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# Laser pyrolysis studies of the thermal decomposition of chlorinated organic compounds. Part 1—acyl chlorides

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The thermal decomposition of chloroacetyl chloride, propanoyl chloride, 3-chloropropanoyl chloride, acryloyl chloride, *E*-2-butenoyl chloride, methacryloyl chloride, and cyclopropanecarbonyl chloride has been investigated using infrared laser-powered homogeneous pyrolysis, together with product analysis using IR spectroscopy, gas chromatography/mass spectrometry, matrix isolation spectroscopy and tuneable diode laser spectroscopy. Decomposition is usually initiated by 1,2-HCl elimination (where possible), followed by further decomposition of ketene products. Reaction pathways have been validated in many cases by the *ab initio* calculation of activation energies.

## Introduction

The thermal decomposition of acyl chlorides has been the subject of some individual investigations, but there seems to have been no previous attempt to construct a comprehensive decomposition scheme. In general, pyrolysis of acyl chlorides is initiated by 1,2 molecular elimination of HCl to afford the corresponding ketene, and this has been widely exploited in the synthesis of ketenes.[1–3] Ketenes are often transient species, whose chemical utility in organic synthesis has long been acknowledged;[2,4–7] for example, hydration of ketene itself was, for many years, a major industrial process in the manufacture of acetic acid.

We have shown that the technique of infrared laser-powered homogeneous pyrolysis (IR LPHP), allied with standard analytical methods and augmented by techniques for the detection and identification of short-lived reaction intermediates and *ab initio* evaluation of the feasibility of reaction routes, is uniquely suited to the elucidation of thermal decomposition reaction mechanisms.[8–11] This has been demonstrated in systems as varied as precursors to chemical vapour deposition,[12–16] various cyclic systems[17,18] and small organic molecules.[19] We have also shown that the pyrolysis of acyl chlorides is a good source of short-lived ketenes for spectroscopic study.[20–22] Here we report a systematic study of a range of acyl chlorides selected to emphasise a number of aspects of their decomposition chemistry.

## Experimental and theoretical methods

### Chemicals

All chlorinated compounds used were of analytical grade quality and obtained commercially. These and $SF_6$ (BOC) were purified before use by repeated freeze-pump-thaw cycles. Materials were handled on rigorously pre-conditioned Pyrex vacuum lines fitted with greaseless J. Youngs taps. Precursor and product identification and analysis (FT-IR spectroscopy and GC-MS) was accomplished using commercial instrumentation in conjunction with comparison with data from authentic samples.

### Infrared laser-powered homogeneous pyrolysis

All static cell pyrolyses utilised the IR LPHP technique. This method has been described in detail elsewhere,[8–11] thus only a brief description is given here. Pyrolysis is performed in a cylindrical Pyrex cell (length 100 mm, diameter 38 mm) fitted with ZnSe windows. Although ZnSe is opaque to infrared radiation below 500 $cm^{-1}$, it has several distinct advantages over cheaper materials, such as NaCl. ZnSe is thermally stable, strong, and non-hygroscopic. Most significantly, ZnSe is highly transparent to the $CO_2$ laser radiation. The pyrolysis cell is filled with between 1 and 2 Torr (1 Torr = 133.3 Pa) of the vapour under study and approximately 10 Torr of $SF_6$. The contents of the cell are then exposed to the output of a free running CW $CO_2$ laser operating at 10.6 μm at a power level sufficient to initiate decomposition of the vapour under study. As shown elsewhere,[8,11] $SF_6$ strongly absorbs the laser radiation, which is then rapidly converted to heat *via* efficient intermolecular and intramolecular relaxation. The low thermal conductivity of $SF_6$ ensures that a strongly inhomogeneous temperature profile is produced in which the centre of the cell may reach temperatures of the order of 1500 K while the cell wall remains at room temperature.[23]

IR LPHP has a number of well-documented advantages. The first of these is that pyrolysis is initiated directly in the gas phase, thereby eliminating the complications frequently introduced by competing surface reactions. The second is that the primary products of pyrolysis are rapidly ejected into the cooler regions of the cell, inhibiting their further reaction. In favourable cases, these products may be accumulated for further investigation. One disadvantage of IR LPHP is that the temperature of the pyrolysis is neither well-defined nor easily determined; comparison with more conventional methods of pyrolysis is thus difficult.

### Analytical methods

In all cases, the reaction is monitored *ex situ* in the first instance using FT-IR spectroscopy. Product identification is confirmed with GC-MS. Infrared spectra were recorded using a Digilab FTS60 FT-IR spectrometer at a resolution of 1 $cm^{-1}$. GC-MS data were recorded using a Hewlett Packard 6890 gas

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chromatograph coupled with a Hewlett Packard 5973 mass selective detector. Samples for GC-MS analysis were extracted through a septum on the pyrolysis cell with a gas tight needle.

## Matrix isolation spectroscopy

A two-stage closed cycle helium refrigerator was used for all matrix isolation experiments. The second stage (heat station) of the cryostat, to which a copper sample holder was in direct contact, was maintained at a temperature between 15 and 20 K for the duration of the experiment. All matrices were collected at this temperature. The matrix isolation assembly was constructed such that any reactive species, generated through IR LPHP or conventional hot-walled pyrolysis of an appropriate precursor, would rapidly co-deposit with the matrix material on the cold sample holder.

The matrix cold cell (the cavity enclosing the cold stage and sample holder) was fitted with two valves, one of which connected to the part of the vacuum line where pyrolysis occurred (the spray-on line). The main vacuum line, to which the spray-on line connected, was coupled to the second valve of the matrix cold cell. An inlet port on the spray-on line, fitted with a needle valve, permitted attachment of a gas bulb containing a mixture of matrix material and degassed precursor. The matrix and precursor gas mix was prepared on a standard vacuum line, at a ratio of between 100 : 1 and 2000 : 1 (dependent on the experiment) at a pressure of at least 200 Torr. The matrix gas used was dependent on the manner in which decomposition was initiated: IR LPHP experiments employed $SF_6$, while conventional hot-walled pyrolysis used Ar as the host gas. Prior to experiment, the entire assembly (excluding the gas bulb) was evacuated using rotary (Edwards E2M5 two stage) and oil diffusion (Edwards EO2) pumps. The valve connecting the spray-on manifold to the main vacuum line was then closed and a pressure of source gas, of the order of 0.15 Torr, introduced through the needle valve.

In experiments that employed conventional hot-walled pyrolysis, the precursor was decomposed in silica tubes (8 mm i.d.) heated to between 673 and 1073 K (dependent on experiment) with a 300 mm long electric oven. In IR LPHP initiated decomposition, laser radiation was directed at a ZnSe fronted reaction cell through which the gaseous mixture flowed. The reaction products were collected at the conductively cooled copper block within 170 mm of the pyrolysis tube or reaction cell. At the cessation of the experiment, the matrix cold cell was disengaged from the vacuum line and the cold stage, to which the sample holder was appended, and rotated 90° to permit FT-IR analysis. The temperature of the cold sample holder was maintained at between 15 and 20 K during spectrum acquisition.

