Rate Coefficients and Mechanisms of the Reaction of Cl-Atoms with a Series of Unsaturated Hydrocarbons Under Atmospheric Conditions

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ABSTRACT: Rate coefficients and/or mechanistic information are provided for the reaction of Cl-atoms with a number of unsaturated species, including isoprene, methacrolein (MACR), methyl vinyl ketone (MVK), 1,3-butadiene, *trans*-2-butene, and 1-butene. The following Cl-atom rate coefficients were obtained at 298 K near 1 atm total pressure: $k(\text{isoprene}) = (4.3 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (independent of pressure from 6.2 to 760 Torr); $k(\text{MVK}) = (2.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; $k(\text{MACR}) = (2.4 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; $k(\textit{trans}\text{-2-butene}) = (4.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; $k(\text{1-butene}) = (3.0 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Products observed in the Cl-atom-initiated oxidation of the unsaturated species at 298 K in 1 atm air are as follows (with % molar yields in parentheses): CH_2O (9.5 ± 1.0%), HCOCl (5.1 ± 0.7%), and 1-chloro-3-methyl-3-buten-2-one (CMBO, not quantified) from isoprene; chloroacetaldehyde (75 ± 8%), CO_2 (58 ± 5%), CH_2O (47 ± 7%), CH_3OH (8%), HCOCl (7 ± 1%), and peracetic acid (6%) from MVK; CO (52 ± 4%), chloroacetone (42 ± 5%), CO_2 (23 ± 2%), CH_2O (18 ± 2%), and HCOCl (5%) from MACR; CH_2O (7 ± 1%), HCOCl (3%), acrolein (≈3%), and 4-chlorocrotonaldehyde (CCA, not quantified) from 1,3-butadiene; CH_3CHO (22 ± 3%), CO_2 (13 ± 2%), 3-chloro-2-butanone (13 ± 4%), CH_2O (7.6 ± 1.1%), and CH_3OH (1.8 ± 0.6%) from *trans*-2-butene; and chloroacetaldehyde (20 ± 3%), CH_2O (7 ± 1%), CO_2 (4 ± 1%),

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and HCOCl (4 ± 1%) from 1-butene. Product yields from both *trans*-2-butene and 1-butene were found to be O_2-dependent. In the case of *trans*-2-butene, the observed O_2-dependence is the result of a competition between unimolecular decomposition of the $CH_3CH(Cl)—CH(O\bullet)—CH_3$ radical and its reaction with O_2, with $k_{decomp}/k_{O2} = (1.6 \pm 0.4) \times 10^{19}$ molecule cm^{-3}. The activation energy for decomposition is estimated at 11.5 ± 1.5 kcal mol^{-1}. The variation of the product yields with O_2 in the case of 1-butene results from similar competitive reaction pathways for the two β-chlorobutoxy radicals involved in the oxidation, $ClCH_2CH(O\bullet)CH_2CH_3$ and $\bullet OCH_2CHClCH_2CH_3$. Int J Chem Kinet 35: 334–353, 2003

INTRODUCTION

The extent to which Cl-atoms impact the chemistry of the troposphere has been debated over the years [e.g., 1–11]. While it is now generally considered that Cl-atoms play only a minor role on tropospheric oxidation processes on a global scale [6,7,9], it is thought that they may exert some influence in the boundary layer, particularly in marine and coastal environments [1–4,8,10]. For example, heterogeneous chemistry involving sea-salt aerosols is thought to provide a source of Cl-atom precursors, particularly in the presence of NO_x (e.g., in polluted coastal regions) [1,2,8]. The influence of heterogeneous sea-salt chemistry is particularly evident in the Arctic springtime, where changes in hydrocarbon mixing ratios are clearly the result of Cl-atom (and, in the case of some hydrocarbons, Br-atom) chemistry [e.g., 12,13]. It has also recently been proposed [14,15] that Cl-atoms produced in the photolysis of Cl_2 emitted from industrial processes may enhance hydrocarbon oxidation rates and ozone production in urban environments, specifically Houston, Texas.

Finlayson-Pitts and coworkers [16–19] have proposed the use of unique reaction products resulting from the reaction of Cl with isoprene (a major biogenic emission, which is present in the marine boundary layer) and 1,3-butadiene (a major anthropogenic emission) as atmospheric markers for the occurrence of Cl-atom chemistry. For example, using a combination of infrared and GC/MS detection methods, laboratory experiments [17] have shown that 1-chloro-3-methyl-3-buten-2-one (CMBO) is formed following Cl-atom addition to isoprene, though its yield has yet to be quantified [17]. Similarly, the formation of 4-chlorocrotonaldehyde (CCA) in substantial yield following Cl-atom addition to 1,3-butadiene has been observed in laboratory experiments [18,19].

Recent field experiments [15,20] have indeed demonstrated the presence of CMBO and CCA in ambient air. Clearly, in order to interpret these field data and to quantify levels of Cl-atoms in the troposphere, accurate rate coefficient and yield data for reaction of Cl with these unsaturated species and their by-products are needed. Furthermore, a more fundamental understanding of the pathways involved in these oxidations is desired. Cl-atom-initiated oxidation of unsaturated species proceeds in large part via the formation of β-chloroalkoxy radicals (e.g., $ClCH_2CH_2O$ from reaction of Cl with ethene [21]). While it has been established that unimolecular decomposition of these species (via C—C bond cleavage) is not a favorable process for smaller (C_2 and C_3) hydrocarbons [21–25], studies of larger β-chloroalkoxy radicals are lacking.

In this work, measurements of the rate coefficients for, and/or end products of, the reactions of Cl-atoms with isoprene, methyl vinyl ketone (MVK), methacrolein (MACR), and 1,3-butadiene are reported and compared with previous literature data. In addition, studies of the rate coefficient and mechanism of the reaction of Cl with both *trans*-2-butene and 1-butene are reported, and product data are interpreted in terms of the behavior of the β-chloroalkoxy radicals involved.

EXPERIMENTAL

All experiments were conducted in a stainless steel environmental chamber, which has been described previously [26,27]. The chamber is constructed of stainless steel, is 2 m in length, and has a volume of 47 L. The chamber is interfaced to a Bomem Fourier transform spectrometer (operating in the infrared) via a set of Hanst-type multipass optics that provided an optical path length of 32.6 m. Photolysis of gas mixtures in the chamber was carried out using the filtered (235–400 nm) output of a Xe-arc lamp. Temporal profiles of starting materials and reaction products were monitored primarily using FTIR spectroscopy. Infrared spectra were recorded over the range 800–3900 cm^{-1}, with a spectral resolution of 1 cm^{-1}. For some experiments, products were also identified using a gas chromatography/mass spectrometer (GC/MS) system [28]. For GC/MS analysis, samples were withdrawn from the chamber via a 1/8″ PFA Teflon tube and collected on a 1/16″ Silcosteel trap held at −145°C. To avoid reaction of Cl_2 with organics in the cold trap prior to injection, a procedure similar to that described in Wang and

Finlayson-Pitts [18,19] was used to remove excess Cl_2 upstream of the cold trap. For this purpose, a Gelman GF/C 47-mm glass fiber filter coated with a solution of 1% (w/v) sodium carbonate in a 1% (v/v) glycerol in 1:1 methanol–water solution was placed in a Teflon filter holder and all samples were drawn through the filter at ∼100 mL min^{-1} prior to trapping. Typically, 10–25 mL at STP was trapped. The trap was then warmed and the contents injected onto a chromatographic column (Agilent Technologies, HP-624, 20 m × 20 mm i.d., 1.1-μm film) installed in a custom oven enclosure. The compounds were eluted into a mass spectrometer (Agilent Technologies, 5973), which was run in full scan mode. The column was held at 35°C for 1 min and then heated at 20°C min^{-1} to 120°C, and was held there for a total run time of 8 min.

Rate coefficients for reactions of Cl with isoprene, MVK, MACR, *trans*-2-butene, and 1-butene were determined via FTIR spectroscopy, using standard relative rate procedures [e.g.,16,27,29–31], with propane, propene, and ethene used as the reference compounds. In most cases, mixtures of Cl_2, the unsaturated species under study, and one of the reference species were photolysed in synthetic air at a total pressure of 700–720 Torr. For isoprene, studies were also conducted over a range of pressures (6–760 Torr) in either air or N_2. Detailed experimental conditions for specific experiments are given in the Results section.

The rate of disappearance of the unsaturated species under study (UNSAT) relative to the reference compound (REF) was monitored by FTIR spectroscopy, and rate coefficient ratios, $k_{\text{UNSAT}}/k_{\text{REF}}$, were determined as follows:

$$\frac{k_{\text{UNSAT}}}{k_{\text{REF}}} = \frac{\ln([\text{UNSAT}]_o/[\text{UNSAT}])}{\ln([\text{REF}]_o/[\text{REF}])}$$

Absolute values for the rate coefficients for reaction of Cl with isoprene, MVK, MACR, *trans*-2-butene, and 1-butene were obtained from currently recommended [32] expressions for reaction of Cl with propane, $k = 1.43 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (independent of pressure), propene, $k = 2.63 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (at 700 Torr total pressure), and/or ethene, $k = 0.99 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (at 700 Torr total pressure). Each rate coefficient ratio was obtained from four to eight irradiations of at least two fills of the chamber. The ratio of the concentrations of the species under study and the reference compound was varied by at least a factor of 2 between runs. No significant variation in the measured rate coefficient ratio was observed in any case, suggesting that there were no effects of secondary chemistry or of spectral interferences in the measurements.

Product yield experiments involved the photolysis of mixtures of Cl_2 and the unsaturated species under study in 700 Torr of O_2/N_2 diluent in the absence of NO_x (see Results section for further details). Typically, four to eight irradiations of the chamber contents were conducted (each of duration 15–60 s), and an IR spectrum was recorded following each irradiation (with the photolysis lamp blocked). Most products (CH_2O, CO_2, CH_3OH, peracetic acid, 3-chloro-2-butanone, CH_3CHO, acrolein) were quantified via spectral stripping routines, using standard spectra obtained in our laboratory. Other species were quantified using infrared absorption cross-section data from the following sources: HCOCl [33], chloroacetaldehyde [21], chloroacetone*, and CH_3COCl [34].

Chemicals were obtained from the following sources: isoprene, MVK, *trans*-2-butene, 1-butene, 1,3-butadiene, 3-chlorobutan-2-one (all Aldrich, 99% or better); MACR (95%, Aldrich); propene (Matheson, UHP); propane (Linde, instrument grade); ethene (Linde, CP grade); Cl_2 (Matheson, UHP); NO (Linde, UHP). Gases were used as received. Liquids (isoprene, MVK, MACR) were degassed by several freeze-pump-thaw cycles before use. These minor components of the mixture were added to the reaction chamber via expansion from smaller calibrated volumes, while N_2 (boil-off from a liquid N_2 dewar) and O_2 (UHP Grade, U.S. Welding) were added directly to the chamber.

