THERMAL DESORPTION STUDIES
OF ACETYL AND BROMOACETYL CHLORIDE
ON A Cu(111) SURFACE

by

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Abstract

The work in this thesis presents results for the adsorption and decomposition of acetyl and bromoacetyl chloride performed for the first time on any metal surface, and in this case on Cu(111). Results from temperature programmed desorption experiments show that acetyl and bromoacetyl chloride adsorb molecularly at 100 K, and undergo reaction in the monolayer when the surface is heated. Moreover, a chemical displacement technique is used to establish that the decomposition temperature is near 138 K for adsorbed acetyl chloride on Cu(111). This technique also provides evidence that the acetyl chloride decomposition occurs through the C-Cl bond cleavage. During the displacement experiments a new peak is observed at 167 K and is attributed to the formation of acetophenone from the coupling reaction of adsorbed acetyl groups and transient phenyl radicals. Also some preliminary results are shown for bromoacetyl chloride decomposition. For acetyl chloride on Cu(111), the activation energy of the C-Cl bond cleavage is about 11% of the gas phase bond energy, which implies that Cu-Cl bond formation and C-Cl bond scission occur cooperatively. The dissociation reaction is proposed to occur via a thermally-activated electron transfer involving a π*, σ* coupling mechanism.
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Chapter 1

Introduction

1.1 General

In today's industrial society, heterogeneous catalysis has a crucial place. The majority of industrial chemical reactions occur on the surface of catalysts. Heterogeneous catalysis is also widely employed in petroleum refining, and plays an increasingly important role in organic synthesis. Moreover, surface reactions are useful in bioregulation and, in particular, the control of air pollution [1].

Most heterogeneous catalysts are metals and metal oxides, and some of the common metal catalysts include Fe, Ni, Pt, Cu, Ag and Cr. The efficiency of the catalyst depends on the chemisorption of one or more of the reactants on the surface. Furthermore, the identification and the location of the surface species provide information which is essential to understand heterogeneous catalysis. However, the mechanisms of only a few heterogeneously catalyzed reactions are known.

All industrial catalytic reactions occur at high pressures which complicates the examination of the surface reactions due to gas phase collisions. Therefore, ultrahigh vacuum conditions are useful to insure that an actual surface property is measured by a specific technique. Consequently, a more fundamental understanding of the surface reaction
Several surface analysis techniques have been developed to provide information on the diverse properties of the surface-adsorbate system. The kinetics and mechanism on a molecular level can be determined by temperature programmed desorption (TPD) method (also known as thermal desorption spectroscopy, TDS) and temperature programmed reaction (TPR). In favourable cases, one can identify the rate-determining reactive intermediates and it gives a complete map of the reaction network. The use of quantitative mass spectrometry allows one to differentiate the rate of evolution of distinct products from the surface.

Many surface science experiments have focused on the dissociation of rather simple molecules adsorbed on a surface [2-3]. However, these studies have not explicitly addressed the question of possible intramolecular energy transfer for an adsorbed species. Thus the study of acetyl chloride and bromoacetyl chloride on a noble metal surface, like copper, may provide some insight into the fundamental mechanism of intramolecular electronic energy transfer.

In summary, this thesis focuses on the determination of the kinetics and mechanism involved in the decomposition of a complex molecule on a metal surface. The first part of this chapter introduces a brief review of the electron transfer process from a metal substrate to the adsorbed species. Subsequently, the literature of surface dissociative reactions induced by the photo-excitation of a substrate electron is presented. This review provides a comparison between the photo-induced dissociation reaction in the gas-phase and on the substrate. Then, a literature review about the adsorbate decomposition on the surface not involving photo-excited electrons is given, followed by a presentation of the aim of this study.

The second chapter is focused on the elements pertinent to the analysis of the temperature programmed desorption spectra. In addition, ultrahigh vacuum conditions are
discussed and the different components of the system are introduced. In the third chapter, the thermal desorption of iodomethane is presented, followed by a discussion of the results obtained from the temperature programmed desorption experiments for acetyl and bromoacetyl chloride adsorbed on a Cu(111) single-crystal surface. The last chapter comprises some concluding comments and suggested experiments for future research.

1.2 Review of Metal Surface Electron Transfer

In general, reactions can be regarded as an electron transfer process, where an exchange of electrons takes place between one orbital and another. One of the possible excitation states for the resulting excited molecule is a repulsive ion state which promotes a dissociative reaction, as illustrated in Figure 1-1 for a diatomic molecule. This type of excitation generally implicates electron capture by an antibonding orbital with respect to some bond by an electron from an external source. The electronic transitions from the ground state of the molecule to the repulsive ion state are ruled by the Franck-Condon principle, since the electronic transition in a molecule is so rapid that the nuclear separation can be considered to be unchanged, and consequently only vertical transitions can take place.

The potential energy interaction of a metal substrate and an adsorbate can be viewed by a potential curve just as displayed in Figure 1-1, with transfer from the metal of an electron from below the Fermi level. Since the potential energy curve of the repulsive state shown has no minimum, this excitation is followed by dissociation.

When a molecule is adsorbed on a metal surface, the energy for vertical electron transfer from the Fermi level of the adsorbate/metal surface to the adsorbed molecule in its equilibrium geometry involves two important contributions. Firstly, one has to consider the work function, $\phi$, for the adsorbate-covered surface, which is the energy required to place an electron from the Fermi level at infinity. The second contribution corresponds to the energy required to bind the electron to the physisorbed molecule,
Figure 1-1: Schematic potential curves for a diatomic molecule (AB) in an excited repulsive state.
which is estimated as the gas phase vertical electron attachment threshold, VEA. In addition, the energy for the electron transfer is lowered by the effects of image charge attraction and electronic polarization of the surrounding adsorbates, as presented in Figure 1-2. Moreover the chemisorption of a molecule on the metal substrate can lead to rehybridization, which induces bonding and antibonding shifts, as a result of the interactions between the adsorbate and the substrate orbitals. Thus the energy required for the electron transfer would also depend on the nature of the hybridization. However in this study, the possible orbital shifts due to chemisorption are not taken into account during the electron transfer process.

In extreme cases, electron transfer from the metal is exoenergetic even when the adsorbate is in its ground state, leading to electron harpooning, similar to the gas phase reactions of alkali atoms with halogen molecules or halides. Such a mechanism was proposed for the decomposition of bromomethane, CH₃Br, on potassium promoted Ag(111) at 100K [4]. In that system, the dissociation process was observed to be independent of the surface temperature, which suggests that the energy barrier is easily overcome even at 100 K. Hence the vertical electron transfer from the Fermi level of potassium-covered Ag(111) to CH₃Br is energetically favoured due to the small value of the surface work function, and the strong electron affinity of bromomethane.

1.3 Literature Review of Surface Photochemistry

Lately an increasing amount of study has been aimed towards the photochemistry of adsorbed molecules on metal surfaces [3]. These investigations have demonstrated that photo-irradiation of metal-adsorbate systems can lead to photodesorption, photodissociation and photoreaction; and this competes with the strong quenching of electronically excited state by substrate metals. In an early study on the photochemistry of ketene, CH₂CO, on Pt(111) by Roop et al. [5], it was demonstrated by temperature programmed desorption and secondary ion mass spectrometry that the photolysis of CH₂CO is compet-
Figure 1-2: Schematic diagram showing the energy for the electron transfer from the Fermi level of the adsorbate/metal determined by the work function of the surface, the vertical affinity, and also by the stabilization of charge on the surface by the substrate and adlayer polarization.
itive with quenching by the metal. In addition, it was speculated that photofragmentation leads to carbon-carbon bond dissociation to give adsorbed $\text{CH}_2$ and CO.

Two photo-induced mechanisms are proposed to account for the photodissociation process on metal surfaces. The first one implies the direct photoexcitation of an adsorbate to a repulsive electronically excited state. The second process is substrate excitation, involving charge transfer of the excited substrate electron to an anti-bonding orbital of the adsorbate via dissociative electron attachment, DEA, producing an unstable negative anion. Various techniques have been employed to elucidate the underlying mechanism and from the results obtained plausible conclusions about the mechanism were deduced.

From a series of experiments by White and co-workers using Hg-lamp sources on methyl halides ($\text{CH}_3\text{X}$; $\text{X}=$Br, I) and ethyl chloride on Ag(111) [6-8], it has been demonstrated that photo-induced dissociation is wavelength dependent. Different dissociation cross sections and different wavelength dependences have been found for physisorbed multilayers compared to chemisorbed monolayers, and they can be use to indicate the mechanism. For the direct excitation pathway, the wavelength dependence should be very similar to the one observed in the gas phase or condensed phase adsorbate. This direct excitation process is often detected in the case of multilayers since the initial excitation strictly occurs within the adsorbate and the substrate influence can be neglected. The small difference sometimes observed is due to stabilization by metal electrons of the electron-hole pair created in the adsorbate, leading to a red shift in threshold. The photolysis of chemisorbed monolayers are strongly red-shifted compared to the gas phase species and this effect is consistent of substrate mediated excitation process. In these situations, the photon energy thresholds were less than the energy of the work function of the metal substrate, implying electron tunneling or hopping. Therefore photon excited sub-vacuum level electrons formed in the substrate are particularly important to the indirect photofragmentation occurring in the first layer of adsorbate adjacent to the metal. From a molecular point of view, the closest comparison for an adsorbate-substrate
complex is an organometallic molecule. In many cases, the photolysis of organometallic species, which generally results in metal-ligand and intra-ligand bond dissociation, might be expected to correspond to the photodesorption and dissociation of adsorbates on surfaces. Hence, an alternative mechanism that could account for the photochemistry observed is a “localized” charge-transfer process due to the adsorption of photons by an adsorbate-substrate complex analogous to an organometallic molecule. However, such a mechanism depends on how similar the bonding interactions between the adsorbed molecules on metal surfaces are to organometallic complexes.

The previous studies mentioned make use of standard surface science techniques to monitor the photoproduct left at the surface. Another experimental approach used to investigate the photodissociation processes at the gas-metal interface is the characterization of the dynamics of photofragments escaping from the surface. Cowin and co-workers have studied the photofragmentation of CH$_3$Cl adsorbed on Ni(111) and resolved two photodesorption channels [9]. Time-of-flight (TOF) experiments of CH$_3$Cl following pulsed irradiation at 193 nm showed ejection of CH$_3$, Cl and CH$_3$Cl; and only CH$_3$ and CH$_3$Cl were ejected at 248 nm. Moreover, no photolysis took place at 351 nm. The TOF spectra of CH$_3$ fragments at 193 nm displayed two different arrival time peaks corresponding to fragment energies of 0.6 and 1.3 eV. The fast peak (higher translational energy) was assigned to dissociation resulting from direct excitation, since it remained at all coverages and the wavelength onset between 248 and 351 nm is as would be expected for unperturbed photodissociation in the gas phase. The 0.6 eV peak was ascribed to substrate photon absorption followed by dissociative electron attachment to the adsorbate. TOF spectra of CH$_3$ at 248 nm, where the gas phase cross section for dissociation is negligible, displayed only one peak which was very similar to the slow peak in the 193 nm TOF spectra. Thus this evidence suggested that the CH$_3$ fragment energy of 0.6 eV are produced by the same mechanism for both wavelengths. Furthermore electrons from the metal can escape the surface and travel through multilayers since the photon energies used exceed the work function of the surface. But the electron-driven processes
might only take place within the first few layers due to the limited mean free paths of the electrons in the adsorbate. A dynamical study of the photodissociation of CH$_3$I on Ag(111) at 248 nm performed by Jensen et al. also indicates that substrate mediated excitation is still an important contribution to the photofragmentation process up to the first five layers adjacent to the surface [10].

Recently a relation between photoelectron yields and bond dissociation rates was shown by White and co-workers for CH$_3$Cl on clean Pt(111) and C-covered Pt(111) [11]. For both systems the photoelectron yield and the photo-driven rate of C-Cl bond fission were measured as a function of the CH$_3$Cl coverage. No photolysis, in both cases, was observed with photons below 4.3 eV which is slightly lower than the work function. Consequently the substrate sub-vacuum level electrons do not lead to dissociation. In contrast, the use of an unfiltered Hg-arc, $\lambda > 230$ nm, induced the photofragmentation of CH$_3$Cl by attachment of photoelectrons, corresponding to photo-excited electrons with energy above the vacuum level. Since gas phase CH$_3$Cl does not absorb wavelengths above 230 nm, it is expected that no direct excitation occurs for multilayers and if this is the case, the observed photodissociation should correlate with the photoelectron yield. The results obtained were described in a satisfactory manner by a simple kinetic model assuming a photoelectron-induced fragmentation path and a first-order rate equation in both the concentrations of CH$_3$Cl and photoelectrons for clean and C-covered Pt(111) over a wide adsorbate coverage. Hence, in this particular case photoelectrons play an important role in the photolysis of multilayers of CH$_3$Cl on the surface.

Another series of studies conducted by White and co-workers focused on the photochemistry of phosgene, Cl$_2$CO, on Ag(111), Pt(111) and Pd(111) [12-15]. The adsorption of Cl$_2$CO on the three surfaces at about 100 K is molecular and no detectable thermal decomposition is observed during temperature programmed desorption experiments. On Pt(111), Ag(111) and Pd(111), the photodissociation in the monolayer regime, happens with higher cross section and lower photon energy thresholds than in the gas phase. The
dissociation products are Cl and CO for all three surfaces. It has been demonstrated that all the Cl is retained on all surfaces, while only a small fraction of CO is retained on Pt(111) and none on Ag(111) and Pd(111). The threshold for the photolysis of phosgene on Ag(111) was found to be 2.6 eV for the first monolayer and the red shift was qualitatively explained by a sub-vacuum electron model. A study of the evolution of CO during the photolysis of phosgene was also performed on Ag(111) and allowed calculation of the initial cross section and the photodissociation rate. The resulting value of the cross section exceeds the gas phase optical absorption cross section and is in the range of $10^{-18} - 10^{-19}$ cm$^2$. In addition, the cross section was shown to depend on the wavelength.

In another set of experiments, Ukraintsev et al. studied the role of the local work function in surface electron attachment processes for the photofragmentation of CH$_3$Br on Xe covered-Pt(111), by using a 4.03 eV photon energy [16]. The local work function of a surface contrasted to its macroscopic value, evaluated far from the surface, is of primary importance in the photodissociation of an adsorbate induced by substrate excitation; since it directs the energetic positioning between adsorbate and substrate electronic states. Time-of-flight experiments were used to monitor the photo-induced fragmentation of CH$_3$Br adsorbed on Xe multilayers deposited on CH$_3$Br covered Pt(111). The dissociative electron attachment, DEA, of the topmost layer reflects the evolution of the local work function towards its macroscopic value as a function of the thickness of the Xe layer. The energy of the photo-excited substrate electrons is limited by the conduction band of the Xe layer and the energy resulting from the irradiation with 4.03 eV photons. Therefore the photo-excited electrons arriving at the topmost layer of CH$_3$Br have energies between -0.5 and $h\nu - \phi = -0.27$ eV with respect to the vacuum level, with $\phi$ equal to 4.3 eV for the macroscopic work function of a monolayer of CH$_3$Br on Pt(111). The energy for DEA of a CH$_3$Br molecule located in the topmost layer was calculated using a Born-Haber cycle. This energetic cycle takes into consideration the energy required to attach a substrate derived photoelectron to CH$_3$Br as being the vertical electron affinity, VEA, in the gas phase. The Born-Haber cycle also examines the factors affecting the
adsorption on the surface of the transient anion, CH$_3$Br$^-$, like stabilization by electronic polarization of surrounding adsorbate, the image charge attraction by the substrate and the stabilization by the physisorptive forces resembling those of the neutral molecule. The DEA energy for CH$_3$Br in the topmost layer, where image charge attraction is negligible, was found to be in resonance with electrons at the bottom of the Xe multilayer.

