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Rate constants for the reactions of chlorine atoms with a series of unsaturated aldehydes and ketones at 298 K: structure and reactivity

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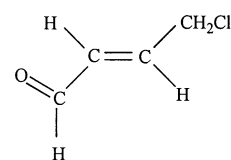
The kinetics and mechanisms of chlorine atom reactions with the products of organic oxidations in the atmosphere are of interest for understanding the chemistry of coastal areas. We report here the first kinetics measurements of the reactions of atomic chlorine with 4-chlorocrotonaldehyde and chloromethyl vinyl ketone, recently identified as products of the reaction of chlorine atoms with 1,3-butadiene. The reactions with acrolein, methacrolein, crotonaldehyde, methyl vinyl ketone and crotyl chloride were also studied to probe structure-reactivity relationships. Relative rate studies were carried out at 1 atm and 298 K using two different approaches: long path FTIR for the acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone reactions with acetylene as the reference compound, and a collapsible Teflon reaction chamber with GC-FID detection of the organics using *n*-butane or *n*-nonane as the reference compounds for the entire series. The average absolute rate constants (in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) determined using these techniques are as follows: acrolein (2.5 ± 0.7); methacrolein (2.9 ± 0.8); crotonaldehyde (3.2 ± 0.9); methyl vinyl ketone (2.0 ± 0.5); 4-chlorocrotonaldehyde (1.6 ± 0.4); chloromethyl vinyl ketone (2.0 ± 0.2); crotyl chloride (2.5 ± 0.2). The reported errors are $\pm 2\sigma$ and include a reference rate constant error of 20% for acetylene, 10% for *n*-butane and 3% for *n*-nonane. These values are in good agreement with previous literature reports for the acrolein, methacrolein and methyl vinyl ketone reactions, while that for crotonaldehyde is 33% larger. The rate constant for acetylene using *n*-butane as the reference compound was also measured to be $(5.23 \pm 0.91) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ), in excellent agreement with the currently recommended value at 1 atm and 298 K. The effect of structure on reactivity of these compounds is discussed and it is shown that these fast reactions will be a major loss process for these compounds in coastal marine areas at dawn.

Introduction

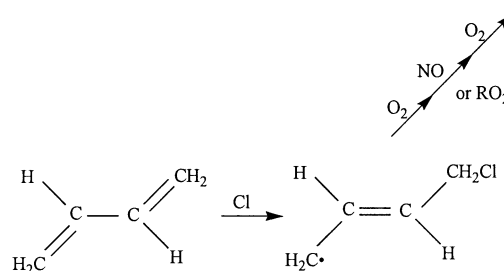
Atomic chlorine is generated in the marine boundary layer from reactions of sea salt particles.^{1–6} In addition, chlorine atom chemistry has been observed in the Arctic at polar sunrise^{7–13} and may have occurred in the plumes from the burning of oil wells in Kuwait due to the presence of brine.^{14–21} Molecular chlorine, Cl_2 , a precursor to atomic chlorine has been measured in marine air masses at concentrations up to ~ 150 ppt (parts per trillion).²² Non-HCl inorganic gaseous chlorine compounds, hypothesized to be mainly Cl_2 ranging from 13 to 127 ppt were measured indirectly using mist chambers at coastal sites.^{23,24} Photolyzable chlorine compounds^{25–27} have also been identified in the Arctic during surface ozone depletion in the spring. Such photolytically labile chlorine compounds will be photolyzed at sunrise and generate chlorine atoms.

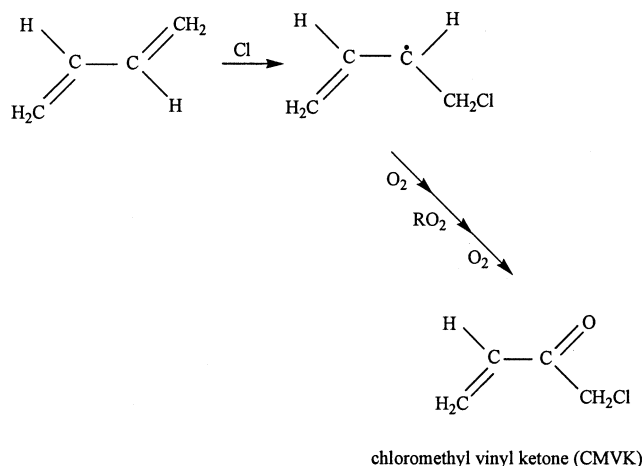
The rate constants for chlorine atom reactions with organic compounds reactions are about one to two orders of magnitude faster than the corresponding OH reactions. In the early morning hours when OH concentration is small ($\sim 10^5 \text{ cm}^{-3}$) and the atomic Cl concentration may be of the order²³ of 10^4 to 10^5 cm^{-3} , chlorine atoms could be the most important oxidant in the marine boundary layer. However, direct measurements of chlorine atom concentrations are not available. A potential approach is to measure unique chlorine-containing compounds formed from Cl-organic reactions. Recent studies

from this laboratory have shown that isoprene^{28,29} and 1,3-butadiene^{30,31} react with chlorine atoms to form unique, chlorine-containing aldehydes and ketones. Because these are formed only through chlorine atom chemistry, they can be used as “markers” for chlorine atoms in the lower atmosphere. For example, 4-chlorocrotonaldehyde (CCA) is formed in both the presence and absence of NO, while chloromethyl vinyl ketone (CMVK) is formed only in the absence of NO.³¹



