

Phosgene formation from adsorption of carbon tetrachloride on oxygen modified Ir(111)

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Abstract

The production of phosgene was observed when a pure carbon tetrachloride molecular beam was impinged on an oxygen modified Ir(111) surface. We propose a mechanism involving the partial surface decomposition of the CCl_4 molecule to CCl_2 which subsequently reacts with adsorbed oxygen to form phosgene. Phosgene formation was maximized at an oxygen surface coverage of approximately 0.3 ML. Increasing the surface temperature resulted in a decrease in formation of COCl_2 , as competing reactions became important, especially the rapid and more complete decomposition of CCl_4 on the surface prior to reaction with oxygen. © 2001 Elsevier Science B.V. All rights reserved.

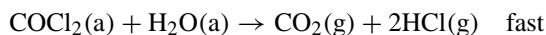
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1. Introduction

The use and production of carbon tetrachloride has been discouraged since its classification as an ozone depleting material by the Montreal Protocol [1]. However, carbon tetrachloride is still present as an unwanted by-product in the production of many chlorinated chemicals such as chloroform and dichloromethane, resulting in problematic chemical waste [2]. Among possible treatment methods, catalytic combustion is seen as advantageous for the disposal of dilute halocarbon wastes due to its relatively low energy cost and low temperature (300–500°C). Noble metal catalysts, including iridium on alumina, have been shown to be active for the both the partial

and complete oxidation of hydrocarbons [3]. However, many of these catalysts suffer from deactivation when exposed to chlorinated organics [4,5]. The cause of deactivation and mechanisms by which these reactions proceed are not precisely known and are the subjects of continued study [6].

Rossin and Farris report that the oxidation of chloroform with humid air on a platinum catalyst may proceed through a phosgene intermediate on the surface [7]. Although they report no phosgene in their final products, the production of HCl in favor of Cl_2 leads the authors to conclude that the reaction proceeds as presented below:



This mechanism implies that chloroform likely hydrodechlorinates to an adsorbed CCl_2 species on the

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surface after adsorption although, this has not been experimentally verified.

The production of phosgene from carbon tetrachloride has been observed on both water covered and “dry” MgO films when irradiated with an ultraviolet (193 nm) laser [8]. In addition, temperature programmed desorption (TPD) experiments following the irradiation of CCl₄ at 100 K showed the evolution of C₂Cl₄ from the “dry” surface at 240 K, a significantly higher surface temperature than observed in the desorption of intact C₂Cl₄ from MgO. This implies that CCl₂ species created from the photolytic decomposition of CCl₄ are stable on the surface until 240 K whereupon they combine and desorb in a reaction limited manner. Phosgene was thought to be created in a similar manner with CCl₂ reacting with either adsorbed water (wet surface) or the MgO substrate (dry surface). No phosgene was observed to form without the use of the UV radiation source.

A number of investigators have examined the behavior of carbon tetrachloride on a variety of single crystalline transition metal surfaces: Fe(1 1 0), Ag(1 1 1), Ru(0 0 1), and Ni(1 1 0). Using vibrational spectroscopy, carbon tetrachloride was found to dissociate completely on Ni(1 1 0) even at temperatures as low as 108 K [9]. However, Smentkowski et al. found that CCl₂ species which formed on an Fe(1 1 0) surface when exposed to carbon tetrachloride at 90 K, could desorb as a diradical at ~177 K or combine and desorb as C₂Cl₄ at ~198 K [10,11]. At least a portion of the CCl₂ formation is attributed to the presence of defect sites [12]. Similarly, these CCl₂ species were believed to form on Ag(1 1 1) resulting in formation of C₂Cl₄ (which desorbed at ~270 K) [13]. Sack et al. also found evidence of partial dissociation of carbon tetrachloride for fractional coverages (the first 0.13 ML) on the surface of Ru(0 0 1) at 100 K [14]. While the current article is confined to the behavior of CCl₄ on an O-modified Ir(1 1 1) surface, the authors hope to comment on the behavior of CCl₄ on unmodified Ir(1 1 1) in another publication [15].