It was also observed that the monolayer of CH$_3$Br on Pt(111) preceding the deposition of the overlayers controls the photo-excited substrate electrons travelling through the Xe conduction band. If the CH$_3$Br coverage adsorbed directly on the Pt(111) surface is not completed, then island formation leads to a two dimensional variation of the local work function on the surface. The in-plane fluctuations of the local work function decrease as the distance $z$, away from the surface and at which the local work function is evaluated, is increased until its macroscopic value is reached. Hence this investigation of the three dimensional variation of the local work function has provided a quantitative indication for the observed dissociation dynamics for the CH$_3$Br/Xe/CH$_3$Br/Pt(111) system.

Lamont et al. examined the photodissociation of CH$_3$Br on Cu(111) and they observed that their results agreed with a charge transfer mechanism with a threshold energy of about 2.6 eV [17]. Also by increasing the work function of the substrate with various pre-adsorbed bromine coverage, they found that the onset for the reaction shifted to higher energy accordingly. Therefore the work function of the surface limits the energy of the sub-vacuum level photo-excited electrons which can tunnel into an anti-bonding orbital of the adsorbate by resonance.

In summary, researchers have shown by the use of various techniques that the photo-induced fragmentation of the intra-adsorbate bonds at the adsorbate/metal interface frequently competes efficiently with substrate quenching. Most studies examined the photodissociation of rather simple molecules, like methyl halides on several surfaces, which involve the formation of a transient excited species and the subsequent carbon-halogen bond cleavage. The fragmentation proceeding through substrate mediated excitation
pathway has been demonstrated for various systems and plays a particularly important role for the first few monolayers of the adsorbate adjacent to the metal surface. The direct excitation pathway should also be considered, especially in multilayers where this dissociation mechanism is very effective. Since the wavelength, the adsorbate and the metal substrate used during experiments influence the choice of the excitation pathway, it is of interest to distinguish their effects to determine the dynamics of these systems and more commonly, to further one's understanding of the adsorbate-surface interactions.

1.4 Literature Review of Surface Thermal Reactions

In recent studies of thermal reactions, using conventional temperature programmed desorption, the decomposition of iodomethane, CH$_3$I, was investigated by Bent and co-workers [18-20]. On a Cu(110) surface, they observed that methyl groups are formed by dissociative adsorption of CH$_3$I at temperatures above 180 K and are thermally stable up to 400 K [18]. Above this temperature two reaction pathways occur depending on the surface methyl coverage. At very low coverages, methyl group disproportionate to yield methane and ethylene and it was determined that the reaction follows first-order kinetics. At higher coverages methyl groups couple to produce ethane and the reaction seemed to be consistent with second-order kinetics. The bond enthalpy for Cu(110)-CH$_3$ has also been determined to be 33 ± 8 kcal/mol. In subsequent experiments conducted on Cu(111), the evolution of methyl radicals during the thermal decomposition of submonolayers of CH$_3$I was observed at two different temperatures, 140 and 470 K [19-20]. The low temperature pathway was assigned to carbon-iodine bond scission in iodomethane, whereas, the mechanism at 470 K can be regarded as the Cu-CH$_3$ bond homolysis of chemisorbed methyl groups generated during the decomposition of the parent molecule. This temperature is equivalent to a Cu-CH$_3$ bond energy of around 29 kcal/mol, which is in good agreement with the value of 26 kcal/mol obtained from the bond-order-conservation model [21].
The mechanism occurring at 140 K is deduced to be possible given the reaction thermodynamics. From organometallic chemistry [22], the reduction of alkyl halides by metal complexes can be described by two mechanistic possibilities which are

**Atom Transfer**  
\[ R - X + M^n \rightarrow [R* + XM^{(n+1)}] \rightarrow R - M^{(n+2)} - X \]

**Electron Transfer**  
\[ R - X + M^n \rightarrow [R - X^* + M^{(n+1)}] \rightarrow R - M^{(n+2)} - X \]

The atom transfer mechanism involves the formation of radicals via the transfer of the halogen from the alkyl group to the metal. In the case of CH$_3$I on Cu(111), one can intuitively presume that the C-I bond scission is balanced by the formation of a Cu-I bond of similar strength. On the other hand, in an electron transfer process, the halogen remains bound to the carbon during the rate-limiting step and the subsequent radical formation is the result of fragmentation of the radical-anion. Since adsorbed iodine atoms on copper are ionic to some degree, it is suggested that the electron transfer from the metal to the iodine takes place at some point during the iodine atom transfer, for the evolution of methyl radicals at a low temperature from CH$_3$I/Cu(111).

The energetics for electron transfer as a function of thermal excitation of the C-I bond were examined by using a thermochemical cycle, similar to the one developed by Ukraintsev and co-workers [16,23]. From this cycle, the energy, $E_D$, required for dissociative electron transfer was derived and is given by

\[ E_D = \phi - VEA[CH_3I(g)] - E_im - E_{pol} \]  

(1.1)

where $\phi$ is the work function of the adsorbate-covered surface, $VEA[CH_3I(g)]$ is the vertical electron affinity in the gas phase CH$_3$I, $E_im$ is the image charge attraction and $E_{pol}$ is the electronic polarization of the surrounding adsorbates. The resulting value of 3.1 eV ($\sim$ 72 kcal/mol) was estimated and is actually much larger than the measured activation energy of 8.5 kcal/mol for the C-I bond dissociation. However, several effects...
Figure 1-3: Potential energy curves for the Cu(111)/iodomethane and Cu(111)/anion systems as a function of C-I internuclear separation, from Lin and Bent [20].
can lower this energy barrier, especially the stretching of the C-I bond. This peculiar effect is illustrated quantitatively in Figure 1-3, by plotting the energy for the adsorbed CH$_3$I and CH$_3$I$^-$ systems as a function of the C-I internuclear separation, as described by Lin and Bent [20]. The potential energy curves are harmonic potentials, with the gas phase C-I bond energy (2.4 eV) defining the CH$_3$I/Cu curve; whereas the CH$_3$I$^-$/Cu curve is described by the vertical electron transfer energy (3.1 eV) and the enthalpy of change of the reaction ($\leq$ 0.17 eV). The C-I bond separation for the formation of Cu-I and methyl radicals is assumed to be 1.6 Å, based on known ionic and copper Van der Waals radii.

At the point where the CH$_3$I/Cu and CH$_3$I$^-$/Cu curves intersect in Figure 1-3, electron transfer is thermoneutral for the vibrationally-excited iodomethane. This configuration requires a thermal energy of 0.7 eV. The experimental value of 0.37 eV is less than that estimated but the difference can be ascribed to the approximations used in the model. For instance, the iodine bonding to the metal, which would lower the crossing point, is not considered while establishing the neutral CH$_3$I/Cu curve. Thus thermally activated dissociative electron transfer is a plausible mechanism for the evolution of methyl radical at 140 K.

The surface studies of the photolysis and the thermal decomposition of rather simple adsorbates on a metal surface have shown that electron transfer from the substrate to the adsorbate plays an important role in the fragmentation process. In particular, this mechanism was shown to be important for submonolayers of alkyl halides on copper surfaces, although the influence of several variables are not completely understood. In the case of submonolayers of more complex molecules adsorbed on metal surface, one could suppose that the excitation pathway leading to dissociation involve the attachment of metal electrons to the adsorbate and possible intra-adsorbate electron transfer.
1.5 Objectives of This Research

The incentive for the work presented in this thesis is driven in part by the concern posed by the release of chlorinated compounds into the environment and the potential health hazards [1]. Thus, it is of interest to study the reactions occurring on metal surfaces, since the metal can act as a catalyst for the degradation of halogenated hydrocarbons. In addition, the hydrocarbon produced during the decomposition of the halogenated compound on the metal may be studied as a transient intermediate common to other surface processes. Previous studies of halogenated compounds on copper surfaces have mostly been focused on mono- and multi-halogenated alkanes [32,36], and a few investigations for carbonyl compounds, such as acetone, formaldehyde and acetaldehyde on single Cu(110) crystal were also performed [24]. This work examines, for the first time, the surface reactions of acetyl chloride and bromoacetyl chloride on a Cu(111) surface.

This first objective of this study is to determine if a thermal reaction occurs after depositing the adsorbate on the metal substrate at 100 K. Thermal desorption spectroscopy is employed to distinguish between the molecular desorption and the thermal dissociation process in the monolayer regime.

In the case of thermal decomposition of the species on the surface, the evolution of possible products is monitored by temperature-programmed reaction. From the information obtained, the reaction pathways can be deduced, and in turn the bond cleaved during the decomposition process can be established. Moreover, the determination of the energy barrier for the surface reactions is also possible.

Once the bond through which the dissociation occurs is assigned, the dissociation temperature is established by the chemical displacement technique. By assuming first-order reaction kinetics, the activation energy for the bond dissociation can be calculated and the results obtained provide some insight into the possible reaction mechanism.
Chapter 2

Experimental Section

All surface science experiments were conducted in a turbomolecular and ion pump ultra-high vacuum chamber, shown in Figure 2-1 with a base pressure of $6 \times 10^{-10}$ torr. The principal components of the system include a single-pass cylindrical mirror analyzer for the Auger electron spectrometer (AES), a quadrupole mass spectrometer (QMS) which is placed in a differentially pumped shield, a 5-degrees of movement manipulator with sample holding and heating, and a closed-cycle helium refrigerator is used to cool the sample via a copper braid. The chamber also contains an ion sputtering gun for sample cleaning and two sapphire leak valves for gas dosing. Further discussion of the vacuum chamber, its main components and sample handling are presented first, and later the procedure for the experiments and the data analysis are considered.

2.1 Ultrahigh Vacuum System

While performing experiments on a well-characterized solid surface, it is important to maintain a surrounding vacuum for two main reasons. Firstly, the characterization of the surface at the atomic level is an important restricting factor imposed on the vacuum. Since the technique sensitivities range from $10^{-1}$ to $10^{-5}$ atom layers, it is evident that surface contamination poses a serious problem. In most situations, the main cause of
Figure 2-1: Schematic diagram of the UHV chamber.
contamination is due to the residual gas present in the vacuum chamber. Even in small quantities, it can influence the outcome of the experiment or the analysis of the results. Therefore to prevent the interference from the surrounding gas and to preserve the composition of the surface during an experiment, a base pressure in the ultrahigh vacuum (UHV) about $10^{-10}$ torr is essential. Secondly, several surface analytical techniques use ions or electrons to probe a particular surface property. These probing particles require a long mean free path, \( \lambda \), to ensure that they can reach the analyzer before colliding with gas molecules. By applying the kinetic theory of gases, the mean free path, \( \lambda \), of a pure gas at a certain pressure is given by

\[
\lambda = \frac{RT}{\sqrt{2\pi \sigma^2 PN_A}}
\]

where \( R \) is the gas phase constant, \( T \) is the gas temperature, \( \sigma \) is the collision diameter of the molecule, \( P \) is the pressure and \( N_A \) is the Avogadro constant. By assuming that the only gas present in the system is nitrogen at $6 \times 10^{-10}$ torr and 298 K, one obtains a mean free path of approximately 80 km. Since \( \lambda \) is much larger than the dimensions of the chamber, the gas molecules collide far more often with the chamber walls than with one another or the probing particles.

During a surface science experiment, an adsorbed monolayer of molecules is obtained by exposing the surface to the species, at a given ambient pressure, for a certain lapse of time that can be determined. From the kinetic theory of gases, one can establish a relationship between the flux of incident molecules colliding with the surface in unit of area per second and the ambient pressure as

\[
F(\text{molecules/cm}^2/\text{sec}) = \frac{PN_A}{\sqrt{2\pi MR}}
\]

where \( P \) is the ambient pressure, \( T \) is the gas temperature, \( M \) is the molecular mass of the adsorbate and \( R \) is the gas constant. By using \( M = 28 \text{ g/mol} \) for nitrogen gas at 298 K and a pressure of $1 \times 10^{-8}$ torr, one obtains a flux, \( F \), of $\gtrsim 10^{14}$ molecules/cm$^2$/sec.
Hence at this pressure, $\geq 10^{14}$ molecules are adsorbed on the surface in one second, if a sticking coefficient of unity is assumed. The sticking process involves loss of energy from the molecule when it collides with the surface and as a result the molecule remains on the substrate. Since $10^{14}$-$10^{15}$ molecules/cm$^2$ corresponds to one layer, the unit of gas exposure conveniently used is $10^{-6}$ torr-sec and is called the Langmuir. At higher pressures, the surface may be covered in less than a second since the exposures are greater than 1 Langmuir. At pressures below $10^{-8}$ torr, $10^2$ to $10^3$ seconds may elapse before the surface is completely covered. Thus UHV conditions are necessary to obtain and maintain a clean surface.

The UHV chamber is constructed from stainless steel which is widely used, since it is a strong material, bakeable at elevated temperatures due to its low vapour pressure and not readily oxidized. The UHV seals between components of the system consist of a soft copper gasket compressed between a pair of flanges with knife edges. In order to obtain a UHV environment from atmospheric pressure, the following pumping sequence is used:

(i). Firstly, the chamber is pumped down to 600 torr by an oil-free diaphragm pump connected to the vent valve.

(ii). The rough pumping is then completed by a mechanical pump which is connected in series with the turbomolecular pump. The two-stage vane pump (Alcatel 2010) which is employed, has a base pressure of $10^{-3}$ torr.

(iii). Once a pressure in the range of $10^{-3}$ torr is reached, the turbomolecular pump (Varian Turbo-V 250) is started to achieve a pressure of $10^{-7}$ torr in an hour. The pumping action is produced by rotating the turbine at 56,000 rpm within the slotted stator. The edge speed of the rotor is comparable to molecular velocities. Therefore a molecule receives a significant component of the velocity in the direction of the pump exhaust, when it is hit by one of the rotor blade. A comparison of the pumping speed of nitrogen and hydrogen gas, which are 250 and 200 litres/sec, respectively, shows that H$_2$ remains in the chamber for a longer period of time than N$_2$. Although the pumping speed
is almost the same for all gases; the compression ratio, defined by the ratio of outlet to inlet pressure, is related to the nature of the gases being removed. Since the logarithm of the compression ratio is approximately proportional to the square root of the molecular weight of the gas, the compression ratio for oil vapours backstreaming from the pump bearings or from the pump exhaust is very high. Consequently the turbomolecular pump provides an oil-free vacuum.

(iv). The pressure is then reduced in the range of $10^{-8}$ torr in half an hour, by opening the gate valve that isolates the main ion pump (Thermionics IP200) from the chamber. This pump operates by sustaining a discharge, confined in an intensified magnetic field, between a cylindrical-cell anode made of stainless steel and a titanium cathode. When a potential of 5 kV is placed across the electrodes, the discharge is produced by field emission. The molecules are pumped out of the system by two mechanisms. Firstly, the gas molecule is ionized in the discharge and then it is accelerated into the cathode with enough kinetic energy to be permanently imbedded. In addition, titanium sputtered off the cathode due to ion bombardment, deposits on the anode to produce a clean surface that reacts with active gases through chemisorption. The speed of the ion pump is 200 litres/sec and it can be used as a pressure gauge, since the positive-ion current drawn by the pump is directly proportional to the pressure.