RESULTS AND DISCUSSION

Rate Coefficients

Isoprene. The rate coefficient for reaction of Cl with isoprene (k_1) was determined relative to k_2 over a range of pressures (6.2–760 Torr), from the photolysis of mixtures of Cl_2, (1.8–3.5) × 10^{15} molecule cm^{-3}; isoprene, (2.3–8.5) × 10^{14} molecule cm^{-3}; and propane, (7–14) × 10^{14} molecule cm^{-3} in either synthetic air or N_2 diluent.

$$\text{Cl} + \text{isoprene} \rightarrow \text{products} \tag{1}$$

$$\text{Cl} + \text{propane} \rightarrow \text{products} \tag{2}$$

As previously noted by Ragains and Finlayson-Pitts [16], a slow dark reaction occurs between isoprene and Cl_2. Under the conditions employed in our experiments (i.e., relatively low [Cl_2]), and based on a rate coefficient of 1×10^{-20} cm^3 molecule^{-1} s^{-1} measured in our laboratory, the effect of this dark reaction was minimal.

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*Wallington, T. J. personal communication.

Observed isoprene concentrations were corrected by no more than 4% to account for its occurrence.

Representative relative rate data are plotted in Fig. 1, and all measurements are summarized in Table I. No evidence of any variation in the ratio k_1/k_2 with either total pressure or diluent gas identity was noted; the nonweighted mean of all data gives $k_1/k_2 = 2.99 \pm 0.27$. Using $k_2 = 1.43 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [32], a value of $k_1 = (4.3 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is obtained. In all cases in this paper, uncertainties in measured rate coefficient ratios are 1σ, precision only. Uncertainties quoted for absolute rate coefficient data include a (typically 10%) contribution for the uncertainty in the reference rate coefficient data.

Numerous measurements for k_1 at 298 K have been reported in the recent literature [16,29,31,35–38], over a range of total pressures and using a variety of relative and absolute techniques. As shown in Fig. 2, these data all fall within the range (2.6–5.6) × 10^{-10} cm^3 molecule^{-1} s^{-1}. The atmospheric pressure data of Bierbach et al. [35] and Fantechi et al. [29] lie slightly above the bulk of the measurements, though the differences are not outside the combined uncertainties of the various data sets. The lowest pressure data of Ragains and Finlayson-Pitts [16] (below 0.25 Torr) show a slight decrease in k_1 with decreasing pressure, though no fall-off is evident in the Bedjanian et al. [36] data obtained at slightly higher pressure. The available data suggest a slight increase in k_1 with pressure, from about 3.5×10^{-10} cm^3 molecule^{-1} s^{-1} near 1 Torr to 4.5×10^{-10} cm^3 molecule^{-1} s^{-1} near 1 atm, although, given the uncertainty inherent in the data, a mean value of $k_1 = (4.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (the average of all data obtained between 0.25 and 760 Torr) also provides an adequate description.

MVK. The rate coefficient for reaction of Cl with MVK, k_3, was determined relative to both propane (k_2) and propene (k_4), from the photolysis of mixtures of Cl_2 [(6–13) × 10^{15} molecule cm^{-3}], MVK [(4–7) × 10^{14} molecule cm^{-3}], and either propane [(1.0–1.4) × 10^{15} molecule cm^{-3}] or propene [(3.5–5.6) × 10^{14} molecule cm^{-3}], in 700 Torr synthetic air. The measured ratios $k_3/k_2 = 1.50 \pm 0.12$ and $k_3/k_4 = 0.81 \pm 0.07$ (see Fig. 3), combined

$$\mathrm{Cl + MVK \rightarrow products} \tag{3}$$

$$\mathrm{Cl + propene \rightarrow products} \tag{4}$$

with the literature values for $k_2 = 1.43 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $k_4 = 2.63 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [32], yield values for k_3 of (2.15 ± 0.32) and (2.27 ± 0.30) × 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. Averaging these values yields $k_3 = (2.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This value is in excellent agreement with other recently published data for this reaction obtained near atmospheric pressure, $k_3 = (2.1 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [31], $k_3 = (2.0 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [30], and

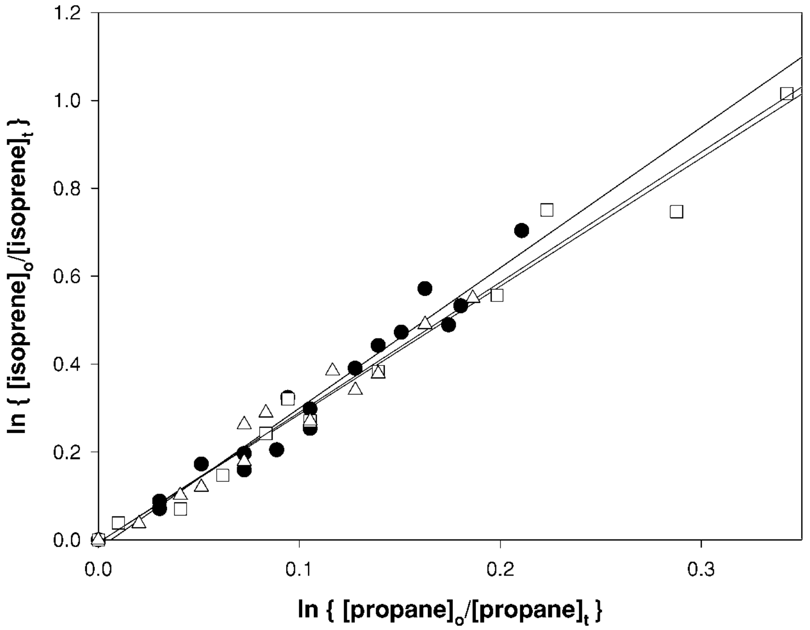


Figure 1 Decays of isoprene relative to those of propane at 296 K at different total pressures and in the presence of air (filled symbols) or N_2 (open symbols): triangles, 6.2 Torr; circles, 260 Torr; squares, 760 Torr.

Table I Summary of Rate Coefficient Data Obtained in This Study

Compound	Reference Compound	Pressure (Torr)	Measured Rate Coefficient Ratio	Absolute Rate Coefficient (10^{-10} cm^3 $molecule^{-1}$ s^{-1})
Isoprene	Propane	6.2 (N_2)	2.91	4.16
Isoprene	Propane	760 (N_2)	2.89	4.13
Isoprene	Propane	270 (air)	3.05	4.36
Isoprene	Propane	760 (air)	3.26	4.66
Isoprene	Propane	112 (air)	2.82	4.03
Isoprene	Propane	46 (air)	3.01	4.30
MVK	Propane	700 (air)	1.50	2.15
MVK	Propene	700 (air)	0.81	2.27
MACR	Propane	700 (air)	1.77	2.53
MACR	Propene	700 (air)	0.82	2.16
trans-2-Butene	Propene	700 (air)	1.54	4.0
1-Butene	Propene	700 (air)	1.12	2.9
1-Butene	Ethene	700 (air)	3.17	3.1

All data were obtained at 296 K.

$k_3 = (2.0 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} [39]. A flow-tube determination of $k_3 = (1.0 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} [40], made at a total pressure of 1.6 Torr, indicates a pressure dependence to the rate coefficient.

MACR. The rate coefficient for reaction of Cl with MACR, k_5, was determined relative to both k_2 and k_4,

$$\text{Cl} + \text{MACR} \rightarrow \text{products} \qquad (5)$$

from the photolysis of mixtures of Cl_2 [(5–16) × 10^{15} molecule cm^{-3}], MACR [(2.2–7.0) × 10^{14} molecule cm^{-3}], and either propane [(1.0–1.5) × 10^{15} molecule cm^{-3}] or propene [(2.0–3.5) × 10^{14} molecule cm^{-3}], in 700 Torr synthetic air. As shown in Fig. 4 and in Table I, rate coefficient ratios $k_5/k_2 = 1.77 \pm 0.15$ and $k_5/k_4 = 0.82 \pm 0.07$ were determined. With $k_2 = 1.43 \times 10^{-10}$ and $k_4 = 2.63 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} [32], values for k_5 of $(2.53 \pm 0.39) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and $(2.16 \pm 0.39) \times 10^{-10}$ cm^3

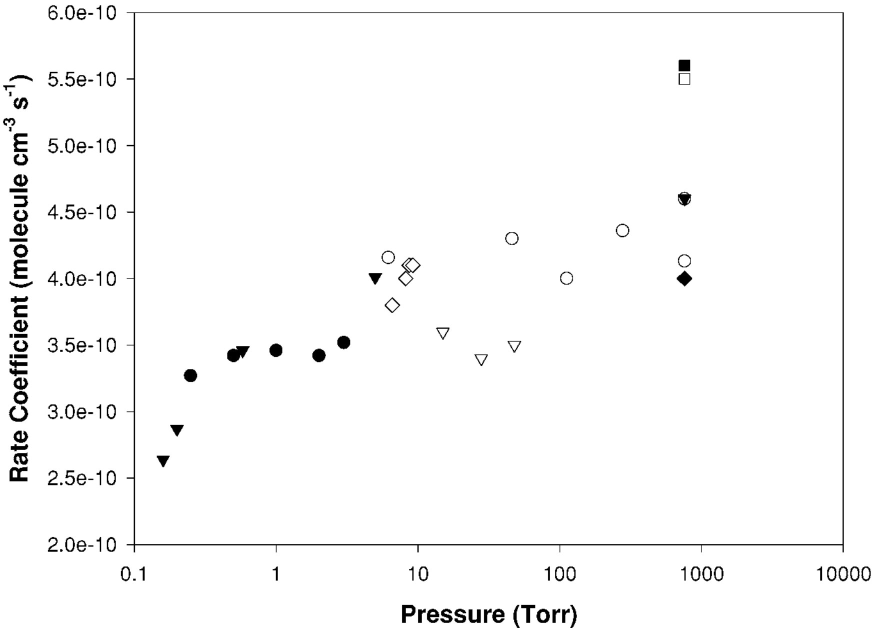


Figure 2 Summary of rate coefficient measurements for the reaction of Cl with isoprene as a function of pressure (all data at 296–300 K). Solid triangles, Ref. [16]; solid circles, Ref. [36]; open diamonds, Ref. [37]; open triangles, Ref. [38]; solid diamonds, Ref. [40]; solid square, Ref. [29]; open square, Ref. [35]; open circles, this work.