2. Experimental

All experiments were conducted with a supersonic molecular beam scattering apparatus consisting of an ultra high vacuum chamber, which routinely achieves

base pressures of less than 1×10^{-10} Torr, and a quadruply differentially pumped source. The UHV chamber is equipped with an electron energy loss spectrometer, an Auger electron spectrometer, a quadrupole mass spectrometer (QMS), low energy electron diffraction optics (LEED), and an ion sputtering gun. A more detailed description of the chamber is reported elsewhere [16]. The iridium crystal was mechanically polished to within 0.4° of the (1 1 1) face and spot welded to tantalum wires which were subsequently attached to a translation/rotation manipulator. The sample was heated resistively with proportional-integral-derivative control and cooled conductively via either a liquid nitrogen filled reservoir (for cooling to 77 K) or by continuously flowing room temperature air through the same unfilled reservoir (for cooling to 300 K). Supersonic beams were produced by expansion of pure carbon tetrachloride (99.9% purity, Aldrich) vapor above room temperature liquid carbon tetrachloride through a ceramic nozzle with a 0.008 in. (203 μ m) aperture. The circular beam spot of 29 mm² was centered on the 80 mm² sample surface. An average beam energy of 0.074 eV was measured under these conditions using a standard time of flight technique [17].

The iridium sample was initially cleaned by repeated sputtering (1×10^{-5} Torr Ar, 0.5 keV, sample current 5–6 μ A) with subsequent annealing in oxygen at 5×10^{-7} Torr at 600 K for 10 min. Oxygen doses at 77 K and annealing in vacuum to 1550 K were used to maintain a clean surface. The clean Ir(1 1 1) surface showed the expected LEED pattern and Auger spectra.

Oxygen coverages were determined by relating the TPD area for mass 32 to O₂ dosage. Oxygen was back-filled at 300 K at approximately 1×10^{-7} Torr through a leak valve. The exposure was determined by integrating the partial pressure of O₂ over the dose time. Subsequent TPD measurements monitoring mass 32 were performed at 10 K/s to obtain a curve of oxygen dosage versus coverage. Saturation oxygen coverage was assumed to be 0.5 ML as has been previously shown by Hagen et al. [18].

Phosgene formation was determined using a modified King and Wells technique [16,19–21]. After applying the appropriate oxygen dose at 300 K, masses 117 (CCl₃⁺) and 63 (COCl⁺), the primary mass cracking fragments of carbon tetrachloride and phosgene,

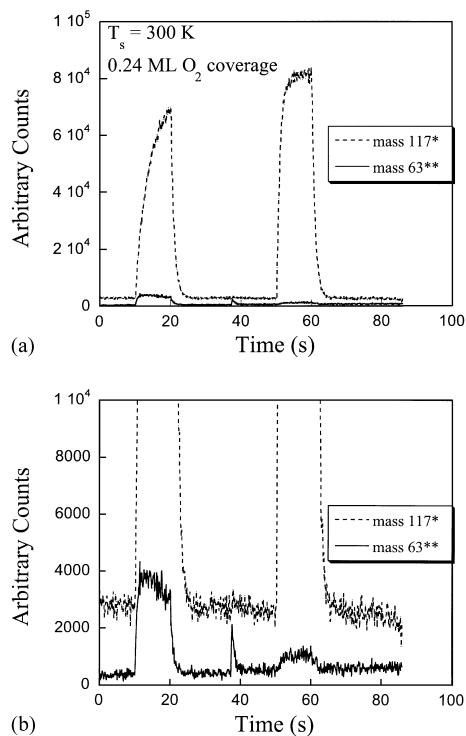


Fig. 1. (a) Example King and Wells type experiment showing production of phosgene from oxygen covered Ir(1 1 1) monitoring mass 63 and mass 117 signals: surface temperature = 300 K; oxygen coverage = 0.24 ML. First pulse is reflected off sample, second pulse is reflected off aluminum flag. See text for further details. Asterisk (*) denotes primary cracking fragment of CCl_4 and double asterisks (**) denote primary cracking fragment of COCl_2 . (b) Closeup of part (a) focusing on mass 63 signal.