(v). To obtain a pressure much below $10^{-8}$ torr, it is necessary to bakeout the system and its components in order to remove water and hydrocarbons, which are outgassed slowly from the walls. This procedure accelerates the rate of desorption at which the gas molecules leave the internal surfaces. Therefore a decrease in the surface coverage is achieved and after cooling the chamber to room temperature, the rate of desorption is significantly lowered. The bakeout is set for 20 hours at a temperature of 150°C. In addition, the bakeout is assisted by the use of a Phototron lamp installed in the UHV system. Once the bakeout is completed, the filaments of the components are degassed for 2 hours and the heater band of the turbomolecular pump is turned on for an hour.
The pressure of the system is monitored by an ion gauge (K.J.Lesker IG-4400) after turning on the turbo pump for half an hour. The ion gauge works on the principle of ionizing a fraction of the gas molecules by electron impact and collecting the resulting positive ions. These ions produce an electrical current flow to the ion collector circuit. The magnitude of this current is a function of pressure.

2.2 Principal Components of the Chamber

2.2.1 Auger Electron Spectroscopy

The Auger electron emission occurs when a core hole is created by ionizing an atom with an electron beam of sufficient energy and the subsequent filling of this core hole gives rise to the ejection of an Auger electron. Since the kinetic energy of the Auger electron is a fundamental function of the atomic energy levels involved, a direct elemental identification is obtained by measuring the Auger energies from the surface. The detection of low kinetic energy Auger electrons of short mean-free path outside the surface provides a sensitive probe for chemical composition.

The Auger electron spectrometer (Omicron/CMA 100) is equipped with a single-pass retractable cylindrical mirror analyzer (CMA), which corresponds to a band-pass filter and thus can only collect electrons close to a certain energy. However, the single-pass CMA is very effective due to its very high transmission, considering that the primary electron beam is highly focused and irradiates an area (less than 25 μm) much smaller than the acceptance area of the analyzer. Thus the CMA gives a high sensitivity at moderate energy resolution and has a high signal to noise ratio. The sensitivity of the Auger electron spectroscopy is about 1 percent of the monolayer and strong inelastic scattering makes AES surface sensitive for kinetic energies of more than a few eV, and with the exception of hydrogen and helium, all elements are detectable. One of the most important application of AES is qualitative analysis which allows one to test the chemical
cleanliness of the sample before beginning a fundamental surface science study. No AES spectra are presented in this work since the primary use of the AES, in our system, was to verify the surface cleanliness which was routinely achieved after the cleaning procedure described in Section 2.4.

2.2.2 Quadrupole Mass Spectrometry

The quadrupole device is a dynamic mass analyzer where a set of time dependent forces influences the ion trajectories. The analyzer, also known as mass filter, is composed of a parallel array of four round cylindrical rods mounted in a square configuration. Opposite pairs are coupled together, and an electric field within the mass spectrometer is produced by applying radiofrequency and direct current potentials between the pairs.

Electrons emitted from an iridium filament are used to ionize gas molecules in the ionizing volume. The ionizing electrons are accelerated to the ionizing volume by the potential produced by the electron energy supply. This potential is called the electron energy and is nominally the energy of the ionizing electrons within the ionizing volume. During normal operation the electron energy is set at some standard value, since the ionizing efficiency of the bombarding electrons is a function of the electron energy.

Ions are removed from the ion region and directed into the focusing lens system by the field produced by the extractor. In principle, the extraction of positive ions into the mass filter is achieved with a negative extractor potential with respect to the ion region. However, it is often observed that a positive extractor potential with respect to the system ion region gives good signals. The use of a positive extractor potential is necessary to partially cancel the presence of strong fields which direct ions out of the ion region. The lens system focuses the ions into the mass analyzer for the system greatest sensitivity and resolution.

The ideal mass spectrometer is composed of four parallel electrodes having hyperbolic cross-sections. A potential \( \phi(t) = U + V \cos(2\pi ft) \), where \( U \) is a dc voltage and \( V \)
is the peak amplitude of a radiofrequency $f$ is applied to adjacent electrodes, while opposite electrodes are electrically connected, as illustrated in Figure 2-2(b). Under these circumstances, the equipotential surfaces are symmetric hyperbolic cylinders and the potential along the z axis is zero. In practice, round cylindrical rods are generally employed to approximate the potential generated by hyperbolic rods.

Ions are injected into the mass filter with a certain velocity along the $z$ direction, and transverse motion is induced by the rf and dc fields perpendicular to the $z$ axis. For the $x$ direction, the trajectory of light ions is easily influence by the rf potential and becomes unstable whenever the rf component is greater than the dc component. Thus only high masses would reach the exit aperture of the quadrupole without colliding with the $x$ electrodes. For this reason, the $x$ direction can be defined as a high-pass mass filter. At the same time, in the $y$ direction, heavy ions trajectories are diverged from the $z$ axis as a result of the dc voltage. However, the lighter ions are stabilized by the rf potential when its amplitude and frequency are such as to “rectify” the ion trajectory. Hence the $y$ direction corresponds to a low-pass mass filter. The combined effect of both directions provides a mass analyzer with a certain pass-band. Mass scanning is accomplished by varying the amplitude of $V$ and $U$, while keeping the ratio between them constant. This constant $U/V$ ratio allows ions of different $m/z$ ratios to pass between the electrodes and reach the detector [25].

The ion beam emerging from the exit aperture of the quadrupole is detected by an electron multiplier. Direct photon and metastable pick up from a line of sight connection to the ion source are a potential problem. Random and untunable background noise could result if these particles strike the first dynode. This difficulty is overcome by placing the multiplier in an offset position parallel to the line of exit of ions from the mass filter, as shown in Figure 2-2(a). The positive ions exiting the quadrupole analyzer are focused into the first dynode, which is maintained at a voltage of $-2000$ volts, through the entrance apertures of two earthed shielding plates. The multiplier and mass filter enclosures are
Figure 2-2: Schematic diagrams for (a) the arrangement of the quadrupole mass spectrometer with the electron multiplier fitted in an offset position, and (b) the electrode structure required to generate the potential.
also at ground potential. Hence neutrals, metastables and photons do not strike the first
dynode and pass out of the multiplier enclosure through a smaller exit aperture. The
multiplied ion signal appears at the collection dynode which is held at ground potential
for positive ion collection.

It is often necessary to limit the angle of acceptance into the mass spectrometer,
especially for temperature programmed desorption experiments. Such a restriction can
be realized by positioning the centre of the sample at a short distance from the aperture at
the end of a drift tube connected to the mass analyzer. Two skimmers of 4 mm of diameter
can be used to remove signal originating from other parts of the system to obtain optimum
background suppression. The shielded mass spectrometer is differentially pumped by
two 20 litres/sec ion pumps. Hence the specimen and the mass spectrometer can only
communicate via the aperture. If the intensity of the signal is weak, the restricted
angle of acceptance provided by the two skimmers may diminish the collected signal
intensity below detection levels. The presence of the second skimmer may restrict the
number of ions, which have passed through the first skimmer, from reaching the analyzer
and reactive species may react with the wall of the drift tube before they are detected.
Consequently, the data obtained for the TPD spectra of acetyl and bromoacetyl chloride
were collected by using only one skimmer of 4 mm of diameter, positioned at the end of
the drift tube.

Figure 2-3 represents a schematic diagram of the selectivity and efficiency of the
shielded mass spectrometer, which has an ionizer aperture of 3 mm of diameter. The
efficiency of this setup is obtained by calculating the ratio of the solid angle of a cone
as indicated in Figure 2-3(a) to that of the hemisphere, which is given by \((1 - \cos \theta)\).
The value for the efficiency is approximately \(5 \times 10^{-5}\) which indicates a low sensitivity,
assuming an isotropic distribution, but it is highly selective for angle-resolved measure-
ments. The collection area at the sample distance is four times smaller than the area
of the sample which implies that the mass spectrometer should only detect the species
Figure 2-3: Schematic diagrams representing the ionizer and the two skimmers apertures with the sample for (a) the efficiency and (b) the selectivity of the mass filter.
desorbing from the centre of the sample, if the latter is in the line-of-sight of the analyzer.

2.2.3 Closed-cycle Helium Cryostat

In surface science applications, the sample is often cooled to temperatures approaching 100 K to allow the intact adsorption of species on the surface, which do not adsorb, or otherwise decompose at higher temperatures. The cooling system is a two-stage cryogenic refrigerator which uses helium gas to obtain cold temperatures (APD Cryogenics). The cooling of the sample is achieved via a copper braid connected to the refrigerator head, with a pumping power of two Watts at a temperature of 20 K.

2.2.4 Ion Sputtering Gun

Since a clean surface is essential in surface science analysis, techniques have been devised to accomplish this in situ cleaning. One of these methods uses ion bombardment to remove several atomic layers of a surface. This can be achieved by an ion gun (Physical Electronics PHI 04-161) which produces a beam of energetic inert gas ions to sputter etch solid surfaces.

The ion sputtering gun is designed to produce ions within the ionization chamber by accelerating electrons from a hot tungsten filament into the anode region using a bias of 180 V. The ions are directed toward the open end of the chamber and focused by a lens system to create a beam of variable size at the target surface which is grounded. The energy of the ions incident on the sample surface is equal to the positive potential applied to the anode. The filament current usually required is 2.5 A and the electron emission current should not exceed 30 mA during use. Also the potential applied to the focusing electrode determines the beam size of the surface.

This technique is effective in the removal of impurities but it is often necessary to anneal out the damage caused by ion bombardment. Once a cleaned surface has been
prepared, it is then possible to study the reaction between reacting species and the surface without having to take into account surface contamination.

### 2.3 Sample Handling

#### 2.3.1 Manipulator

In surface studies, the crystal sample is usually the subject of an extended investigation. Thus precise positioning of the crystal is essential for either analytical techniques or for cleaning treatment of the surface. This is achieved here by mounting the sample on a manipulator composed of a UHV specimen translator (Fisons OMNIAX 100), a rotary drive (Fisons RD2) and a specimen holder (Fisons SH2). The manipulator is mounted vertically below the UHV chamber and it is equipped with vacuum feedthroughs for the thermocouple and the electrical power to resistively heat the sample.

Two rotational motions can be achieved with the present manipulator. The axial rotation is obtained by rotating the shaft about its axis; while the azimuthal rotation can be accomplished via a push rod, placed in the centre of the shaft, setting a precision mechanism in motion. The axial and azimuthal rotations are limited to $\pm 180^\circ$ and $\pm 108^\circ$, respectively. Three translational degrees of movement enable accurate positioning of the sample. The head of the manipulator is driven in the x and y directions by the x-y stage which is parallel to the flange it is mounted on, and a perpendicular motion to the latter is provided by the z stage connected to the x-y stage. A stainless steel bellows allows a flexible vacuum seal between the chamber and the x-y-z translational stages. The distance travelled in the x and y directions is determined by the diameter of the bellows while its length limits the z translational motion. The travel limits for the x, y and z translations are $\pm 12.5$, $\pm 12.5$ and 100 mm, respectively. Hence these five degrees of movement permit the sample to be accessible to the different analytical facilities and
to perform angle dependent measurements.

2.3.2 Sample Holder Assembly

In the course of a surface science experiment, it is frequently useful to cool the sample below room temperature to achieve adsorption of the species on the substrate and to trap the possible reaction intermediates. In addition, sample heating to temperatures above 1000 K is also required during the cleaning or the thermal desorption techniques. Consequently a relatively simple and economical sample holder, shown in Figure 2-4, was devised and constructed to provide effective and rapid cooling and heating of the sample.

The design of the sample holder includes the use of a single crystal sample that is a 10 mm diameter, 2 mm thick disc. It is mounted on a molybdenum resistive button heater (Spectra-Mat) by using a 0.010 inch diameter chromel wire, as illustrated in Figure 2-5. This is accomplished by looping the wire around the stem of the heater and twisting it to the length of about 35 mm. The crystal is first held in place by wrapping the two threads of chromel around the grooves edges of the crystal. Next it is maintained securely against the base of the button heater by twisting the ends of the wire tightly around the stem of the heater. The button heater is then inserted into a narrow opening in a (1.5 \times 1.0 \times 1.0 \text{ cm}^3) OFHC (oxygen-free high conductivity) copper mounting block. The copper block is fastened to a mounting stainless steel plate through a 4-40 bolt and four insulating sapphire beads (1 mm in diameter). The bolt is insulated from the stainless steel plate by a ceramic spacer. Thus this mounting block is thermally and electrically isolated from the other mounting parts. Furthermore the mounting plate can be removed without disturbing the sample fit to it.

The limits imposed to obtained efficient cooling and heating of the sample were taken in consideration while designing the sample holder. The cooling of the crystal is achieved by connecting the closed-cycle helium cryostat to the copper block via a thick, flexible copper braid, which is electrically, but not thermally, insulated from the cryostat by a
Figure 2-4: Schematic diagram of the sample holder assembly.
sapphire disc. The copper braid is placed between the Cu block and the mounting plate. This arrangement enables the heat to be drawn from the sample to the cryostat through the high thermal conductance of the copper braid. Thus it is possible to cool the crystal from 1000 K to 90 K in half an hour, since the Cu block, button heater and sample are in close contact with each other and sapphire beads isolated them from the rest of the mounting components. This rapid cooling action is necessary to prevent the adsorption of a critical amount of residual gases onto the crystal surface during the time required to reach a temperature of 90 K.

The assembly devised to provide efficient heating of the crystal surface is as follows: one of two copper lugs is tightened down against the Cu block with a small bolt. The other lug is fastened by a 2-56 bolt, which is electrically insulated from the mounting block by two ceramic spacers placed on either side of the block. The bolt hole is also large enough so that the bolt never touches the Cu block. However the copper lug is trapped between two stainless steel washers and is in immediate electrical contact with the 3% Re/W wire set into the button heater. The two copper lugs are connected to the electrical power leads attached to the vacuum feedthrough on the manipulator. Thus the sample can be heated to temperatures over 1200 K through thermal conductance of the heat produced by applying a current across the molybdenum heater. The temperature of the surface is controlled by a DC power supply, which is coupled to an independent temperature controller (Eurotherm 818P4) with temperature feedback. The temperature controller is also equipped with a programmable Proportional-Integral-Differential (PID) circuit, which allows the generation of a constant temperature ramp. The thermocouple used to monitor the surface temperature supplies the necessary voltage for feedback control. Consequently the sample can be heated at a reproducible rate or maintained to a certain temperature for an extended period of time.

The temperature of the crystal is measured by using chromel-alumel thermocouple junctions inserted into 0.7 mm diameter and 2 mm deep hole drilled in the side of the
(1) Loop a chromel wire around the stem of the button heater and twist the wire to a length of about 35mm.

(2) Wrap the crystal with this wire assembly and make sure that the hole for the thermocouple is facing the point where the wires are connected.

(3) The crystal is attached to the button heater by wrapping the loose ends of the wire around the thick contact of the button heater making sure that the thin contact is bent in the direction opposite to the thermocouple hole in the side of the crystal. Tighten the wire assembly using pliers.

Figure 2-5: Steps to mount the crystal sample on the button heater.
sample. The choice of this thermocouple is directed by its melting temperature, the temperature range to be monitored and its non-reactivity with the crystal.

The copper block can be quickly disassembled to permit a change of the crystal/heater unit. In addition, the mounting block is shielded by a tantalum sheet which is level with the surface crystal. The sheet is spotwelded to the stainless steel mounting plate and it also covers the sides of the block. Therefore signal at the quadrupole mass spectrometer due to the desorption of species from the Cu block is repressed. The grounding of the crystal is achieved by linking one of the electrical feedthrough of the manipulator to ground.