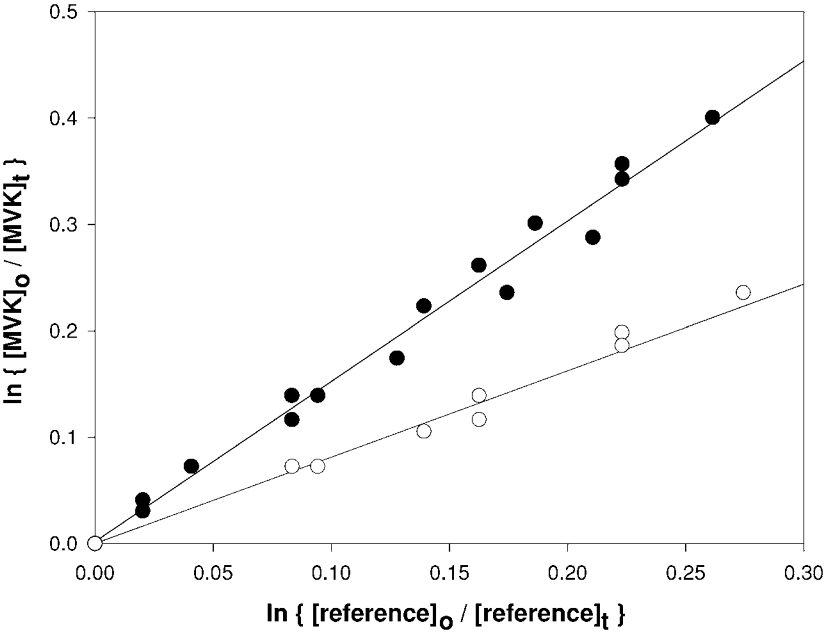


Figure 3 Decays of MVK versus those of propane (filled circles) or propene (open circles) in 700 Torr air at 296 K.

molecule^{-1} s^{-1} are derived. Averaging these data yields $k_5 = (2.35 \pm 0.40) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This value is somewhat smaller than data published by Canosa-Mas et al. [31,40] [$k_5 = (3.2 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at atmospheric pressure, and $k_5 = (3.3 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 1.6 Torr total pressure] and by Wang et al. [39] [$k_5 = (2.9 \pm 0.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}]. Although all determinations agree within the quoted uncertainties, the disagreement between our value and the atmospheric pressure value of Canosa-Mas et al. [31] is surprising, given the similarity in technique. A nonweighted average of the four separate determinations of k_5 yields an average value of $k_5 = (2.9 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

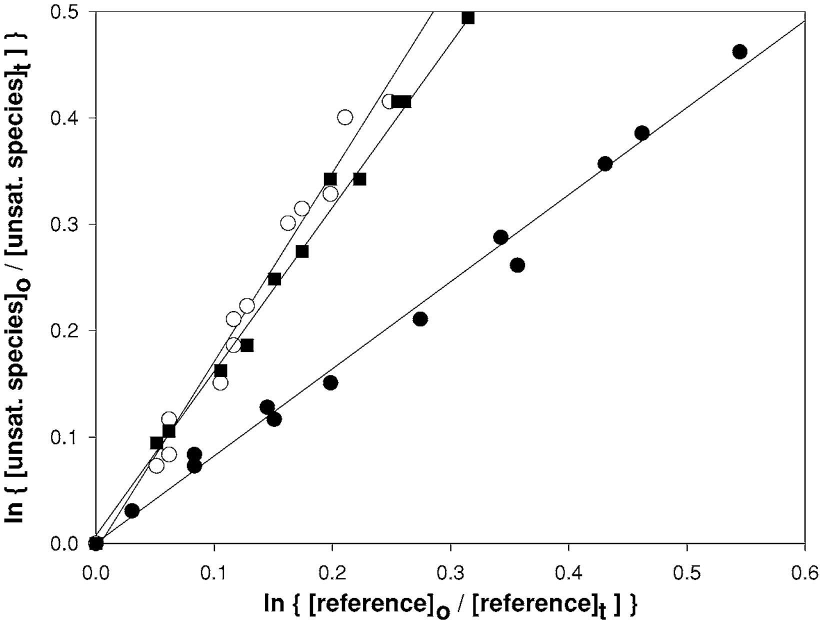


Figure 4 Decays of MACR (circles) and *trans*-2-butene (squares) versus those of propane (open symbols) or propene (filled symbols).

Trans-2-butene and 1-Butene. The rate coefficient for reaction of Cl with *trans*-2-butene, k_6, was made relative to k_4, from the photolysis of mixtures of Cl_2 [$\approx 1.2 \times 10^{16}$ molecule cm^{-3}], *trans*-2-butene [$(1.1–1.5) \times 10^{15}$ molecule cm^{-3}], and propene [$(2.8–5.6) \times 10^{14}$ molecule cm^{-3}], in 700 Torr synthetic air.

$$\text{Cl} + \textit{trans}\text{-2-butene} \rightarrow \text{products} \qquad (6)$$

The rate coefficient ratio k_6/k_4, obtained from the data shown in Fig. 4, is found to be 1.54 ± 0.12, which yields $k_6 = (4.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

For studies of the rate coefficient for reaction of Cl with 1-butene, k_7, both propene (k_4) and ethene (k_8) were used as the reference compounds:

$$\text{Cl} + \text{1-butene} \rightarrow \text{products} \qquad (7)$$

$$\text{Cl} + C_2H_4 \rightarrow \text{products} \qquad (8)$$

Experiments involved the photolysis of mixtures of Cl_2 [$(3–5) \times 10^{15}$ molecule cm^{-3}], 1-butene [$(7–12) \times 10^{14}$ molecule cm^{-3}], and either propene or ethene [$(2.8–4.2) \times 10^{14}$ molecule cm^{-3}], in 700 Torr synthetic air. Relative rate data are shown in Fig. 5, from which the following rate coefficient ratios are obtained: $k_7/k_4 = 1.12 \pm 0.06$ and $k_7/k_8 = 3.17 \pm 0.20$. Using $k_4 = 2.63 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $k_8 = 0.99 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 700 Torr total pressure yields $k_7 = (2.9 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $(3.1 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, from which an average value of $k_7 = (3.0 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} can be reported.

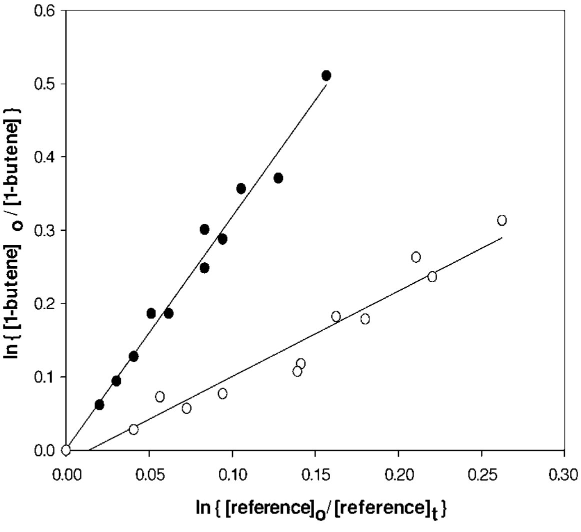


Figure 5 Decays of 1-butene versus those of ethene (filled circles) and propene (open circles) in 700 Torr air at 296 K.

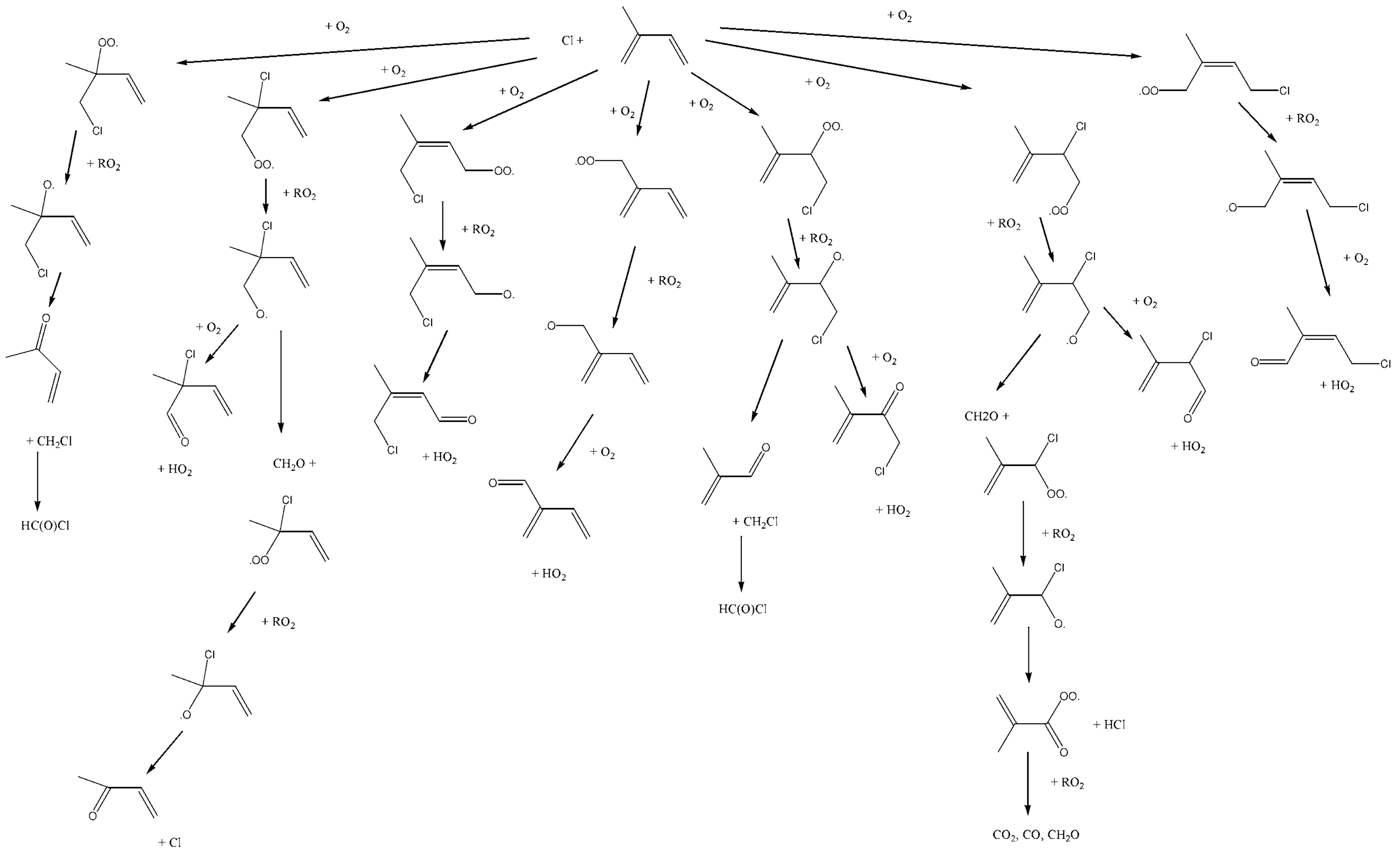
There are now a few measurements [41–44] available in the literature with which to compare our k_6 and k_7 data. For 1-butene, our value of $(3.0 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is in reasonable agreement with two very recent reports [$(3.5 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [42] and $(3.4 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [41]], though somewhat higher than an earlier value reported by Stutz et al. [43], $(2.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Our value for k_6, $(4.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, is slightly higher than two recent reports, $(3.3 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [41] and $(3.4 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [44], though all values agree within the mutual uncertainties. Our values seem reasonable on the basis of the structures of the compounds involved. The finding of very similar values for k_4 and k_7 is consistent with near identical reactivity of the terminal alkene moieties in propene and 1-butene, while the higher degree of substitution about the double bond in *trans*-2-butene leads to a larger value for k_6.

