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# The ultraviolet photochemistry of condensed-phase acetyl chloride

Brad Rowland<sup>1</sup>, Wayne P. Hess<sup>\*</sup>

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

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#### Abstract

Ultraviolet (UV) irradiation of amorphous and crystalline samples of solid acetyl chloride produces metastable HCl  $\cdot$  ketene complexes in a 1:1 ratio following S<sub>1</sub> photoexcitation. The HCl  $\cdot$  ketene complex is the only product observed following UV irradiation of either amorphous or crystalline samples. The condensed-phase reaction mechanism contrasts starkly with that of the gas phase mechanism that produces Cl and CH<sub>3</sub>CO radicals by prompt photolysis, followed by dissociation of internally excited CH<sub>3</sub>CO to form CO and CH<sub>3</sub> in a non-concerted process.

#### 1. Introduction

The release of chlorinated hydrocarbons into the environment is a potential threat to terrestrial ecosystems and ground water supplies [1]. Chlorocompounds are present in hazardous wastes and in the soil subsurface at industrial and defense waste sites, such that the energetic processes of chlorine-containing compounds impact the storage and processing of mixed hazardous waste and the disposition of contaminated soils. Previously, we have studied the photodissociation of acetyl chloride molecules under isolated conditions in a molecular beam [2,3], and found that the gas phase photodissociation is described by sequential reactions

 $CH_{3}COCl + h\nu \rightarrow CH_{3}CO^{\#} + Cl^{*}/Cl, \qquad (1)$ 

$$CH_3CO^{\#} \rightarrow CH_3 + CO.$$
 (2)

Reaction (1) leads to rapid scission of the C–Cl bond producing ground Cl  $({}^{2}P_{3/2})$  and spin–orbit excited Cl\*  $({}^{2}P_{1/2})$  atoms, and vibrotationally excited acetyl radicals. In the 236 nm photolysis of acetyl chloride, the mean translational energy release is 18 kcal/mol with an average release of 9.9 kcal/mol into Cl translation [2,3]. The mean internal energy of the acetyl radical is 19 kcal/mol, which is sufficient to overcome the  $\approx$  18 kcal/mol barrier to breaking the C–C bond as described in reaction (2). The gas phase photochemistry of acetyl chloride is unusual because it does not follow the well known Norrish type I reaction that is characteristic of asymmetrically substituted aldehydes and ketones [4,5]. The

<sup>\*</sup> Corresponding author. E-mail: wp\_hess@pnl.gov.

<sup>&</sup>lt;sup>1</sup> AWU Postdoctoral Research Associate, E-mail: jb\_rowland@pnl.gov.

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usual Norrish type I photochemical mechanism involves cleavage of the weaker  $\alpha$ -bond following  $(\pi^* \leftarrow n)$  photoexcitation to the lowest singlet excited state localized on the carbonyl group. Therefore, the weaker C-C bond in acetyl chloride would be expected to break preferentially over the C-Cl bond following S<sub>1</sub> excitation [4,5]. Acetyl chloride photodynamics might also be expected to resemble the high-temperature chemistry of alkyl chlorides that yield HCl and alkene products through elimination.

In the present study of UV-irradiated amorphous and crystalline acetyl chloride samples, we extend the previous gas phase work into the condensed phase. Our goal here is to explore photodissociation processes, which are more closely related to those occurring in mixed-waste storage tanks and in the large-scale remediation of chlorinated wastes, by investigating the condensed-phase reaction mechanism for UV excitation of acetyl chloride – a system that is well studied under isolated conditions [2,3,5,6].

Although no studies report the radiation-induced photochemistry of neat liquid or solid acetyl chloride, Kogure et al. have studied UV photolysis of acetyl chloride molecules isolated in an argon matrix [7]. Their results show that UV photolysis of matrix isolated acetyl chloride leads to the formation of ketene and HCl molecules in a caged dimer complex, which can be described by

$$[H_3CCOCI]_{matrix} + h\nu \rightarrow [HCI \cdot H_2C = C = O]_{matrix}.$$
(3)

The formation of the HCl · ketene complexes was attributed to an elimination reaction. However, the mechanism for product formation, which could be a concerted elimination or a stepwise reaction, was not discussed [7]. In a related study, the reaction of acetyl bromide to form a dimer complex of ketene and HBr was investigated using ab initio methods. This study concluded that the HBr elimination reaction is endothermic with an enthalpy of 21.3 kcal/mol [8]. As such, a caged HBr · ketene complex may be regarded as metastable.