The IR LPHP matrix isolation experiment could be modified such that the path between the reaction cell and cold stage was restricted. By employing a length of Pyrex with an aperture (0.5 mm) at one end, an extremely short-lived species would be prevented from reaching the cold stage before reacting further. Consequently, it was possible to differentiate to some extent between short-lived intermediate species based on lifetimes.

The use of an aperture to restrict gas flow elevated the pressure of $SF_6$ in the IR LPHP cell. At a given laser power, the effective temperature was significantly higher than that attained when the restriction was not employed. This was reflected in the laser power required to initiate decomposition: compounds that decomposed when the gas flow was restricted remained intact even at the highest laser power when the gas flow was unrestricted. The modification of the matrix isolation assembly, while inhibiting the collection of very short-lived species, allowed IR LPHP of compounds that would otherwise not decompose.

## Calculation methods

It was necessary to execute a number of theoretical calculations in order to corroborate a proposed species, or pyrolysis scheme. The former was realised by calculating the vibrational frequencies of the species in question and comparing them with the post-pyrolysis infrared spectrum. This was particularly useful for systems in which a substituted ketene intermediate was proffered. Such species possess a characteristic carbonyl stretching frequency between 2100 and 2200 $cm^{-1}$, the precise position of which is determined by the substituent present.[24] A proposed species was verified by comparing the observed value with the value calculated.

The feasibility of a proposed pyrolysis scheme could be evaluated by determining the relative activation energies involved. For the most part, this involved calculating the activation barrier to dehydrochlorination, the predominant decomposition route, and comparing this value with that of an alternate system, whose actual pyrolysis temperature (*i.e.*, the laser power required to initiate decomposition) was known. It was found that theory agreed well with experiment; a system calculated to possess higher activation energy required a higher decomposition temperature.

All theoretical calculations were executed using the PC Spartan ′02 molecular orbital program.[25,26] PC Spartan ′02 provides a full range of molecular mechanics and quantum chemical methods, and it was found that the density functional theory method at the B3LYP level with the 6-31G* basis set[27] provided sufficiently accurate results. Relative values of the activation energies of various reaction pathways were considered to be of greater value in predicting mechanism than absolute values. As a benchmark, the activation energy for 1,2-elimination of HCl from chloroethane was calculated as 252 kJ $mol^{-1}$, very comparable with the experimentally determined value[28] of 243 kJ $mol^{-1}$.

## Tuneable diode laser spectroscopy

The combination of IR LPHP and tuneable diode laser spectroscopy (TDLS) provides an ideal and novel technique by which to generate and characterise *in situ* the high-resolution spectra of a transient species. The transient species is generated in a specially adapted cell (the multipass cell) through IR LPHP of an appropriate precursor, and spectroscopically probed *in situ* with a diode laser source.

The semiconductor diode used in this investigation was one of four available and emitted infrared light between 1950 and 2200 $cm^{-1}$, ideal for the detection of transient ketene species. The frequency of the output laser mode was broadly determined by regulating the current and temperature settings with a Laser Photonics TDL controller. The maximum temperature and current allowed was of the order of 123 K and 1000 mA, respectively.[29]

The output laser beam was reflected from an Al collimating mirror and passed through a grating monochromator, which was used to select and isolate a discrete frequency. The beam was then split, with 90% entering the multipass cell for signal detection and, for the purpose of referencing, the remaining 10% relayed through a germanium etalon that could be used as an internal calibrant. The level of accuracy at which the position of absorption bands were measured in this investigation (the characterisation of high resolution spectra was not executed) was such that an internal calibrant was not required; the accuracy attained *via* the grating monochromator was sufficient.

The cell was constructed such that the incoming diode beam was reflected between two adjacent gold plated mirrors, thereby increasing the effective path length to approximately 2 m. The $CO_2$ laser beam entered the cell perpendicular to the diode laser, through a ZnSe window located at the front of the multipass cell. IR LPHP of the cell contents (of the order of 1 Torr of precursor and 4 Torr of $SF_6$) was confined to the centre of the cell where the diode laser beam was focused. This improved the probability of detecting the transient species. The output diode laser beam exited the multipass cell diagonally opposite to the point where it had entered, and passed into the detector module.

## Results

### Calculations

We have conducted a series of calculations on representative systems containing the CCl–CH unit in order to assess the relative significance of HCl elimination and re-addition in the systems studied here. The results are shown in Table 1. In addition, we have calculated the activation energy for 1,4-elimination from *Z*-1-chlorobut-2-ene and *Z*-2-butenoyl chloride (and its reverse).

The activation energy for 1,2-elimination of simple chloroalkanes lies close to 250 kJ $mol^{-1}$. This is somewhat decreased by the substitution of electron-withdrawing groups at the Cl-bearing carbon (*e.g.*, by 25 kJ $mol^{-1}$ for two F), and conversely increased by substitution of electron-withdrawing groups at the H-bearing carbon (*e.g.*, by 61 kJ $mol^{-1}$ for two F). This effect is even more marked on substitution by C═O, so that elimination of HCl from acyl chlorides requires on the order of 200 kJ $mol^{-1}$, and from α-chloroaldehydes on the order of 320 kJ $mol^{-1}$. As expected, 1,4-elimination of HCl, where available, is more facile. Thus *Z*-1-chlorobut-2-ene requires 174 kJ $mol^{-1}$ to produce 1,3-butadiene, and 1,4-HCl elimination from the *Z* isomer of butenoyl chloride needs only 161 kJ $mol^{-1}$. Finally, we have assessed the importance of direct decarbonylation accompanied by a 1,2-Cl shift. In acetyl chloride itself, the activation energy for this process is calculated at 364 kJ $mol^{-1}$, and is unlikely to be competitive with HCl elimination.

It is interesting to view the changes in geometry of the transition state; these are shown in Fig. 1 for the case of $CH_3COCl$, together with the relative energies of all species involved in HCl eliminations. As expected for this somewhat endothermic process, the transition state is product-like; for example, the C–C bond length is reduced from 1.504 to 1.405 Å, approaching the ketene C═C bond length of 1.315 Å. Likewise, the C–C–O angle is increased from 128° to 174°, close to the linear 180° in ketene.

In acetyl chloride itself, the only substantial products observed in LPHP at moderate powers are ketene and HCl; at higher powers, products of decarbonylation of ketene (largely CO and the ethylene product of recombination of the resultant carbene $CH_2$) are detectable. There is no evidence of either direct decarbonylation, which would result in chloromethane, radical-initiated processes, or breakdown products of the reverse re-insertion of HCl to form chloroacetaldehyde. Decarbonylation of higher ketenes is likely to depend heavily on the nature of substituent, as we have observed.