Product Distributions

Isoprene. Major reaction pathways expected following addition of Cl to isoprene in NO_x-free air are shown in Scheme 1 [16,17,29,37,45–47]. Reactions of peroxy radicals with HO_2 (to form a variety of organic hydroperoxides) are not shown, nor are the products likely to arise from the molecular channels of the various RO_2–RO_2 reactions. Major products anticipated from the chemistry include [16,17,29,37,45] CMBO; four isomers of chloro-methyl-butenal (CMBA); MVK and MACR with HCOCl as their coproduct; formaldehyde with various coproducts including MVK and chloromethyl vinyl ketone (ClMVK); and 2-methylene-3-butenal and HCl, which arise via abstraction from the methyl group.

Previous studies, based on observed HCl yields, have shown that abstraction accounts for ≈15% of the reaction [16,29,37]. Other previously observed products include HCOCl (8 ± 5% [16], 4.7 ± 3.3% [29]), MVK (9 ± 5%) [17], as well as CMBO and three isomers of CMBA, which were identified by GC/MS [17]. Although not strictly quantitative, the GC/MS studies pointed to the likelihood of substantial yields of the CMBO/CMBA species.

Our studies involved the photolysis of mixtures of Cl_2, $(1.0–3.7) \times 10^{15}$ molecule cm^{-3}, and isoprene, $(0.27–1.89) \times 10^{15}$ molecule cm^{-3}, in 700–740 Torr synthetic air. The only products observable via IR spectroscopy were formaldehyde (9.5 ± 1.0%) and HCOCl (5.1 ± 0.7%), as shown in Fig. 6. No MVK (<4%) or MACR (<4%) was observed. While our HCOCl yield agrees favorably with previous studies [16,29],



Scheme 1 Major reactions occurring in the reaction of Cl-atoms with isoprene in NO_x-free air.

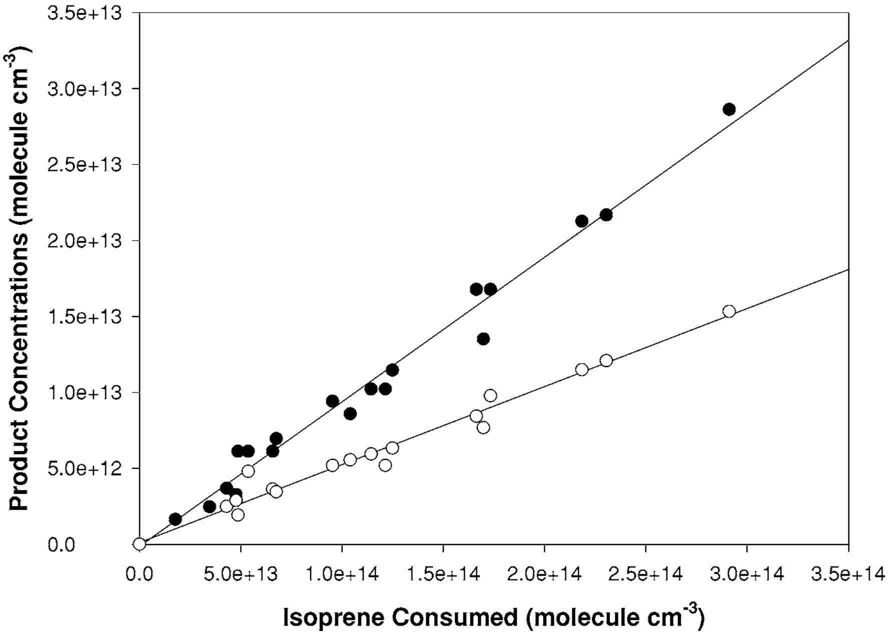


Figure 6 Product data obtained in the reaction of Cl with isoprene in 700 Torr air at 296 K. Filled circles, CH_2O; open circles, HCOCl.

our upper limit for MVK lies on the low end of the Nordmeyer et al. [17] value. Also, Fantechi et al. [29] postulated that MACR was formed in their experiments, but subsequently destroyed. Our experiments, conducted under conditions of low isoprene conversion ($<10\%$ in most cases) and hence negligible product consumption, clearly exclude any appreciable MACR formation in this system. The observation of formaldehyde (not previously reported, but apparent in the spectra of Fantechi et al. [29]), coupled with the very low yield of MVK, implies that either ClMVK is produced in the chemistry (see Scheme 1) or that the $CH_2{=}C(CH_3)CHClCH_2O\cdot$ radical is formed and subsequently decomposes to generate formaldehyde and other products. The most likely chemistry occurring subsequent to this decomposition is as follows:

$$CH_2{=}C(CH_3)CHClCH_2O\cdot\ (+O_2)$$
$$\rightarrow CH_2{=}C(CH_3)CHClO_2\cdot + CH_2O$$
$$CH_2{=}C(CH_3)CHClO_2\cdot + RO_2$$
$$\rightarrow CH_2{=}C(CH_3)CHClO\cdot + RO + O_2$$
$$CH_2{=}C(CH_3)CHClO\cdot\ (+O_2)$$
$$\rightarrow CH_2{=}C(CH_3)C(O)O_2\cdot + HCl$$
$$CH_2{=}C(CH_3)C(O)O_2\cdot + RO_2$$
$$\rightarrow CH_2{=}C(CH_3) + CO_2 + RO + O_2$$
$$CH_2{=}C(CH_3) + O_2 \rightarrow\rightarrow CH_2O, CO, CO_2$$

In conjunction with the FTIR product measurements, studies were also conducted using the GC/MS instrument. Though not quantitative at this time, these measurements revealed the presence of CMBO and three isomers of CMBA (identified via comparison with [17]), as well as MVK and MACR. Relative intensities seen in the chromatograms were similar to those observed by Nordmeyer et al. [17].

Examination of Scheme 1 reveals that the expected products from the reaction of Cl with isoprene can be categorized as either (a) CMBO and isomers of CMBA, obtained from reaction of O_2 with the various alkoxy radicals, or (b) four-carbon oxygenates and simple coproducts, such as HCOCl and CH_2O, which arise via alkoxy radical decomposition processes. The low yields of the readily detectible HC(O)Cl and CH_2O, and of some of the key four-carbon species expected as coproducts (MVK and MACR), point to the likelihood of high yields of CMBO and CMBA, as was concluded previously by Nordmeyer et al. [17]. These general conclusions are also supported by recent theoretical studies [45–47] which show that decomposition reactions of the six possible alkoxy radicals are relatively slow, and thus that high yields of CMBO (25–30%) and CMBA (45–50% total yield of the four possible isomers) should be obtained. Note, however, that one quantitative discrepancy exists between the theoretical predictions [45] and our observations; theoretically predicted yields of MVK and HCOCl, via decomposition of the $ClCH_2C(O\cdot)(CH_3)CH{=}CH_2$ radical, are significantly higher (≈15%) than our observations (≈5% or less). Experiments to quantify CMBO and CMBA products of the Cl-initiated oxidation of isoprene, which would provide context for atmospheric measurements of these species and would provide further data for comparison with theory [45], are planned in our laboratory.

MVK. Products of the Cl-initiated oxidation of MVK were determined using FTIR spectroscopy via the photolysis of Cl_2, (3.3–5.0) × 10^{15} molecule cm^{-3}, and MVK, (4.4–6.6) × 10^{14} molecule cm^{-3}, in 720 Torr synthetic air. Products observed (see Fig. 7) included chloroacetaldehyde ($ClCH_2CHO$, yield 75 ± 8%), CO_2 (58 ± 5% yield), CH_2O (47 ± 7% yield), as well as CH_3OH (≈8% yield), HCOCl (7 ± 1% yield), and peracetic acid (≈6% yield). The observed products account for 70 ± 9% of the reacted MVK; organic hydroperoxides, arising from reaction of peroxy radicals with HO_2, likely account for a large fraction of the remaining carbon.

The large yield of chloroacetaldehyde implies that the majority (at least 75%) of the Cl-atom addition to MVK occurs at the terminal carbon, and that the decomposition of the resulting oxy radical is via CH_3CO elimination (see Scheme 2). The acetylperoxy radical produced via this route will generate CO_2, CH_2O, peracetic acid, acetic acid, and CH_3OH. The combined yields of these species implies an acetylperoxy radical yield of 64 ± 10%, similar to that of the chloroacetaldehyde coproduct.

Internal addition of Cl to MVK results in the production of the $CH_3C(O)CH(Cl)CH_2O$ radical, which may undergo decomposition, isomerization, or reaction with O_2 (see Scheme 2 [29]). On the basis of the chemistry of the 1-butoxy radical [43] and data on 1-butene oxidation given below, we conclude that isomerization [$k \approx (1–2) \times 10^5\ s^{-1}$ [48]] should be the dominant fate of this radical, resulting in the production of CH_2O, CO_2, and HCOCl (see Scheme 2 [29]), though decomposition will likely lead to a similar end-product distribution. The very low observed HCOCl yield is thus consistent with the occurrence of only a small amount of internal addition.

The only previous studies of the Cl-initiated oxidation of MVK were brief investigations by Fantechi et al. [29] and Canosa-Mas et al. [40]. Products identified in [29] were chloroacetaldehyde, HCOCl, methylglyoxal, CH_2O, HCl, CO, and CO_2; no yields are reported. Methylglyoxal was not observed in our study. Elimination of CH_2Cl from the $CH_3C(=O)CH(O\cdot)CH_2Cl$ radical, as proposed by Fantechi et al. [29] to account for the methylglyoxal formation, will not compete with the more favorable $CH_3C(O)$ elimination, and thus the production of methylglyoxal in this system seems unlikely. The CO observed by Fantechi et al. [29], but not seen in our work, may result from oxidation of the primary CH_2O product. Canosa-Mas et al. [40] report the observation of chloroacetaldehyde and CH_2O (in agreement with our work, though no yield data were given), and CO (yield ≈0.05). They also conclude that external addition of Cl to the MVK double bond leads to