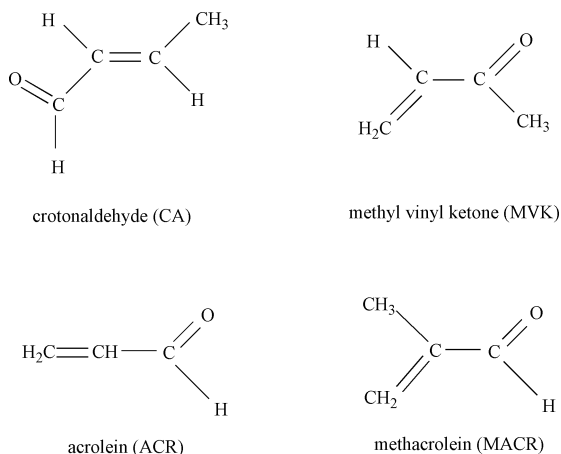
4-chlorocrotonaldehyde (CCA)





In order to use such compounds to quantify the concentration of chlorine atoms in air, their rates of removal must be known. Loss of these products occurs by reaction with OH, O₃, NO₃ and chlorine atoms, as well as by photolysis. Loss through Cl reactions could be the most important process in the early morning hours when CCA and CMVK are generated.

We report here relative rate studies at room temperature and 1 atm pressure for the reactions of chlorine atoms with 4-chlorocrotonaldehyde (CCA) and chloromethyl vinyl ketone (CMVK). To further understand the structural features that control reactivity of unsaturated aldehydes and ketones, the reactions with acrolein (ACR), methacrolein (MACR), crotonaldehyde (CA), and methyl vinyl ketone (MVK) were also studied using the same techniques:



Kinetics studies of the reactions of chlorine atoms with ACR, MACR, CA and MVK have been reported recently,^{32–35} but there are no reports of the rate constants for the CCA or CMVK reactions. Our combined data set permits probing structure-reactivity relationships for this series of unsaturated aldehydes and ketones. In addition, ACR is the major product from the OH-butadiene reaction, MACR and MVK from the OH-isoprene reaction, and MVK from the Cl-isoprene reaction. Their rate constants with Cl atoms will contribute to a better understanding of isoprene and 1,3-butadiene chemistry in coastal regions.

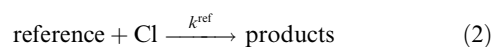
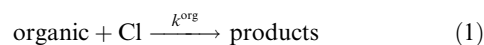
Crotonaldehyde and methyl vinyl ketone are structurally analogous to CCA and CMVK, respectively. In order to probe for the impact of substitution of a chlorine atom for a hydrogen atom on a carbon adjacent to a double bond, the rate constant for the reaction of chlorine atoms with crotyl chloride (CH₂ClCH=CHCH₃) was also measured. Finally, since acety-

lene was used as the reference compound in one set of experiments and *n*-butane or *n*-nonane in another, the relative rate constant for acetylene compared to *n*-butane was also measured to ensure there were no systematic errors due to the use of different reference compounds.

Experimental

Rate constants were measured at room temperature (298 ± 3) K and 1 atm in air or N₂ using the relative rate technique with two different approaches: (1) a borosilicate glass chamber with long path FTIR detection, and (2) Teflon[®] reaction chambers with GC-FID detection. In both cases, a mixture of the analyte and a reference compound, for which the rate constant for reaction with Cl atoms is known, was introduced into the reaction chamber. Relative rates were carried out in air or N₂ to check for potential interference from OH chemistry. Molecular chlorine was added to generate chlorine atoms and was photolyzed using a set of blacklamps surrounding the reaction chambers. These lamps emit radiation in the 300–450 nm range with a maximum intensity at ~360 nm, providing a good overlap with the Cl₂ absorption spectrum. Photolysis was typically carried out in increments of 1 to 5 min, depending on the compound and reaction conditions. The lamps were turned off to stop the reaction during sampling. Total photolysis times were 6 to 30 min. The loss of the organic and reference compound with reaction time were measured either by FTIR or by GC-FID as described in more detail below.

The organic and the reference compound react simultaneously with the chlorine atoms, with rate constants k^{org} and k^{ref} , respectively:



As described in detail elsewhere,⁶ the simultaneous decay of the organic and the reference compound from their initial concentrations at time $t = 0$, [org]₀ and [ref]₀, to [org]_{*t*} and [ref]_{*t*} at time t is given by eqn. (I):

$$\ln\{[\text{org}]_0/[\text{org}]_t\} = (k^{\text{org}}/k^{\text{ref}})\ln\{[\text{ref}]_0/[\text{ref}]_t\} \quad (\text{I})$$

Thus, a plot of $\{\ln [\text{org}]_0/[\text{org}]_t\}$ versus $\{\ln [\text{ref}]_0/[\text{ref}]_t\}$ should be linear through the origin with a slope equal to the ratio of rate constants $k^{\text{org}}/k^{\text{ref}}$. A major advantage of the relative rate approach is that accurate measurements of absolute concentrations of the organic and reference compounds are not required.

Chemicals

The chemicals used were as follows: *n*-butane (Matheson, 99.5%); acetylene (Air Products, Industrial Grade); *n*-nonane (Aldrich, 99+%); acrolein (Arcos, 97%); methacrolein (Aldrich, 95%); methyl vinyl ketone (Aldrich, 99%); crotonaldehyde (Aldrich, 99+%, predominantly *trans*-); crotyl chloride (Aldrich, 95%, predominantly *trans*-); N₂ (Oxygen Service Company, Ultrahigh Purity, >99.999%); air (Oxygen Service Company, Ultrahigh Purity). The gases were used as received. Acrolein, methacrolein, methyl vinyl ketone and crotonaldehyde were subjected to several freeze–pump–thaw cycles prior to vaporizing a measured pressure into 5 L bulbs; N₂ was then added to a known total pressure to give a mixture of the organic in N₂ that was subsequently expanded into the 0.5 L bulb and flushed into the reaction chamber. 4-Chlorocrotonaldehyde and chloromethyl vinyl ketone were synthesized according to the procedures described by Wang and Finlayson-Pitts,³¹ and directly injected into the diluent gas stream as it filled the reaction chamber.