respectively (parent ion peaks are not detectable), were monitored while the molecular beam of carbon tetrachloride was delivered in two 10 s pulses at a flux of about 0.003 ML/s. Fig. 1a and b show an example of the data collected. At 10 s a shutter is opened to allow the beam to enter the scattering chamber and to impinge upon the sample. At 20 s, the shutter is closed and the scattered carbon tetrachloride is pumped away. At 38 s a beam blocking flag in the scattering chamber is moved in front of the sample, which is intended to act as an inert surface. The rise in the mass 63 signal here is an experimental artifact due to the movement of the flag. At 50 s the shutter is opened again allowing the beam to impinge on the blocking flag and at 60 s, the shutter is closed again. The mass

117 signal allowed for a measurement of the carbon tetrachloride delivered to the surface while the mass 63 signal allowed for a measurement of the phosgene produced. A secondary mass cracking fragment (mass 65) due to isotopic variation in Cl was observed in the spectra at the correct proportion providing confidence in the identification of phosgene as the reaction product. However, we did not compare our experimentally produced result with a phosgene standard. Fragmentation patterns for carbon tetrachloride were in good agreement with those reported in the literature [22]. For experiments involving elevated surface temperatures, after oxygen was dosed at 300 K, the surface was heated and the temperature was allowed to stabilize for approximately twenty seconds before beginning the modified King and Wells experiment. The amount of oxygen on the surface was found to be nearly constant over the course of the experiment. Between experiments, oxygen was backfilled at 300 K and the surface was heated to 1550 K to remove any residual chlorine and carbon that may have been deposited by complete dissociation of the carbon tetrachloride.

In Fig. 1b, one can clearly see that phosgene is produced when the carbon tetrachloride beam impinges on the Ir(1 1 1) sample. However, there also appears to be some phosgene produced when the carbon tetrachloride beam is reflected off the beam blocking flag. This result can be explained in three ways. First, the blocking flag used in these experiments is aluminum, which can adsorb some oxygen during backfilling. Therefore, phosgene may be produced from reaction between the carbon tetrachloride beam and adsorbed oxygen on the flag. Similarly, other surfaces in the chamber can adsorb oxygen which may also result in the appearance of a low phosgene background. Finally, a small portion of carbon tetrachloride that reflects off the aluminum flag will absorb on the sample (front, back and sides) and may then react to form phosgene. While it is somewhat difficult to differentiate between the first and the second mechanisms, a sequence of three modified King and Wells experiments was performed to show the third mechanism dominates the formation of mass 63 when reflecting the beam off the flag. First, a typical modified King and Wells experiment was performed during which some mass 63 is produced when reflecting the beam off the flag with some arbitrary coverage of oxygen on the sample.

Immediately following the experiment, oxygen was removed from the sample by heating it to 1550 K. Upon cooling of the sample, a second modified King and Wells experiment was promptly performed in which almost no mass 63 (less than 1/10 of the latter case) was produced by reflecting the beam off the flag. This result indicates that either the majority of the phosgene produced during the first modified King and Wells experiment was produced as a result of surface reactions on the oxygen modified Ir(1 1 1) surface from scattered CCl_4 , or that oxygen on other surfaces that was responsible for phosgene formation in the first experiment had since reacted and was therefore unavailable for reaction in the second experiment. A third modified King and Wells was performed in which the oxygen covered sample was allowed to sit in vacuum for 15 min (about twice as long as the time between the first two experiments) before exposure to the beam. If oxygen on other surfaces of the chamber was responsible for the formation of phosgene in the first experiment, we would expect that no phosgene would be formed in our third modified King and Wells experiment, as the oxygen would have been depleted over time, just as between the first and second experiments. However, the formation of phosgene when the beam was reflected off the flag in this third experiment indicates that secondary collisions with the oxygen covered sample are indeed the primary mechanism for these mass 63 traces. Additionally, the mass 63 signals from the beam reflecting off the flag and the sample are maximized under the same conditions.