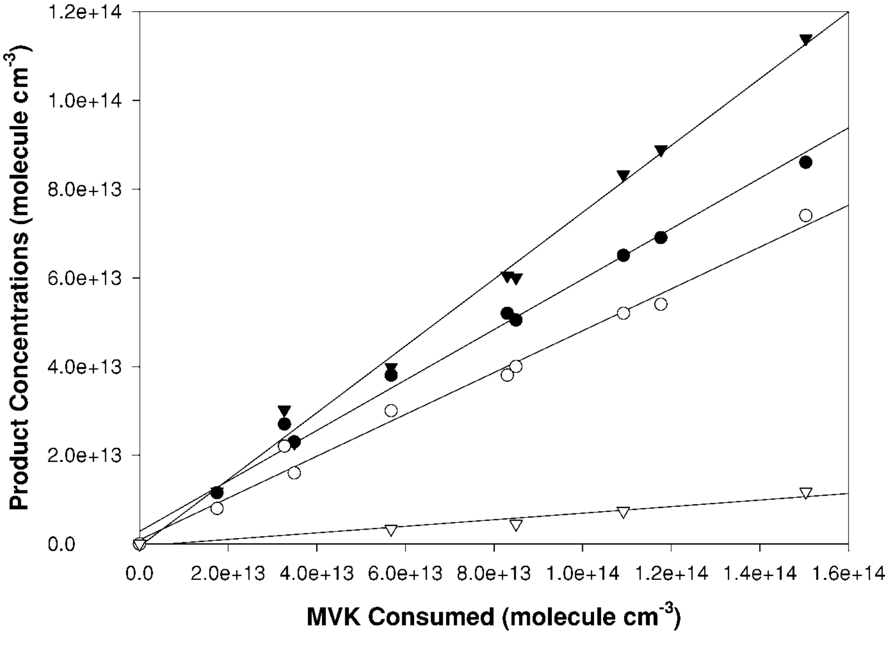
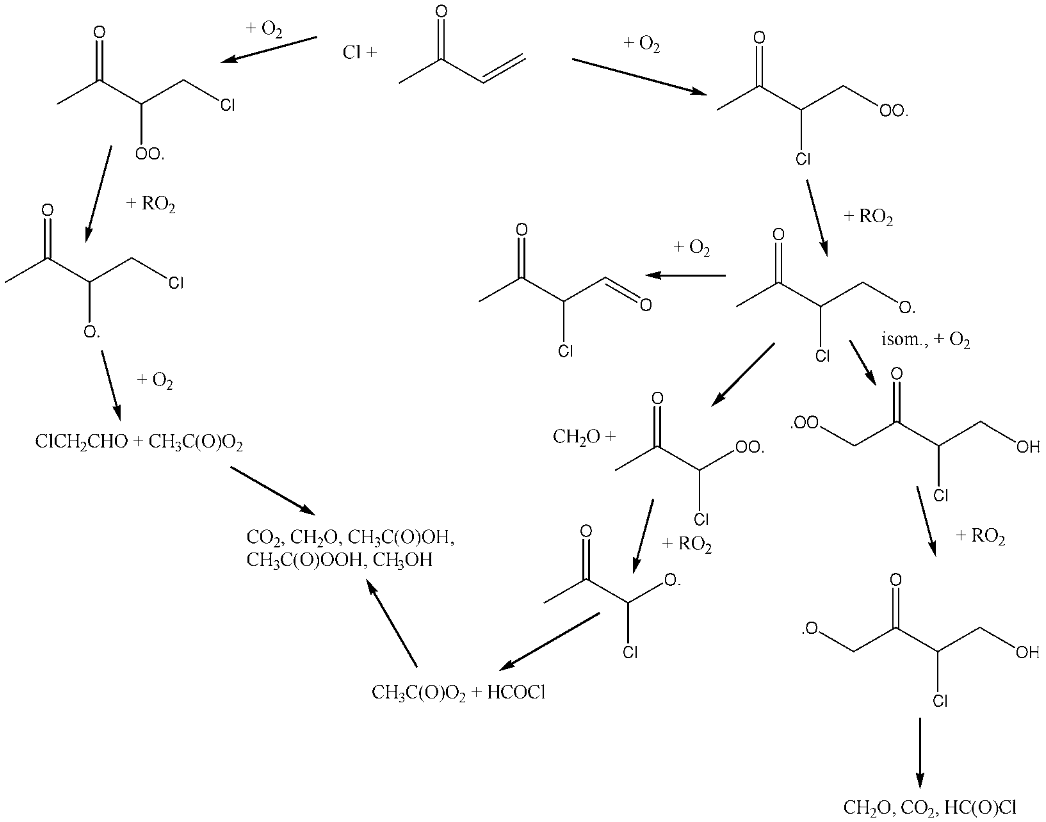


Figure 7 Product yield data obtained in the reaction of Cl with MVK in 700 Torr air at 296 K. Filled triangles, chloroacetaldehyde; filled circles, CO_2; open circles, CH_2O; open triangles, HCOCl.



Scheme 2 Major reactions occurring in the reaction of Cl-atoms with MVK in NO_x-free air.

the major observed products (chloroacetaldehyde and CH_2O).

MACR. FTIR spectroscopy was used to determine the end products of the Cl-initiated oxidation of MACR, via the photolysis of mixtures of MACR, (2.1–7) × 10^{14} molecule cm^{-3}, and Cl_2, (2.1–5.6) × 10^{15} molecule cm^{-3}, in 710 Torr synthetic air. Products observed (see Fig. 8) included CO (52 ± 4% yield), chloroacetone (42 ± 5% yield), CO_2 (23 ± 2% yield), CH_2O (18 ± 2% yield), and HCOCl (≈5% yield), which account for 55 ± 7% of the reacted carbon. As with any study conducted in a NO_x-free environment, organic hydroperoxides likely contribute much of the remaining carbon.

Three major reaction pathways are available for the Cl/MACR reaction, addition to either end of the double bond, and abstraction of the aldehydic hydrogen (see Scheme 3). Addition to the terminal carbon should yield chloroacetone and CO in equal yields, thus indicating that at least 42% of the reaction proceeds via this pathway (undetected hydroperoxide, $ClCH_2C(CH_3)(OOH)CHO$, could also result from terminal addition). Abstraction, as is the case in the reaction of OH with MACR [49,50], should lead to the formation of ≈2 CH_2O, 0.4 CO, and 1.6 CO_2 and this appears to account for about 11% of the reaction (based on the observed yield of CH_2O and the yield of CO in excess of that of chloroacetone). Acetyl chloride, CH_3COCl, a likely product of internal addition, was not observed (yield <2%). The other possible end product of internal addition is $HC(O)CCl(CH_3)CHO$. Although no strong, unidentified carbonyl absorption features were present in the product spectra, this species could have a fairly low vapor pressure and thus be rapidly removed from the gas phase. However, on the basis of the behavior of other β-chlorinated alkoxy radicals (see discussion below), it is likely that decomposition will be a major fate of the $HC(O)—CCl(CH_3)—CH_2O$ radical, and thus large yields of $HC(O)—CCl(CH_3)CHO$ are not likely. Nonetheless, with the information available at present, it is not possible to exclude a significant occurrence of Cl-atom addition to the internal carbon in MACR.

A brief investigation of the mechanism of the reaction of Cl with MACR was carried out by Fantechi et al. [29]. They report the formation of methylglyoxal, HCOCl, formic acid, HCl, CO, CO_2, and possibly CH_2O, though no quantitative information is given. From an examination of their Fig. 4, it

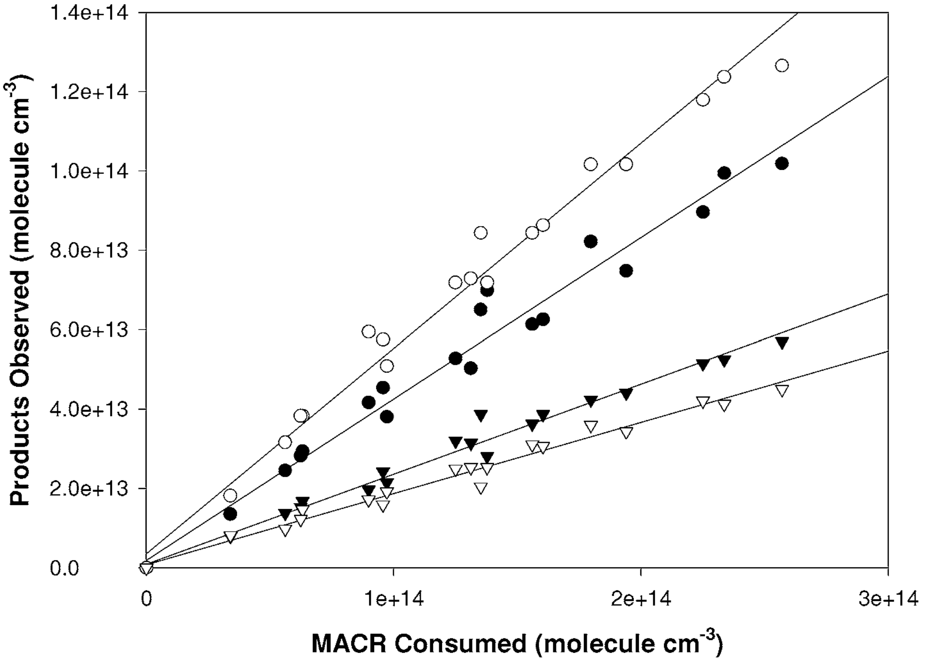
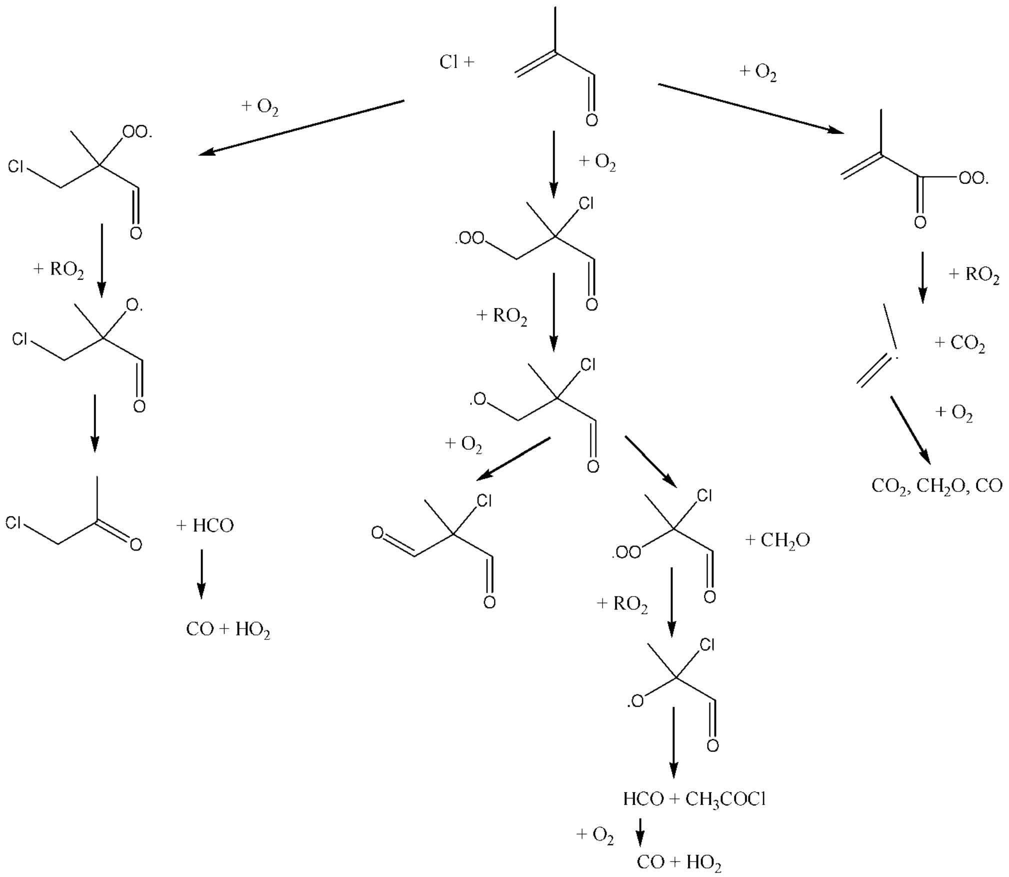


Figure 8 Product data obtained in the reaction of Cl with MACR in 700 Torr air at 296 K. Open circles, CO; filled circles, chloroacetone; filled triangles, CO_2; open triangles, CH_2O.



