supports a possible interpretation based on alteration of the entropy of the process. In addition, studies by the same author(53) on coadsorbed CO and H₂ show a new, low temperature H₂ desorption when sufficient CO is coadsorbed, suggesting a new chemical state of H on the surface. In a paper presented by Ertl and coworkers(54) regarding CO chemisorption on Pd(100)-C, a figure is presented (figure 2) which shows effects similar to those described in this report, but in the studies of CO adsorption on carbon covered platinum conducted by Somorjai and

coworkers(55), this effect was not duplicated. Only a decrease in peak area as carbon coverage increased was noted. Thus the literature of coadsorption states of CO and H₂ does not give a clear answer regarding the origins of observed changes in desorption spectra. In the absence of evidence to the contrary, the results reported here for the coadsorption systems will be explained in terms of lateral interactions, but as indicated in the foregoing discussion, alternate explanations could be equally valid.

Both carbon and oxygen affect the extent of these interactions but superimposed on this are geometric constraints arising from the structure of the C or O layer. In the case of carbon, a structural interpretation of the state of the carbon is not readily available. No low energy electron diffraction patterns were ever observed from the decomposed benzene layers, but the previously mentioned changes in the Auger electron spectra suggest a carbon layer that is graphitic in character, at least at high coverages. Studies on the surface chemistry of both Ru(001) and Os(001) conducted in this laboratory using hydrocarbon molecules suggest that carbon overlayers do not substantially affect the decomposition of those molecules, but instead simply cause a decrease in the intensity of the thermal desorption spectra. This implies that the carbon forms patches on the surface, a conclusion which has also been reached by Somorjai and coworkers(55) in a similar study of CO chemisorption on Pt(111), and these patches merely act to lower the available surface area.

For a noninteracting carbon overlayer one would expect to see a CO thermal desorption spectrum which displays the same characteristics as observed for desorption from the clean surface, only at a reduced relative intensity, but the data demonstrate a preferential decrease in the intensity of the high temperature peak. This implies that the carbon overlayer interacts directly with the chemisorbed CO in a fashion which is repulsive in nature, and affects both high and low coverages of CO equally strongly.

The results obtained with hydrogen tend to cloud this interpretation somewhat as the low exposure data and the tailing observed at high exposure imply that an attractive interaction exists. However the main peak in the D₂ desorption spectrum for high exposures does undergo a slight shift downwards in temperature which also implies a repulsive interaction. Thus D₂ and C interact differently depending on coverage.

Oxygen chemisorption has been studied extensively on Ru(001)(51) and it has been shown that the observed p(2x2) low energy electron diffraction pattern arises from three domains of (1x2) structure that are rotated with respect to one another for high coverages and a single domain of (2x2) structure at low coverages. In addition, Weinberg, et al.(51b) have demonstrated with high resolution electron energy loss spectroscopy that the chemisorbed oxygen atoms lie in three-fold hollow sites. On the other hand the vibrational data(49) obtained for CO chemisorption on Ru(001) suggests that CO prefers to

bond to that surface via a single metal atom in on-top sites. In one interpretation, the compression state which forms at high coverages is caused by an incommensurate lattice. This state would force the CO molecules to either tilt substantially or to move off the on-top site altogether (although no evidence of bridge-bonded CO was obtained). The coadsorption of oxygen in three-fold hollow sites would serve to isolate the CO molecules from one another and prevent the formation of the strained compression state, especially if at least a slight repulsive interaction between the CO and O atoms existed.

The data presented here support this assumption since the low temperature CO thermal desorption state is preferentially decreased. This implies that the formation of the close-packed state of CO which produces strong lateral interactions between the CO molecules does not occur. In addition the existence of slight repulsive CO-O interactions is suggested by the slight decrease in the peak maximum of the high temperature CO desorption observed for high O coverages. However, several studies have been done on coadsorbed CO and O on the Ru(001) surface(15b,52) and the results obtained depended greatly on the experimental parameters such as order of adsorption and kind of pretreatment of the oxygen adsorbate. It is expected that similar effects could be produced on Os(001).