2.3.3 Sample Preparation

Once the sample is introduced in the vacuum system, it may need some treatments before any measurements are performed. In particular, cleaning is required since the surface contamination may prevent or change the outcome of an experiment. In this research, the procedure used to achieve the in situ removal of impurities is a combination of heat and ion bombardment. The advantages of this method are that heating enables the desorption of adsorbed species, while ion sputtering eliminates the possible surface impurities segregated from the bulk by heating. Hence oxygen, carbon and sulfur which are the primary impurities, are removed. The damages produced by the sputter etching are annealed out by heating the sample at a higher temperature than the one used during the ion bombardment. Consequently the surface is cleaned to a level compatible with the contamination constraints placed on the vacuum chamber. Although the surface orientation was not verified by low-energy electron diffraction (LEED) optics, literature techniques using a similar experimental protocol have demonstrated that surface cleanliness and orientation were usually achieved after such a treatment [18,49].
2.3.4 Gas Handling Manifold and Backfilling of the Chamber

Surface science studies typically involve the analysis of changes in the properties of the surface as a result of the reaction between the sample surface and gases or vapours. The reacting species are directed in a controlled manner into the UHV system, and the gases or vapours can be admitted singly, sequentially or as a mixture. The gas admission device consists of gas cylinders or glass ampules, fitted with glass-to-kovar seals, attached via a demountable joint and a control valve to the stainless steel manifold. A vacuum in the range of $10^{-3}$ torr can be achieved in the manifold by a two-stage mechanical oil pump and the pressure is monitored by a thermocouple gauge. The manifold is connected to a high quality sapphire leak valve (Varian 951-5106) which enables the gas to enter the chamber. For safety reasons, an additional control valve is required when the pressure in the manifold reaches atmospheric pressure or above during gas mixing. The manifold was baked under vacuum at a temperature of 70°C for 36 hours to desorb water and other impurities. The liquid samples used are transferred to glass ampules and purified by several freeze-pump-thaw cycles under vacuum. The purity of each compound is verified in situ by the mass spectrometer.

It is important to control and measure the amount of gas that is admitted in the chamber during an experiment. Hence a certain ambient partial pressure of gas for a specified period of time is allowed by backfilling of the chamber via a precision leak valve. All exposures are measured in Langmuirs (L) where $1 \times 10^{-6}$ torr-sec is equal to 1 Langmuir. While we measure the relative amount of each gas precisely, the absolute dosage is not known accurately as this depends upon the molecule specific correction factors to the ion gauge sensitivity.

2.4 Experimental Procedure

The UHV system described previously is equipped to perform temperature programmed desorption (TPD) and laser induced photodissociation experiments. The work presented
in the thesis is exclusively centered on results obtained from TPD measurements.

The Cu(111) crystal (Monocrystals Inc., 99.999%) is cleaned, with the ion pump isolated from the system, by ion bombardment using $5 \times 10^{-5}$ torr of Argon, a beam voltage of 1.5 kV and an electron emission current of 23 mA for 30 min at a temperature of 850 K. This process is followed by annealing in UHV at 950 K for 10 min. The surface cleanliness is verified by AES and it is briefly annealed back at 950 K due to the possible damage or chemical changes created by the incident electrons. When the crystal reaches a temperature of $\sim 95$ K, the gases are adsorbed onto the sample by backfilling the chamber, with the gate valve connecting the ion pump to the chamber closed to minimize distortion of the pumping elements or metallization of the insulators. It should be noted that the exposures are not corrected for different ion gauge sensitivities. The sample is then positioned in the line of sight of the mass spectrometer and about 12 mm away from the sampling aperture. The emission current is set at 2.5 mA and an electron impact ionization energy of 70 eV is used. The TPD spectra are obtained by recording the current of a specific ionic species with the mass spectrometer tuned to that mass-to-charge ratio, as a function of temperature. The QMS and the temperature controller are interfaced to a PC for data storage and a linear heating rate of 1.1 K/sec is used. Between each TPD experiment a clean surface is restored by annealing the crystal at a temperature of 960 K for 3 min.

Reagents were obtained from the following sources: bromoacetyl chloride, TCI (95%); iodobenzene (98%), iodomethane (99%), and acetyl chloride (98%), Aldrich.

2.5 Data Analysis

When the temperature of a sample is increased rapidly, gas is desorbed from the surface. An instantaneous rise in pressure is observed as a result of the increased rate of evolution of the gas due to the surface heating. The analysis of this increase of the gas density should, in principle, provide information on the number and the nature of the
desorbing species and on the kinetics of their evolution. Two different procedures can be used to perform desorption experiments which are: flash desorption and temperature programmed desorption. The first method implies that the temperature rise is accomplished rather rapidly, which results in a desorption rate much greater than the pumping rate required to remove the gas from the system. In this case, the pressure of the system is proportional to the integration of the desorption rate over time. The second procedure relies on the concept that during the desorption cycle, the gas which desorbs rapidly can be removed by effective pumping, while the surface is heated rather slowly. In this case, the heating rate should be selected in accordance with the pumping speed of the system; since the proportion of desorbed species should be characteristic of the desorption process occurring at the surface and the increase of pressure around the crystal should not be so large that re-adsorption may ensue. In temperature programmed desorption (TPD), the pressure rise is therefore proportional to the desorption rate.

The rate of desorption of adsorbed species from a surface may be given by the general Arrhenius equation

\[
\frac{-dn}{dt} = vn^x \exp(-E_d/RT)
\]  

(2.3)

where

- \(n\) = surface concentration
- \(v\) = frequency factor
- \(x\) = order of the desorption reaction
- \(E_d\) = activation energy of desorption
- \(T\) = absolute temperature.

Assuming that the activation energy and the frequency factor for desorption are independent of coverage, the rate law for desorption usually can be deduced from kinetics, with an overall order that may correspond to a series of reactions. However, a desorption process generally involves an elementary step. For a zeroth-order desorption, the rate is not a function of coverage. This reaction order could correspond to desorption of
the multilayer or from edges of a large cluster of adsorbate, where the removal of a molecule does not affect the kinetics of the reaction. Another common order observed for the desorption is first-order kinetics. In this case, the rate slows down since the concentration of adsorbed species decreases with time.

In temperature programmed desorption (TPD), the data is obtained under an experimental system where the pumping speed is suitably high around the crystal compared with the desorption rate. In a TPD spectrum a maximum desorption rate is indicated as a peak pressure at some temperature \( T_{\text{max}} \), where the condition for the maximum desorption rate is derived from the Arrhenius equation by differentiating and equating \( d^2n/dt^2 = 0 \) at \( T = T_{\text{max}} \). For a first-order reaction, the following equation is obtained

\[
\frac{E_d}{RT_{\text{max}}^2} = \nu \frac{dt}{dT} \exp\left(-\frac{E_d}{RT_{\text{max}}}\right) \tag{2.4}
\]

The heating rate \( (dT/dt) \) is an experimental parameter, and if a value for \( \nu \) is assumed, the activation energy \( E_d \) can be derived by solving Equation 2.4. One should note that the factor \( n \), the surface density of adsorbed species is not included in Equation 2.4. This implies for a first-order reaction with a fixed activation energy that the peak temperature is independent of the surface coverage. In the situation where the temperature of the peak shifts to lower temperatures with increasing coverage, the reaction can be assigned to a second-order process. The differentiation of the second-order rate equation yields an expression containing \( n \) explicitly

\[
\frac{E_d}{RT_{\text{max}}^2} = 2n_{\text{max}} \nu \frac{dt}{dT} \exp\left(-\frac{E_d}{RT_{\text{max}}}\right) \tag{2.5}
\]

In second-order desorption kinetics, the peak temperature shape is symmetric about \( T_{\text{max}} \) so that \( n_{\text{max}} \), the surface concentration at \( T_{\text{max}} \), is \( n_0/2 \) where \( n_0 \) is the initial concentration. Consequently, Equation 2.5 can be rewritten as

\[
\frac{E_d}{RT_{\text{max}}^2} = n_0 \nu \frac{dt}{dT} \exp\left(-\frac{E_d}{RT_{\text{max}}}\right) \tag{2.6}
\]
The activation energy of desorption and the frequency factor can be determined by a "complete" desorption analysis, which can also be applied to systems where the heat of adsorption is dependent on coverage. This type of analysis involves a series of experiments using different initial coverages or different heating rates. Hence for a fixed surface coverage, \( n \), one could determine the different desorption rates at different temperatures. In addition, a plot of \( (dn/dt)_{n=constant} \) as a function of \( 1/T \) yields the activation energy of desorption for a given coverage and the intercept of the plot gives the frequency factor. However, such experiments are not performed frequently.

Equation 2.4 can be solved numerically if \( \nu \) and \( n_0 \) are known quantities. Also, as a useful approximation, Redhead has demonstrated that the relationship between \( E_d \) and \( T_{max} \) is almost linear, and for \( 10^{13} > T_{max} (\max) > 10^8 \), it is given to \( \pm 1.5 \) percent by

\[
E_d/RT_{\max} = \ln \frac{\nu_1 T_{\max}}{\beta} - 3.64 \tag{2.7}
\]

with \( \beta = dT/dt \) [26]. Although the Redhead analysis may lead to serious errors especially when applied to a desorption process which is not positively first-order, it can yield a useful estimate of the desorption energy since the sensitivity of results to errors is diminished by the logarithmic dependence on \( \nu_1 \). Similar and more complex treatments can be conducted for higher orders of reaction.

The value of the frequency factor is estimated by using transition-state-theory, which assumes that the distribution function for the reactants and products is the equilibrium one and that the rate of the reaction is obtained by a one way flux calculation. The frequency factor for the \( N^{th} \) order of reaction of the \( i \) species is given by

\[
\nu_n = \left(\frac{kT}{h}\right)Q_0 \prod_{i=1}^{N} Q_i
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( h \) is the Planck's constant, \( Q_i \)
is the partition function of the reactant species $i$ and $Q^\neq$ is the partition function for
the activated complex. For a first or pseudo-first order reaction, the expression for $\nu$ is
$kT/h$, which has a typical value of $10^{13} \text{ sec}^{-1}$. Another useful model to determine the
frequency factor is the harmonic oscillator, which equates the frequency to the number
of vibration per second and is expressed by

$$\nu = \frac{1}{2\pi} \left( \frac{k}{m} \right)^{\frac{1}{2}}$$

where $k$ is the force constant and $m$ is the mass of the molecule. Values of the vibrational
frequency are generally of the order of $10^{13} \text{ sec}^{-1}$.

Another parameter that can assist the interpretation of the TPD spectra is the analysis of the shape of the desorption peaks. A schematic indication of the expected peak symmetries for various orders of desorption reactions was presented by Madix, based on the analysis performed by Redhead (Figure 2-6) [27]. Thus the shape of the desorption peak can, in theory, be used to resolve the order of the desorption process. Consequently, a second-order reaction is identified when the areas of the low and high temperature halves of the desorption peak are almost equal and thus a symmetrical peak is displayed. The first-order peak is asymmetrical with the area of the lower temperature side of the peak larger than the higher temperature side. For a zero-order process the area of the higher side of the desorption peak is almost equal to zero and the peak moves to higher temperatures as the coverage increases. In this situation, the desorption energy is determined by a logarithmic plot of the area under the curve of the desorption rate versus the inverse of the temperature for a certain coverage. This plot yields a straight line of slope $E_d/R$.

In addition to probing bond energies, TPD are useful for providing quantitative information about the number of species adsorbed, if the ion gauge is calibrated. During the heating cycle, the mass spectrometer registers a signal proportional to the number of adsorbed species leaving the surface at each instant. Hence the area under the desorption peak can be viewed as a measure of the surface concentration of that species. Since the
Figure 2-6: Theoretical indication of the dependence of desorption peak shape on the order of the desorption reaction by Madix [27].

\[ E = 25.0 \text{ kcal mole}^{-1} \]
\[ C_i = 9.2 \times 10^{14} \text{ molecules cm}^{-2} \]
\[ \beta = 10 \text{ K s}^{-1} \]
absolute temperature $T$ is a linear function of time $t$, the area corresponds to $\int p(t)dt$, where $p(t)$ is the partial pressure of the gas as a function of $t$ after the desorption has begun.

In spite of the difficulties and complexities which hinder proper interpretation of thermal desorption spectra, this technique contributes an abundance of useful data. With care very valuable qualitative and semi-quantitative conclusions can be reached concerning the interaction and the nature of the adsorbed species, and their approximate desorption energies. Furthermore, during the heating cycle a molecule adsorbed on the surface may surmount a dissociation barrier rather than the activation barrier for desorption. Information on the surface reaction kinetics can be deduced from such an effect and it represents the concept of temperature programmed reaction spectroscopy [28-29].
Chapter 3

Thermal Dissociation of Alkyl and Acetyl Halides on a Cu(111) Surface

3.1 Alkyl Halide Decomposition on Copper Surfaces

Several studies have demonstrated that thermal decomposition of alkyl halides can generate the corresponding alkyl groups on copper surfaces [30-36]. The dissociation temperature of alkyl halides on metal substrates increases in the order of iodides < bromides < chlorides; in agreement with gas phase carbon-halogen bond energies: C-I ~ 55 kcal/mol; C-Br ~ 70 kcal/mol and C-Cl ~ 85 kcal/mol. The reactivity of alkyl halides on metal surfaces is also influenced by the competition between the rate of desorption of the species and the rate of carbon-halogen bond dissociation. From studies of the effect of alkyl chain length on the carbon-halogen bond dissociation on copper surfaces, it was shown that the activation energy for the dissociation is independent of the chain length, even though the heat of molecular adsorption increases by 1.3 kcal/mol per CH₂ unit [32]. The minimal effect of the alkyl chain length on the dissociation kinetics suggests that the transition state for carbon-halogen bond is similar to the flat-lying configuration assumed for the molecular adsorption. In another set of experiments, Lin et al. found that the carbon-halogen bond dissociation rates decrease in the order of tertiary, secondary and
primary alkyl halides [35]. Changes in the reaction thermodynamics partially explain the differences in the dissociation temperatures for the various alkyl chain structures. Steric and electronic effects are also proposed as plausible factors responsible for the changes observed in the dissociation rate.

The products of the carbon-halogen bond scission of an alkyl halide are generally the corresponding alkyl group and halogen atom bound to the metal surface. However in concurrence with the formation of adsorbed methyl groups, methyl radical ejection into the gas phase has been detected at low temperatures during the decomposition of bromomethane on K-promoted Ag(111) [4] and of iodomethane on clean Cu(111) [19]. In both cases, the dissociation mechanism involves electron transfer from the substrate to the adsorbed species as previously discussed in Section 1.2. The observed reaction channels for chemisorbed methyl groups on copper surfaces are: C-Cu homolytic bond cleavage to form gas phase methyl radicals, $\alpha$-elimination to produce adsorbed methylene and hydrogen atoms, hydrogenation to form methane and C-C bond formation as evidenced by the evolution of ethane and ethylene. The formation of ethylene on Cu(110) is proposed to occur through the reaction of CH$_2$ with methyl groups to form ethyl groups, followed by $\beta$-hydride elimination [18]. For longer chain of adsorbed alkyl groups, the primary reaction observed is $\beta$-hydride elimination, at temperatures above 200 K, to produce the corresponding alkene and H$_2$ [31]. In addition, at coverages approaching the monolayer saturation on Cu(111), alkyl coupling and disproportionation products detected at temperatures below 200 K are presumed to be formed during the carbon-halogen bond dissociation [33].