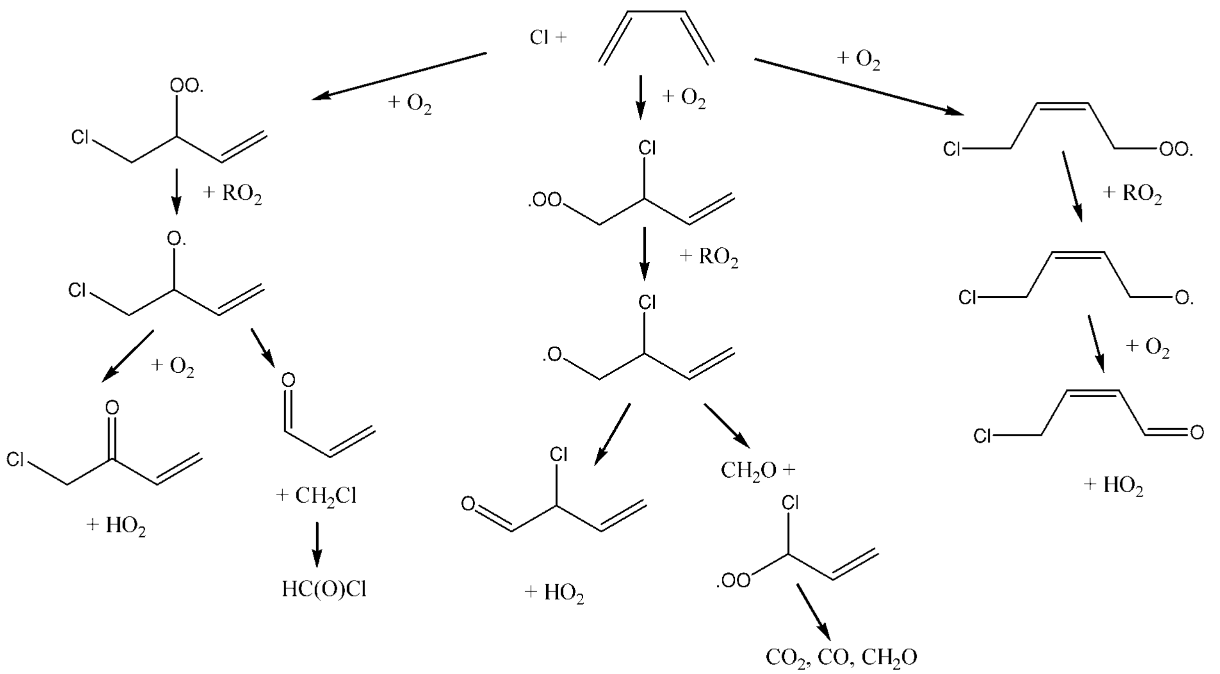
Scheme 3 Major reactions occurring in the reaction of Cl-atoms with MACR in NO_x-free air.

appears that chloroacetone (1743, 1365, 1225 cm^{-1}) has been misidentified as methylglyoxal (1731, 1366, 1229 cm^{-1}). Additional chloroacetone absorption features at 1428, 810, and 725 cm^{-1} are also evident in their product spectrum, as are absorptions due to CH_2O.

More recently, Canosa-Mas et al. [40] identified chloroacetone ($41 \pm 4\%$ molar yield), CH_2O ($23 \pm 2\%$), CO ($75 \pm 6\%$), and HCl ($18 \pm 2\%$) as products of the Cl-initiated oxidation of MACR. Although their yields of chloroacetone and CH_2O are similar to ours, their CO yield is significantly higher. Our conclusions regarding the mechanism are similar to those drawn by Canosa-Mas et al. [40]. Their HCl yield indicates an 18% channel to abstraction, similar to our less direct conclusion derived on the basis of the yields of CO, CO_2, and CH_2O.

1,3-Butadiene. Major reactions expected to occur following the addition of Cl to 1,3-butadiene are shown in Scheme 4 [18,19]. Three alkoxy radicals are likely to be produced: $ClCH_2CH(O\cdot)CH{=}CH_2$ from external addition, $ClCH_2CH{=}CHCH_2O\cdot$ from external addition followed by allylization; and $CH_2{=}CH{-}CH(Cl)CH_2O\cdot$ from internal Cl addition. Likely end products include ClMVK, from reaction of $ClCH_2CH(O\cdot)CH{=}CH_2$ with O_2; HC(O)Cl and acrolein, following decomposition of $ClCH_2CH(O\cdot)CH{=}CH_2$; CCA, from reaction of $ClCH_2CH{=}CHCH_2O\cdot$ with O_2; 2-chloro-3-butenal, from reaction of $CH_2{=}CH{-}CH(Cl)CH_2O\cdot$ with O_2; and CH_2O, CO, and CO_2, following decomposition of $CH_2{=}CH{-}CH(Cl)CH_2O\cdot$. Studies performed by Wang and Finlayson-Pitts [18,19], using a combination of FTIR, GC/MS, and atmospheric pressure ionization–MS, have identified CCA (29% yield), ClMVK (19%), acrolein (6%), CH_2O, and possibly 2-chloro-3-butenal as products of the Cl-initiated oxidation of 1,3-butadiene in NO_x-free air. A number of chlorinated hydroxybutenes, the result of the occurrence of the "molecular channels" of various RO_2/RO_2 reactions, were also identified.

In our studies, both FTIR and GC analyses were used to investigate the products of the the reaction of Cl with 1,3-butadiene. Experiments consisted of the photolysis of mixtures of Cl_2 [$(1.1–3.1) \times 10^{15}$ molecule cm^{-3}] and 1,3-butadiene [$\approx 2.8 \times 10^{15}$ molecule cm^{-3}]. Although yields were quite small (see Fig. 9), CH_2O (with a yield of $7 \pm 1\%$), HCOCl ($3 \pm 1\%$), and acrolein ($\approx 3\%$, not shown) were clearly observed in the infrared. Numerous other product absorption features were observed, including bands centered near 978, 1067, 1107, 1275, 1340, 1414, 1721, 2736, 2815, and 2970 cm^{-1}. Although these absorption features could not be identified, they appear very similar in position and intensity to the peaks shown in Fig. 2 of Wang and Finlayson-Pitts [19], many of which were identified as belonging to CCA and ClMVK [19]. However, without authentic reference spectra for these species, we are not able to quantify their presence in our product spectra.



Scheme 4 Major reactions occurring in the reaction of Cl-atoms with 1,3-butadiene in NO_x-free air.

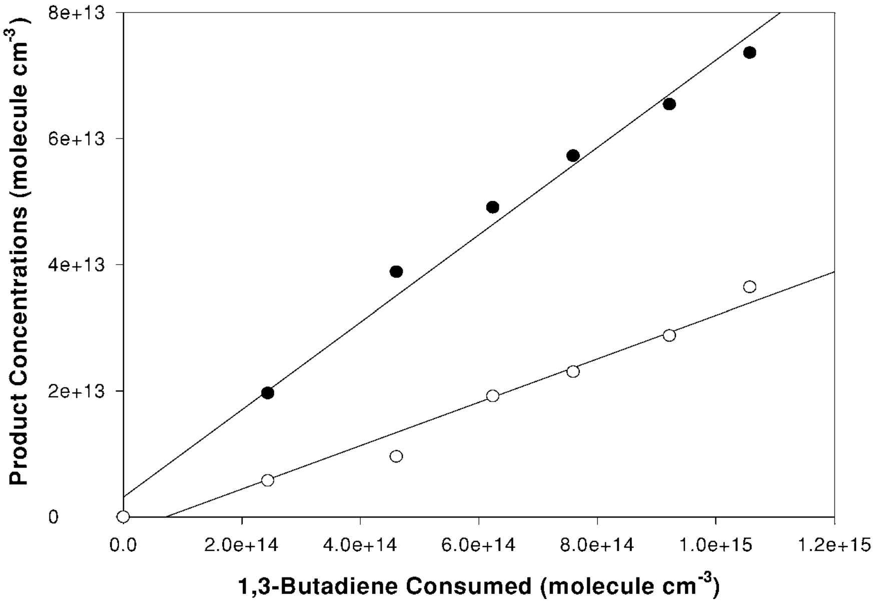


Figure 9 Product data obtained in the reaction of Cl with 1,3-butadiene in 700 Torr air at 296 K. Filled circles, CH_2O; open circles, HCOCl.

The similar yields of HCOCl and acrolein observed in our study are consistent with their simultaneous formation from the decomposition of the $ClCH_2{-}CH(O\cdot)CH{=}CH_2$ radical, as described above and as is shown in Scheme 4:

$$ClCH_2{-}CH(O\cdot)CH{=}CH_2$$
$$\rightarrow ClCH_2 + CH_2{=}CH{-}CHO$$
$$ClCH_2 + O_2 \rightarrow\rightarrow HCOCl$$

The observed CH_2O may result from the decomposition of the $CH_2{=}CH{-}CHCl{-}CH_2O$ radical:

$$CH_2{=}CH{-}CH(Cl)CH_2O$$
$$\rightarrow CH_2{=}CH{-}CHCl + CH_2O$$

Subsequent chemistry of the $CH_2{=}CHCHCl$ likely generates the vinyl radical, a further source of CH_2O.

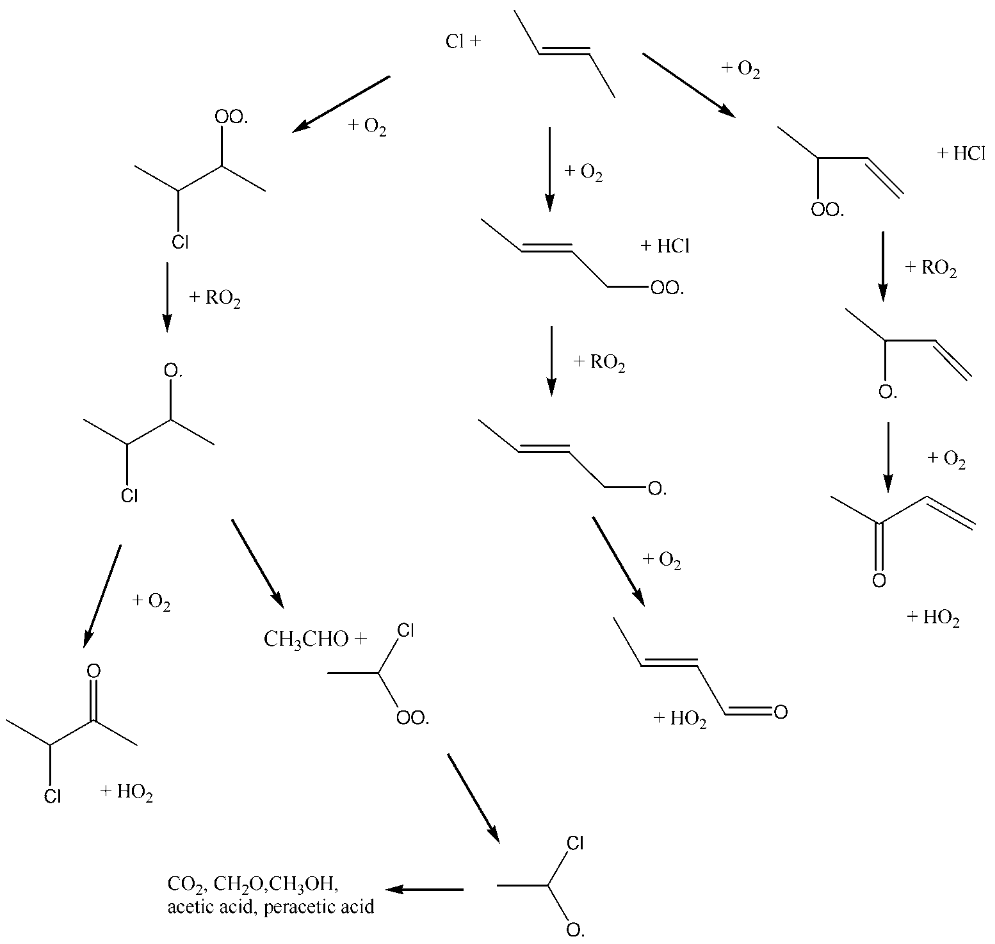
$$CH_2{=}CH{-}CHCl + O_2 \rightarrow CH_2{=}CH{-}CHClO_2$$
$$CH_2{=}CH{-}CHClO_2 + RO_2$$
$$\rightarrow CH_2{=}CH{-}CHClO + RO + O_2$$
$$CH_2{=}CH{-}CHClO$$
$$\rightarrow HC(O)Cl + CH_2{=}CH \rightarrow\rightarrow CO, CO_2, CH_2O$$