**Table 1** Activation energies (in kJ $mol^{-1}$) for elimination and addition of HCl in representative systems. First five entries refer to 1,2 reaction, last two to 1,4 reaction

| Compound | $E_a$ Elimination | $E_a$ Addition |
|---|---|---|
| $CH_3CH_2Cl$ | 252 | 138 |
| $CH_3CF_2Cl$ | 227 | 109 |
| $CF_2HCH_2Cl$ | 313 | 218 |
| $CH_3COCl$ | 199 | 63 |
| $CHOCH_2Cl$ | 317 | 255 |
| *Z*-$CH_3CH{=}CHCH_2Cl$ | 174 | 90 |
| *Z*-$CH_3CH{=}CHCOCl$ | 161 | 45 |

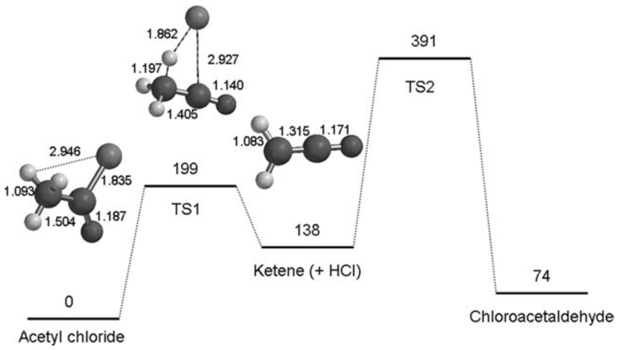


**Fig. 1** Bond lengths (in Å) and energies (in kJ $mol^{-1}$) of (a) starting material, (b) transition state (TS1) and (c) product for 1,2-HCl elimination from $CH_3COCl$, together with energies of transition state (TS2) and products for reverse addition.

### Chloroacetyl chloride

The thermolysis[30–34] and photolysis[35] of chloroacetyl chloride has been studied by a number of workers with an express focus on the initial decomposition step, specifically, molecular elimination of HCl. The dehydrochlorination of chloroacetyl chloride yields the unstable ketene derivative, chloroketene. Microwave,[31] photoelectron[32,34] and IR spectra[35,36] have been reported for chloroketene. Xu and co-workers have used laser-induced fluorescence excitation spectroscopy to identify and characterise the product of chloroketene decarbonylation, namely chloromethylene.[30]

In the present work, the dominant stable products at threshold laser powers were CO and HCl, $CH_2Cl_2$ and the *E*- and *Z*-isomers of 1,2-dichloroethene in the approximate ratio of 2 : 1 : 1. At higher laser powers (*i.e.*, temperatures), trichloroethene (up to 28%), chloromethane (up to 13%), chloroform (up to 7%) and traces of 1,1,2,2-tetrachloroethane, chloroethene and dichloroethyne were also observed. A partial gas chromatogram of high temperature products is shown in Fig. 2.

A short-lived absorbance band was observed in the post-pyrolysis infrared spectrum at 2154 $cm^{-1}$ and ascribed to chloroketene.[36] The intermediate ketene was also detected directly by IR spectroscopy in both an Ar and $SF_6$ matrix (dilution 2000 : 1). At 16 K, an intense band at 2147 $cm^{-1}$ (2149 $cm^{-1}$ in a $SF_6$ matrix), attributable to the cumulenic stretch, $\nu_2$, of chloroketene, was observed. Davidovics and co-workers[35] observed chloroketene following photolysis of chloroacetyl chloride in a Xe matrix at 2141 $cm^{-1}$. In the present study, chloroketene was also detected directly in the gas phase by TDL spectroscopy. At 2145, 2158 and 2195 $cm^{-1}$, a series of absorption bands developed while the contents of the cell were exposed to the output of a CW $CO_2$ laser. The spectrum returned to its original state within 5 min of the cessation of irradiation. These observations are consistent with the centre of the jet-cooled IR spectrum at 2157.2 $cm^{-1}$ reported by Liu *et al.*[36]

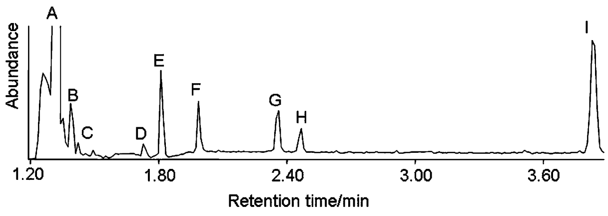
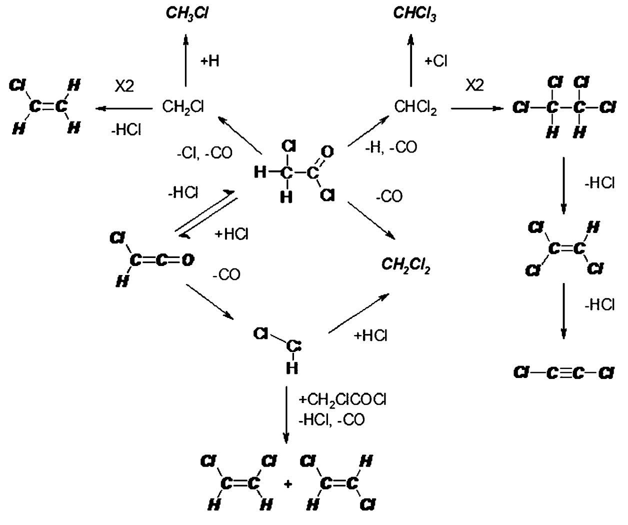


**Fig. 2** Partial gas chromatogram of the products of IR LPHP of chloroacetyl chloride: A = $SF_6$; B = chloromethane; C = chloroethene; D = dichloroethyne; E = dichloromethane; F = *E*-1,2-dichloroethene; G = *Z*-1,2-dichloroethene; H = chloroform; I = trichloroethene; 1,1,2,2-tetrachloroethane was observed at 9.6 min.

The formation of chloroketene is consistent with molecular dehydrochlorination of chloroacetyl chloride. This is in agreement with earlier investigations that have concentrated on the initial decomposition step.[30–35] The increase in the intensity of absorbance bands ascribed to chloroacetyl chloride during the acquisition of a spectrum, at the expense of the band ascribed to chloroketene, indicates that molecular dehydrochlorination is reversible. The absence of dichloroacetaldehyde, the product resulting from *anti*-Markovnikov addition of HCl to chloroketene, suggests that dehydrochlorination (at least during the time when the cell contents were not exposed to laser irradiation) is unidirectional. The theoretical investigations described above support this proposition: production of chloroacetyl chloride through Markovnikov addition of HCl to chloroketene is significantly lower in activation energy than that associated with the formation of dichloroacetaldehyde.

The use of ketenes as carbene precursors is well known; decarbonylation of a ketene, of which chloroketene is an example, will give the analogous carbene.[37] Decarbonylation of chloroketene will yield chloromethylene.[30] The production of the *E* and *Z* isomers of 1,2-dichloroethylene may formally be accounted for through direct recombination of chloromethylene; more likely in practice, however, is insertion into a C–H bond of the starting material, followed by loss of HCl and CO and finally 1,2-H rearrangement of the resulting carbene. Statistically, one would expect the yield of each to be approximately equivalent, which, as illustrated in Fig. 2 by the comparable intensities of their respective peaks in the gas chromatogram, is indeed the case. Likewise, insertion of chloromethylene into the copious HCl product accounts for the formation of dichloromethane (as described above, energetic considerations render the direct decarbonylation route less probable).