Long path FTIR

The reaction chamber was a 20 L borosilicate glass cylinder containing White cell optics with a base path of 1 m and a total path length of 40 m. This was housed in the external sampling compartment of an FTIR spectrometer (Mattson Research Series) which had an MCT detector. The spectra were obtained using a total of 64 scans at 1 cm^{-1} resolution. Reactants were introduced directly into the cell by expansion from a glass manifold system. Photolysis of Cl_2 was accomplished using eight Sylvania 350 blacklights (30 W, F30T8/350BL) arranged around the outside of the cell.

The rotational line of the $\equiv\text{C-H}$ stretch at 3260 cm^{-1} was followed for acetylene (C_2H_2). For acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone, the peaks at 920, 933, 972 and 952 cm^{-1} respectively were followed. In separate experiments using either C_2H_2 or the analyte alone with Cl_2 , it was established that these peaks are free of interference from products. CCA and CMVK were not studied using FTIR because CCA had a rapid loss to the glass walls of the cell, and there was no distinctive peak for CMVK that we could use to follow this compound unequivocally.

Acetylene was chosen as the reference compound because it has unique infrared bands associated with the $\equiv\text{C-H}$ stretch, while alkane or alkene oxidation products often have infrared spectra similar to those of the parent compounds. Because the bimolecular rate constant for the C_2H_2 reaction ($k^{\text{bi}} = 5.27 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 1 atm, 298 K)³⁶ is smaller than those for the analytes [$(2-3) \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$], the net loss of acetylene during these runs was typically less than 15%, compared to losses of up to 60% for the analytes. The use of *in-situ* FTIR avoids the introduction of uncertainties due to sampling; hence the data precision is higher than for the Teflon reaction chamber studies and reliable data can be generated, despite the differences in rate constants for the reference compound and the analytes.

Concentrations used were in the range of 10–70 ppm for the organics, 20–70 ppm for acetylene, and 10–70 ppm for Cl_2 . Experiments were also performed in the absence of photolysis to check for dark reactions and obtain an estimate of the precision associated with the measurements for use in the error analysis as described elsewhere.³⁷ No dark reactions were observed under the conditions used here. The standard deviations (1σ) of the average absorbances of the peaks of interest for the unreacted mixtures in the dark were typically less than 0.5%. The simple averages of the data in each diluent gas (air or N_2) were used to obtain rate constant ratios and a simple average of these two values was used to calculate the final rate constant for the FTIR studies.

Teflon reaction chambers with GC-FID detection

Different Teflon reaction chambers having volumes ranging from 35 to 50 L when fully inflated were used. Non-chlorinated organics and Cl_2 were introduced into the reaction chamber by flushing a measured pressure of each compound in a known volume (0.5 L) into the chamber using a stream of the diluent gas (either air or N_2). Chlorinated liquid organics and nonane were vaporized by injecting a known volume of the liquid into the stream of diluent gas as it filled the reaction chamber. The reference compounds used for non-chlorinated compounds and for chlorinated compounds were *n*-butane and *n*-nonane, respectively. Concentrations were in the range of 30–95 ppm for the organics, 8–64 ppm for *n*-butane, 18–50 ppm for nonane, and 10–68 ppm for Cl_2 . The Cl_2 was photolyzed to generate chlorine atoms using a set of blacklamps (Sylvania 350, 20 W, F20T12/350BL).

The reactant mixture was withdrawn from the collapsible chambers by pumping slowly through the sampling loop of a gas sampling valve (Valco Instruments or Carle Gas). The

sampling loop pressure was then allowed to equilibrate with the reaction chamber prior to injection. The reactants were followed with time using GC-FID (Hewlett Packard Model 5890 and Series II). Three different GC columns were used. An SPB-1 column (Supelco, $60\text{ m} \times 0.53\text{ mm}$) was run at 40°C , giving a retention time of 3.9 min for methyl vinyl ketone and 1.5 min for acetylene. A GS-Q column (J&W Scientific, $30\text{ m} \times 0.32\text{ mm}$) was run at 170°C for 5 min and then temperature programmed to 210°C at a rate of $20^\circ\text{C min}^{-1}$; retention times varied from 2.4 min for acrolein to 4.6 min for crotonaldehyde. An RTX-2330 column (Restek Corporation, $30\text{ m} \times 0.25\text{ mm}$) was operated isothermally at 55°C for methacrolein, which had a retention time of 2.0 min. The RTX-2330 column was also used for chlorinated compounds: for CCA, the column was run at 20°C for 3 min and then increased to 150°C at a rate of $10^\circ\text{C min}^{-1}$, giving a retention time for CCA of 11.5 min. For analysis of CMVK, the column was operated at 0°C for 3 min and then increased to 60°C at a rate of $10^\circ\text{C min}^{-1}$, giving a CMVK retention time of 11 min.