Thus, the overall occurrence of internal addition followed by $CH_2{=}CHCH(Cl)CH_2O$ decomposition only need be about 4% to account for the observed CH_2O.

GC/MS analysis of the Cl-initiated oxidation of 1,3-butadiene indicated the presence (in decreasing order of abundance) of CCA, ClMVK, and acrolein though, as was the case with isoprene, these data were not quantitative.

Trans-2-butene and 1-Butene. Product studies for the reaction of Cl-atom with *trans*-2-butene were carried out at 1 atm pressure, over a range of O_2 partial pressures, from the photolysis of mixtures of Cl_2 [(2.0–8.4) × 10^{15} molecule cm^{-3}] and *trans*-2-butene [(0.6–1.2) × 10^{15} molecule cm^{-3}] in O_2 (25–600 Torr) and N_2 (100–700 Torr). Products observed were 3-chloro-2-butanone, CH_3CHO, CH_2O, CH_3COCl, CH_3OH, and CO_2, which are all expected following addition of Cl to *trans*-2-butene (see Scheme 5). Abstraction has been shown to be a minor, but measurable, channel in the reaction of Cl with isoprene, ethene, and propene [16,29,37,51,52]. In the case of *trans*-2-butene, abstraction from the CH_3 group would generate either crotonaldehyde or MVK, neither of which are observed in our experiments (MVK yield <4%; crotonaldehyde yield <5%). The finding of less than 10% abstraction in the Cl/*trans*-2-butene reaction is in disagreement with a recently published structure–reactivity scheme for Cl/alkene reactions [41], which predicts ≈15–20% abstraction for this reaction.

As shown in Fig. 10, reaction product yields were found to be O_2-dependent, with the 3-chloro-2-butanone yield increasing with increasing O_2 partial pressure, and the yields of the other product



Scheme 5 Major reactions occurring in the reaction of Cl-atoms with *trans*-2-butene in NO_x-free air.

species decreasing. These observations can be rationalized (see Scheme 5) in terms of competing fates of the CH_3CHCl—$CH(O)CH_3$ radical, decomposition (to yield CH_3CHO, CH_2O, CH_3COCl, CH_3OH, and CO_2) and reaction with O_2 (to yield 3-chloro-2-butanone). Note that the O_2-dependence of the CH_3COCl yield is weaker than for the other species; its formation is simultaneously anticorrelated with $[O_2]$ [through the competition between reactions (9) and (10)]

$$CH_3CH(Cl){-}CH(O){-}CH_3 \rightarrow CH_3CHO + CH_3CHCl \qquad (9)$$

$$CH_3CH(Cl){-}CH(O){-}CH_3 + O_2 \rightarrow CH_3{-}CH(Cl)C({=}O)CH_3 + HO_2 \qquad (10)$$

and positively correlated with $[O_2]$, through the chemistry of the CH_3CHClO radical [53] (see Scheme 5).

For quantitative analysis of the competition between decomposition (9) and reaction with O_2 (10), yields of 3-chloro-2-butanone and CH_3CHO were considered, since these are direct products of the $CH_3CH(Cl)$—$CH(O\cdot)$—CH_3 chemistry. The O_2-dependence of the yields of these species can be expressed as follows:

$$Y\{CH_3CH(Cl)C({=}O)CH_3\} = Y(RO\cdot) \times [k_{10}[O_2]/k_9/\{k_{10}[O_2]/k_9 + 1\}] + A \qquad (I)$$

$$Y\{CH_3CHO\} = Y(RO\cdot)/\{k_{10}[O_2]/k_9 + 1\} + A' \qquad (II)$$

where $Y(RO\cdot)$ is the yield of the $CH_3CH(Cl)$—$CH(O\cdot)$—CH_3 radical. The constants A and A' account for the formation of these species from other O_2-independent sources (for example, $CH_3CH(Cl)$-$C({=}O)CH_3$ may result from the molecular channels of the reactions of $CH_3CH(Cl)$—$CH(OO\cdot)$—CH_3 with other peroxy radicals present in the system). A simultaneous four-parameter $[Y(RO\cdot), k_9/k_{10}, A, A']$ fit (shown

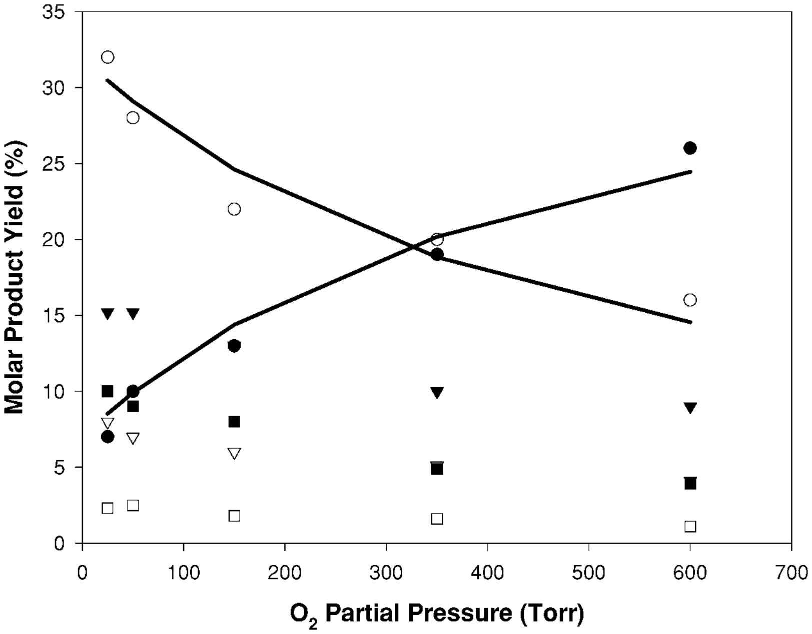


Figure 10 Product yield data in the reaction of Cl with *trans*-2-butene, as a function of O_2 partial pressure at 296 K. Open circles, acetaldehyde; open triangles, CO_2; filled circles, chlorobutanone; filled squares, CH_2O; filled triangles, CH_3COCl; open squares, CH_3OH. Solid lines denote results of fits of Eqs. (I) and (II) to the yields of 2-chloro-butanone, and acetaldehyde; see text for details.

as the solid curves in Fig. 10) of the data yields the following results: $Y(\text{RO}\cdot) = 0.32 \pm 0.04$, $A = 0.07 \pm 0.02$, $A' = 0.00 \pm 0.02$, and $k_9/k_{10} = (1.6 \pm 0.4) \times 10^{19}$ molecule cm^{-3}. With some reasonable assumptions, the measured k_9/k_{10} ratio can be used to obtain approximate kinetic and thermodynamic parameters for the decomposition reaction (9). Reactions of alkoxy radicals with O_2 are typically of order 1×10^{-14} cm^3 molecule^{-1} s^{-1} [48]. With this assumption, and an assumed A-factor for k_9 at atmospheric pressure of $2 \times 10^{13}\,\text{s}^{-1}$ [54], an activation barrier for k_7 of 11.5 ± 1.5 kcal mol^{-1} can be estimated, thus yielding $k_9 \approx 2 \times 10^{13} \exp(-5750/T)\,\text{s}^{-1}$. The chemistry of the 3-chloro-2-butoxy radical is thus very similar to the structurally similar 3-bromo-2-butoxy radical [55], which was shown to also undergo both reaction with O_2 and unimolecular decomposition at room temperature.

The chemistry occurring following reaction of Cl with 1-butene was also examined via FTIR spectroscopy, from the photolysis of mixtures of Cl_2 [(3–4) $\times 10^{15}$ molecule cm^{-3}] and 1-butene [$\approx 7 \times 10^{14}$ molecule cm^{-3}] at 700 Torr total pressure (O_2 partial pressure 25–600 Torr; balance N_2). In all experiments, $ClCH_2CHO$ (chloroacetaldehyde), HCOCl, CH_2O, and CO_2 were observed. Also present in the product spectra was a carbonyl absorption band centered near 1744 cm^{-1}, that could not be assigned to any specific species. As shown in Fig. 11, the yields of all four identifiable products (chloroacetaldehyde, CH_2O, CO_2, and HCOCl) were observed to decrease with increasing O_2 partial pressure. This observation points to the occurrence of competing pathways in the chemistry of the two β-chlorinated alkoxy radicals derived from Cl addition to 1-butene, $CH_3CH_2CH(O)CH_2Cl$, and $CH_3CH_2CH(Cl)CH_2O$.