In order to determine the initial reaction probabilities, the observed QMS signals for masses 117 and 63 must be corrected for the effect of pumping speed as outlined by Rettner et al. [23]. First, the pumping speed time constant for mass 117 may be determined from the declining edge of a trace of a carbon tetrachloride beam scattering off the saturated surface after the beam is blocked from entering the scattering chamber. The pumping speed time constant for mass 63 may be determined from examination of the declining edges of mass 63 signal traces from experimental data. The time constants for both phosgene and carbon tetrachloride were found to be ~ 0.8 s. Rettner et al. demonstrate that the effect of a time constant τ , on a step function where the signal goes from a baseline value $I(t < t^*) = 0$ to $I(t = t^*) = I'$,

yields

$$I(t) = I' \left[1 - \exp \left(- \left(\frac{t - t^*}{\tau} \right) \right) \right]$$

where I represents the relevant mass counts from the quadrupole mass spectrometer, and t^* represents the time at which the shutters are opened and the beam is allowed to enter the scattering chamber. For a linear function such as $I' = I_0(t - t^*)$ this gives

$$I(t) = I_0 + m(t - t^*) - \left(\exp \left(- \frac{(t - t^*)}{\tau} \right) \right) (I_0 + m(t - t^*))$$

The above function was fit to experimental data in order to determine appropriate values for I_0 , which is the value needed for computing the initial reaction probability. For roughly half of the data analyzed, a linear function could not provide an adequate fit of the mass 63 trace for the entire 10 s pulse. For these cases, and indeed for all the data, we fit linear functions to what we judged to be the upper and lower bounds for the mass 63 signal and used this information to estimate uncertainties. We then used the average of these two bounds in the determination of the initial signal levels, which we used in computing the reaction probabilities. We have labeled our four initial signal values (corrected for pumping speed): I_s^{63} , I_f^{63} , I_s^{117} , I_f^{117} with the subscripts indicating reflection off the sample (s) and flag (f).

In addition to corrections for pumping speed, the QMS signal intensities of mass 63 and 117 must be related to the relative amounts of phosgene and carbon tetrachloride that these signals represent by means of a mass spectrometry scaling factor [19]. This scaling factor is a function of the ratio of pumping speeds, the relative electron impact ionization cross sections and the ratio of mass filter transmission probabilities for these two species. While the ionization cross section of carbon tetrachloride is well known [24], the authors were unable to locate any data in the literature reporting the ionization cross section of phosgene. Furthermore, the mass filter transmission probability of phosgene could not be determined with accuracy without the use of a phosgene standard, which was not possible due to safety considerations. Therefore, the authors can only report relative reaction probabilities and for the purposes of this paper we assume that the

mass spectrometry scaling factor between phosgene and carbon tetrachloride is unity.

As mentioned above, we also need to consider the formation of phosgene off surfaces other than the sample. Therefore, we have determined the initial amount of phosgene formed by the background, I_b^{63} , by multiplying the amount of carbon tetrachloride reflected from the oxygen covered surface in each experiment by the ratio of the mass 63 signal to the mass 117 signal for the case of reflection of the beam off the clean surface.

$$I_b^{63} = (I_s^{117}) \left(\frac{I_s^{63}}{I_s^{117}(\text{O}_2 \text{ coverage} = 0, T_s = 300 \text{ K})} \right)$$

By subtracting this value from the mass 63 signal for beam reflection off the sample, we determine the initial phosgene signal attributed to reaction on oxygen modified Ir(1 1 1), I_s^{63*} .

$$I_s^{63*} = I_s^{63} - I_b^{63}$$

The initial phosgene formation probability per incident CCl_4 molecule (P_i) in each experiment was calculated to be the ratio of the initial phosgene signal formed by reaction on the oxygen modified Ir(1 1 1) surface and the mass 117 signal off the aluminum flag (the amount of CCl_4 dosed).

$$P_i = \frac{I_s^{63*}}{I_f^{117}}$$

In addition to examining the phosgene formation probability per incident carbon tetrachloride molecule, the fraction of chemisorbed carbon tetrachloride that reacted on the surface to form phosgene can also be quantified. The initial phosgene formation probability per chemisorbed carbon tetrachloride (P_c) was calculated by dividing the corrected mass 63 signal by the difference between the mass 117 signal reflected by the sample and the blocking flag.