Although carbenes do abstract atomic hydrogen,[37] this is limited to their triplet states and is therefore unlikely to account for the remaining products. What seems more likely is that C–Cl bond homolysis plays an increasing role at higher temperatures; C–Cl bond energies are typically of the order of 320–330 kJ mol$^{-1}$.[38] Loss of either Cl from chloroacetyl chloride, followed by loss of CO, yields the chloromethyl radical, $CH_2Cl$; these may abstract H from starting material to form the observed $CH_3Cl$, or recombine to form 1,2-dichloroethane, which will readily lose HCl at these higher temperatures to yield chloroethene. The Cl atoms produced will abstract H from starting material, followed by CO loss to yield the dichloromethyl radical, $CHCl_2$; these may abstract Cl from the starting material, recombine to yield tetrachloroethane and thence trichloroethene and dichloroethyne. All possible pathways and observed products are illustrated in Scheme 1.



**Scheme 1** Proposed reaction scheme for chloroacetyl chloride IR LPHP; observed products in ***bold italics***.

## Propanoyl chloride

Propanoyl chloride has been identified and used as a precursor to methyl ketene. Bock and co-workers observed that the thermal elimination of HCl from a number of acyl chlorides, including propanoyl chloride, generated the analogous ketene.[39] A radical mechanism was proposed to describe the dehydrohalogenation of the parent compound. An extensive investigation of the decomposition of propanoyl chloride has, however, not been executed.

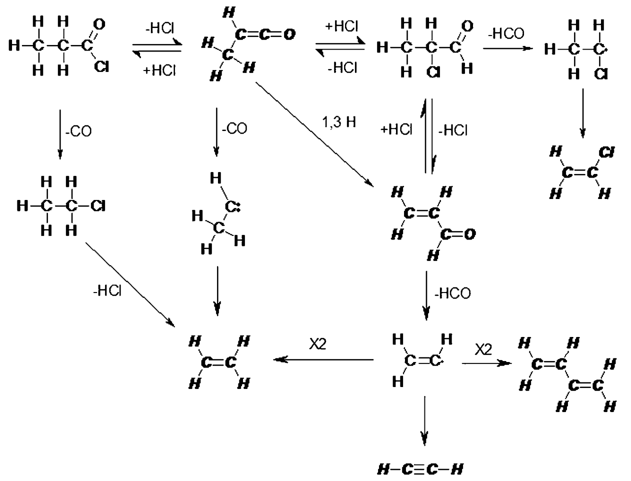
In the present study, the stable products of propanoyl chloride pyrolysis at threshold powers were identified as HCl and CO, and 1,3-butadiene (40%), ethylene (26%), acetylene (18%), chloroethene (10%) and acrolein (2-propenal, 6%); the last became less significant at higher laser power (*i.e.*, temperature), while others were largely unaffected. Chloroethane, the decarbonylation product, was detected in trace amounts. A transient band at 2133 cm$^{-1}$ was ascribed to methyl ketene. Bands ascribed to starting material increased during the acquisition of a spectrum at the expense of methyl ketene and HCl.

Methyl ketene was also detected directly by IR spectroscopy in an Ar matrix (dilution 2000 : 1). At 16 K, an absorbance band at 2124 cm$^{-1}$ with a shoulder at 2129 cm$^{-1}$, attributable to the cumulenic stretch, $\nu_2$, of methyl ketene, was observed. Two weaker peaks were observed at 2137 and 2144 cm$^{-1}$, the former ascribed to CO. Johnstone and Sodeau detected absorbance bands in the post-photolysis spectrum of acrolein, at 2126 and 2129 cm$^{-1}$ that they ascribed to methyl ketene.[40] The appearance of two additional signals at 2138 and 2146 cm$^{-1}$, the former ascribed to CO and the latter a complexed CO–ethylidene pair, was also reported. The absorbance band at 2144 cm$^{-1}$ observed in the present work coincides approximately with that observed by Johnstone and Sodeau.[40]

In the present work, the IR LPHP of propanoyl chloride was monitored *in situ* by TDL spectroscopy. At 2122 and 2145 cm$^{-1}$, blanket absorption that is ascribed to methyl ketene was observed when the contents of the cell were exposed to the output of the $CO_2$ laser. Individual peaks were resolved using a lock-in amplifier. Subsequent to irradiation the spectrum returned to its original state within several minutes.

The increase in propanoyl chloride, at the expense of methyl ketene and HCl as the spectrum was acquired, indicates the reversibility of dehydrochlorination. Our theoretical investigations predict Markovnikov addition of HCl to methyl ketene to yield propanoyl chloride as opposed to 2-chloropropanal, the *anti*-Markovnikov addition product. It is possible that at elevated temperature the activation barrier to formation of 2-chloropropanal is overcome; the fact that this compound was not detected indicates that it decomposes under these conditions. Molecular elimination of HCl from 2-chloropropanal yields methyl ketene or 2-propanal (acrolein), the latter consistent with dehydrochlorination across the C(2)–C(3) bond. An alternative facile mechanism for the formation of acrolein involves a 1,3-H shift in methyl ketene, a process whose activation energy is calculated to be 303 kJ mol$^{-1}$.

It is known that homolytic cleavage of the C(1)–C(2) bond in acrolein will yield the formyl and vinyl radicals;[41] similarly, homolytic fragmentation of 2-chloropropanal will afford the formyl and α-chlorinated ethyl radicals. Seetula[42] has shown that the predominant decomposition route for an α-chlorinated ethyl radical is through scission of the $C_\beta$–H bond (the weakest bond) to yield chloroethene, a significant product in this investigation. The formation of acetylene and ethylene, and 1,3-butadiene, is consistent, respectively, with the disproportionation and combination of vinyl radicals. It is likely, therefore, that the formation mechanism (specifically, elimination of HCO from acrolein) is significant, resulting in a high



**Scheme 2** Proposed reaction scheme for propanoyl chloride IR LPHP; observed products in ***bold italics***.

concentration of vinyl radicals. The formation of ethylene is also consistent with decarbonylation of methyl ketene, followed by rearrangement of the resultant ethylidene species. A proposed scheme for IR LPHP of propanoyl chloride is given in Scheme 2.