The mixture was first sampled in the dark to test for potential losses of the organic or reference compound by a dark reaction with Cl_2 , as has been observed for isoprene at higher reactant concentrations in earlier studies.²⁹ No dark reactions were observed under the conditions used here. These dark runs were also used to obtain an estimate of the precision associated with the measurements for use in the error analysis.³⁷ The standard deviations (1σ) of these replicate measurements were typically less than 5%. Experiments were also carried out with the individual reference compound or the analyte alone with Cl_2 to ensure that the reactions did not produce species with the same retention times as the reactant peaks. In addition, all analytes were subjected to the blacklamp radiation alone to ensure that there were no unrecognized photochemical reactions occurring in the absence of the chlorine atom source.

Weighted averages of the runs in each diluent gas, using weights $w = 1/\sigma^2$, were used to obtain rate constant ratios in air and nitrogen. Weighted averages of the combined runs in N_2 and in air were used to calculate the final rate constant for the GC-FID. This approach was taken since the error from individual runs was higher than that in the FTIR studies, leading to an underestimate of the errors if analyzed as for the FTIR studies.

Results

FTIR studies

Fig. 1 shows a typical set of spectra before and after 10 min total photolysis for an acetylene–acrolein– Cl_2 mixture. Fig. 2 shows typical kinetics plots in the form of eqn. (I) for acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone, respectively. The data from the FTIR studies for these compounds are summarized in Table 1.

Teflon chamber studies using GC-FID

Fig. 3 shows typical kinetics plots eqn. (I) for each of the non-chlorinated unsaturated aldehydes and ketones. Fig. 4 shows analogous data for CCA, CMVK and crotyl chloride. These data are also summarized in Table 1.

The Teflon reaction chamber and FTIR studies used different reference compounds, *n*-butane and acetylene, respectively. This could introduce a systematic error if their values relative to each other were inconsistent. In order to test for this possibility, experiments using the Teflon reaction chamber were also carried out for acetylene relative to *n*-butane. Fig. 5 shows some of the kinetics data, which are summarized in Table 1. It is seen that the rate constant for the reaction of chlorine atoms with acetylene based on a rate constant for the *n*-butane reaction³⁸ of $(2.18 \pm 0.22) \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ is

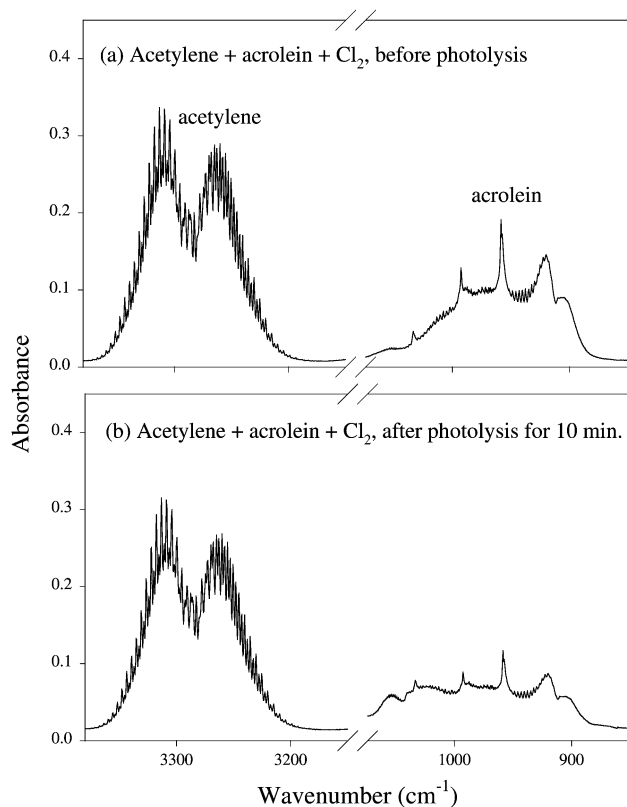


Fig. 1 Typical spectra (a) before photolysis and (b) after 10 min total photolysis time for a mixture of acetylene (67 ppm), acrolein (22 ppm) and Cl_2 (11 ppm) in N_2 .

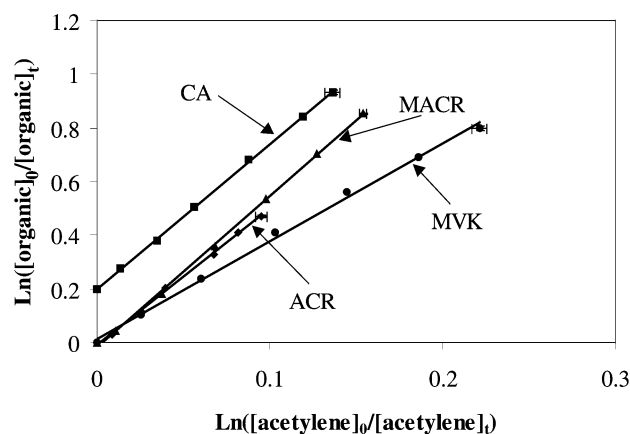


Fig. 2 Typical kinetics plots for loss of acetylene (reference compound) and the organics according to eqn. (1). ■ crotonaldehyde in N_2 ; ▲ methacrolein in air; ◆ acrolein in air; ● methyl vinyl ketone in N_2 . The plot for crotonaldehyde is displaced upwards by 0.2 for clarity of presentation. Typical 2σ errors, calculated as described elsewhere,³⁷ are shown for representative data points.

$(5.23 \pm 0.91) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is in excellent agreement with the recommended value³⁶ of $(5.26 \pm 1.05) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For our experiment, the use of two different reference compounds therefore does not introduce a systematic error into the final absolute rate constants.