As shown in Scheme 6, the $CH_3CH_2CH(O)CH_2Cl$ radical (derived from external Cl addition) has three possible reaction pathways, reaction with O_2 to generate $CH_3CH_2C({=}O)CH_2Cl$, decomposition to generate $ClCH_2CHO$, or decomposition to generate HCOCl. Furthermore, there are no other likely pathways to the production of either $ClCH_2CHO$ or HCOCl, thus indicating that the O_2-dependence of the product yield data for these species can be used directly in the examination of the chemistry of the $CH_3CH_2CH(O)CH_2Cl$ radical. The O_2-dependence of the HCOCl and $ClCH_2CHO$ yields can thus be expressed as follows:

$$Y(\text{HCOCl}) = Y(\text{RO}\cdot) \times \{k_{d1}/(k_{d1} + k_{d2} + k_{O2})\} \qquad \text{(III)}$$

$$Y(\text{ClCH}_2\text{CHO}) = Y(\text{RO}\cdot) \times \{k_{d2}/(k_{d1} + k_{d2} + k_{O2})\} \qquad \text{(IV)}$$

where $Y(\text{RO}\cdot)$ is the formation yield of the $CH_3CH_2CH(O\cdot)CH_2Cl$ radical, k_{O2} is the rate

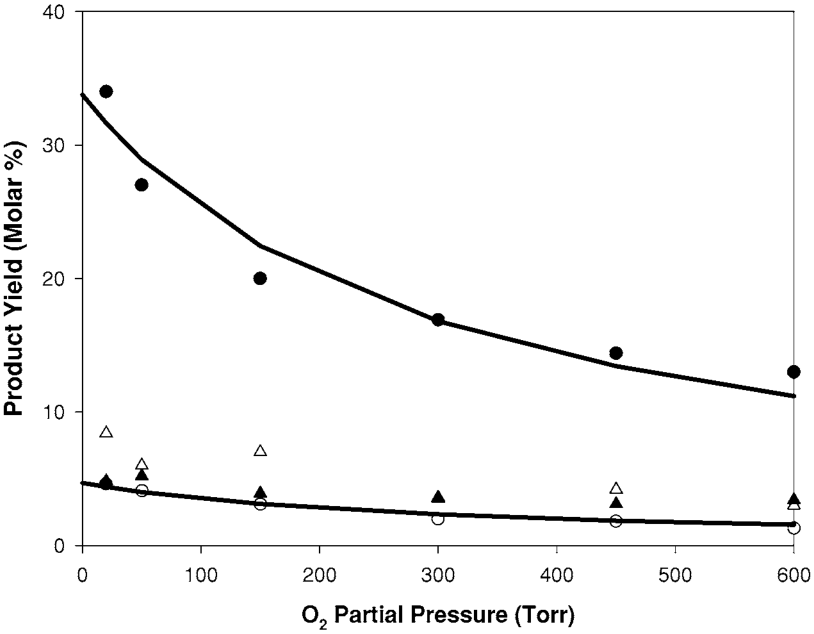
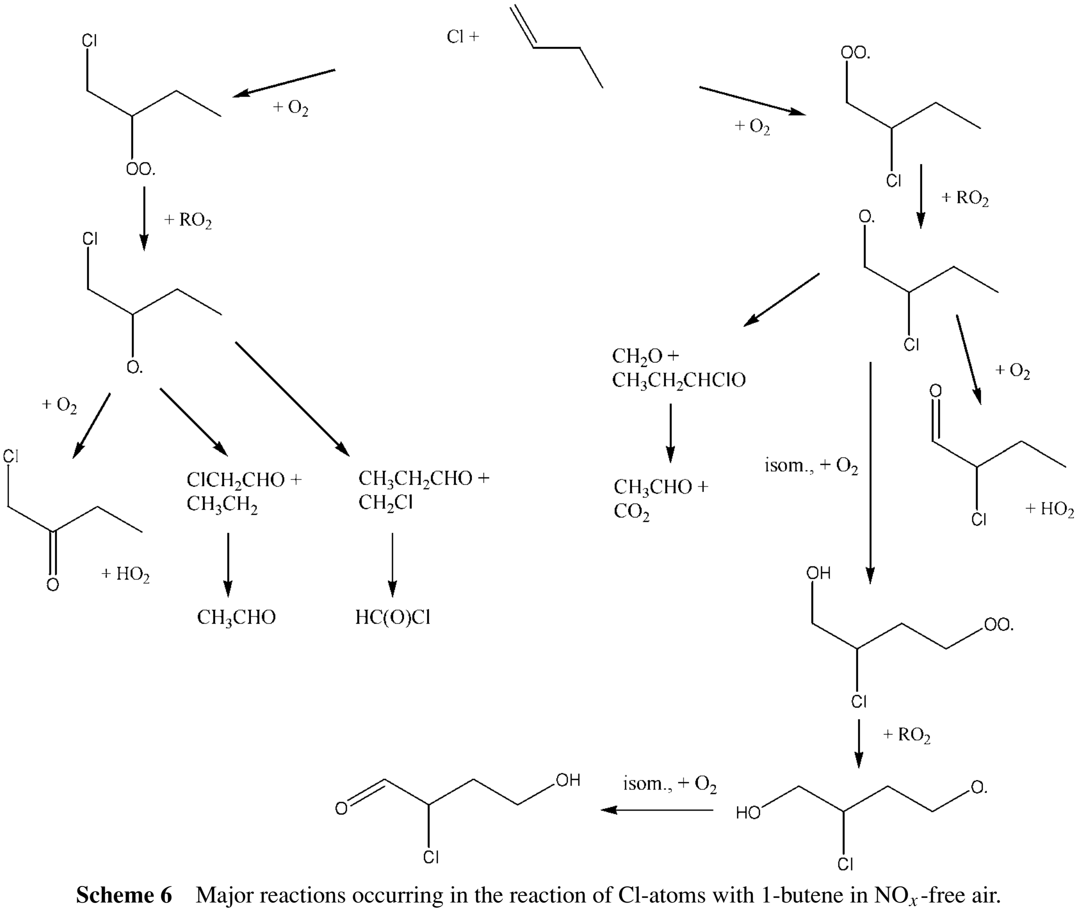


Figure 11 Product yield data in the reaction of Cl with 1-butene, as a function of O_2 partial pressure at 296 K. Filled circles, chloroacetaldehyde; open circles, HC(O)Cl; open triangles, CH_2O; filled triangles, CO_2.



Scheme 6 Major reactions occurring in the reaction of Cl-atoms with 1-butene in NO_x-free air.

coefficient for its reaction with O_2, and k_{d1} and k_{d2} are the rate coefficients for its unimolecular decomposition to HCOCl and $ClCH_2CHO$, respectively. A least-squares fit of the HCOCl and $ClCH_2CHO$ yield data versus O_2, with k_{O2} fixed at 10^{-14} cm^3 molecule^{-1} s^{-1} [43] and with $Y(RO\cdot)$, k_{d1}, and k_{d2} as fit parameters, yielded the following results (shown as solid lines in Fig. 11): $Y(RO\cdot) = 0.38$, $k_{d1} = 1.1 \times 10^4\ s^{-1}$, and $k_{d2} = 8.5 \times 10^4\ s^{-1}$. With the assumption that the A-factors for these decomposition reactions are about $2 \times 10^{13}\ s^{-1}$ at atmospheric pressure [54], activation barriers for the two decomposition pathways of $\approx$12.5 kcal mol^{-1} (for the HCOCl formation channel) and 11.5 kcal mol^{-1} (for the $ClCH_2CHO$ formation channel) are obtained.

Less quantitative information can be obtained regarding the chemistry of the $CH_3CH_2CHClCH_2O\cdot$ radical, which is produced from internal Cl addition to 1-butene. Three pathways are plausible (see Scheme 6): decomposition to give CH_2O (and also CO_2), isomerization to yield an array of multifunctional compounds (including $HOCH_2CH_2CH(Cl)CHO$), and reaction with O_2 to yield $CH_3CH_2CHClCHO$. Clearly, some decomposition is occurring given that both CH_2O and CO_2 are observed, and some reaction with O_2 must also be occurring, since the CH_2O and CO_2 yields decrease with increasing O_2. However, without the ability to quantify the yield of any products derived from the isomerization channel, a quantitative analysis cannot be carried out. Nonetheless, the fact that the decrease in the yields of CH_2O and CO_2 with O_2 partial pressure are similar to those for HCOCl and $ClCH_2CHO$, the barrier to decomposition (and probably isomerization as well) are likely close to 12 kcal mol^{-1}.

Summary of β-Chloroalkoxy Radical Chemistry

The data presented here for a number of β-chlorinated alkoxy radicals, combined with recent theoretical studies [22,45], allow for some general conclusions to be drawn. The available thermodynamic and kinetic data ([22] and this work) for the unimolecular decomposition of some of the simpler β-chlorinated alkoxy radicals are collected in Table II. The decompositions of the β-chlorinated species are characterized by somewhat lower ΔH values (3–5 kcal mol^{-1}) than for the corresponding unsubstituted radical decompositions [54,56,57], which leads to only a modest reduction in the corresponding activation energies (0–2 kcal mol^{-1}). It has been shown [48,58] that the activation energy (E_a) for a series of alkoxy radical decompositions involving a common leaving group is related to the endothermicity of the decomposition (ΔH_d) by the following relationship:

$$E_a = (2.4\text{IP} - 8.1) + 0.36\Delta H_d$$

where IP refers to the ionization potential of the (common) leaving group in eV, and E_a and ΔH_d are in kcal mol^{-1}. Consideration of the data in Table II reveals that, in this context, β-chlorinated alkyl radicals are slightly poorer leaving groups than CH_3 radicals (higher activation energy for a given endothermicity), despite the fact that the ionization potential for CH_2Cl (8.9 eV [59]) is somewhat lower than that of the CH_3 radical (9.8 eV [59]).

Table II Summary of Available Thermodynamic and Kinetic Data for the Unimolecular Decomposition of β-Chlorinated Alkoxy Radicals and Their Unsubstituted Counterparts (Where Available)

Species	ΔH_r	E_a	Reference
3-Chloro-2-butoxy	1.5	11.5	This work
2-Butoxy[a]	4.9	12.2	[54]
1-Chloro-2-butoxy[a]		11.5	This work
2-Butoxy[a]	4.9	12.2	[54]
1-Chloro-2-butoxy[b]		12.5	This work
2-Butoxy[b]	6.4	14.5	[54]
2-Chloro-1-butoxy		≈12	This work
1-Butoxy	10.6	14.9	[54]
1-Chloro-2-propoxy	2.6	13.4	[22]
2-Propoxy	7.8	15.2,14.9	[54,56]
2-Chloro-1-ethoxy	10.2	17	[22]
Ethoxy	13.1	16.8,17.6	[54,57]

[a] Decomposition via rupture of the C2—C3 bond.

[b] Decomposition via rupture of the C1—C2 bond.

Thus, to a first approximation, the atmospheric chemistry of the β-chlorinated alkoxy radicals is similar to that of nonsubstituted (i.e., alkane-derived) species [48,54] of similar size and structure. For example, smaller and less branched species (e.g., ethoxy, propoxy, and their β-chlorinated counterparts) predominantly react with O_2. On the other hand, decomposition plays a role in the atmospheric chemistry of larger, more branched species (such as 2-butoxy, branched C_4 and larger radicals, and their β-chlorinated counterparts). Decomposition plays a slightly larger role in the atmospheric chemistry of some mid-size β-chlorinated species in comparison with their unsubstituted counterparts (for example, 1-chloro-2-butoxy and 2-chloro-1-butoxy).

From the standpoint of the formation of unique atmospheric tracers of Cl-atom chemistry, largest tracer yields are expected from the oxidation of the smaller alkenes (e.g., nearly 100% yield of chloroacetaldehyde from ethene, and chloroacetone from propene are expected [21–25] in the presence of NO_x), while lesser yields are obtained from larger and more branched species (e.g., the yield of 1-chloro-2-butanone from 1-butene is probably about 30% in the presence of NO_x). Reasonably large tracer yields also result from the oxidation of the dienes (1,3-butadiene and isoprene) [16–19,45], since decomposition of the chlorinated oxy radicals formed from these species are not favorable processes [45], often involving the formation vinyl-type radicals.

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