$$P_c = \frac{I_s^{63*}}{(I_f^{117} - I_s^{117})}$$

3. Results and discussion

Fig. 2 depicts the relationship between oxygen surface coverage and the incident carbon tetrachloride

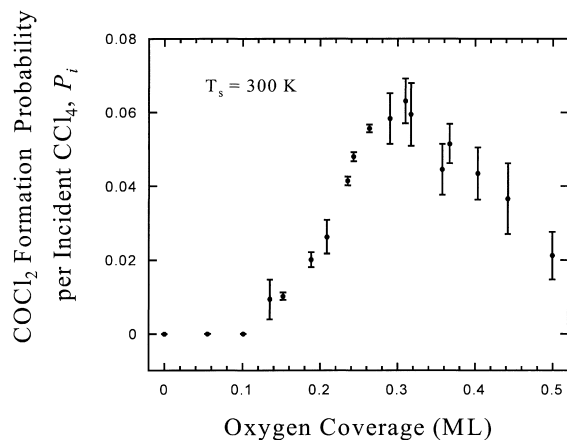


Fig. 2. Dependence of reaction probability of COCl_2 formation from incident CCl_4 on oxygen surface coverage at 300 K.

phosgene formation probability at 300 K. P_i increases with increasing oxygen coverage until passing through a maximum at approximately 0.32 ML, but even at 0.5 ML (saturation coverage under vacuum conditions), P_i still remains 40% of the maximum. Fig. 3 shows the relationship between the chemisorbed carbon tetrachloride phosgene formation probability and oxygen surface coverage. Even for coverages where P_i was maximized, the value of P_c is only 0.2. However, for a saturation coverage of oxygen P_c is computed to be 0.83. This value is consistent with a mass spectrometry scaling factor of one, since a reaction probability greater than one would be unphysical. If the

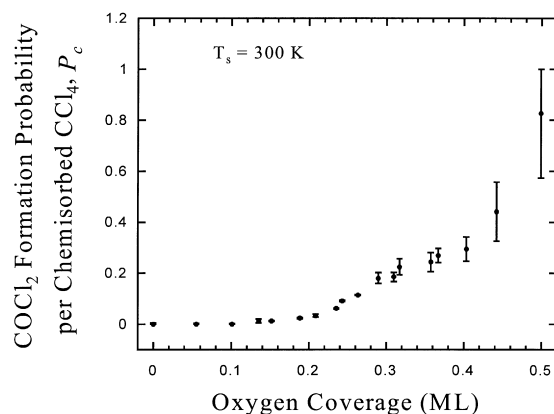


Fig. 3. Dependence of reaction probability of COCl_2 formation from chemisorbed CCl_4 on oxygen surface coverage at 300 K.

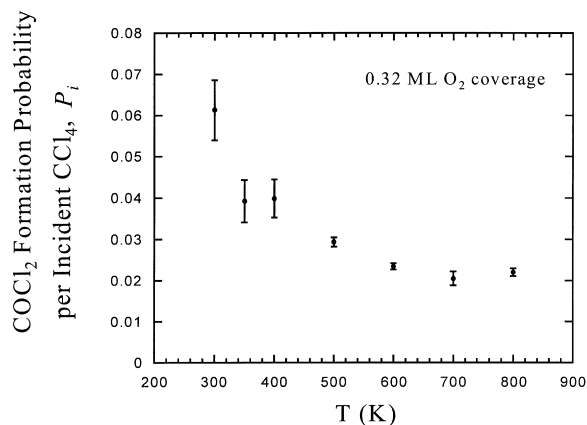


Fig. 4. Dependence of reaction probability of COCl_2 formation from incident CCl_4 on surface temperature.

mass scaling factor is nearly correct, this would also suggest that CCl_4 molecules that actually chemisorb readily encounter surface oxygen for the formation of phosgene. However, the presence of oxygen on the surface can significantly affect the work function and electronic structure of metal surfaces [25] and thus, may correspondingly be partially responsible for the increase in reaction probability shown in Fig. 3.