The desorption spectra for D₂ coadsorbed with oxygen also point to strong repulsive interactions in that the D₂ thermal desorption maximum moves to lower temperature with increasing oxygen coverage.

The subsequent alteration of the D_2 desorption peak also implies a site blocking effect engendered by the coadsorbed oxygen; an effect that is also apparent in the CO-O coadsorption experiments. According to electron energy loss studies(56), hydrogen bonds to metal surfaces in bridge-bonded or three-fold hollow sites, a conclusion supported by the analogy between surface and cluster chemistry (where hydrogen often bonds in bridged positions). Thus the H(D) atoms should physically approach the surface oxygen atoms more closely than CO molecules bonded in on-top sites. Therefore it is not surprising that the magnitude of the shift in desorption maximum for D_2 is significantly larger than that of CO(57).

Phosphorous trifluoride is formally analogous to CO in its bonding capability; both molecules are poor sigma donors and good pi acceptors. Ertl and co-workers(21) concluded from a study of PF_3 chemisorption on several different metal surfaces that M-CO and M- PF_3 bond energies are generally comparable, with the latter being somewhat stronger for a given metal. However, their data on Ru(001)- PF_3 suggested that PF_3 is one of the extreme members of this generalization and is bonded more strongly to the Ru(001) surface than is CO. The thermal desorption spectra from Ru(001)- PF_3 confirmed that fact and also suggested that, due to a weak, low temperature shoulder on the main PF_3 desorption, lateral interactions were also present in the PF_3 adlayer. This, in addition to the similarity of the PF_3 and CO LEED patterns, tends to confirm the formal analogy.

Thus, a general picture of Ru(001)- and Os(001)-small molecule chemistry is beginning to emerge. This picture suggests the existence of repulsive lateral interactions between adsorbates and is supported by the studies on coadsorption states detailed in this thesis. However, it should be noted that the data here are certainly not definitive, especially when the work of other authors discussed above is considered.

BENZENE and BENZENE DERIVATIVES

Chemical and physical studies of benzene chemisorption on surfaces of Ag, Ni, Pd, Pt, Rh, Ir, Fe, and Ru(58) have suggested that benzene is bound molecularly to those surfaces. Extensive spectroscopic studies of many of those systems further established that the benzene molecule is oriented in a plane parallel to the surface(27, 59-63, 65-68). Accordingly, no significant differences are expected for Ru(001)-benzene or Os(001)-benzene.

Consistent with this expectation, the LEED pattern obtained from Ru(001)-benzene ($p(3 \times 3)$) shows a unit cell that just envelops the van der Waals extension for benzene molecules lying flat on the surface. This ordered array would lead to close packing of the benzene molecules. The nearest neighbor distance in osmium is approximately .02 angstroms larger than in ruthenium(70), and benzene forms an ordered $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ array on Os(001), which would also allow benzene to bond parallel to the surface on Os(001).

This mode of bonding is expected to still be predominant in toluene and xylene chemisorption, and has been demonstrated to be so in the case of Pt(111)-toluene(71), but in these cases a new perturbation should arise. Placing the ring flat on the surface will lead to the close approach to the surface of at least one of the methyl C-H bonds (two for xylene), perhaps leading to the formation of a multicenter C-H-M bond(72). This multicenter bond would then lead to a more facile cleavage of that particular C-H bond. In principle, if the energetics of this process were favorable enough, a new thermal desorption peak should appear in the decomposition spectra of a methyl substituted benzene molecule. This aspect of the decomposition could be probed further by selectively labelling the methyl C-H bonds in relation to the aromatic C-H bonds and examining the distribution of the label in the desorption spectra.