### 3-Chloropropanoyl chloride

Piétri and co-workers have recently investigated the photolysis of matrix isolated 3-chloropropanoyl chloride.[43] At $\lambda > 230$ nm, the primary products were reported as acryloyl chloride and 3-chloro-1-propen-1-one,[44] attributable respectively to elimination of HCl across the C(2)–C(3) and C(1)–C(2) bonds (numbered from the oxygen-bearing carbon). Chloroethene was also observed, presumably through decarbonylation of acryloyl chloride or 3-chloro-1-propen-1-one, the latter necessitating rearrangement of the 2-chloroethylidene intermediate. Piétri and co-workers also observed 1,2-propadien-1-one (methylene ketene) and proposed that formation of this species be attributed to dehydrochlorination of acryloyl chloride. A thorough search of the literature has failed to find any additional reference to the decomposition of 3-chloropropanoyl chloride, with the exception of a patent detailing the preparation of acryloyl chloride from gas phase dehydrochlorination of 3-chloropropanoyl chloride.[45]

In the present investigation, the only significant product at low laser power (*i.e.*, temperature) was acryloyl chloride; chloroethene and acetylene were the major products at higher laser power. Presumably, the formation of acetylene is attributable to the dehydrochlorination of chloroethene. In contrast to the post-pyrolysis spectra of chloroacetyl and propanoyl chloride, there were no ephemeral absorbance bands attributable to a short-lived ketene species in the infrared spectrum at ambient temperature.

The low temperature post-pyrolysis FT-IR spectrum of 3-chloropropanoyl chloride, which is shown in Fig. 3, revealed a series of absorbance bands between 2200 and 2100 cm$^{-1}$. Reaction was initiated at 748 K and the pyrolysate co-deposited with Ar (dilution 2000 : 1) at 16 K. The most intense band at 2122 cm$^{-1}$ was attributable to the cumulenic stretch, $\nu_2$, of methylene ketene, and is in agreement with the value (ascribed to the uncomplexed product) reported by Chapman and co-workers.[46] Subsequent decarbonylation of methylene ketene provides an alternate route to acetylene through rearrangement of the ethenylidene intermediate.

A number of weaker absorbance signals were also present at 2099, 2137, 2141 (shoulder) and 2169 cm$^{-1}$. In experiments initiated at a higher temperature, a weak band at 2147 cm$^{-1}$ was observed that has yet to be identified. The peaks at 2137 and 2141 cm$^{-1}$ are ascribed to uncomplexed CO and ketene, respectively; the spectrum of an authentic sample of each, isolated in an Ar matrix, is spectroscopically identical with those peaks observed in the post-pyrolysis spectrum. The trace peak at 2099 cm$^{-1}$ is ascribed to complexed methylene ketene following Piétri *et al.*,[47] who proposed a methylene ketene–HCl complex to account for a signal observed at 2102 cm$^{-1}$.

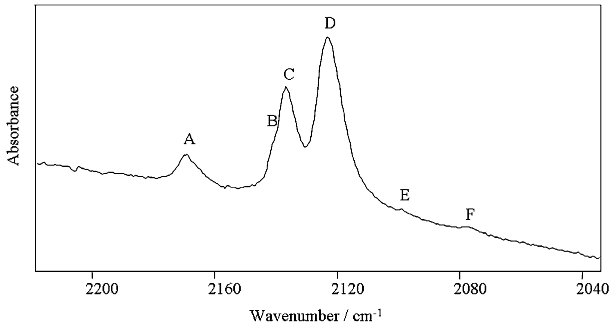
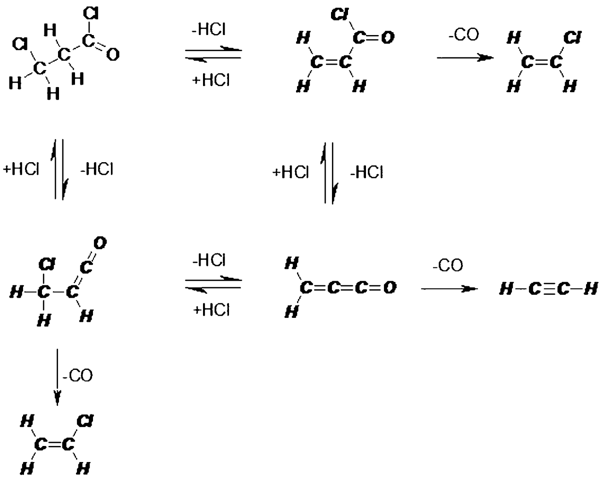


**Fig. 3** FT-IR spectrum of Ar matrix-trapped (16 K) 3-chloropropanoyl chloride after pyrolysis at 748 K: A = 3-chloro-1-propen-1-one; B = ketene; C = CO; D = 1,2-propadien-1-one; E = 1,2-propadien-1-one–HCl complex; F = acryloyl chloride.

The band at 2169 cm$^{-1}$ is ascribed to 3-chloro-1-propen-1-one. In the present work, the scaled[48] frequency of the cumulenic stretch of 3-chloro-1-propen-1-one was calculated at 2148 cm$^{-1}$, which is in reasonable agreement with the frequency observed. It is conceivable that 3-chloro-1-propen-1-one arises from either a 1,3-chlorine shift in acryloyl chloride or dehydrochlorination of 3-chloropropanoyl chloride across the C(1)–C(2) bond. The activation barrier value of the proposed 1,3-chlorine shift must be considered; calculations predict that the 1,3-chlorine shift has a comparable activation energy to that associated with molecular dehydrochlorination of 3-chloropropanoyl chloride and, consequently, represents a practicable pathway. The formation of 3-chloro-1-propen-1-one might also involve *anti*-Markovnikov addition of HCl to the C(2)–C(3) bond of methylene ketene, the most significant pyrolysis product of a transient nature.

IR LPHP of 3-chloropropanoyl chloride was monitored *in situ* using TDL spectroscopy. At 2145 cm$^{-1}$, a series of minor absorption bands, attributable to ketene, developed while the contents of the cell were exposed to the output of a CW $CO_2$ laser. The spectrum obtained was spectroscopically identical to that observed for a pure sample of ketene, procured through pyrolysis of acetyl chloride. A proposed scheme for the pyrolysis of 3-chloropropanoyl chloride, excluding the mechanism responsible for ketene formation, is given in Scheme 3.



**Scheme 3** Proposed reaction scheme for 3-chloropropanoyl chloride IR LPHP; observed products in ***bold italics***.

## Acryloyl chloride

The thermolysis of acryloyl chloride has been studied by Bock and co-workers;[39] the results of photoelectron spectroscopy suggest that the initial decomposition step, specifically elimination of HCl, is simultaneously accompanied by the loss of CO. Ostensibly, the expected product of molecular dehydrochlorination, methylene ketene, was not detected.