Discussion

Rate constants obtained from the FTIR studies and the Teflon reaction chamber studies differ by less than 10% for crotonal-

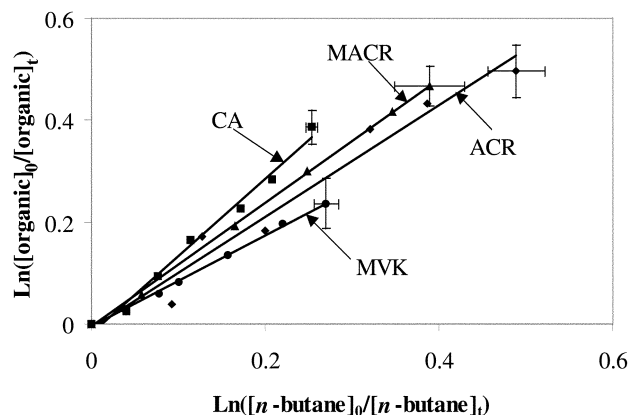


Fig. 3 Typical kinetics plots for loss of *n*-butane (reference compound) and the organics according to eqn. (1). ■ crotonaldehyde in air; ▲ methacrolein in air; ◆ acrolein in air; ● methyl vinyl ketone in air. Typical 2σ errors, calculated as described elsewhere,³⁷ are shown for representative data points. Typical 2σ errors, calculated as described elsewhere,³⁷ are shown for representative data points.

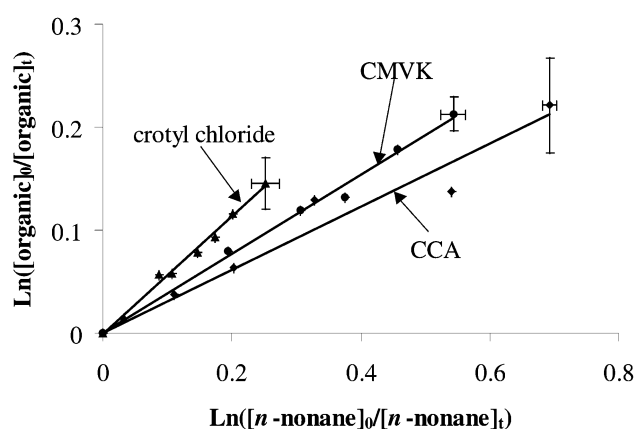


Fig. 4 Typical kinetics plots for loss of *n*-nonane (reference compound) and the chlorinated organics according to eqn. (1). ◆ 4-chlorocrotonaldehyde in N_2 ; ● chloromethyl vinyl ketone in N_2 ; ▲ crotyl chloride in N_2 . Typical 2σ errors, calculated as described elsewhere,³⁷ are shown for representative data points.

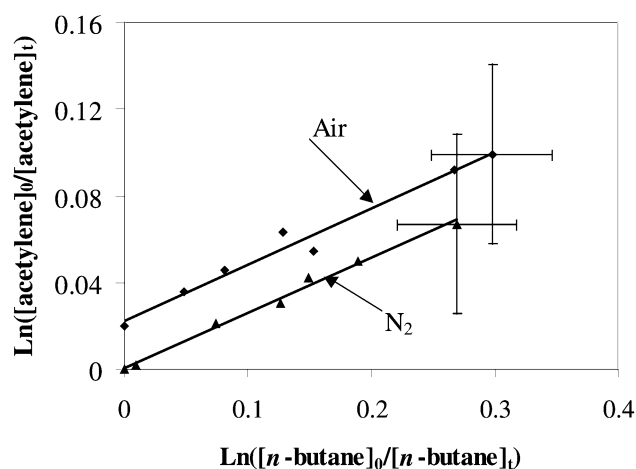


Fig. 5 Typical kinetics plots for the loss of *n*-butane (reference compound) and acetylene according to eqn. (1). ◆ in air; ▲ in N_2 . The data in air have been displaced upwards by 0.02 for clarity of presentation. Typical 2σ errors, calculated as described elsewhere,³⁷ are shown for representative data points.

Table 1 Summary of relative rate measurements for acrolein, methacrolein, crotonaldehyde, methyl vinyl ketone, 4-chlorocrotonaldehyde, chloromethyl vinyl ketone and crotyl chloride at 298 K and 1 atm pressure, and the corresponding absolute values