This has been attempted extensively in this laboratory and in these experiments, but two complicating observations arise immediately when comparing the decomposition spectra of benzene, toluene, and the xylenes on Os(001) and Ru(001). Namely, the striking similarity in desorption spectra contrasts sharply with the change expected with methyl substitution, and the general lack of regiospecificity observed in the decomposition casts doubt on the existence of preferential bond cleavage at the methyl substituent during the thermal decomposition.

Several causes of these observations can be advanced and a few will be presented here. To begin with, an important consideration is

whether the adsorption of methyl substituted benzenes is dissociative or not. If the close approach of the methyl C-H bond to the surface does in fact lead to facile bond cleavage, it is possible that this cleavage occurs upon adsorption.

The previously discussed studies into hydrogen adsorption on carbon covered Os(001) clearly demonstrated a decrease in the amount of hydrogen adsorbed on the surface as the amount of coadsorbed C increased. Thus, it is entirely possible that dissociation followed by recombination and desorption of hydrogen occurs immediately upon adsorption. This type of process is postulated to occur with thiophene and methyl acetate adsorption on Ru(001) (see later sections of this thesis) and for hydrogen sulfide on Ru(001)(19). Thus any discussion based on the assumption that the hydrogen observed in the thermal desorption experiment represents all of the hydrogen in the molecule could be entirely fallacious.

A variation on this postulate is dissociative adsorption, but without the subsequent hydrogen desorption. This would result in a coadsorption state of "free" hydrogen and a partially decomposed intermediate on the surface, and all the complexities inherent in coadsorption states would come into play. In light of this possibility it is interesting to contemplate the hydrogen desorption spectrum of meta-xylene. The low temperature H₂ desorption seems to show behavior similar to the behavior of hydrogen adsorbed on Os(001)-C, perhaps supporting this interpretation in this case.

In the case of dissociation upon adsorption or the case of facile methyl C-H bond cleavage early in the decomposition, a likely intermediate would be a benzyl-like surface species, where extensive conjugation would render all the remaining C-H bonds energetically similar. The net result would be a surface molecule arising from toluene or xylene which would decompose in a similar fashion to benzene itself. It is of interest to note that there are great similarities in the decomposition spectra of benzene, toluene, and xylene on all the Group VIII transition metal surfaces(73) as well as in the decomposition of molecules such as azulene and naphthalene on Pt(111)(74).

With hydrogen being released to the surface during the decomposition process, another complication is the possibility of scrambling of the surface hydrogen into the intermediates. The net result of this process would be total loss of regiospecificity in the remaining steps of the decomposition. Scrambling of this type is illustrated in the decomposition of selectively labelled toluene chemisorbed on Ir(111), where benzene molecules are produced that contain one hydrogen originating from the methyl group of toluene(75).

Dissociative adsorption alone does not explain the observed coverage dependences of the decompositions, where low temperature desorptions of varying relative intensity appear as the coverage is increased. There are several alternative proposals that can be put forth to explain these observations. First, a new chemical state

could arise as the coverage was increased. Second, the low temperature hydrogen desorption which appears at high coverage could actually be there at low coverage, but because of shifts in temperature maxima with coverage, could not be resolved at low coverage. Third, cooperativity effects could be postulated during the decomposition which lead to an easier formation of hydrogen molecules at high coverages, perhaps due to a forced close approach arising from closer packing of the surface species at high coverages.

The first proposition has some basis in fact. Tsai and Muetterties (38b) have shown for benzene chemisorption on Pt(111), two peaks are observed in the molecular thermal desorption spectra. These peaks fill sequentially with increasing exposure, with the lower temperature desorption filling last. By sequentially filling these two peaks with C_6H_6 and C_6D_6 in the manner of the CO experiments discussed in earlier sections, they showed that these two desorption maxima represented chemically differentiable states. In addition, Somorjai and coworkers (76) have studied the chemisorption of benzene on Pt(111) and have detected a change at high coverages which they attribute to the formation of a new chemical state where the ring is now inclined with respect to the surface. Demuth and coworkers (77) have postulated a similar change with coverage for pyridine chemisorption on Ag(111).