In the present study, we probe photo-initiated reactions within thin films of amorphous and crystalline acetyl chloride following 266 nm irradiation. We use Fourier transform infrared (FT-IR) spectroscopy to detect the trapped photoproducts and to observe their kinetic behavior. The photoproducts, and hence reaction mechanism, differ markedly from the gas phase mechanism. The photo-produced HCl · ketene complexes are metastable, and readily back react to reform acetyl chloride at moderately elevated temperatures.

# 2. Experimental

Thin films of acetyl chloride are deposited from  $\approx 10^{-4}$  Torr vapor samples to a thickness of  $\approx 4$ µm on an IR transparent substrate held at 20 K. The acetyl chloride sample is outgassed using several freeze-pump-thaw cycles before deposition, and no impurities, such as water, are observed in the IR spectra of the condensed samples. At a substrate temperature of 20 K, low-density amorphous films form directly. To produce more dense amorphous samples, we warm freshly deposited films to 90 K for  $\approx 5$  min and then recool the samples to 10 K. Crystalline samples are prepared by warming films to 110 K for  $\approx 10$  min and again recooling to 10 K. The 10-min annealing period at 110 K allows the amorphous films to convert into a more ordered crystalline phase. Distinct FT-IR spectra of amorphous and crystalline acetyl chloride films are obtained which may be used to identify the phase of the solid film.

We irradiate the crystalline and amorphous films using the 4th harmonic of a Nd:YAG laser at 266 nm. Samples are irradiated between 1 and 20 h using an average pulse energy of 0.7 mJ at a 20 Hz repetition rate. The diameter of the 266 nm beam is  $\approx 18$  mm which is considerably larger than the  $\approx$  12 mm diameter of the unpolarized polychromatic IR probe beam. Infrared spectra are collected before and after irradiation at a resolution of  $2 \text{ cm}^{-1}$ . To extract vibrational spectra of the photoproducts, we subtract the FT-IR spectrum of a non-irradiated sample from the spectrum of an irradiated sample. The resulting difference spectra display vibrational absorption bands attributable solely to the photoproducts. In typical experiments,  $\approx 8\%$  of the acetyl chloride sample is converted to HCl · ketene complexes, however, in some experiments less than 1% of the original acetyl chloride sample is converted. Assignments of the vibrational modes of the ketene product were guided by ab initio calculations and by published spectra of matrix and solid samples [9,10]. The vibrational modes of acetyl chloride were identified by comparison with the published spectra of matrix isolated [7] and liquid samples [11], and by comparison with the results of ab initio calculations [12]<sup>2</sup>.

#### 3. Results

The IR spectra of amorphous and crystalline acetyl chloride samples are displayed in Fig. 1. When compared, the IR bands of the crystalline sample are much sharper than those of the amorphous sample. The full-width-half-maxima of all the IR bands of the crystalline sample decrease by an average factor of  $\approx 2$  upon conversion from an amorphous to a crystalline film. In addition, distinct doublets are observed for several vibrational bands indicating the presence of a more highly ordered crystalline phase. The relative IR peak heights also change drastically; especially among the C-O stretching (1803 cm<sup>-1</sup>), CH<sub>3</sub> symmetric rocking (1102 cm<sup>-1</sup>), and CClO deformation (592 cm<sup>-1</sup>) modes [12]. The IR band positions, FWHM, and peak heights for these bands are listed in Table 1.