Fig. 4 shows the relationship between the incident carbon tetrachloride phosgene formation probability and surface temperature between 300 and 800 K at constant oxygen coverage (0.32 ML). P_i declines monotonically as the temperature increases. This can be attributed partially to the reduction in carbon tetrachloride sticking with increasing temperature [15] and, as Fig. 5 shows, partially to the reduced phosgene formation probability per chemisorbed carbon tetrachloride with increasing temperature. This suggests that competing reactions may be important. Perhaps the complete decomposition of carbon tetrachloride occurs more rapidly at higher temperatures and since oxygen on the surface will be more mobile and reactive, this could lead to more complete oxidation products, namely CO and CO_2 . Unfortunately, CO and CO_2 production were more difficult to quantify due to a high background. However, when monitoring mass 28 and mass 44 in an analogous manner to the previous experiments, at 800 K, CO and CO_2 evolution were observed when impinging the beam upon the sample.

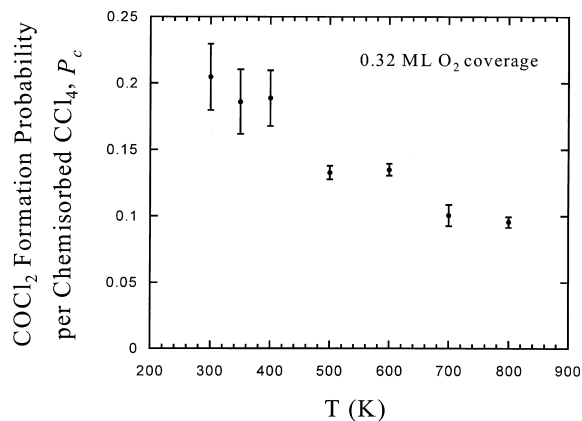


Fig. 5. Dependence of reaction probability of COCl_2 formation from chemisorbed CCl_4 on surface temperature.

Similarly, TPD measurements following phosgene production experiments at lower temperatures showed the presence of both CO and CO_2 which cannot be attributed to background adsorption. Above 800 K, the oxygen desorption rate was high enough to preclude the necessary oxygen coverage desired for comparison.

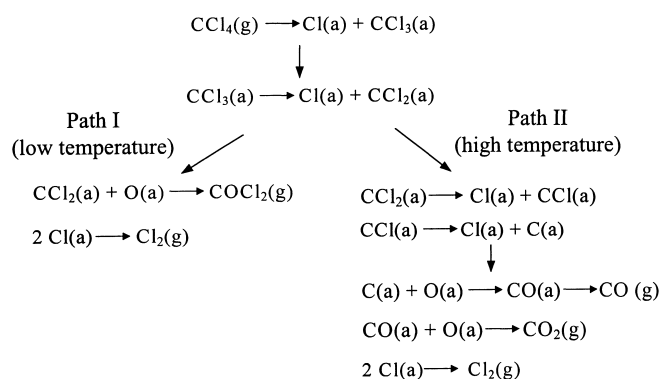
Modified King and Wells type experiments involving oxygen beams and carbon tetrachloride covered surfaces (~ 0.1 – 3.0 L) at 300 K did not result in the production of phosgene. First, a pure molecular oxygen beam (~ 0.088 eV) with a flux of ~ 0.04 ML/s was employed, but the production of phosgene was not detected. Second, a radio frequency generated atomic oxygen source (7.5% O_2 in Ar, a more complete description of a similar source can be found elsewhere [19]) with a flux of ~ 0.003 ML/s was directed at the sample, and again the production of phosgene was not detected. In both cases, subsequent TPD experiments revealed the presence of oxygen on the surface, so carbon tetrachloride did not prevent the adsorption of oxygen.