The second proposition is a difficult one to test. Presumably the labelling studies would shed some light on this, and in fact, there does appear to be a slight preponderance of the hydrogen label

originating from the methyl substituents in the low temperature regions of the decomposition spectra from toluene on Os(001) and Ru(001) and para-xylene on Os(001) at high coverages. However, the data certainly are not conclusive in that while the regioselectivity is even lower at low coverages, the peak height and ratio of the area of the sharp, low temperature desorption to the remainder of the hydrogen desorbed at low coverage does not seem too different from that ratio at high coverage. If the sharp peak was actually composed of two desorptions at low coverage, their resolution at high coverage should result in a noticeable change in this ratio.

The third proposition is equally difficult to prove or disprove. The coadsorption studied of hydrogen on Os(001), as well as the other studies mentioned in that discussion, suggest that strong interactions can exist between coadsorbed species. The LEED studies of the adsorption states formed by benzene and toluene suggest an attempt for the molecules to adsorb into similar ordered arrays. Since the ordering is hindered by the methyl substituent, reasonably strong interactions between the adsorbate molecules are implied. In order to evaluate if the close approach of surface molecules leading to the appearance of the new desorption peak at high coverages, a detailed study of the coverage dependence and mechanism (island formation?) of ordering, correlated to the thermal desorption data, is required and this thesis does not present such a study.

In summary then, the data presented in this thesis on benzene and benzene derivative decomposition show two confusing aspects, the

similarity in the decomposition patterns and the high degree of nonregiospecific bond cleavage. Several causes for these observations have been discussed, but the data presented here do not distinguish between them. Therefore, the explanation of these results rests on the application of other techniques which can specifically address these problems. An excellent example of the type of work necessary to do this is the study by Johnson and coworkers(71) on the decomposition of toluene on Pt(111) with the technique of near edge X-ray absorption fine structure (NEXAFS).

Previous work on the Pt(111)-toluene system has demonstrated its similarity (at least in terms of its decomposition) to the Ru(001) and Os(001) systems. Specifically, multiple peaks are also observed in the hydrogen desorption spectra that display the same general shape and position characteristics, but unlike Os(001) and Ru(001), no coverage dependence was noted. Using NEXAFS, Johnson and coworkers showed that the initial bonding of toluene to the Pt(111) surface occurred as expected, through the pi system of the ring with the ring being flat on the surface. In the subsequent decomposition, it was observed that the first step (as indicated by the first hydrogen thermal desorption) did not result in a change in the ring orientation. However, the second step did; the ring was observed to tilt substantially, leading to the postulate of a C_6H_5-CH or C_6H_5-C intermediate.

Thus on Pt(111) at least, the postulate of facile C-H bond cleavage at the methyl group leading to a benzyl-like intermediate

that is completely coplanar has been substantiated. It is unclear however if a predissociated intermediate could be distinguished from a nondissociatively adsorbed molecule by NEXAFS.

Even though many questions are raised by the data reported herein, one general conclusion and comparison can be made. Extensive desorption of molecular benzene is observed from the nickel group (111) metal surfaces and quantitative or near quantitative displacement of benzene can be achieved on those surfaces. When moving to the Ir(111) surface, the amount of desorbable benzene drops dramatically, and this trend is carried to completion on Ru and Os(001). Ru(001)- and Os(001)-benzene or benzene derivative chemistry is characterized by total decomposition, while moving to the right in the periodic table leads to more and more molecular desorption.

HETEROAROMATIC MOLECULES

The surface chemistry of pyridine, furan, and thiophene on Ru(001) was examined and it was found that as was the case with benzene and benzene derivatives, no molecular desorption was detected. Furan did not appear to have a unique decomposition pattern in that only CO, H₂, and surface carbon were produced and that the CO and H₂ desorptions closely resembled those arising from the adsorption of CO or H₂ on Ru(001)-C.