Fig. 2 displays the difference spectrum obtained for a crystalline film of acetyl chloride following 266 nm irradiation. The HCl and ketene products are readily identified by strong IR absorption bands in the 2750–2350 and  $\approx 2130 \text{ cm}^{-1}$  spectral regions, respectively. Other positive IR bands displayed in Fig. 2 are attributed to the vibrational modes of ketene. The negative IR absorption bands, in the difference spectra, are attributed to loss of acetyl chloride molecules due to photoreaction. The remaining positive IR absorption bands, which *are not* 



Fig. 1. Infrared spectra of amorphous (a) and crystalline (b) acetyl chloride samples; the vibrational absorption bands of the crystalline spectrum are sharper than the bands of the amorphous spectrum, and splitting can be observed in some of the higher frequency bands of (b).

assigned to the vibrational modes of HCl or ketene, are attributed to the red-shifted IR bands of acetyl chloride. The spectral red-shift of the vibrational modes of such 'perturbed' acetyl chloride molecules is caused by close coupling of unreacted acetyl chloride molecules with neighboring HCl · ketene complexes.

The vibrational frequency of gas phase HCl is  $2886 \text{ cm}^{-1}$  with significant spectral red-shifts ob-

Table 1

The IR spectra of condensed-phase acetyl chloride. Infrared band positions, FWHM, and peak heights of the C–O stretching, the CH<sub>3</sub> symmetric rocking, and the CCIO deformation bands of amorphous and crystalline films

| Vibrational mode               | Band center | FWHM | Peak height |
|--------------------------------|-------------|------|-------------|
| amorphous film                 |             |      |             |
| C-O stretch                    | 1803.7      | 30.8 | 1.48        |
| CH <sub>3</sub> symmetric-rock | 1102.2      | 21.9 | 0.97        |
| CCIO deformation               | 592.0       | 26.1 | 0.70        |
| crystalline film               |             |      |             |
| C-O stretch                    | 1804.0      | 31.7 | 0.83        |
| CH <sub>3</sub> symmetric-rock | 1098.4      | 13.1 | 1.32        |
| CCIO deformation               | 592.1       | 9.2  | 1.31        |

<sup>&</sup>lt;sup>2</sup> There is disagreement in the literature over the proper assignment of the 590 cm<sup>-1</sup> band of the acetyl chloride vibrational spectrum. We agree with the assignment of Durig et al. based upon review of ab initio calculations and spectra of the  $d_3$ -acetyl chloride isotope.

served for neat liquid (2785  $\text{cm}^{-1}$ ) and solid (2768  $cm^{-1}$ ) samples [13]. Large spectral red-shifts are observed for the Ar matrix-isolated HCl monomer [7] at  $\approx 2860 \text{ cm}^{-1}$ , for matrix (argon) isolated HCl  $\cdot$  ketene complex [7] at 2679 cm<sup>-1</sup>, for the matrix (argon) isolated HCl · CO complex [14] at 2664 cm<sup>-1</sup>, and for the matrix  $(N_2)$  isolated HCl  $\cdot$  $(CH_3)_2O$  complex [15] at 2280 cm<sup>-1</sup>. The magnitude of the spectral red-shift, and the shape of the product HCl vibrational band indicate that the absorption bands between 2350 and 2750 cm<sup>-1</sup> are attributable to HCl molecules complexed with ketene molecules. The corresponding red-shifted bands of the DCl · ketene complexes are observed in the 1600–1900 cm<sup>-1</sup> region for UV-irradiated  $d_3$ -acetyl chloride.

The intensity of the vibrational absorption bands associated with HCl and ketene decrease markedly as the temperature of a sample is increased. Since the post-irradiated spectra approach the pre-irradiated spectra with warming, we conclude that acetyl chloride molecules are reformed upon warming irradiated samples, and that the condensed-phase photoreaction is reversible. Fig. 3 displays the loss of IR band



Fig. 2. The difference spectrum of a crystalline sample of acetyl chloride; the positive IR absorption bands that are attributed to vibrational modes of ketene and HCl are marked. Other positive and negative bands are attributed to spectral shifting of perturbed but unreacted acetyl chloride. The strong negative bands are due to the loss of acetyl chloride by photoreaction.