### Coupling reaction

$$2 \text{CH}_3\text{CH}_2^* \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$$

### Disproportionation reaction

$$2 \text{CH}_3\text{CH}_2^* \rightarrow \text{CH}_2\text{CH}_2 + \text{CH}_3\text{CH}_3$$

A radical mechanism is proposed to take place based on the similarity between the disproportionation to coupling ratio and that reported for alkyl radicals in the gas phase.
and in solution.

In most cases, alkyl iodides and alkyl bromides undergo dissociative adsorption on copper surfaces while alkyl chlorides desorb from the metal surface at a rate faster than the one for the C-Cl bond dissociation. However, it was observed that both C-Cl bond dissociation and molecular desorption occur for straight-chain alkyl chlorides with more than six carbons on Cu(100) surfaces [32]. In addition, one finds that different substrate crystal planes have different adsorption properties, for instance heats of adsorption and sticking probabilities, and that the structure of the adsorbed species may differ from one surface to another. Based on bromopropane dissociation on Cu(111) and Cu(100) surfaces, it was observed that the carbon-halogen bond dissociation temperature was lowered by approximately 20 K on the Cu(100) more open structure compared to that reported on Cu(111) [32].

### 3.2 Acetyl Chloride Decomposition on Cu(111)

The adsorption of acetyl chloride on a metal surface has not been previously studied. Such experiments might be of interest due to the possible formation of acetyl groups as intermediates. In addition, the dynamics on the surface might be compared to that reported from gas phase studies [37]. Under ultrahigh vacuum conditions, the thermal dissociation of acetyl chloride, \( \text{CH}_3\text{COCI} \), may produce acetyl groups and coadsorbed chlorine atoms on metal surfaces, in analogy to the decomposition of alkyl chlorides, at \( \sim 240 \) K, on Cu(100) surfaces [32]. The \( \text{CH}_3\text{COCl} \) decomposition on metal surfaces can provide some insight in air control pollution; and in heterogeneous industry, the formation of adsorbed acetyl groups on copper surfaces can be important catalytic intermediate for partial oxidation processes. The comparison of the dissociation products of acetyl and alkyl chlorides on a copper surface is established on the similarity of the gas phase C-Cl bond strength of acetyl chloride and chloroethane, which are approximately 83 and 84 kcal/mol, respectively. In addition, the C-Cu bond strength for adsorbed alkyl and acetyl
groups are expected to be similar based on the bond-order-conservation model [21]. The carbon-chlorine bond cleavage seems more probable than the carbon-carbon bond since Cl atoms bind strongly to the surface, even though the C-C bond energy is ~ 80 kcal/mol in the gas phase. In addition, the photolysis of gas phase acetyl chloride demonstrates that C-Cl bond scission is favoured over the C-C bond [37] and thermal decomposition of alkyl halides on copper surfaces indicates that the C-C bond scission does not occur. Moreover, one generally observes that reactions where a single atom is removed dominate over dissociation reactions involving a molecular ligand, despite the order of the bond strengths [38]. The C=O bond dissociation is unlikely due to its strong bond energy, which is ~ 127 kcal/mol in the gas phase. Although acetyl and alkyl chlorides may be viewed as similar chemically, the dissociation mechanism of alkyl chloride may involve the thermal occupation of the $\sigma^*(C-Cl)$, whereas one could assume that the C-Cl bond cleavage involves occupation of the $\pi^*(C=O)$, since the $\pi^*(C=O)$ is located at a lower energy level than the $\sigma^*(C-Cl)$.

The geometry of the molecule on the surface is an important factor which affect the probable reaction pathways. The adsorbate geometry was not determined in this work. However, the geometry of alkyl halides on copper surfaces is that the alkyl chain lies approximately flat on the substrate [32]. Moreover, the molecular adsorption of acetone on Cu(100) is proposed to be via the oxygen and tilted away from the surface normal in the plane of the molecule [39]. The structure of phosgene on Ru(001) is indicated to be the $\eta^1(\text{Cl})$ configuration [40]. For the adsorption of the acetyl chloride, it is assumed that the Cl—end is in direct contact with the surface, however, no further speculations can be made on the actual geometry of adsorbed acetyl chloride.

Several reaction pathways might be expected for the decomposition of acetyl groups and some of them are presented in Figure 3-1. When a layer of chemisorbed acetyl groups is heated, some of the possible reaction pathways considered are the homolytic metal-carbon bond dissociation, the coupling of acetyl groups to produce 2,3-butanedione and
Figure 3-1: Proposed reaction pathways for the decomposition of acetyl chloride on Cu(111).
the further decomposition of the acetyl group on the surface. Under ultrahigh vacuum conditions, the products of the first two reactions are pumped out of the system before readsorption on the crystal can take place. The third reaction can lead to dehydrogenation (β-elimination) to yield adsorbed ketene and hydrogen atoms and/or carbon-carbon bond cleavage may occur. The resulting products adsorbed on the surface are methyl groups and CO with a fraction of unreacted acetyl groups. Thus diverse reactions are subsequently possible. In one of these reactions, ketene may desorb from the surface and hydrogen atoms may react with acetyl groups. Another reaction channel might involve coupling of methyl radicals might to form ethane which can then produce ethylene and formaldehyde in a disproportionation reaction with CO. Since CO adsorbs weakly on copper surfaces, further decomposition of this species is unlikely, but it may suffer addition reaction with other adsorbed species as in Fischer-Tropsch synthesis. Methyl groups on the surface can undergo dehydrogenation (α-elimination) and both H and CH₂ can react with methyl groups to yield methane and ethyl groups, respectively. In addition, H and CH₂ may each couple to produce H₂ and ethylene. Another plausible reaction is the further dehydrogenation of CH₂ to form CH, C and more surface hydrogen.

In ultrahigh vacuum, the probability of these reactions to occur largely depend on the substrate activation. Silver and copper surfaces are relatively inert to promote catalytic reactions. Recent studies of biacetyl on Ag(111) have shown that silver is thermally inactive regarding the scission of C-C, C-H and C=O bonds [41]. In the case of copper, a study of the thermal desorption of acetone on clean Cu(100) indicates that the dominant reaction is molecular desorption for both the multilayer and monolayer [39]. However, copper is an efficient substrate in the dehalogenation of alkyl halides. Carbon-halogen bond dissociation studies have established that the reaction is an elementary event. Moreover, single crystal copper surfaces promote carbon-iodine bond cleavage at temperatures below 150 K. Although C-C bond dissociation is shown as a possible reaction pathway, such a process was not detected for the decomposition of alkyl groups adsorbed on copper surfaces and thus seems unlikely to occur for the decomposition.
of CH$_3$COCl [33]. However, C-H bond cleavage and effective coupling of hydrocarbon fragments was demonstrated by the formation and evolution of methane, ethylene and propylene, during the thermal dissociation of iodomethane on a Cu(111) surface [20].

### 3.3 Bromoacetyl Chloride Decomposition on Cu(111)

From photoinduced and thermal decomposition of alkyl bromides and chlorides on metal surfaces, it was demonstrated that the energy required for the carbon-bromine bond dissociation is less than the one observed for the carbon-chlorine bond. On a Cu(111) surface, the activation energy for the C-Br bond dissociation, assuming first-order kinetics and a frequency factor of $10^{13}$ sec$^{-1}$, is $\sim 11$ kcal/mol compared to approximately 15 kcal/mol for the C-Cl bond scission [32]. This difference in reactivity reflects the trend in the gas phase bond strength of the carbon-halogen bond.

In a study performed by White and co-workers, it has been proposed that the photolysis of 1-bromo-2-chloroethane, BrCH$_2$CH$_2$Cl, on Pt(111) occurs by dissociative electron attachment, DEA [42]. The results obtained by X-ray photoelectron spectroscopy and temperature programmed desorption showed that 230-295 nm photons induced the C-Cl bond dissociation by excited substrate electrons and they were also effective for the C-Br bond dissociation through a combination of direct photon and substrate mediated excitation. However, 295-345 nm photons only induced the C-Br bond scission through photo-excited substrate electrons. Hence the dissociation of the C-Cl and C-Br bonds occurs at different bonds specific threshold wavelengths that correspond to the monohalide analogs. These results suggest that the electronic character of an isolated chromophore is not significantly disturbed by the presence of other chromophores in the same molecule. In addition, according to Kadodwala and Jones, the thermal decomposition of BrCH$_2$CH$_2$Cl on Cu(111) is assumed to occur via the weaker C-Br bond cleavage and the subsequent cleavage of the C-Cl bond [43].

The decomposition of bromoacetyl chloride, BrCH$_2$COCl, on a Cu(111) surface may
take place through three plausible dissociation pathways, assuming the thermal excitation of the $\pi^*(C=O)$ electronic configuration. One of these pathways favours the cleavage of the low energy bond beta to the carbonyl, C-Br at 68 kcal/mol, while the other two involve the cleavage of an alpha bond either C-C at $\sim$ 80 kcal/mol or C-Cl at about 83 kcal/mol [44]. However the C-C bond dissociation is unlikely, based on the same factors considered for the decomposition of acetyl chloride and discussed in the previous section. The geometry of the molecule on the surface is another critical element to consider. Although the orientation of BrCH$_2$COCl on Cu(111) was not established in this study, one would expect the bromine and chlorine ends to be in close contact with the surface.

Hence the thermal degradation of BrCH$_2$COCl on Cu(111), presented in Figure 3-2, could occur through the scission of the C-Br bond or the C-Cl bond, or both. If the C-Br bond dissociates first, the expected products are adsorbed Br atoms and CH$_2$COCl groups which might evolve from the surface, couple to form butanedioyl dichloride, ClCOCH$_2$CH$_2$COCl, or undergo further decomposition when the crystal is heated. In the case where the C-Cl bond cleavage is the primary dissociation pathway, the metal surface is assumed to be composed of BrCH$_2$CO groups and coadsorbed Cl atoms. Upon further warming of the substrate, some of the possible reaction pathways for the BrCH$_2$CO groups are the homolytic metal-carbon bond dissociation, a coupling reaction to produce 1,4-dibromo-2,3-butanedione, or degradation. Another dissociation pathway is the cleavage of both the C-Br and C-Cl bonds. Ketene, CH$_2$CO, which can evolve from the crystal, and coadsorbed bromine and chlorine atoms are the proposed products of this reaction. The bromine and chlorine atoms should remain bound to the metal throughout any ketene reaction on the surface. The thermal degradation of ketene on copper could be view as the cleavage of the carbon-carbon bond to form CH$_2$ and CO on the surface. Subsequently, CH$_2$ may undergo a coupling reaction to yield ethylene or decompose to produce CH, and surface carbon and hydrogen. The probability of these reaction pathways to occur depends on the same factors considered for the thermal degradation of acetyl chloride on Cu(111).
Figure 3-2: Proposed reaction pathways for the decomposition of bromoacetyl chloride on a Cu(111) surface.
3.4 Temperature Programmed Desorption Measurements

All TPD spectra are presented without a baseline subtraction. However, to obtain the area of the desorption peak, it was often necessary to subtract a calculated slope to eliminate any background effects. A binomial smoothing was applied to all the spectra. The number of times the smooth operation was used on a selected collection of data was 33, where 33 data points are equivalent to 1 K. The binomial smoothing allows one to convolve the data with normalized coefficients derived from the Pascal's triangle at a level corresponding to the 'smoothing' parameter and operates by combining the same number of neighboring points before and after the point being smoothed. Visual inspection shows that no significant loss of information is detected between the smoothed and the original spectrum.

A variable tail is observed in most TPD spectra and it could be assigned to the desorption from other parts of the sample assembly due to thermal conductance, when the crystal is heated. Another factor to consider is the finite pumping speed, such that the baseline pressure increases with time and the rate of desorption. Furthermore, when the mass spectrometer is on for long periods of time, desorption from parts of the mass analyzer could occur as a result of the heat produced by the filament. In addition, the ionizer becomes less stable which can affect the recording of the data.

3.5 Results and Interpretation

3.5.1 Iodomethane (CH$_3$I)

The thermal desorption of molecular iodomethane was performed as a test. Moreover, the results obtained from this set of experiments may be compared to the literature. Figure 3-3 displays the TPD spectra for the adsorption of iodomethane, CH$_3$I, on Cu(111) at
95 K. For this set of experiments the integration is straightforward. At exposures above 6 L, a first peak is observed at 125 K, and its temperature shifts upwards to 130 K with increasing exposure. A second peak appears at about 118 K for high exposures and it is assigned to multilayer condensed iodomethane, since its area increases steadily with exposure without saturation. The temperature of this peak also shifts up from 118 K to 126 K as the coverage goes up. The temperature peaks observed for the second layer (125 K) and the multilayer (118 K) desorption of CH₃I on Cu(111) are in good agreement with that reported for the CH₃I desorption from Pt(111), which are 124 K and 112 K for the first and second overlayer, respectively [45]. The small difference in the desorption temperature could be assigned to a thermocouple gradient. In addition, the shape of the TPD peaks are similar for both surfaces. The shape of the multilayer peak and the observations presented above agree with zeroth-order desorption kinetics as anticipated for the evolution of multilayer CH₃I. For the peak associated with the second layer, its shape and the upward shift of the peak temperature with increasing coverages suggest a first-order desorption kinetics and attractive interactions between the adjacent molecules. The inset shows the integrated area of the 126 and 130 K temperature peaks as a function of coverages of iodomethane. The absence of desorption for exposures less than 6 L implies reaction of the CH₃I molecules on the surface. Therefore, it is concluded that ~ 5.5 L exposure corresponds to a monolayer of iodomethane and that a 11 L exposure correlates with saturation of the second layer. The CH₃I yield changes linearly for exposures above 6 L on Cu(111) indicating that the sticking probability of the molecules on the surface is constant for the second and subsequent layers.

For exposures above two monolayers, the TPD spectra displayed in Figure 3-3 show a desorption peak at about 244 K which increases with exposure. Two plausible interpretations are proposed for the origin of this peak. Firstly, the CH₃I⁺ evolution observed at high-temperature might be attributed to the desorption from surface defect sites. In a study performed by Jenks et al., the desorption of alkene on sputtered versus annealed copper surfaces demonstrates that a high-temperature peak is due to the defects produced
Figure 3-3: Temperature programmed desorption for the molecular evolution of iodomethane on Cu(111) monitoring m/e=142. The desorption yield of iodomethane as a function of exposure is plotted in the inset. The flat regions on 6 L and 7 L spectra are due to data acquisition failure.
by ion bombardment [46]. It is evident that a corrugated surface can bind molecules more strongly than an ideal one. This effect is due to the deeper potential energy well for a defect site than a terrace site, as a result of the increased coordinate unsaturation. If intact molecular desorption is occurring at 244 K, this may indicate that decomposition of CH$_3$I requires an array of sites not available at the defect. However, the desorption yield becomes so large at high exposures that this must be associated with the multilayer, and such a high-temperature peak cannot be attributed to multilayer desorption from the Cu(111) single crystal. The second possible reason for the detection of a peak at 244 K is the desorption of condensed iodomethane molecules adsorbed on other parts of the system, particularly the copper block and braid of the sample holder assembly. Since CH$_3$I exposures are accomplished by backfilling of the chamber, adsorption on different components of the chamber cannot be prevented. Thus it is plausible that when the crystal is heated to 244 K, the desorption of iodomethane from the copper block and braid takes place due to a temperature gradient effect.