Organic	Technique (reference)	Diluent gas (no. of runs)	$k^{\text{org}}/k^{\text{ref}} (\pm 2\sigma)^a$	Average $k^{\text{org}}/k^{\text{ref}} (\pm 2\sigma)^b$	$k^{\text{org}} (\pm 2\sigma) / 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1 c, d}$	Overall average $k^{\text{org}} (\pm 2\sigma) / 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1 e}$	
Acrolein [CH ₂ =CH-CHO]	FTIR (C ₂ H ₂)	N ₂ (8)	4.99 ± 0.57	5.10 ± 0.23	2.68 ± 0.55	2.53 ± 0.72	
		air (10)	5.22 ± 1.02				
	GC-FID (<i>n</i> -butane)	N ₂ (5)	1.14 ± 0.25		1.09 ± 0.19		2.38 ± 0.47
		air (4)	1.04 ± 0.27				
Methacrolein [CH ₂ =C(CH ₃)-CHO]	FTIR (C ₂ H ₂)	N ₂ (4)	6.13 ± 0.84	5.88 ± 0.50	3.09 ± 0.67	2.86 ± 0.76	
		air (9)	5.63 ± 1.34				
	GC-FID (<i>n</i> -butane)	N ₂ (6)	1.18 ± 0.13		1.21 ± 0.12		2.64 ± 0.37
		air (5)	1.23 ± 0.03				
Crotonaldehyde [CHO-CH=CHCH ₃]	FTIR (C ₂ H ₂)	N ₂ (3)	5.38 ± 0.48	5.79 ± 0.82	3.05 ± 0.75	3.16 ± 0.93	
		air (3)	6.20 ± 1.32				
	GC-FID (<i>n</i> -butane)	N ₂ (3)	1.50 ± 0.26		1.50 ± 0.21		3.27 ± 0.56
		air (3)	1.49 ± 0.33				
Methyl vinyl ketone [CH ₂ =CHC(O)CH ₃]	FTIR (C ₂ H ₂)	N ₂ (3)	3.67 ± 0.45	0.903 ± 0.074	1.93 ± 0.46	1.95 ± 0.52	
		air (3)	^f				
	GC-FID (<i>n</i> -butane)	N ₂ (7)	1.01 ± 0.07		1.97 ± 0.27		
		air (7)	0.950 ± 0.272				
4-Chlorocrotonaldehyde [CHO-CH=CHCH ₂ Cl]	GC-FID (<i>n</i> -nonane)	N ₂ (3)	0.332 ± 0.10	0.333 ± 0.086	1.61 ± 0.42	1.61 ± 0.42	
		air (1)	0.339 ± 0.172 ^g				
Chloromethyl vinyl ketone [CH ₂ =CHC(O)CH ₂ Cl]	GC-FID (<i>n</i> -nonane)	N ₂ (4)	0.436 ± 0.054	0.420 ± 0.044	2.02 ± 0.22	2.02 ± 0.22	
		air (3)	0.388 ± 0.074				
Crotyl chloride [CH ₂ Cl-CH=CHCH ₃]	GC-FID (<i>n</i> -nonane)	N ₂ (3)	0.510 ± 0.024	0.514 ± 0.048	2.48 ± 0.24	2.48 ± 0.24	
		air (3)	0.559 ± 0.090				
Acetylene [C ₂ H ₂]	GC-FID (<i>n</i> -butane)	N ₂ (3)	0.257 ± 0.150	0.240 ± 0.034	0.523 ± 0.091	0.523 ± 0.091	
		air (5)	0.223 ± 0.074				

^a As described in the text, this is the simple average for the FTIR runs. For the experiments in the Teflon chambers with GC-FID, this is the weighted average of the runs, where each run was weighted by $w = 1/\sigma^2$. ^b Simple average of runs in N₂ and in air for FTIR studies and weighted average for combined runs in N₂ and in air for GC-FID studies. ^c The rate constants for the reference compounds were taken as $(5.26 \pm 1.05) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ) for Cl + C₂H₂ at 1 atm and 298 K,³⁶ $(2.18 \pm 0.22) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ) for Cl + *n*-C₄H₈³⁸ and $(4.82 \pm 0.14) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ) for Cl + *n*-nonane³⁸ which has been adjusted to the recommended value of $k(\text{Cl} + n\text{-C}_4\text{H}_8)$. ^d Errors include 20% error cited for the Cl + C₂H₂ rate constant, 10% in the Cl + *n*-butane rate constant and 3% in the Cl + *n*-nonane rate constant. ^e Error cited is $(\sigma_{\text{FTIR}}^2 + \sigma_{\text{GC}}^2)^{1/2}$ where σ_{FTIR} is the uncertainty in the absolute rate constant obtained in the FTIR studies shown in the previous column and includes the uncertainty in the Cl + C₂H₂ rate constant, and σ_{GC} is the uncertainty in the absolute rate constant obtained in the Teflon chamber studies shown in the previous column and includes the uncertainty in the Cl + *n*-C₄H₈ rate constant. ^f Runs in air were significantly faster than in N₂, 5.19 ± 0.48 (2σ), suggesting some interference. As a result, these runs were not included in the average. ^g The error is from one individual run in air.

dehyde and methyl vinyl ketone, and less than 15% for acrolein and methacrolein. Table 2 compares the rate constants measured in this study to those available in the literature. Our rate constants for methacrolein and methyl vinyl ketone are within 10% of those of Canosa-Mas *et al.*,³³ and an earlier preliminary study of methyl vinyl ketone.³² Our rate constant for acrolein is also in reasonable agreement with that of Canosa-Mas *et al.*;³⁴ it is ~25% larger than that reported by Ullerstam *et al.*,³⁵ although the two values are within the combined experimental errors. Our value for crotonaldehyde is 33% larger than the value reported by Ullerstam *et al.*,³⁵ although it again is within the combined error limits of the two studies.

It is interesting that the rate constant reported here for acrolein is within experimental error of that reported for the propene reaction in a number of studies, $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1 atm and room temperature.³⁹⁻⁴⁵ If an analogy can be drawn to the structurally similar alkenes, then cro-

tonaldehyde might be expected to have a rate constant similar to that of *trans*-2-butene. The *trans*-2-butene rate constant has been reported to be $3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Ullerstam *et al.*³⁵ (with the 10% correction described in Table 2), which is in excellent agreement with a value of $3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured in unpublished studies in this laboratory.⁴⁵ The rate constant measured in this study for crotonaldehyde, $3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is indeed the same as that of the corresponding alkene. The rate constant for methacrolein, $2.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is also similar to that of its corresponding alkene, isobutene ($3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).⁴⁵

Structure and reactivity of unsaturated aldehydes and ketones

Although all the reactions are fast, approaching collision controlled, differences between the rate constants can be used to

Table 2 Comparison of rate constants at 1 atm pressure and 298 K to literature values