Fig. 3. The difference spectra taken at temperatures of 10 K (a) and 90 K (b) for an amorphous film of acetyl chloride. The IR intensity of the strong positive IR band, which is attributed to the C-O stretch of ketene at 2130 cm<sup>-1</sup>, decreases by a factor of  $\approx 4$  in warming from 10 to 90 K. A similar strong decrease in absorption intensity for HCl and ketene bands (and proportional gain in acetyl chloride band intensity) is observed in the difference spectra of a crystalline acetyl chloride film held at 80 K for several hours. No significant sublimation of the acetyl chloride samples occurs at these temperatures.

intensities as an amorphous sample is warmed from 10 to 90 K. The loss of HCl  $\cdot$  ketene products and the reformation of acetyl chloride reactant is observed in the difference spectra of both crystalline and amorphous samples. The kinetics of the reverse reaction for complexes trapped within crystalline or amorphous matrices of acetyl chloride are also similar. Metastable HCl  $\cdot$  CH<sub>2</sub>CO complexes back-convert at temperatures above  $\approx 50$  K.

# 4. Discussion

The gas phase photoproducts described in reactions (1) and (2) are not observed in UV-irradiated acetyl chloride films. While it is not necessarily surprising that no radical products were trapped in the solid acetyl chloride matrix, it is surprising that the only observed products formed in the solid state are entirely absent in the gas phase photochemistry. We observe no evidence for intermolecular reaction channels, that is, chemistry involving attack of a neighboring acetyl chloride molecule by a Cl atom or an acetyl radical. In addition, secondary products, that could be attributed to the reaction of UV-irradiated ketene molecules with neighboring molecules, are not observed. The gas phase photochemistry of ketene has been studied extensively [16–18] and irradiation at wavelengths shorter than 313 nm are known to lead to CO,  $CH_2$ , and  $C_2H_4$  products. No indication of these products is observed in the difference spectra of UV-irradiated amorphous or crystalline acetyl chloride films. This evidence strongly suggests that a different reaction mechanism dominates the condensed-phase photochemistry.

The formation of the HCl · ketene complex proceeds through either a direct elimination or a stepwise caged abstraction mechanism. The direct elimination reaction forms the HCl · ketene complex by a concerted reaction path, and presumably produces well oriented products. The stepwise caged abstraction mechanism proceeds by dissociation of the C-Cl bond, caging of the Cl atom by the solid sample, and finally, abstraction of an H atom from the geminate CH<sub>3</sub>CO radical. We would not expect well oriented products from a stepwise abstraction mechanism. A potential problem with this mechanism is that abstraction reactions are notoriously sensitive to bond strength display a marked propensity to attack the weakest available bond. For example, H atom abstraction from CH<sub>3</sub>OH by OH radical (a pseudo halogen) may proceed by either methyl H atom abstraction, to form CH<sub>2</sub>OH, or by hydroxyl H atom abstraction, to form CH<sub>3</sub>O. At room temperature, the gas phase reaction occurs almost exclusively through methyl H atom abstraction even though the C-H bond is only 10% weaker than the O-H bond [19]. Consider the bond strengths and dissociation barriers of the C-H and C-C bonds in CH<sub>3</sub>CO radical. The H-CH<sub>2</sub>CO bond strength is relatively small at 42 kcal/mol [20], however, the CH<sub>3</sub>-CO bond strength is even less at  $\approx 10$  kcal/mol [20]. Indeed, the barrier to CH<sub>3</sub>-CO dissociation is measured to be only 17 kcal/mol [21]. It would seem that the methyl radical would provide a much more suitable target for abstraction by the Cl atom (provided steric factors are negligible). Furthermore, we observe no CH<sub>3</sub>Cl or CO product. These facts argue in support of a direct elimination mechanism.



Fig. 4. Schematic diagram of the thermochemistry of the gas- and condensed-phase photoproducts observed following UV excitation of acetyl chloride. The barrier to the formation of HCl and ketene from acetyl chloride has not been reported. The figure uses the barrier of 53.5 kcal/mol estimated for the analogous acetyl bromide reaction [22]. This value is well within the range reported for many HCl and HBr elimination reactions from halogenated alkanes and alkenes. The enthalpy at 298 K for (a) was calculated by using the  $\Delta H_{\rm f, 298 \ K}$  values of liquid HCl, ketene, and acetyl chloride [23]. The enthalpy values,  $\Delta H_{\rm f, 0 \ K}$ , for (b), (c), and (d), which describe the thermochemistry of the gas phase photodissociation of acetyl chloride, were obtained from Refs. [20,21,23], respectively.