The desorption yield of $m/e^+ = 142$, CH$_3$I$^+$, at 244 K as a function of exposure is displayed in Figure 3-4. From this figure, two points are noted. Firstly, at low exposures, the desorption peak does not grow with exposure and furthermore no desorption is detected. Secondly, at high exposures, the temperature peak grows without saturation with exposure. In addition, for coverages above two monolayers, the desorption yield appears to increase linearly with coverage. Thus on the basis of the analysis presented above, the high-temperature peak does not seem to be the result of CH$_3$I molecular desorption surface from surface defects. It is therefore concluded that adsorption of iodomethane multilayer on the sample holder is the cause of the observed desorption peak at 244 K for coverages greater than two monolayers. This higher temperature peak is also detected for the desorption of acetyl and bromoacetyl chloride. However, the delay for the desorption of iodomethane and bromoacetyl chloride is not observed in the case of acetyl chloride and it may indicate that decomposition of CH$_3$I and BrCH$_2$COCl is facile even on the sample holder assembly.
Figure 3-4: Plot of the iodomethane desorption yield for the temperature peak at 244 K as a function of coverage, monitoring m/e=142.
The desorbing reaction products following adsorption of submonolayers of iodomethane on a Cu(111) surface were studied by Bent and co-workers [20]. The results obtained provide evidence for methyl radical production and metal alkyl formation at 140 K. The adsorbed methyl groups are stable up to 400 K, where they either desorb as methyl radical or decompose to produce methane, ethylene, propylene and ethane at higher exposures. Other experiments using surface vibrational spectroscopy showed that in fact the radical evolution at 140 K corresponds to the temperature at which the carbon-iodine bond cleavage occurs to form adsorbed methyl groups [30].

3.5.2 Acetyl Chloride (CH$_3$COCl)

The temperature programmed desorption spectra for the evolution of acetyl chloride from Cu(111) at different exposures are presented in Figure 3-5. The evolution of CH$_3$COCl was monitored by $m/e^+ = 42$, CH$_2$CO$^+$, since the molecular ion at $m/e^+ = 78$ cannot be detected due to fragmentation in the mass analyzer, as seen in the mass spectra obtained by backfilling the chamber and also as demonstrated in the literature [47]. The inset displays the TPD peak area at 127 K, which corresponds to the desorption yield, as a function of exposure. For exposures above 4.5 L, a linear increase is observed for the molecular desorption yield, and for exposures less than 4.5 L no molecular desorption is detected. These results provide evidence that at low coverages, acetyl chloride adsorbed on the metal undergoes a reaction. A monolayer of acetyl chloride is defined as being equal to a 4.5 L exposure.

The value obtained for a monolayer of acetyl chloride appears to be reasonable compared with the value for the monolayer of iodomethane. This comparison is based on the estimated square area for acetyl chloride and iodomethane, using Van der Waals radii to determine the size of the molecule [48]. The calculated surface densities are $5.41 \times 10^{14}$ cm$^{-2}$ and $3.31 \times 10^{14}$ cm$^{-2}$, which correspond to one molecule per every 3.3 Cu atoms for CH$_3$I and one molecule per every 5.3 Cu atoms for CH$_3$COCl. Assuming a sticking coefficient of unit, the flux of molecules striking the surface indicates that for
Figure 3-5: TPD spectra of acetyl chloride on Cu(111) monitoring the evolution of m/e=42 (the molecular ion peak is not observed due to fragmentation). The desorption yield of acetyl chloride as a function of exposure is plotted in the inset.
exposures corresponding to the observed monolayer of each species, the actual coverage would be $9.39 \times 10^{14}$ cm$^{-2}$ and $1.05 \times 10^{15}$ cm$^{-2}$ for iodomethane and acetyl chloride, respectively. From surface science studies of the adsorption of CH$_3$I on Pt(111) [45], French and Harrison have determined that the actual saturation coverage is close to this estimated value. In the case of acetyl chloride, the actual coverage is three times greater than the one estimated by Van der Waals radii. This could be the result of crowding on the surface greater than the bulk density. However, the monolayer values for these two species may not coincide to the observed ones since all exposures are uncorrected for different ion gauge sensitivities.

Similarly to the TPD spectra obtained for iodomethane, a desorption peak is detected at high temperature for acetyl chloride, monitoring $m/e^+ = 42$. The integrated area of the desorption peak at 239 K is plotted as a function of the exposure in Figure 3-6. It is observed that the desorption yield increases linearly with exposure, without saturation. In addition, the difference between the low-temperature and the high-temperature peaks for acetyl chloride is approximately the same as the one observed for iodomethane. This evidence indicates that the desorption from surface defects is not probable since one might expect different desorption temperatures for CH$_3$I and CH$_3$COCl molecules evolving from defect sites. Hence, the origin of the high-temperature peak is attributed to the desorption of condensed acetyl chloride on the sample holder. Moreover, the high-temperature peak detected at the monolayer coverage is also assigned to molecular desorption from the sample holder, where acetyl chloride decomposition is inhibited due to the presence of impurities.

For an exposure of 6 L, a desorption peak is observed at about 138 K. At higher exposures this peak is displayed as a shoulder of the multilayer peak at 125 K, which shifts to 127 K as the coverage is increased. This shoulder peak is qualitatively similar to the second layer desorption peak observed for iodomethane. The high-temperature detected for the second layer desorption indicates that this layer is more strongly bound than the
Figure 3-6: Plot of the acetyl chloride desorption yield at the 239 K temperature peak as a function of coverage, monitoring m/e=42.
multilayer. It should be pointed out that this second layer may correspond to either the adsorption of a complete layer onto the monolayer or the adsorption of the “second half” of the first layer. The shift of the shoulder peak at 138 K towards lower temperatures as the coverage is increased could indicate the presence of repulsive adsorbate-adsorbate interactions as the acetyl chloride molecules are adsorbed more closely together until multilayer condensation is achieved. The desorption process is expected to follow a zeroth-order reaction for the multilayer, whereas the evolution of the second layer may be assumed to be first-order kinetics.

The molecular desorption of acetyl chloride was also studied by monitoring $m/e^+ = 35$, Cl$^+$, and is presented in Figure 3-7. Although an insufficient number of TPD spectra were collected, the inset shows the peak area as a function of exposure. The monolayer is extrapolated and corresponds to 4 L, which is in good agreement with the 4.5 L value obtained for the monitoring of CH$_2$CO$^+$ evolution. In another set of TPD experiments, $m/e^+ = 28$, CO$^+$, was monitored and the TPD spectra are displayed in Figure 3-8. The desorption yield as a function of exposure is shown in the inset. The monolayer is defined by 4.4 L, which is consistent with the results obtained previously and a linear increase is observed for exposures above 4.5 L on Cu(111). Even for coverages below the monolayer, one notes a low-temperature peak near 165 K. This desorption peak might be assigned to a decomposition product containing CO group. However, this does not seem probable since referring to the inset of Figure 3-8, the integration of this peak is constant at low exposures. From CO adsorption studies on Cu(111) surfaces, it is observed that the desorption of CO occurs between 130 and 171 K [49]. Thus the temperature peak at 165 K might be attributed to background gases or the evolution of impurities, containing carbon monoxide. The TPD spectra obtained for $m/e^+ = 35$, Cl$^+$, and 28, CO$^+$, both exhibit the same shoulder peak due to the second layer, as observed during the TPD experiments monitoring $m/e^+ = 42$, CH$_2$CO$^+$.

A comparison of the mass intensities for acetyl chloride desorption at 127 K for $m/e^+$
Figure 3-7: TPD spectra for the desorption of acetyl chloride on Cu(111) monitoring the evolution of m/e=35. The inset shows the integrated peak area at 126 K as a function of exposure.
= 28, 42 and 35, at 10 L and 20 L coverages, shows that the normalized mass ratio of CO:CH₂CO:Cl is 1:0.6:0.08 and it is the same for the high and low coverages. In addition, the same data treatment was applied to the temperature peak observed at about 240 K, for coverages of 10 L and 20 L and both normalized mass ratios are similar to that reported for the desorption peak at 127 K. It is therefore concluded that only one species, acetyl chloride, is detected by \( m/e^+ = 28, 42 \) and 35 at all coverages and for both desorption peaks.

Since no molecular desorption is detected in TPD experiments for acetyl chloride, for coverages up to one monolayer, one can postulate that dissociative adsorption of the parent molecule takes place on the surface. At higher exposures, molecular desorption is observed at ~ 126 K and the desorption yield increases linearly with exposure. These observations imply that the sticking coefficient is constant and that dissociation of the adsorbate does not take place in the multilayer. This second assumption is supported by the TPD studies of alkyl halides on copper surfaces, where direct contact of the adsorbate with the substrate is required for the dissociation process to occur. For the dissociative reaction of CH₂COCl in the monolayer, various surface reactions which are presented in Figure 3-1, could occur and the mechanism could be resolved by monitoring the evolution of the possible products. After dosing 2 monolayers to insure complete coverage of the copper surface, the evolution of \( m/e^+ = 15, 16, 30, 44, 86 \) which correspond respectively to CH₃ radicals, methane, ethane, acetaldehyde and 2,3-butanedione, were monitored. No desorption peak was detected for all the proposed products, even though methyl radical ejection is thought to occur during the thermal decomposition of iodomethane on Cu(111) [20]. By considering the reaction mechanisms of CH₃I and CH₃COCl on a metal surface, one might suggests that physisorbed CH₃ radicals have a shorter lifetime on the substrate and thus radical desorption dominates, whereas CH₃CO radicals have a longer lifetime on the surface due to a deeper physisorption well caused by the CO group, so that subsequent chemisorption to form adsorbed acetyl groups dominates. Also, we might have a low detectability of the radical intermediate, which should decrease in the
Figure 3-8: TPD spectra of acetyl chloride on Cu(111) monitoring the evolution of m/e=28. The desorption yield of acetyl chloride at 127 K as a function of exposure is plotted in the inset.
order R > CH₅ > CH₃CO*, due to the products not reaching the mass spectrometer as a result of their high reactivity resulting in their adsorption on the walls of the chamber and the drift tube. In addition, if the product is oriented at a large angle from the surface normal, the intensity of the signal could be diminished, since all TPR spectra were taken at normal incidence of the surface.

Although the results for the product desorption do not allow the determination of which bond is cleaved during the decomposition, it might be assumed that C-Cl bond cleavage takes place, by comparison with the dissociative adsorption of alkyl chlorides on a Cu(100) surface [35]. The photochemistry of condensed-phase and gas phase acetyl chloride seems to corroborate the proposed dissociation pathway [37,50]. In addition, evidence that the CH₃COCl decomposition occurs via C-Cl bond scission is provided in this work by chemical displacement experiments, as will be discussed in the next section.

3.5.3 Displacement Experiments

The temperature of the C-Cl bond dissociation in acetyl chloride was determined by using the technique of chemical displacement [51-52]. This technique is based on the concept that weakly adsorbed species can be displaced from the monolayer by an adsorbate which bind more strongly to the surface. For hydrocarbons monolayers on copper surfaces, this displacement process takes place at temperatures as low as 100 K. Studies of displacement processes of hydrocarbons adsorbed on copper surfaces have indicated that chemical displacement is driven by a thermodynamic force, where the adsorbate with the larger enthalpy of adsorption displaces the adsorbate with the lower adsorption enthalpy. From a study performed by Xi and Bent, it is estimated that the heat of adsorption of iodobenzene on Cu(111), \( \Delta H_{ads} \), is \( \lesssim 15 \) kcal/mol [53]. The enthalpy of adsorption of CH₃COCl on a Cu(111) surface has not been reported and was not determine in this work. However, as discussed in Section 3.6, the heat of adsorption of acetyl chloride is estimated as 11-12 kcal/mol. Molecularly intact acetyl chloride can therefore be displaced to a weakly bound, physisorbed second monolayer on Cu(111) by
an excess of iodobenzene, C₆H₅I. However, when the surface is heated at a high enough temperature before dosing the displacing agent, irreversible decomposition of CH₃COCl occurs in the monolayer. As discussed later, the decomposition product species bind to the surface much more strongly and are not displaced.

In the present studies, the C-Cl bond scission temperature is established by applying the following protocol. After the deposition of 4 L of CH₃COCl on clean Cu(111) at 100 K, the surface was briefly annealed up to various temperatures to induce bond dissociation. Subsequently, the reaction was quenched by cooling the surface back to 100 K and any undissociated CH₃COCl molecules were displaced to the multilayer by dosing C₆H₅I. The iodobenzene dose was 15 L which is equivalent to approximately 3 monolayers since it has been determined that 5 L corresponds to one monolayer of C₆H₅I adsorbed on Cu(111) [53]. The TPD spectra, monitoring m/e⁺ = 42, taken after this experimental protocol are presented in Figure 3-9. During this set of experiments, sputtering and annealing to reproduce a clean surface were necessary prior to each TPD spectrum, as a result of carbon deposition. Two low-temperature peaks are observed in all the spectra, one at 127 K and another at 167 K. The first peak is assigned to the desorption of the displaced acetyl chloride layer since the peak temperature is the same at which acetyl chloride multilayer desorption occurs, in the absence of the displacing agent. By comparison with the TPD area obtained in Figure 3-5, most of the CH₃COCl initially adsorbed on Cu(111) is displaced to the multilayer at the annealing temperature of 100 K. But, approximately ≤ 20 % of the adsorbed CH₃COCl is not displaced by iodobenzene. This actually agrees with our estimate that the difference between the heat of adsorption of the two species, which is ≤ 4 kcal/mol, is on the order of the thermal energies. It would then be expected that some entropic randomization of iodobenzene and acetyl chloride would occur in the monolayer.

The inset displays the integration of the low temperature peak at 127 K as a function of annealing temperature. The curve obtained shows that the displaced CH₃COCl
Figure 3-9: Determination of the dissociation temperature for acetyl chloride on Cu(111) by chemical displacement experiments described in the text. TPD spectra were obtained by monitoring m/e=42 evolution. The inset shows the TPD peak intensity for the desorption peak at 127 K as a function of annealing temperature.
yield decreases due to an increased CH₃COCl dissociation for higher annealing temperatures. Differentiation of this curve gives the rate of dissociation for acetyl chloride molecules which has a maximum at 138 K. This maximum is equivalent to a temperature programmed reaction, TPR, peak temperature. We roughly estimate that the anneal/quench procedure used here is equivalent to a linear heating rate of about 0.1 K/s. Our estimated activation energy of 9.2 kcal/mol assuming a first-order reaction and frequency factor of 10¹³ sec⁻¹, is affected by less than 1 kcal/mol, if the heating rate is changed by an order of magnitude.

A high-temperature desorption peak is observed at about 236 K and is attributed to desorption of condensed acetyl chloride adsorbed on the sample holder, as seen with the non-displacement experiments. However, the temperature peak at 167 K is new and provide further evidence that the decomposition of acetyl chloride occurs via the C-Cl bond scission. This peak is assumed to be the result of a coupling reaction between iodobenzene and adsorbed acetyl groups on Cu(111). This is based on TPR studies performed by Xi and Bent where coupling reactions between chemisorbed phenyl groups and alkyl radicals occur immediately upon decomposition of the corresponding alkyl iodide [54]. The thermal dissociation of the C-I bond in C₆H₅I on clean Cu(111) happens at approximately 175 K [53], near the temperature where we observe the new desorption peak. It is proposed that benzene radicals produced during the thermal dissociation of iodobenzene react with adsorbed acetyl groups to form acetophenone, C₆H₅COCH₃, which desorbs promptly from the surface. A study of the cross coupling reaction between iodomethane and adsorbed phenyl groups on a Cu(110) surface was performed by Kash et al. [55]. Their experiments provide evidence that the low-temperature desorption of toluene is driven by a radical mechanism upon dissociation rather than a reaction between chemisorbed methyl and phenyl groups.