In investigations by Piétri and co-workers, it was shown that at $\lambda > 230$ nm, acryloyl chloride was photolytically decomposed to methylene ketene *via* 1,2-HCl elimination, and 3-chloro-1-propen-1-one[44] *via* 1,3-chlorine migration.[47] The latter rapidly decomposed to 2-chloroethylidene and CO, with rearrangement of the former affording chloroethene, a secondary pyrolysis product. Subsequent decarbonylation of methylene ketene resulted in the formation of acetylene through rearrangement of the ethenylidene intermediate. The non-concerted mechanism inferred is inconsistent with the mechanism proposed by Bock and co-workers.[39]

Piétri and co-workers were able to corroborate the presence of 3-chloro-1-propen-1-one by comparing the value calculated for the cumulenic stretch, specifically 2146 cm$^{-1}$ (after scaling), with the absorbance bands observed in the infrared spectrum between 2139 and 2145 cm$^{-1}$. Moreover, 3-chloro-1-propen-1-one derived from the photolysis of 3-chloropropanoyl chloride at $\lambda > 230$ nm was reported to be spectroscopically similar to that observed from the photolytically induced 1,3-chlorine shift of acryloyl chloride. It is important to note, however, that the production of 3-chloro-1-propen-1-one from the photolysis of 3-chloropropanoyl chloride is accompanied by the formation of acryloyl chloride.[43] The decomposition of acryloyl chloride at $\lambda > 230$ nm effects the formation of methylene ketene and 3-chloro-1-propen-1-one;[47] consequently, it would appear that the execution of such an experiment so as to corroborate the existence of the latter is somewhat redundant.

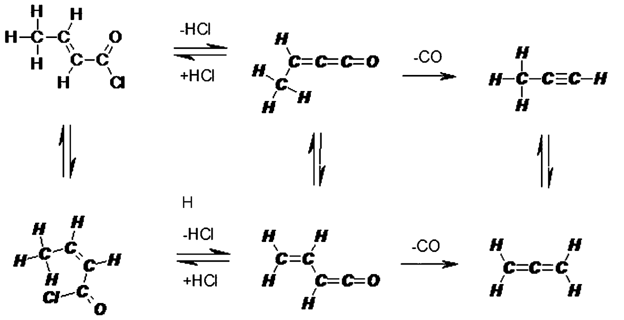
In the present work, acryloyl chloride was exposed to the output of a CW CO$_2$ laser. The products observed were consistent, for the most part, with the mechanism associated with the thermal decomposition of 3-chloropropanoyl chloride; acryloyl chloride is a major primary product of 3-chloropropanoyl chloride pyrolysis.

## *E*-2-Butenoyl chloride

The thermal or flash vacuum pyrolysis of *E*-2-butenoyl chloride has been investigated by a number of workers.[49–51] A combination of tandem mass spectrometry and low temperature (77 K) infrared spectroscopy was used by Maquestiau and co-workers to detect vinyl ketene and ethylidene ketene following flash vacuum pyrolysis.[49,50] Ethylidene ketene, while observed with tandem mass spectroscopy, was not detected in the low temperature infrared spectrum; it was argued that the high efficiency of fragmentation of the ethylidene ketene ions would allow detection, even if the concentration of such ions was extremely low. In the low temperature post-pyrolysis spectrum of *E*-2-butenoyl chloride, vinyl ketene was observed at 2118 cm$^{-1}$.

Mohmand and co-workers[51] used photoelectron spectroscopy to investigate the thermal decomposition of *E*-2-butenoyl chloride; formation of ethylidene ketene was ascribed to 1,2-HCl elimination. Conversely, vinyl ketene, which was also observed, was attributed to 1,4-HCl elimination. Additionally, it was proposed that at higher temperature, ethylidene ketene rearranges to the thermodynamically more stable vinyl ketene.

In the present investigation, we report the infrared LPHP of *E*-2-butenoyl chloride. The stable decomposition products are accounted for in Scheme 4 and include HCl, CO, propyne and a little 3-butenoyl chloride. A trace amount of *Z*-2-butenoyl chloride was observed, consistent with isomerisation of the starting material. The formation of allene, which was observed at higher laser power, is ascribed to rearrangement of propyne; thermal interconversion of propyne and allene at high temperature is a well-known process.[52] A transient band at 2134 cm$^{-1}$ is attributed to vinyl ketene and appears to have a much longer lifetime than either chloroketene or methyl ketene. In fact, when sufficient quantities were generated by extensive pyrolysis of the starting material, it was even possible to detect vinyl ketene using GC-MS.



**Scheme 4** Proposed reaction scheme for *E*-2-butenoyl chloride IR LPHP; observed products in ***bold italics***.

The formation of vinyl ketene is consistent with the very facile molecular 1,4-elimination of HCl from *Z*-2-butenoyl chloride; the conformation of *E*-2-butenoyl chloride apparently precludes such a process. Dehydrochlorination of *Z*-2-butenoyl chloride is evidently rapid, as it was detected in only trace amount. The decarbonylation of vinyl ketene coupled with a hydrogen shift provides a route to propyne, a significant product in this investigation.

The low temperature post-pyrolysis FT-IR spectrum of *E*-2-butenoyl chloride revealed a number of bands between 2200 and 2100 cm$^{-1}$. The pyrolysate was co-deposited with Ar (dilution 2000 : 1) at 16 K. The most intense absorbance band at 2127 cm$^{-1}$ is ascribed to uncomplexed vinyl ketene and is in accord with the value reported by Maquestiau and co-workers.[49,50] Brown and co-workers[53] and Bjarnov[54] have reported the infrared and microwave spectra of vinyl ketene generated by pyrolysis of vinylacetic anhydride. The cumulenic stretch of vinyl ketene in the gas phase was observed at 2137 cm$^{-1}$.[54] Brown and co-workers observed matrix-isolated (77 K) vinyl ketene at 2130 cm$^{-1}$.

A weak band that was observed at 2109 cm$^{-1}$ is ascribed to ethylidene ketene; on annealing to 20 K, this peak decayed, to be replaced by a broad absorbance band at 2094 cm$^{-1}$. Wentrup and Lorencak observed ethylidene ketene at a comparable frequency, following the pyrolysis of an alternative precursor.[55] Decarbonylation of ethylidene ketene provides an alternate reaction path to propyne through rearrangement of the intermediate carbene.

Vinyl ketene and ethylidene ketene were also detected in a SF$_6$ matrix (dilution 2000 : 1) where initiation of the reaction is homogeneous. At 16 K, a weak absorbance band at 2125 cm$^{-1}$ was observed and ascribed to uncomplexed vinyl ketene; an intense band at 2100 cm$^{-1}$ was assigned to ethylidene ketene. The relative intensities of the bands ascribed to vinyl and ethylidene ketene reflect a preference for ethylidene ketene formation, in contrast to the spectra obtained from an Ar matrix. It is likely, therefore, that the mechanism responsible for the formation of vinyl ketene, specifically molecular 1,4-elimination of HCl from *Z*-2-butenoyl chloride, is heterogeneous in nature.

In both Ar and SF$_6$ matrices vinyl ketene increased at the expense of ethylidene ketene on annealing the matrix to 25 K. In matrix experiments that employed a restriction in the gas flow between reaction (the pyrolysis cell or furnace) and collection (the cold stage), the intensity of the peak assigned to ethylidene ketene was reduced; conversely, the band ascribed to vinyl ketene intensified. These results are consistent with the conversion of ethylidene ketene to vinyl ketene through a facile 1,3-hydrogen shift and suggest that the lifetime of ethylidene ketene is significantly shorter than that of vinyl ketene.