Compound	$k \pm 2\sigma / 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference
Acrolein	2.5 ± 0.7^a	This work
	2.0 ± 0.3^b	Ullerstam <i>et al.</i> ³⁵
	2.2 ± 0.3	Canosa-Mas <i>et al.</i> ³⁴
Methacrolein	2.9 ± 0.8^a	This work
	3.2 ± 0.5	Canosa-Mas <i>et al.</i> ³³
Crotonaldehyde	3.2 ± 0.9^a	This work
	2.4 ± 0.4^b	Ullerstam <i>et al.</i> ³⁵
Methyl vinyl ketone	2.0 ± 0.5^a	This work
	2.0 ± 0.2	Finlayson-Pitts <i>et al.</i> ³²
	2.1 ± 0.5	Canosa-Mas <i>et al.</i> ³³

^a Error includes that in the values used for the reference compounds as well, 20% for the acetylene reaction³⁶ and 10% for the *n*-butane reaction.^{38, b} Adjusted upwards by $\sim 10\%$ to a rate constant for $\text{Cl} + \text{C}_3\text{H}_6$ of $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In the Ullerstam *et al.* studies,³⁵ propene was used as the reference compound with a value for the rate constant of $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on the work of Kaiser and Wallington.⁴¹ However, this value is for the addition pathway at 1 atm; there is also a small contribution of a net abstraction pathway in the $\text{Cl} + \text{propene}$ reaction, leading to a total rate constant at 1 atm and 298 K of $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

probe the contributions of the different functional groups to the kinetics. The 2σ experimental errors associated with our measurements of the relative values are in the range of 7–16%, significantly less than the 50% difference in rate constants from methyl vinyl ketone to crotonaldehyde. Thus, some insight can be gleaned into structure-reactivity relationships for this series of unsaturated aldehydes and ketones.

The simplest compound studied here, acrolein (ACR), has two potential reaction sites: the double bond to which the chlorine atom can add, and the aldehydic hydrogen, which can be abstracted. The rate constant can be viewed as the sum of the rate constant for each reaction site:

$$k^{\text{ACR}} = k^{\text{C=C}} F^{\text{-CHO}} + k^{\text{-CHO}} F^{\text{C=C}} \quad (\text{II})$$

where the F factors take into account neighboring group effects.^{38,46,47}

An estimate for $k^{\text{C=C}}$ can be obtained from the chlorine atom reaction with propene, where the rate constant^{39–45} for the addition portion of the reaction at 1 atm is $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reaction of propene, which has 21 vibrational degrees of freedom over which the energy in the adduct can be spread, is not quite at the high pressure limit at 1 atm;⁴¹ given that ACR has only 18 vibrational degrees of freedom, its addition reaction would be expected to be displaced from the high pressure limit to a greater extent so that a value of 2.3×10^{-10} may be an overestimate for addition to the double bond in ACR.

The rate constant for chlorine atoms with the aldehyde group ($k^{\text{-CHO}}$) can be obtained from the difference between the known rate constant for the reaction of Cl with CH_3CHO and that for chlorine atoms with a methyl group. Structure-reactivity relationships for chlorine atom reactions with a series of alkanes^{38,46,47} give a rate constant for the reaction of Cl with a methyl group of $(3.0\text{--}3.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constant for $\text{Cl} + \text{CH}_3\text{CHO}$ has been measured by a number of groups and the results have been reviewed by Atkinson³⁸ and Tyndall and coworkers.^{48,49} Tyndall *et al.*⁴⁸ recommend a value of $7.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. If abstractions from the methyl group and the aldehydic hydrogen are additive, and using a value for Cl with a methyl group of $3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k^{\text{-CHO}}$ must be $4.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Thus, using eqn. (II) above, if the F factors are both 1.0, the rate constant for ACR is expected to be approximately $(2.3 + 0.5) \times 10^{-10} = 2.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is in reasonable agreement with our measured value of $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, particularly when it is recognized that the value of $k^{\text{C=C}}$ using propene at 1 atm may be overestimated.

Ullerstam *et al.*³⁵ measured rate constants for acrolein and crotonaldehyde that are smaller than for propene and *trans*-2-butene, respectively. They concluded that the aldehyde group lowers the reactivity of the double bond, offsetting the increased contribution expected from abstraction of the aldehydic hydrogen. In our studies, however, the rate constants are essentially the same for the unsaturated aldehydes and the corresponding alkenes.

Methacrolein (MACR) and crotonaldehyde (CA) are isomers that can be regarded as addition of a methyl group to acrolein, but in different positions. Thus they might be expected to have the same rate constant, which is in fact the case, to within 10%.

One approach to understanding the rate constants for MACR and CA is to treat them as the sum of reaction with acrolein and abstraction of an allylic hydrogen from the methyl group. In the case of simple alkene reactions, there are two reaction paths: (1) addition to the double bond, and (2) net abstraction of an allylic hydrogen, part of which occurs by an addition–elimination reaction.^{29,41,44} Based on studies of the propene and isoprene reactions, the net abstraction at 1 atm pressure typically contributes $\sim 10\text{--}15\%$ of the total reaction.^{39–45,50–52} In the case of propene, this corresponds to an abstraction rate constant of $0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Thus, the rate constants for MACR and CA would be expected to be larger than that for acrolein by $0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, or a total of $2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. However, the rate constant for acrolein, with 18 vibrational degrees of freedom, is not likely in the high pressure limit, whereas the rate constants for MACR and CA, with 27 vibrational degrees of freedom, would be expected to be close to the high pressure limit. Thus the contribution from the acrolein portion of the molecule may be underestimated using this approach. Given that, the measured values of $2.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for MACR and $3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CA are in good agreement with this analysis.