Figure 3-10 displays the integrated area of the temperature peak at 167 K as a function of the annealing temperature. The desorption yield increases with annealing tempera-
Figure 3-10: Plot of the desorption yield at 167 K as a function of the annealing temperature, monitoring m/e=42.
tures up to 135 K, followed by a decrease for higher temperatures. The reaction kinetics of adsorbed acetyl groups with phenyl radicals to form acetophenone is assumed to follow second-order kinetics. The desorption peak at 167 K for annealing temperatures below 135 K can be attributed to the possible decomposition of acetyl chloride at a temperature as low as 100 K. However, as discussed earlier, iodobenzene might not totally displace adsorbed acetyl chloride and so it is probable that the non-displaced CH₂COCl undergoes decomposition, when the surface is heated up to ~ 138 K. The number of adsorbed acetyl groups and Cl atoms on the metal surface are expected to increase with annealing temperatures above 135 K. Moreover, these adsorbed products are not displaced by C₆H₅I and can effectively block active site for the decomposition of iodobenzene resulting in a decreasing yield for phenyl radical formation as the annealing temperature is increased. For annealing temperatures above 135 K, the decrease in the desorption yield of acetophenone can be explained by the decrease in the product of the concentration of adsorbed acetyl groups and phenyl radicals. Interestingly, Xi and Bent have reported that as the annealing temperature for the formation of a submonolayer of phenyl groups is increased, the toluene yield from phenyl groups reacting with CH₃I increases and then plateaus [54]. The different shape observed for the acetophenone yield might be due to the different coverage of the adsorbed species, which is near the monolayer saturation for acetyl chloride.

3.5.4 Bromoacetyl Chloride (BrCH₂COCl)

The surface chemistry of bromoacetyl chloride on Cu(111) can provide an interesting comparison with the results obtained for acetyl chloride. In particular, the cleavage of the C-Br bond might be expected before that of the C-Cl bond. The thermal desorption results for BrCH₂COCl on Cu(111) monitoring m/e⁺ = 79, ⁷⁹Br⁺ isotope, are presented in Figure 3-11. The molecular ion is not observed, and presumably has a low detectability at the mass spectrometer. This assertion is supported by the literature data for chloroacetyl chloride [47]. The inset shows the desorption yield at 174 K as a function
Figure 3-11: TPD spectra of bromoacetyl chloride on Cu(111) monitoring the evolution of m/e=79 (the molecular ion peak is not observed due to fragmentation). The inset displays the desorption yield as a function of exposure.
of exposure. The absence of molecular desorption for exposures below 6.7 L indicates that BrCH\textsubscript{2}COCl reacts with the surface and this value defines the monolayer. Also for exposures above 6.7 L, the desorption yield increases linearly. We also monitored the evolution of \( m/e^+ = 35, \text{Cl}^+ \), and the TPD spectra are presented in Figure 3-12. The integrated area of the temperature peak at 174 K is plotted in the inset as a function of exposure, and the monolayer corresponds to the same value obtained for the \( m/e^+ = 79 \) evolution. This monolayer value of 6.7 L for bromoacetyl chloride on a Cu(111) surface agrees with that found for iodomethane and acetyl chloride. Based on the square root of the mass ratio of CH\textsubscript{3}COCl and BrCH\textsubscript{2}COCl, one obtains a value of 6.4 L for a monolayer of BrCH\textsubscript{2}COCl on Cu(111). The slight difference between this value and the one obtained experimentally may be due to a different adsorption geometry on the substrate. In addition, the ion gauge sensitivity, the size of the molecule, the sticking coefficient of the species striking the surface and the presence of contamination are factors that affect the value of the monolayer.

In both TPD experiments monitoring \( m/e^+ = 35 \) and 79, a desorption peak is detected at 160 K, for low coverages, and this desorption peak moves toward 174 K with increased coverages. Moreover, an examination of the peak shape shows that the desorption kinetics follows zeroth-order. A high-temperature peak at about 308 K is also observed for both \( m/e^+ \) and is attributed to the multilayer desorption of bromoacetyl chloride adsorbed on the sample holder. For an exposure of 25 L, a desorption peak is detected at 150 K for the \( ^{79}\text{Br}^+ \) evolution; and two distinct peaks are observed below 174 K for \( m/e^+ = 35 \), one at 133 K and the other at 150 K. To date no explanation is proposed to account for these desorption peaks associated with the multilayer.

Figure 3-13 displays the evolution of \( m/e^+ = 28, \text{CO}^+ \), for BrCH\textsubscript{2}COCl exposures above 5 L on Cu(111). The TPD spectra obtained for \( m/e^+ = 28 \) are quite different from the ones presented in Figure 3-11 for \( m/e^+ = 79 \) evolution. Firstly, for exposure above 15 L, two low-temperature desorption peaks are observed at 162 K and 174 K, for
Figure 3-12: TPD spectra of bromoacetyl chloride on Cu(111), monitoring the evolution of m/e=35. The inset shows the peak area as a function of exposure.
$m/e^+ = 28$ evolution. Secondly, the large background of the TPD spectra in Figure 3-13 for high exposures, is presumably due to the presence of impurities during the backfilling of the chamber by bromoacetyl chloride. The peak at 174 K is associated with the multilayer desorption of BrCH$_2$COCl as confirmed by monitoring the evolution of Cl$^+$ and $^{79}$Br$^+$. In addition, a high-temperature peak is detected at 307 K and is similar to that observed for $m/e^+ = 35$ and 79 TPD spectra. Hence, this peak is assigned to the multilayer desorption of bromoacetyl chloride from the sample holder. The temperature difference between the desorption peaks at 307 K and 174 K is approximately equal to the one between the peak at 162 K and that expected for CO multilayer desorption. The desorption peak at 162 K is thus reasoned to be the result of the desorption of carbon monoxide from the colder sample holder. The possible sources of CO contamination are the gas-handling manifold, the decomposition of BrCH$_2$COCl in the ampule, and residual gas in the ultrahigh vacuum chamber. By comparing the desorption temperature of the acetyl chloride multilayer with its enthalpy of vaporization ($\sim 7.4$ kcal/mol [56]), the enthalpy of vaporization of bromoacetyl chloride can be estimated as about 10.8 kcal/mol, so that its room vapour pressure is $\sim 7$ torr compared to $\sim 284$ torr for acetyl chloride. The pressure of the dosing line is approximately $10^{-2}$ torr at the thermocouple gauge, and probably higher at the chamber inlet, so that the BrCH$_2$COCl gas during backfilling of the chamber may contain on the order of 1% of carbon monoxide or other background gases.

Since for exposures below the monolayer BrCH$_2$COCl molecules do not desorb intact, thermal dissociation is assumed to take place. From the proposed reaction pathways in Figure 3-2, the possible products are butanediyl dichloride, 1,4-dibromo-2,3-butane-dione, CH$_2$COCl and BrCH$_2$CO radicals, ketene, carbon monoxide and ethylene. The molecular ion of the first four products may not be detected due to their fragmentation pattern in the analyzer. Moreover, CH$_2$COCl and BrCH$_2$CO radicals could react with any hydrogen present in the system and form acetyl chloride and bromoacetaldehyde, respectively. It is also possible that CH$_2$ reacts with hydrogen to produce methyl...
Figure 3-13: TPD spectra of bromoacetyl chloride on Cu(111) for exposures above 5 L, monitoring m/e=28.
radicals and subsequently methane. For a coverage of one monolayer, no thermal desorption is observed for CH$_3$, $m/e^+ = 15$, and CH$_4$, $m/e^+ = 16$. In addition, $m/e^+ = 44$ and 86, which are plausible ion fragments of butanediyl dichloride and/or 1,4-dibromo-2,3-butanedione, were also monitored and no peak temperature was detected. The reasons for these observations are analogous to the ones proposed for the lack of detection of acetyl chloride products in Section 3.5.2.

However, the TPD spectra monitoring the evolution of $m/e^+ = 28$, in Figure 3-14, show a low-temperature desorption peak, at coverages below the monolayer. The desorption peak for exposures up to 5 L of bromoacetyl chloride is first detected at 171 K and then shifts to 145 K. As for acetyl chloride, this peak may be the result of dissociation product, or it may be assigned to the desorption of submonolayer of background carbon monoxide adsorbed on the metal substrate. The TDS are similar to the results reported by Kristein et al. for the desorption of CO adsorbed on Cu(111) [49]. As the coverage of BrCH$_2$COCl is increased the desorption peak shifts to a lower temperature possibly due to repulsive adsorbate-adsorbate interactions.

Significantly, a desorption peak was observed for $m/e^+ = 42$, CH$_2$CO$^+$, for exposures below the monolayer, and TPR spectra are presented in Figure 3-15. The $m/e^+ = 42$ evolution could be the result of ketene desorbing from the surface or it could represent the desorption of one or several products which are fragmented in the ionizer. In addition, this evolution may be due to the detection of impurities present in bromoacetyl chloride. Although the origin of the $m/e^+ = 42$ signal was not confirmed in this study, the peak area is thought to correspond to the product yield of a surface reaction. The TPR spectra obtained show two temperature peaks, one at 121 K and another at 168 K. The desorption peak at 168 K is attributed to the multilayer desorption of BrCH$_2$COCl, as shown earlier for $^{79}$Br$^+$ evolution. The inset shows the product yield of both peaks as a function of exposure. Although, this set of experiments was performed only once, it is speculated that the low-temperature $m/e^+ = 42$ evolution indicates either a lower temperature of
Figure 3-14: TPD spectra for submonolayer coverages of bromoacetyl chloride on Cu(111), monitoring the evolution of m/e=28.
Figure 3-15: TPR spectra for submonolayer coverages of bromoacetyl chloride, monitoring the evolution of m/e=42. The inset displays the desorption yield as a function of exposure.
decomposition for BrCH$_2$COCl than the one estimated for CH$_3$COCl occurring at 121 K, or possibly earlier with desorption of the ketene product at 121 K. In addition, the large quantitative increase observed between the 4 L and 5 L coverages is presumably due to a $\beta$-halogen elimination, assuming a preferential C-Br bond cleavage and resulting in the formation of ketene, as shown in Figure 3-16. The elimination reaction takes place when adsorption of the radical group or reaction within the monolayer is not feasible.

The chemical displacement technique was employed again in an attempt to determine the temperature at which BrCH$_2$COCl dissociates. The displacing agent used was iodobenzene, and the experimental procedure was similar to the one described previously in Section 3.5.3. However, no displaced peak for the $m/e^+ = 35$ evolution is observed at annealing temperatures below the multilayer desorption temperature. The heat of adsorption of BrCH$_2$COCl is estimated as $\sim$ 15-16 kcal/mol, by assuming that the difference between the adsorption energies of ethane and bromoethane corresponds to the additive binding energy of a Br atom in CH$_3$COCl. The enthalpy of adsorption for iodobenzene is $\leq$ 15 kcal/mol as previously mentioned. The inability of C$_6$H$_5$I to displace BrCH$_2$COCl from monolayer sites can be attributed to the similitude of the adsorption energy of the two species or that BrCH$_2$COCl binds more strongly to the metal surface than C$_6$H$_5$I.

### 3.6 Discussion

From TPD studies of alkyl chlorides on copper surfaces performed by Lin and Bent [32], it has been determined that no decomposition takes place for C$_1$-C$_6$ alkyl chlorides in the monolayer regime. However, when the alkyl chain contains more than six carbons, molecular desorption and C-Cl bond cleavage occur jointly. The dissociation temperature is estimated as $\sim$ 250 K, which corresponds to an activation energy of about 15.5 kcal/mol assuming a frequency factor of $10^{13}$ sec$^{-1}$. The gas phase C-Cl bond strength for alkyl chlorides and acetyl chloride is similar and has a value of approximately 83 kcal/mol. As a first approximation, one might expect the C-Cl bond dissociation temperature
Figure 3-16: Proposed mechanism for the formation of ketene on the surface for a coverage between 4 L and 5 L.
for CH$_3$COCl to be similar to that reported for alkyl chlorides. However, the thermal
dissociation of acetyl chloride on Cu(111) occurs at 138 K from the results obtained
by chemical displacement experiments. If we assume a first-order reaction and a pre-
exponential factor of $10^{13}$ sec$^{-1}$ for this process, then the calculated activation energy is
equal to 9.2 kcal/mol. By assuming a ± 2 order of magnitude uncertainty in the value
of the pre-exponential factor, the activation energy has an uncertainty of ± 2 kcal/mol.
For the acetyl chloride, the activation energy of the C-Cl bond cleavage is about 11%
of the gas phase bond energy compared to ~ 19% in the case of alkyl chlorides. In
both cases, it is implied that copper-chlorine bond formation and carbon-chlorine bond
scission take place concurrently. In addition, the low dissociation temperature at 138 K
implies that the presence of the CO group lowers the energy barrier for the C-Cl bond
scission. A model is presented below to examine the effects of the carbonyl group during
the decomposition of acetyl chloride on a Cu(111) surface.

The enthalpy of change for the formation of adsorbed acetyl groups and Cl atoms
can be estimated from the thermodynamical cycle in Figure 3-17(a). The gas phase C-Cl
bond strength in acetyl chloride is well-known and is approximately 83 kcal/mol, but
otherwise several approximations must be used. The heat of adsorption of CH$_3$COCl
and CH$_3$CO cannot be determined since they do not desorb from the substrate in the
monolayer regime. The bond enthalpy for Cu-CH$_3$CO is evaluated to be about equal to
29 kcal/mol, which corresponds to the Cu-CH$_3$ bond enthalpy determined on Cu(111)
[20]. This value is used on the basis that the adsorbed configuration of CH$_3$CO is via
the carbon of the carbonyl group, which presumably is similar to the $\eta^1$(C) configuration
for CH$_3$ chemisorbed on a Cu(111) surface. The heat of adsorption of acetyl chloride
is estimated by comparing the heat of adsorption of butane on Cu(100), $\Delta H_{ads} = 9.0$
kcal/mol [39], to the additive bonding energies of a chlorine atom and an oxygen atom.
The substitution of a CH$_3$ group by a Cl atom in butane increases its heat of adsorption
by ~ 1.3 kcal/mol, based on the heat of desorption of chloropropane on Cu(100) [32].
Moreover, a surface science study of the adsorption of organic molecules on clean Cu(100)
Figure 3-17: Schematic diagram of the thermodynamical cycle for (a) the adsorption of acetyl groups and Cl atoms and (b) the adsorption of Cl atoms on a Cu (111) surface.
by Sexton and Hughes indicates that the heat of adsorption of acetone is 1.1 kcal/mol greater than that reported for butane [39], if one of CH$_2$ groups in the latter is replaced by an oxygen atom. The heat of adsorption of acetyl chloride on Cu(111) is therefore calculated to be approximately 11-12 kcal/mol. The Cu-Cl bond enthalpy is not known, however, it can be estimated to approximately 72 kcal/mol from another thermochemical cycle presented in Figure 3-17(b). In this cycle, an activation energy of $\sim$ 61 kcal/mol is used for the evolution of CuCl, based on the TPD studies of chlorine adsorbed on Cu(111) by Bent and co-workers [35]. In addition, the gas phase Cu-Cl bond strength is well-known and has a value of 91 kcal/mol under standard conditions at 298 K [57]. Moreover, the Cu-Cu bond energy on Cu(111) is evaluated from the heat of sublimation of copper to be about 80 kcal/mol [57]. Thus the enthalpy change for the adsorption of acetyl groups and chlorine atoms on the surface is estimated as $-7$ kcal/mol.