Pyridine decomposition also was not as highly structured as the decomposition of the hydrocarbons discussed previously, and produced only H₂, HCN, N₂, and surface carbon. The hydrogen desorption

produced from pyridine adsorbed at room temperature showed two maxima, but they were of approximately equal intensity and were not well resolved. Lowering the adsorption temperature to -160°C simply lowered the onset of decomposition, as signalled by the H_2 desorption, to approximately 0°C and resulted in an even more poorly resolved hydrogen desorption. Studies with $2,5\text{-d}_2$ -pyridine gave no clearcut evidence of regioselective bond breaking, although a very slight excess of D_2 could be seen at the onset of the hydrogen desorption.

As was the case with almost all molecules studied, thiophene produced no molecular desorption and no carbon containing products were detected. Only hydrogen was observed in the gas phase. If adsorption was conducted at room temperature on $\text{Ru}(001)$, a broad hydrogen desorption was detected at approximately 290°C only at high coverages, but for adsorption at -160°C a new, coverage dependent peak arose at lower temperatures. At even higher exposures a third peak developed in between the other two desorptions. Apparently the hydrogen used to populate these desorptions was desorbed immediately upon adsorption of the thiophene molecule at room temperature. Previous studies of H_2S chemisorption on $\text{Ru}(001)$ (19) indicated that the first amounts of hydrogen sulfide adsorbed decomposed and immediately desorbed hydrogen gas. Thus the postulate of decomposition upon adsorption, followed by desorption is not unreasonable.

$\text{Ru}(001)$ -thiophene chemistry produced clear evidence of a stereoselective decomposition. When $2,5\text{-d}_2$ -thiophene was adsorbed

on the clean surface at -160°C at intermediate and low coverages, the low temperature desorption contained all the D atoms, and none were found in the high temperature desorption. In fact, when adsorption was conducted at room temperature, no deuterium atoms could be detected in the desorption spectra at all.

Surface sulfur altered these results substantially. By preferentially removing the carbon from thiophene residues, sulfur could be left on the surface, although this was always in quantities of less than one quarter monolayer as estimated from the LEED patterns of the adsorbate. When labelled thiophene was adsorbed on these surfaces, the clear regioselectivity was lost and substantial deuterium was observed in all the hydrogen desorption peaks, both for adsorption at room and low temperature.

One reasonable mechanism of decomposition which would explain this interesting type of regioselectivity would be an extraction of H_2S very early in the decomposition, followed by desorption of the hydrogen from this decomposition product. One complication on this picture, however, is the previously mentioned study on hydrogen sulfide chemisorption behavior. In that study, adsorption was conducted at low temperature and for the levels of sulfur examined here, desorption of hydrogen should have been immediate. Perhaps the lower temperature desorption is actually decomposition limited or perhaps cooperativity effects are again coming into play. Unfortunately, these studies cannot answer those questions.

Osmium produced slightly different results upon chemisorption of thiophene. Like Ru(001), no gaseous products were detected other than hydrogen, but the coverage dependence of the hydrogen desorption spectra was different. Again like Ru(001), there were three desorption maxima for hydrogen production from a saturation layer of thiophene on Os(001). The lowest temperature peak did show the same type of coverage dependence as observed on Ru(001), but the desorption appearing between the other two was present at all coverages on Os(001). In studies with 2,5-d₂-thiophene, clear regiospecificity in the decomposition was not detected. All peaks had deuterium content in them, although the amount dropped off as the temperature in the flash increased. An additional difference was the failure of surface sulfur to alter the deuterium distribution.

In order to further probe the steric requirements of the thiophene decomposition, the technique of methyl group substitution was again employed and the chemisorption behavior of 3-methyl- and 2,5-dimethylthiophene was examined. In similar studies on the Ni(100) surface(78), regioselectivity was established in the decomposition by the appearance of increased hydrogen desorption at higher temperatures from 3-methylthiophene and at lower temperatures from 2,5-dimethylthiophene relative to the hydrogen desorption from thiophene itself. However, the analogous studies on Ni(111)(78) did not produce such clean results and this is also true for the results reported here for Os(001).