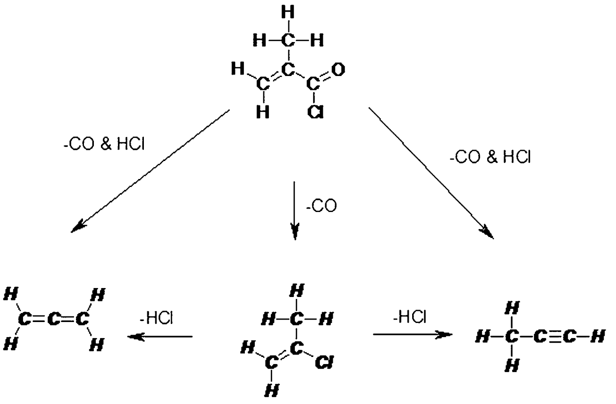
In contrast to the pyrolysis of chloroacetyl and propanoyl chloride, a decrease in bands assigned to the ketene species was not accompanied by an increase in the bands ascribed to *E*-2-butenoyl chloride. This result precludes the addition of HCl to ethylidene ketene across the C(1)–C(2) bond. The formation of 3-butenoyl chloride is consistent with Markovnikov addition of HCl to the less transient vinyl ketene across the C(1)–C(2) bond. The addition of HCl to vinyl ketene across the C(3)–C(4) bond, while affording either 4-chloro-1-buten-1-one or 3-chloro-1-buten-1-one (the latter in accord with Markovnikov's rule) can be discounted; there were no absorbance bands attributable to these products in the low temperature post-pyrolysis spectrum of *E*-2-butenoyl chloride. Moreover, theoretical calculations predict formation of 3-butenoyl chloride from the addition of HCl to vinyl ketene.

## Methacryloyl chloride

The decomposition of 2-methyl-2-propenoyl chloride (methacryloyl chloride) has not been studied previously; it was selected here as a benchmark example of an acyl chloride with no facile 1,2- or 1,4-dehydrochlorination routes. In the present work the laser powered homogeneous pyrolysis of methacryloyl chloride was investigated using infrared spectroscopy at both ambient and low (16 K) temperature. The major stable products, identified as CO, HCl, propyne and allene, are accounted for in Scheme 5. The direct decarbonylation product, 2-chloropropene, was also detected in trace amount. There were no absorbance bands attributable to a short-lived ketene species in the post-pyrolysis infrared spectrum at ambient temperature.

The molecular dehydrochlorination of methacryloyl chloride is restricted to the much less facile 1,3-HCl elimination, affording either propyne or, following rotation of the C(O)Cl group, allene; the absence of a β-hydrogen precludes 1,2-HCl elimination and, consequently, formation of a ketene. Our observations illustrate this point: the low temperature spectrum of the Ar matrix-isolated products of methacryloyl chloride thermolysis was devoid of bands ascribed to a short-lived ketene species. In the spectral region between 2200 and 2100 cm$^{-1}$ there was only one peak observed at 2137 cm$^{-1}$, attributable to CO.

The elimination of HCl is accompanied by concurrent loss of CO. Calculations predict that the activation barrier value for propyne formation is comparable to that of allene and significantly higher than for those acyl chlorides that are capable of eliminating HCl across two adjacent carbon atoms. The conditions required for the successful decomposition of methacryloyl chloride reflect this result: IR LPHP of methacryloyl chloride employed a considerably higher laser power (*i.e.*, temperature) than for each of the other acyl chlorides investigated. It is likely that the conditions pertaining to the pyrolysis of methacryloyl chloride are sufficient to initiate the thermal interconversion of propyne and allene, a well-known process at high temperature.[52]



**Scheme 5** Proposed reaction scheme for methacryloyl chloride IR LPHP; observed products in ***bold italics***.

## Cyclopropanecarbonyl chloride

The pyrolysis[34,39,49,50] and photolysis of matrix-isolated[56] cyclopropanecarbonyl chloride has been investigated by several workers. Decomposition commences through elimination of HCl, affording cyclopropylidene ketene. Maquestiau and co-workers[49,50] and Monnier and co-workers[56] observed this transient species directly using low temperature (77 and 15 K, respectively) FT-IR spectroscopy. Bock and co-workers[34,39] were unable to confirm the presence of cyclopropylidene ketene and consequently proposed that dehydrochlorination was accompanied by concomitant loss of CO.

There is some debate as to whether the subsequent decay of cyclopropylidene ketene occurs in a concerted or stepwise manner; decarbonylation may be simultaneously accompanied, or subsequently succeeded, by ring opening. In any case, allene is the ultimate product. In a study of the photolysis of matrix-isolated cyclopropanecarbonyl chloride, Monnier and co-workers[56] observed chlorocyclopropane; it was argued that this was the product of cyclopropylidene insertion into the single bond of HCl and, consequently, corroborated a non-concerted mechanism. It is worth noting, however, that the direct decarbonylation of cyclopropanecarbonyl chloride will yield chlorocyclopropane directly.

In the present investigation, the only stable pyrolysis products were identified as HCl, CO and allene; the formation of chlorocyclopropane could not be confirmed. At ambient temperature there was no evidence of the transient cyclopropylidene ketene.

The low temperature post-pyrolysis spectrum of cyclopropanecarbonyl chloride in both an Ar and SF$_6$ matrix (dilution 2000 : 1) revealed a number of bands between 2200 and 2100 cm$^{-1}$. At 16 K, an intense band at 2175 cm$^{-1}$ (2168 cm$^{-1}$ in a SF$_6$ matrix) was observed, which was ascribed to the cumulenic C=C=O stretch of uncomplexed cyclopropylidene ketene. A number of workers have isolated and spectroscopically investigated cyclopropylidene ketene at low temperature.[50,56–59] The uncomplexed ketene, procured through thermolysis of the 1-pyrazoline-3,5-dione derivative, was observed by Maier and co-workers[57] at 2176 and 2154 cm$^{-1}$. Conversely, the absorbance band pattern observed between 2145 and 2125 cm$^{-1}$ by Monnier and co-workers[56] was ascribed to the complexed ketene. All other reports of cyclopropylidene ketene give the cumulenic stretch in this region and, consequently, indicate the complex.

There was no evidence to suggest that the dehydrochlorination of cyclopropanecarbonyl chloride process is reversible; absorbance bands ascribed to starting material did not increase during the acquisition of a spectrum at the expense of HCl. Subsequent decarbonylation of cyclopropylidene ketene may be simultaneously accompanied, or subsequently succeeded, by ring opening. Although we were unable to isolate the cyclopropylidene intermediate, a stepwise mechanism cannot be discounted.