The proximity of neighboring acetyl chloride molecules, in the condensed film, may induce  $S_1 \rightarrow S_0$  internal conversion prior to dissociation of the C-Cl bond. The condensed-phase reaction would then proceed from highly excited levels of the ground electronic state surface  $S_0$  (it is possible that intersystem crossing to the  $T_1$  surface could be induced in the condensed film, however, this mechanism should then proceed as a normal Norrish type I process). Absorption of a 266 nm photon provides sufficient energy to surmount the estimated barrier to HCl elimination on the  $S_0$  surface. Fig. 4 displays the relevant thermochemistry for the gas- and condensed-phase reactions.

A plausible geometry of the caged  $HCl \cdot ketene$ dimer complex locates the HCl molecule above and parallel to the plane of the ketene molecule. This proposed  $HCl \cdot ketene$  geometry is consistent with the frequency shifts that are observed for the IR band spectra for the out-of-plane CCO bend at  $532 \text{ cm}^{-1}$ , the  $CH_2$  wag at 600 cm<sup>-1</sup>, and the  $CH_2$  rock at 960  $cm^{-1}$ . The frequency shifts are assigned by comparing these vibrational modes of the HCl · ketene complex with the corresponding vibrational frequencies of solid ketene at 529, 616, and 971 cm<sup>-1</sup>, respectively [10]. The remaining IR bands of the HCl. ketene complex shift less than  $\approx 3 \text{ cm}^{-1}$  from their corresponding solid assignments. The vibrational frequency shifts determined for the HCl · ketene complex within amorphous films are nearly identical to the shifts observed within crystalline films, which suggests that similar structures exist for the complexes trapped in the two phases and that the spectral band shifts result largely from HCl-ketene interactions.

Initial kinetic measurements of the back reaction (the reverse of reaction (3)) do not indicate a significant barrier to acetyl chloride reformation. Furthermore, no physically reasonable pre-exponential factor can be extracted from the preliminary measurement of the reverse reaction rate. That is, the determined A factor is many orders of magnitude smaller than that expected for a condensed-phase reaction (we expect a pre-factor of roughly  $A = 10^{13} \text{ s}^{-1}$  for well aligned caged reactants). At such low temperatures, a mechanism in which the H atom tunnels to form an acetyl radical followed by rapid addition of the chlorine atom to reform acetyl chloride could explain such behavior. However, the back-reaction rates for both  $d_3$ - and  $h_3$ -acetyl chloride samples are equivalent, within error limits, and do not directly support a tunneling mechanism. The similar back-reaction rates for H and D isotopes does not rule out a tunneling mechanism, however, since the tunneling coordinate could be coupled and controlled by the motion of the much heavier Cl atom.

# 5. Conclusions

The condensed-phase photochemistry of acetyl chloride is distinctly different from that of the gas phase. Photoexcitation of a gas phase acetyl chloride molecule leads to direct ejection of a chlorine atom producing an internally excited acetyl radical,  $CH_3CO^{\#}$ , which may undergo further dissociation

into CO and CH<sub>3</sub> [2,3]. Irradiation of low-temperature films of acetyl chloride does not produce any species attributable to the gas phase photodissociation mechanism. The lack of such photoproducts and the known thermochemistry support a direct elimination reaction mechanism, but a caged abstraction process has not been conclusively ruled out. Since a direct elimination mechanism will likely produce well oriented products, we have initiated polarized FT-IR measurements to discriminate such effects and further elucidate the reaction mechanism. The reverse reaction that reforms acetyl chloride at low temperatures (50-100 K) is particularly intriguing since the preliminary kinetic measurements implicate a tunneling mechanism, yet experiments using deuterated acetvl chloride have failed to confirm this mechanism. We have planned HCl and ketene co-deposition experiments to investigate this possibility further. We are continuing the study of the UV photoreactions of solid acetyl chloride using FT-IR spectroscopy, ab initio calculations, and kinetic studies of both amorphous and crystalline samples.

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