The major problem in interpreting the data is the observed coverage dependence of the hydrogen desorption spectra. In the decomposition of 2,5-dimethylthiophene for example, the low temperature desorption grows in intensity and then stops, to be followed by a growth in intensity of the intermediate temperature desorption. In the case of 3-methylthiophene, this type of behavior is not observed, but there is no clear enhancement of one desorption peak over the other, all seem to be equally enhanced. For 2,5-dimethylthiophene there does seem to be preferential enhancement in the low temperature desorption region, but two peaks benefit from this enhancement. The net conclusion forced upon us is that no clear conclusion regarding the stereochemical requirements of the decomposition can be made, which was the analogous conclusion drawn from the Ni(111) studies.

INORGANIC AND ORGANIC CYANIDE COMPOUNDS

The cyanides were the only group of hydrocarbon molecules studied that produced molecular desorption with adsorption at room temperature. Even in these cases however, decomposition was the major process occurring in the thermal desorption experiment, with nitrogen being a common decomposition product for all molecules studied. When the molecule contained hydrogen (fluorine), molecular hydrogen and hydrogen cyanide (HCN) were also observed to desorb. Lowering the adsorption temperature usually produced either new molecular desorptions or alterations in relative peak intensities of the desorptions observed

after adsorption at room temperature (neglecting multilayer desorption, which was evident with all molecules). These desorptions probably represent less than one quarter of the total material adsorbed, based on AES estimates (which were often complicated by chemical effects), and thus do not represent major surface species unlike the chemistry evidenced on Ni surfaces(78).

The molecular orbital structure of the nitrile functionality has great similarity to that of CO(72), and in coordination chemistry, nitriles often bond in a fashion analogous to that of CO, as both a sigma donor and a pi acceptor(79). However, examples are also known of nitriles bonding strictly through the pi system of the cyanide group in an π^2 fashion(80). Nitrile bonding to surfaces should not be substantially different and in fact both modes could be equally likely. Figure 1 illustrates these two modes for a model compound, acetonitrile.

A functionalized nitrile bonded to the surface in an π^2 fashion would lead to the close approach of the hydrogens in the substituent to the surface, as illustrated in B of Figure 1. Given the apparent ease with which such C-H bonds are cleaved in substituted aromatics and heteroaromatics such a structure as B should produce extensive decomposition. The mixed results on both the Ni group metals, where a disagreement exists on the extent of reversible adsorption on Pt(111)(81,82), and on Os(001) and Ru(001) tends to suggest the possibility of both types of bonding to the surface, with only the

relative populations being affected by surface topography (including number of defects) and adsorption temperature. Avery(81a) has postulated that CH_3CN bonds to $\text{Pt}(111)$ via an η^2 complex, as in B, rather than via an η^1 complex (A) as was postulated for $\text{Ni}(111)$ (83) and studies with several nitriles on Ni surfaces(78) indicated a high, but not complete, degree of reversibility.

The nitriles studied here as well as on the Ni surfaces represent an attempt to alter the preferred bonding mode of the nitrile by altering both the electronic and steric constraints imposed by the substituent. With CH_3CN as the starting point, the CF_3 group should foster electron withdrawal from the cyanide functionality, resulting in a favoring of mode B in the bonding. This implication is supported by the complex desorption behavior of CF_3CN on Ru and Os(001). Replacing the CH_3 group with a vinyl or t-butyl group should certainly increase the bulk of the substituent and should also bring the hydrogen atoms in the substituents closer to the surface, favoring more extensive decomposition. In fact, the vinyl functionality could serve as a second major bonding site in that molecule. The lesser amount of molecular desorption of pivalonitrile and acrylonitrile from Ru and Os(001) again support this interpretation. Cyanogen and HCN on the other hand, offer another complexity, as dissociative adsorption is now even more feasible. Other authors have invoked the existence of different types of cyanogen adsorbates on surfaces(41) and the multiple peak character of the thermal desorption spectra also suggest multiple types of surface species.