There were several weaker bands at 2187, 2152 (2146 cm$^{-1}$ in a SF$_6$ matrix) and 2128 cm$^{-1}$, the peaks at 2187 and 2128 cm$^{-1}$ only evident in experiments that used an Ar matrix. On annealing an Ar matrix to 20 K, the absorbance band at 2128 cm$^{-1}$ intensified at the expense of the peaks at 2187 and 2175 cm$^{-1}$. The peak at 2152 cm$^{-1}$ remained unchanged. The post-pyrolysis spectra of Ar matrix-trapped cyclopropanecar-

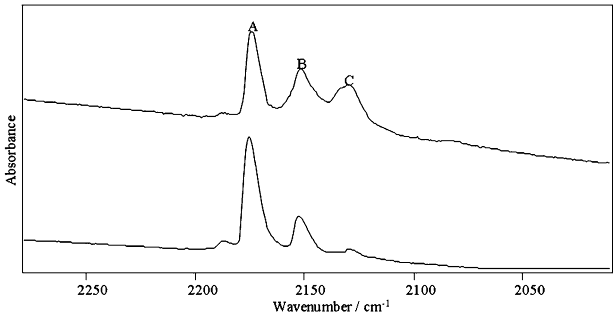


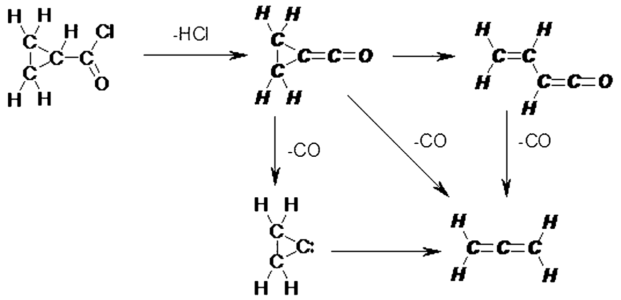
**Fig. 4** Post-pyrolysis FT-IR spectra of Ar matrix-trapped cyclopropanecarbonyl chloride at 20 K (above) and 16 K (below): A = cyclopropylidene ketene; B = 4-chloro-1-buten-1-one; C = vinyl ketene.

bonyl chloride at 16 and 20 K are illustrated in Fig. 4. The annealing pattern of the peaks observed indicates three distinct products. The absorbance band at 2187 cm$^{-1}$ is attributable to cyclopropylidene ketene, on account of its similar behaviour, on annealing, to the peak at 2175 cm$^{-1}$. The band at 2128 cm$^{-1}$ is ascribed to vinyl ketene; the low temperature spectrum of an authentic sample (procured through pyrolysis of *E*-2-butenoyl chloride) is spectroscopically identical with the band observed in this study.

The increase in vinyl ketene at the expense of cyclopropylidene ketene is consistent with isomerisation of the latter through heterolytic cleavage of the three-membered ring with a 1,3-H shift. The fact that vinyl ketene was not observed in the gas phase, or at low temperature in a SF$_6$ matrix, suggests that the mechanism responsible is heterogeneous in nature; in each case, decomposition is initiated by IR LPHP, thereby inhibiting reaction at the surface. Furthermore, decomposition of vinyl ketene has been shown to yield propyne, which was not detected in this investigation. Maquestiau and co-workers could find no spectroscopic evidence for the isomerisation (ring opening) of cyclopropylidene ketene to vinyl ketene.[50]

The band at 2152 cm$^{-1}$ is ascribed to 4-chloro-1-buten-1-one. The mechanism responsible for the formation of 4-chloro-1-buten-1-one involves heterolytic cleavage of the three-membered ring with a 1,3-chlorine shift. Calculations have shown that this mechanism represents a practicable decomposition route with activation energy of 250 kJ mol$^{-1}$. Moreover, the scaled[48] cumulenic stretch of the ketene is calculated at 2153 cm$^{-1}$, which is in excellent agreement with that observed. The decarbonylation or dehydrochlorination of 4-chloro-1-buten-1-one will afford 3-chloro-1-propene or vinyl ketene, respectively; the fact that the former was not observed renders this assignment tentative at present. It is possible, however, that 3-chloro-1-propene rapidly decomposes under these conditions; certainly, formation of allene (a significant product) is consistent with the molecular dehydrochlorination of 3-chloro-1-propene.

In the present study, we report the first detection of cyclopropylidene ketene in the gas phase by TDL spectroscopy. At 2177 cm$^{-1}$, a series of absorption bands, attributable to cyclopropylidene ketene, was observed when the contents of the cell were exposed to the output of a CW CO$_2$ laser. The spectrum returned to its original countenance immediately following cessation of irradiation. We have yet to analyse the rotational spectrum of cyclopropylidene ketene. Additionally, a series of minor absorption bands appeared at 2164 cm$^{-1}$, which is ascribed to ketene; the spectrum obtained was spectroscopically identical to that observed for an authentic sample of ketene procured through pyrolysis of acetyl chloride. Absorption signals attributed to ketene were discernible for up to 10 min after irradiation had ceased. A proposed pyrolysis scheme for cyclopropanecarbonyl chloride, without the mechanism responsible for the formation of 4-chloro-1-propen-1-one (which has not been definitively characterised) and ketene (which is formed in trace amount) is illustrated in Scheme 6.



**Scheme 6** Proposed reaction scheme for cyclopropanecarbonyl chloride IR LPHP; observed products in ***bold italics***.

## Conclusions

The pyrolysis of the selected acyl chlorides was initiated through molecular 1,2-HCl elimination, affording (with the exception of methacryloyl chloride, which does not possess a β-hydrogen) the ketene. The molecular dehydrochlorination of *Z*-2-butenoyl chloride (effected through isomerisation of the *E* form) was restricted to 1,4-HCl elimination, yielding vinyl ketene. Dehydrochlorination of a compound that possesses a second chlorine atom could occur in two ways. For example, the pyrolysis of 3-chloropropanoyl chloride effected formation of 3-chloro-1-propen-1-one and acryloyl chloride through HCl elimination across the C(1)–C(2) and C(2)–C(3) bonds, respectively.

The reversibility of dehydrochlorination was illustrated in systems where a relatively stable ketene was generated; during spectrum acquisition, bands ascribed to the precursor increased at the expense of those assigned to the ketene. The orientation of electrophilic addition was not restricted to that expected from Markovnikov's rule; presumably, the barrier to the *anti*-Markovnikov product was exceeded under IR LPHP conditions.

The decomposition of the ketene primarily involved homolytic loss of the carbonyl group, yielding the analogous carbene. In several intermediate ketenes, a 1,3-hydrogen migration was also proposed to account for an observed end product; a hydrogen shift in cyclopropylidene ketene was accompanied by heterolytic cleavage of the three-membered ring and resulted in the formation of vinyl ketene. The predominant reaction of a simple carbene (possessing a single carbon atom) involved combination or abstraction. In contrast, rearrangement of a more complex carbene (by insertion of the divalent carbon at the $C_\beta$–H bond) may account for the formation of several unsaturated products; for example, the formation of acetylene following the pyrolysis of acryloyl chloride is consistent with rearrangement of the intermediary carbene, ethenylidene.

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