The largest absolute error is actually in the value obtained for the heat of adsorption of a Cl atom on the substrate. Also, one might speculate that if a change in orientation occurs with the loss of the Cl atom, the oxygen atom may affect the bonding of the reactant and product species differently. However, in a study of C$_3$-C$_5$ alkyl bromides on Cu(111) by Lin and Bent [32], it was observed that the dissociation temperature for the C-Br bond scission was the same over the series of alkyl bromides implying that the transition state is not destabilized by the chain length. This study suggested that the observed reorientation of the alkyl chain from flat-lying to stand upright takes place after the dissociation of the C-Br bond.

The rather approximate thermodynamical cycle shown for acetyl chloride on Cu(111) indicates that the radical formation leading to adsorbed species on the surface is feasible. However, the energy barrier for this reaction is of particular interest since it determines whether or not the decomposition process does occur on the metal substrate. For instance, the decomposition of iodomethane on a surface was shown to be thermochemically plausible, and takes place at a low-temperature on Cu(111), but not on Pt(111).
due to the large work function of the platinum surface [45].

As discussed by Lin and Bent in their study of the decomposition of iodomethane on Cu(111) it is assumed that electron transfer from the metal substrate to the iodomethane molecule occurs at some point. It is of interest to us to similarly determine the energy required to transfer an electron from the Fermi level of Cu(111) to adsorbed acetyl chloride, subsequently forming a transient anion leading to dissociation. This energy can be estimated from an energetic cycle, involving an electron removed from the metal substrate, but attracted to the surface by electronic polarization of the substrate and the surrounding adsorbed layer [23]. Finally the energy required to attach the electron to physisorbed \( \text{CH}_3\text{COCl} \) is approximated to the gas phase vertical electron affinity, \( V\text{EA}[\text{CH}_3\text{COCl}(g)] \). Hence the energy required, \( E_D \), for vertical electron transfer from the Fermi level to the equilibrium geometry of adsorbed \( \text{CH}_3\text{COCl} \) is given by

\[
E_D = \phi - V\text{EA}[\text{CH}_3\text{COCl}(g)] - E_{im} - E_{pol}
\] (3.1)

where \( \phi \) is the work function of the adsorbate-covered surface, which was not determined in this study. However, Bent and co-workers have recently conducted experiments monitoring the work function change during surface reactions of alkyl halides on copper surfaces [35]. From their results, the work function change for 4 L of \( \text{CH}_3\text{COCl} \) on Cu(111) is estimated as \(-0.5\) eV, giving a value of \( 4.4\) eV for \( \phi \). The substrate polarization gives rise to the image charge attraction, \( E_{im} \), which can be approximated in the monolayer as \( e^2/4z = (3.6/z) \) eV, where \( z \) is the distance of the charge from the image plane. A value of \( \sim 1.2\) eV is obtained for \( E_{im} \), assuming a radius of \( z = 3 \) Å, based on the liquid density of acetyl chloride [57]. The electronic polarization of the surrounding adsorbates, \( E_{pol} \), can be calculated as \( \chi P^- \), with \( \chi \) representing the "degree" of solvation, and the \( P^- \) is the Born value of \( e^2/2r(1 - 1/e) \), where \( r \) corresponds to the radius of the anion and \( e \) is its dielectric constant. Supposing that the anions are about one third solvated at the monolayer coverage, so that \( \chi = 0.8 \) [23], then \( E_{pol} \) is approximately 0.6
eV, with $P^- = 2.25$ eV given $\epsilon = 15.8$ and $r = 3$ Å, for acetyl chloride. Although the gas phase vertical electron affinity of CH$_3$COCl has not been measured, it is possible to estimate its value as $-0.75$ eV with respect to the vacuum level, by averaging the VEA of phosgene and acetone which are approximately equal to 0 and $-1.5$ eV, respectively [58-59]. The negative sign convention is such that the potential energy curve of this negative ion lies above the potential energy of the neutral molecule in its ground state. This VEA energy should represent electron attachment to an orbital of $\pi^*(C=O)$ character as opposed to $\sigma^*(C-Cl)$ orbital, since the $\pi^*$ orbital lies at a lower molecular energy level than the $\sigma^*$ orbital. However, the energy required for the vertical electron transfer is still as much as $3.35$ eV above the Fermi level. Also, this transfer would not necessarily lead to dissociation since the electron must ultimately occupy the $\sigma^*$ orbital. The VEA to a $\sigma^*$ type orbital for an alkyl chloride is taken as $-3.3$ eV, and the energy for vertical electron transfer from Cu(111) would then be evaluated as $5.9$ eV. However, the actual VEA for the $\sigma^*$ orbital in acetyl chloride is not known.

The measured activation energy of $0.4$ eV for the C-Cl bond dissociation is much smaller than that estimated for direct electron attachment. To explain this difference in energies, thermally-activated electron transfer is considered, as in Bent's studies of iodomethane [20]. Thus, the energy barrier for the electron transfer can be drastically lowered as a result of its dependence on the internuclear separation of the C-Cl bond. This effect is demonstrated in Figure 3-18, which attempts to display the potential energy curves for adsorbed CH$_3$COCl and CH$_3$COCl$^-$ as a function of the C-Cl bond separation. Qualitatively, one observes that as the C-Cl internuclear distance increases, the energy of adsorbed CH$_3$COCl$^-$ decreases while the energy of the neutral molecule increases. At the point where the CH$_3$COCl$^-$/Cu and CH$_3$COCl/Cu potential energy curves intersect, the electron transfer from the metal surface is thermoneutral for vibrationally-excited CH$_3$COCl.

In order to make a quantitative estimate of the energy barrier, it is necessary to
Figure 3-18: Potential energy curves for acetyl chloride on Cu(111) and the anion on Cu(111) systems as a function of the C-Cl internuclear separation. The curves were constructed as described in the text.
know the reactant and product enthalpies for the two paths. These enthalpies have been evaluated above. The shape of the potential energy curves connecting the two sides in Figure 3-18 also needs to be established. The difference between the C-Cl bond length and the sum of the Van der Waals radii of the carbon and the chlorine atoms is estimated as 1.71 Å, which corresponds to the homolytic bond cleavage. For an ionic dissociation, the distance travelled by the Cl atom can be regarded as being equal to the difference in radius of metallic copper and Cu$^{+1}$ ions, which is evaluated as 1.60 Å. In any case, the difference in the reaction coordinate corresponding to the dissociation is approximately taken as 1.6 Å. In addition, the potential energy curves are assumed to be parabolas, i.e. representing harmonic potentials.

In Figure 3-18, electron attachment to the $\sigma^*$ orbital is considered to take place, and the value of 5.9 eV for the VEA is therefore used. The point at which the CH$_3$COCl/Cu and CH$_3$COCl$^-$/Cu curves intersect corresponds to a thermal energy of approximately 1.0 eV. This estimated energy barrier is $\sim$ 0.3 eV higher than the experimental value of about 0.67 eV for alkyl chlorides on a Cu(111) surface [32]. However, several approximations are involved when considering the end point energies and the curves shapes. In particular, the chemisorption of the products during the neutral homolytic cleavage and the adiabatic coupling between the two curves are neglected, and both effects would lower the apparent thermal barrier.

In the case of acetyl chloride, the experimental value obtained for the thermally-activated electron transfer is approximately 0.3 eV below that reported for an alkyl chloride. This difference is a certain indication that the CO group affects the electron attachment to the $\sigma^*$ orbital. One important aspect is that the $\pi^*$ orbital should have a much large cross section for the electron capture, as demonstrated by Pearl et al. [60]. Also, from gas phase studies of dissociative attachment, DA, and intramolecular electron transfer, it is observed that the resonance energy of the $\sigma^*$ orbital in chloromethane is 0.6 eV higher than the one determined for vinyl chloride (H$_2$C=CHCl) [60-62]. From a
study by Closs et al. [63] of intramolecular electron transfer in organic radial anions in solution, they obtained a coupling matrix element of

$$V = V_0 \cdot e^{-\beta(R-R_0)}$$  \hspace{1cm} (3.2)

where $V_0$ is equal to 0.236 eV, $R$ is the donor-acceptor centre-to-centre distance, $R_0$ is equal to 6 Å, and $\beta$ is equal to (1.01/2)Å$^{-1}$. Assuming a similar coupling matrix element, $V$, for acetyl chloride with the distance, $R$, from the Cl atom at 0.8 Å from the C-Cl equilibrium separation to the centre of the C=O bond, equal to ~ 2.8 Å; the coupling matrix element is calculated to be ~ 1.2 eV. The actual coupling energy might be greater than 1.2 eV, if the electron transfer occurs at a distance shorter than 0.8 Å.

Since the $\pi^*$ and $\sigma^*$ orbitals involved in electron transfer are orthogonal by symmetry, this coupling might not be expected. However, very fast electron transfer occurs in aryl halides in solution, and it is suggested that vibrational distortion might help to bypass the symmetry restrictions [64]. In addition, gas phase studies of intramolecular electron transfer in haloalkenes have noted that the C=C bond is unstable with respect to the occupied $\pi^*$ orbital, which might rotate around the bond and allow coupling between the $\sigma^*$ and $\pi^*$ orbitals [65]. The $\pi^*$, $\sigma^*$ coupling in acetyl chloride could have a greater value than the 0.6 eV observed for vinyl chloride, because the $\pi^*$ orbital is more centered around the carbon of the C=O bond. Also strong interactions with the surface may reduce the molecular symmetry. Based on our simple model, presented in Figure 3-18, we evaluate the $\pi^*$, $\sigma^*$ coupling energy in acetyl chloride adsorbed on Cu(111) as 1.0 eV, assuming that the crossing point corresponds to the experimental barrier value of 0.4 eV, corrected for the approximations used by an additional 0.3 eV, by comparison with alkyl chloride data.

Gas phase studies of photofragmentation of acetyl chloride by a Norrish type I reaction demonstrate that at 248 nm the scission of the C-Cl bond dominates over the C-C bond [37]. The bond cleavage is the result of photoexcitation of the $^1[n(O), \pi^*(C=O)]$ electronic
configuration. However, the decomposition of adsorbed acetyl chloride on the substrate probably involves the promotion of a thermally excited electron from a filled metal orbital.

The experiments performed for bromoacetyl chloride on a Cu(111) surface provide preliminary results which imply that bond cleavage readily occurs on the metal surface in the monolayer regime. The photochemistry of gas phase BrCH₂COCl has demonstrated that once local excitation of the carbonyl group is achieved, the C-Cl bond dissociation is favoured over the expected C-Br bond dissociation with a bond cleavage ratio of 2:1[44]. This preferred dissociation pathway is due to the nonadiabaticity in the dynamics of the intramolecular energy transfer. In that case, there is no symmetry restrictions on the electron/hole energy transfer to the Cl. With an electron attachment mechanism, however, it is important that the π*(C=O) and the σ*(C-Br) orbitals could mix more favourably than the π*(C=O) and the σ*(C-Cl) orbitals as a result of a better orbital overlap [65], since the Br atom is not held in the nodal plane of the π* orbital. However, the adsorbate geometry on the metal may drastically alter the coupling between the π*(C=O) and the σ*(C-halogen) orbitals. The results obtained for the thermal decomposition at 174 K on the metal substrate do not permit speculation on which bond is preferentially cleaved. However, once the bond through which the BrCH₂COCl decomposition occurs is established a model analogous to the one described above for acetyl chloride can be proposed.

Finally, an interesting secondary reaction is observed during the chemical displacement technique. The peak detected at 167 K is not associated with CH₃COCl molecular desorption, and is assigned to the formation of acetophenone from a coupling reaction between the adsorbed acetyl group and the benzene radicals. Moreover, the m/e⁺ = 42 evolution implies that the C-Cl bond is the one cleaved during the acetyl chloride decomposition. Although, further experiments were not performed to confirm the identity of the product, it is presumed that acetophenone is formed and then fragmented back to m/e⁺ = 42, CH₂CO⁺, in the analyzer. Also, no fragment is detected at m/e⁺ =
42, from mass spectra taken while backfilling the chamber with iodobenzene. From a study investigating the cross coupling of phenyl groups with alkyl iodides on a copper surface, it is speculated that acetophenone is formed by an Eley-Rideal type mechanism. This process involves the reaction between surface-bound species and a “hot” radical formed during the thermal decomposition of adsorbed iodobenzene, before the bonding and accommodation of the “hot” radical can occur [55].
Chapter 4

Conclusion

4.1 Concluding Comments

In this thesis, the thermal decomposition of submonolayers of acetyl and bromoacetyl chloride condensed on Cu(111) at 100 K, which have not been previously studied, are investigated under ultrahigh vacuum conditions. The TPD/R results obtained indicate that a surface dissociation process takes place at a low-temperature, for acetyl chloride. In addition, the thermal desorption of molecular iodomethane was performed as a test and provides a basis for comparison. Also, preliminary results were obtained for the decomposition of bromoacetyl chloride on Cu(111).

The C-Cl bond cleavage is proposed to occur through the thermal occupation of the $\pi^*(C=O)$. The C-Cl bond dissociation temperature is determined to be 138 K by applying the chemical displacement process, which corresponds to an activation energy of 9.2 kcal/mol compared to 15.5 kcal/mol for alkyl chlorides, assuming a pre-exponential factor of $10^{13}$ sec$^{-1}$ and first-order reaction kinetics. This result implies that intramolecular energy transfer plays an important role in lowering the energy barrier of the C-Cl bond dissociation. In addition, thermodynamical and energetics models show that formation of acetyl groups and chlorine atoms is feasible on the copper surface.
During the chemical displacement technique, the formation of acetophenone is sug­gested due to the temperature peak detected at 167 K. This observation indicates that the adsorbed acetyl group is a stable intermediate and can react readily to form complex carbonyl compounds. Another important aspect of intramolecular energy transfer is the possibility of using an attached "electrophore" on the adsorbate to promote the dissociation of a particular bond.

4.2 Future Research

The study presented here is an exploratory investigation on the mechanism of intra-adsorbate energy transfer and several approaches can be employed to refute or support the assumptions made in this work and expand this research.

1. Use of other surface techniques

TPD/R is the only technique used in this work, it would be of great interest to employ different surface science techniques to confirm the results obtained or to gain a better insight on the factors influencing the surface reactions. For example, high resolution of electron energy loss spectroscopy provides information on the structure of the adsorbed species. Work function change measurements as the temperature of the surface is increased is another means to monitor the evolution of the surface reaction, since the work function is expected to change when a different species is on the surface. Another analytical tool which can be used is near edge x-ray absorption fine structure spectroscopy to determine the binding geometry of the adsorbate on the substrate. AES experiments may also be employed to determine the chemical composition of surface species at a certain temperature, even though the electron exposure might induce a substantial dissociation of the adsorbate [36].

2. Proposed experiments for bromoacetyl chloride on Cu(111)

The bond through which the dissociation process takes place has not been determined
in this study. However, the chemical displacement technique can be employed with a dis­
placing agent that binds more strongly to the surface than bromoacetyl chloride. More­
over, the decomposition of a halogenated hydrocarbon may lead to the evolution of a
coupling product from the reaction between the hydrocarbon radicals with the adsorbed
acetyl group. Consequently, the detection of either chlorine or bromine during the des­
orption of the coupling product should indicate which bond dissociation is kinetically
favoured.

3. Photochemistry of adsorbed acetyl and bromoacetyl chloride on Cu(111)

To investigate the influence of the surface on the branching ratio between competing
reaction pathways of adsorbates on the surface, one can study the branching between two
competitive dissociation channels resulting from the photo-induced electronic excitation
of the adsorbate-substrate system. Furthermore, information on the repulsive forces
acting on the dissociating molecule can be obtained by angle resolved translational energy
distribution of the photofragments desorbing from the surface.
Bibliography