While changes in the appearance of desorption peaks or the development of entirely new desorption peaks with changes in adsorption temperature suggests that one is altering the relative populations of different surface species, an important point to remember is that the majority of the chemistry displayed by all the cyanide compounds on Ru(001) and Os(001) was decomposition. Thus in fact, the alterations described above are probably only minor. However the appearance of multiple desorption maxima and the temperature dependences noted still do suggest that several different types of surface species do exist on the surfaces, even if it is not easy to arbitrarily assign them as A or B types.

In relation to the question of different types of surface species, of great interest was the complex behavior of trifluoroacetonitrile on clean and "dirty" Ru(001) surfaces. To begin with, the multiple peak characteristics of the desorptions, coupled with the broad temperature range of the desorptions ($>300^{\circ}\text{C}$), indicate that at least the high temperature desorptions arise from the recombination of surface radicals. Subsequent readsorption on the residue of CF_3CN that had not been fully decomposed produced fully reversibly adsorbed CF_3CN , which again showed thermal desorption characteristics that differed from those displayed by adsorption on the clean surface.

Trifluoroacetonitrile chemisorption was attempted on a variety of surfaces prepared by adsorbing different molecules and decomposing these to different extents. Almost all the different residues

presented different results, as was illustrated in Figures 15 and 16 of Chapter 3. The details of the desorption spectra depended on both the coverage of the residue and the coverage of CF_3CN . This was illustrated clearly in the chemisorption of CF_3CN on oxygen covered surfaces. While the changes in the chemistry of these coadsorption states are interesting, they illustrate the same difficulty of interpretation as the CO and H_2 on C or O covered $\text{Os}(001)$ or $\text{Ru}(001)$, carried to a higher degree. Thus these studies are only of a preliminary nature and while they illustrate interesting effects, they are not definitive.

In summary, the work reported here on cyanide compound surface chemistry points to the coexistence of multiple surface species. The relative populations appear to be alterable by changing the adsorption conditions and probably the surface topography. Thus some of the disagreements in the current literature could easily be traced to considerations based on these conditions.

OXYGEN CONTAINING COMPOUNDS

Many studies have been completed on oxygen containing compounds on nickel group metal surfaces(84) and on ruthenium surfaces(29,30,85), and the general conclusion that can be drawn from these studies is that ruthenium tends to be more reactive than nickel group metals. Decomposition was also the pervasive result observed in the studies reported in this thesis for $\text{Ru}(001)$ chemistry, and the study of methanol chemisorption on $\text{Os}(001)$ points to the same type of chemistry.

Major decomposition products were CO and H₂, although acetic acid produced CO₂ in addition, but the thermal desorption spectra generally resembled those of CO and H₂ adsorbed on carbon covered surfaces. Since the spectra appear to be desorption limited rather than decomposition limited, no mechanistic information can be gained regarding the decomposition pathway. The only exception to these observations was acetic acid.

Acetic acid decomposition has been studied on the Ni(110) surface by Madix and coworkers(86), and they postulate the formation of an anhydride intermediate in the decomposition. Formic acid has also been studied extensively and its decomposition on Ni(110)(87) and Ru(100)(88) seem to occur via similar mechanisms. Again original postulates were advanced for anhydride intermediates, but in high resolution electron energy loss spectroscopy studies of these reactions(29,87), no vibrations attributable to an anhydride were detected. Based on this, Madix and coworkers(87) postulated that the observed autocatalytic decomposition of formic acid on Ni(110) was mediated by lateral interactions between the adsorbates.