An alternate approach is to regard the MACR and CA reactions as reaction with propene and an additional contribution for abstraction of an aldehydic hydrogen, *i.e.*

$$k^{\text{MACR}} = k^{\text{propene}} + k^{\text{-CHO}} \quad (\text{III})$$

Using a total rate constant^{39–45} for $\text{Cl} + \text{propene}$ at 1 atm pressure of $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the value derived above for $k^{\text{-CHO}}$, the rate constants for Cl with MACR and CA are predicted to be $3.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in excellent agreement with the measured rate constants.

Methyl vinyl ketone has the smallest rate constant of the group, $2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is equivalent to $k^{\text{C=C}}$, $2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, obtained from the ACR (kinetics), assuming $k^{\text{-CHO}} = 0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and our measured rate constant for ACR. This suggests that abstraction from the methyl group, separated from the double bond by a carbonyl group, does not contribute significantly to the reaction. This is consistent with the product studies of Canosa-Mas *et al.*³⁴ in which the lack of observation of HCl as a product put an upper limit of 3% for the abstraction path. As discussed further below, this is also consistent with the fact that the rate constant does not change when a chlorine atom is substituted for a hydrogen atom in the methyl group.

An alternate approach to the MVK reaction is to recognize that since the carbonyl group is unreactive towards chlorine

Table 3 Rate constants and calculated lifetimes with respect to reaction with Cl, OH and O₃ at concentrations typical of dawn

Compound	Cl / 10 ⁵ cm ⁻³		OH / 10 ⁵ cm ⁻³		O ₃ (30 ppb)	
	Rate constant ^a / 10 ⁻¹⁰ cm ³ molecule ⁻¹ s ⁻¹	Lifetime / days	Rate constant ^b / 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹	Lifetime / days	Rate constant ^c / 10 ⁻¹⁸ cm ³ molecule ⁻¹ s ⁻¹	Lifetime / days
Acrolein	2.5	0.46	2.0	5.8	0.28	56
Methacrolein	2.9	0.40	3.4	3.5	1.1	14
Crotonaldehyde	3.2	0.36	3.6	3.2	0.9	17
Methyl vinyl ketone	2.0	0.58	1.9	6.2	4.8	3.3
4-Chlorocrotonaldehyde	1.6	0.72	na ^d	na ^d		
Chloromethyl vinyl ketone	2.0	0.58	na ^d	na ^d		

^a This work. ^b Atkinson⁵⁴ ^c Atkinson *et al.*⁵⁵ ^d na = not known.

atoms, MVK might be expected to have a similar rate constant to that for addition to the double bond in propene (2.3×10^{-10} cm³ molecule⁻¹ s⁻¹) with an additional contribution (3.0×10^{-11} cm³ molecule⁻¹ s⁻¹)^{38,46,47} for abstraction from the methyl group. However, the measured rate constant is actually smaller than that measured for propene alone, suggesting that the adjacent ketone group must decrease the reactivity. Such an effect has been observed by Olsson *et al.*⁵³ in their studies of chlorine atom reactions with ketones. For example, the rate constant for the acetone reaction was a factor of 35 smaller than that for ethane. The electron-withdrawing properties of the oxygen must lead to this reduction in rate constant. Electronic structure calculations might provide some insight into this effect.

Impact of chlorine substitution on rate constant

The rate constant for chloromethyl vinyl ketone is the same, within experimental error, as that of methyl vinyl ketone. If the reaction occurs only through addition to the vinyl group, substitution of a hydrogen atom by chlorine on the terminal methyl group does not alter the rate constant, consistent with our observation and that of Canosa-Mas *et al.*³⁴ that abstraction represents less than 3% of the overall reaction.

However, substitution of a chlorine atom in crotonaldehyde produces a dramatic drop of 50% in the rate constant. Kaiser and Wallington⁴¹ reported a 25% reduction in the rate constant of the Cl atom reaction with allyl chloride (CH₂ClCH=CH₂) compared to that with propene. Since the abstraction path is only about 10% of the overall reaction, the chloromethyl group must also slow the addition pathway. Our value for crotyl chloride (CH₂ClCH=CHCH₃), $(2.5 \pm 0.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, is 24% smaller than the rate constant for the alkene analog, *trans*-2-butene,^{35,45} consistent with the propene-allyl chloride results.

4-Chlorocrotonaldehyde might be expected to show a similar trend, that is a reduction of ~25% in the rate constant compared to crotonaldehyde. The 50% reduction observed here is larger than anticipated, with the rate constant for CCA of 1.6×10^{-10} cm³ molecule⁻¹ s⁻¹ being even smaller than the value of 2.3×10^{-10} cm³ molecule⁻¹ s⁻¹ for addition to the double bond in propene at 1 atm. There may be unrecognised interactions between the p orbital of the chlorine atom, the π bond between the carbon atoms, and the carbonyl group in CCA. Electronic structure calculations would help to clarify this and other potential factors that contribute to the reduced rate constant for CCA compared to CA.

Atmospheric implications

Photolysis of Cl₂ and other photolyzable chlorine species generates chlorine atoms with a peak concentration estimated to

be ~10⁵ atoms cm⁻³ at dawn.²³ Table 3 shows the calculated lifetimes for each of the compounds studied here with respect to reactions with Cl, OH and O₃ at typical concentrations at dawn; the removal of these compounds by chlorine atoms in coastal areas at dawn will be faster by approximately an order of magnitude or more compared to removal by reactions with OH or O₃ for a short period. When field measurements of CCA become available, they can be combined with the kinetics data presented here and the kinetics and mechanistic data for the Cl-butadiene reaction²⁹⁻³¹ to estimate chlorine atom concentrations in coastal regions at dawn.

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