Due to the prompt observation of phosgene when the carbon tetrachloride beam strikes the oxygen covered sample, one might surmise that an Eley–Rideal-type mechanism is responsible for the formation of phosgene. The lack of production of phosgene by the oxygen beams on the carbon tetrachloride covered surface may also suggest an Eley–Rideal mechanism. However, temperature programmed desorption experi-

ments were performed to gain further insight into the mechanism of phosgene formation.

The surface was exposed to various oxygen coverages at 77 K, followed by exposure to the CCl_4 beam at 77 K. The subsequent TPD measurements indicated the production of phosgene with the peak at ~ 175 K. These results are virtually identical to the results from investigations of the desorption of adsorbed phosgene from Pt(1 1 1) [26], which indicate a desorption limited mechanism is responsible for the production of phosgene on Ir(1 1 1) in our experiments. TPD experiments following a sequential exposure of carbon tetrachloride prior to oxygen on Ir(1 1 1) at 77 K also

the subsequent TPD experiment. These results can be explained by a mechanism in which the lifetime of adsorbed CCl_2 is critical to the formation of phosgene. As temperature is increased, the lifetime of CCl_2 is shortened. This would also provide an explanation for the results in which no phosgene was observed when impinging oxygen beams at a carbon tetrachloride covered surface. If the lifetime of adsorbed CCl_2 at 300 K is short, CCl_2 may have decomposed in the time between carbon tetrachloride dosing and contact by the oxygen beams. We propose the following simple Langmuir–Hinshelwood-type kinetic model as given below.



showed the production of phosgene. This result seems to oppose an Eley–Rideal-type mechanism, since the order of the exposure had no effect on the production of phosgene, indicating that both carbon tetrachloride and oxygen are thermally accommodated adsorbed species at the time of reaction. Furthermore, the formation of phosgene would require a somewhat complicated Eley–Rideal mechanism involving the scission of two C–Cl bonds and the formation of a C=O bond, all within the Eley–Rideal framework. Such a highly concerted mechanism seems unlikely. Additionally, the strong surface temperature dependence of this reaction seems counterintuitive to an Eley–Rideal mechanism.

Additional temperature programmed desorption experiments, similar to those described above, were performed in which the temperature of the oxygen covered sample was held constant at various values between 77–150 K during carbon tetrachloride exposure. As the surface temperature during the CCl_4 dosage was increased, less phosgene was revealed in

In our model, carbon tetrachloride that sticks to the surface will readily release two chlorine atoms to the surface in a stepwise manner, resulting in the formation of a quasi-stable CCl_2 species on the surface. The CCl_2 may either react with adsorbed oxygen to form phosgene (Path I) or it can continue to decompose to elemental chlorine and carbon (Path II). As surface temperature is increased, Path II becomes favored over Path I, but for the temperature range of the experiments presented in this article both paths appear to be active. If the CCl_2 molecule takes Path II, the carbon can be further oxidized to CO and CO_2 . Auger and TPD experiments indicate that chlorine will desorb from Ir(1 1 1) over a broad temperature range from ~ 550 –1000 K. This result is in good agreement with results obtained on Pt(1 1 1) [27].

However, it is easy to imagine that an alternative mechanism could be responsible for the production of phosgene, the oxidation of carbon from completely decomposed carbon tetrachloride followed by the chlorination of carbon monoxide. In fact, phosgene is

commercially produced by reacting CO and Cl₂ over an activated carbon catalyst [28]. However, when exposing a partially CO covered surface at 300 K to the carbon tetrachloride beam there was no evidence of phosgene formation. The dissociative chemisorption of carbon tetrachloride was substantially reduced by the presence of CO, but not completely eliminated (~20% sticking of CCl₄ following a 1.1 L CO exposure).

4. Conclusions

Phosgene is produced on the oxygen modified Ir(1 1 1) surface when exposed to carbon tetrachloride. We propose that the formation of phosgene occurs via the presence of CCl₂ surface species formed during the decomposition of carbon tetrachloride. Adsorbed CCl₂ readily reacts with adsorbed oxygen and can desorb as an intact phosgene molecule. Competing reactions involving the oxidation of completely dissociated carbon tetrachloride become significant as the surface temperature increases.

Acknowledgements

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