When the work of these other authors is compared to the data presented herein, the significant point to be noted is the similarity in the coverage dependences of the CO and CO₂ desorptions. In both acetic acid decomposition on Ru(001) and formic acid decomposition on Ru(100), a similar shift up in the desorption maximum of the CO₂ desorption and a concomitant shift down in the CO desorption maximum

as coverage was increased was observed. This similar behavior suggests similar intermediates, even if the identity of these intermediates is still in question. The pervasive evidence for strong lateral interactions on Ru(001) suggests that this may be an alternative explanation of the observed shifts.

SUMMARY

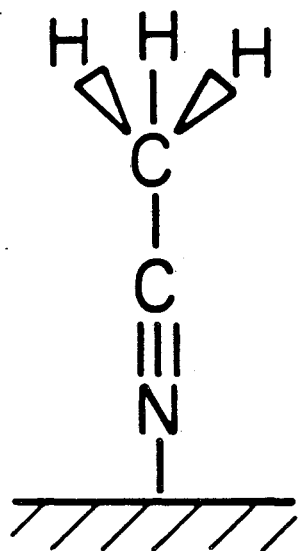
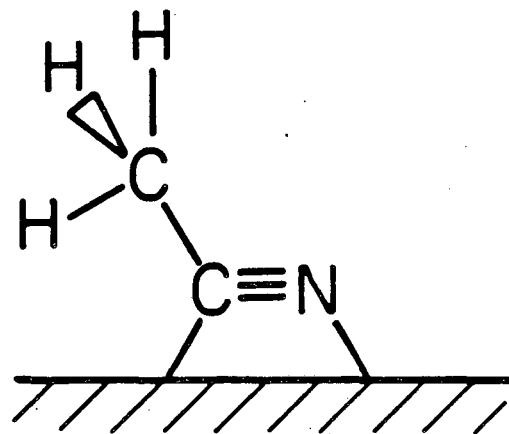
These studies have shown that in general the Ru(001) and Os(001) surfaces favor decomposition of complex molecules, to an extent where molecular desorption is rarely observed. While the reactivity of Ru and Os is substantially higher than the nickel group metals, the decomposition of similar on all these surfaces. However where molecular desorption occurs from Ru(001) and Os(001), multiple forms of chemisorption seem to be indicated. In addition, the greater coverage dependences suggest that lateral interactions play a more significant role on Ru and Os(001) than on the close packed planes of the nickel group metals.

The preponderance of decomposition reactions on ruthenium and osmium surfaces suggest that the active agent in high pressure catalytic reactions is not the clean surface, but a surface contaminated by decomposition products, materials adsorbed from the ambient, or combinations of these. Unfortunately, these surfaces could not be studied under UHV conditions as the molecules of interest generally would not chemisorb on their own decomposition residues. Nevertheless it was demonstrated in several cases that atomic

adsorbates such as C, S, O, and P could significantly alter thermal desorption profiles originating from molecules coadsorbed with these contaminants.

Future work on the chemistry of the molecules studied here is definitely needed. Thermal desorption spectrometry in general is very good at pointing out directions to explore, but very poor in providing definitive, clearcut answers, and these studies are a case in point. For some molecules, possible initial steps in the decomposition have been indicated, while for others no such information was gained. In other cases, lateral interactions were suggested to cause many of the observed desorption properties of the decomposition products. Only the application of a variety of spectroscopic techniques combined with analogous studies on other surfaces will be able to verify these suggestions.

Figure 1. Nitriles have two possible bonding geometries available to them when bonding to a metal surface. These are illustrated above for acetonitrile.

**A****B**

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9. Miscellaneous polyatomic inorganic molecules studied on Ru(001) are sulfur hexafluoride²⁰, phosphorous trifluoride²¹, and ammonia²².
10. Saturated hydrocarbons studied on Ru(001) include ethane²³, cyclopropane^{23,24}, cyclohexane^{23,25}, and cyclooctane²³.
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