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Kinetics and Mechanism of the Reaction of Cl Atoms with 2-Methyl-1,3-butadiene (Isoprene) at 298 K

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The reaction of chlorine atoms with isoprene (2-methyl-1,3-butadiene) may be important in the marine boundary layer. The kinetics and mechanisms of this reaction have been studied at 760 Torr and 298 K using the photolysis of Cl_2 as the chlorine atom source. Product studies in air were carried out using 40 m path length FTIR spectrometry. Rate constants were determined in either air or N_2 using a relative rate technique and GC-FID to follow the decay of isoprene relative to *n*-butane. For comparison, the kinetics of the chlorine atom reactions with isoprene-d_8, 1,3-butadiene, and 1,3-butadiene-d_6 were also studied at 1 atm in air or N_2 at 298 K. The rate constant ratios determined with *n*-butane as the reference compound are as follows: isoprene (2.16 ± 0.17); isoprene-d_8 (1.79 ± 0.22), 1,3-butadiene (2.01 ± 0.11); 1,3-butadiene-d_6 (1.85 ± 0.10) ($\pm 2\sigma$). The corresponding absolute rate constants, based on a value for *n*-butane of $2.11 \pm 0.18 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, are as follows: isoprene (4.6 ± 0.5); isoprene-d_8 (3.8 ± 0.6); 1,3-butadiene (4.2 ± 0.4); 1,3-butadiene-d_6 (3.9 ± 0.4) ($\pm 2\sigma$), all in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Both the kinetics studies and the HCl yields determined using FTIR show that the net abstraction of an allylic hydrogen is a small but significant fraction, 15 ± 4% ($\pm 2\sigma$), of the overall reaction at 1 atm. The major organic products appear to be unsaturated chlorine-containing carbonyl compounds which remain unidentified. The atmospheric implications are discussed.

Introduction

Atomic chlorine is now known to be a major oxidant for organics in the Arctic at ground level in the spring at polar sunrise.[1−3] While the source of these tropospheric chlorine atoms remains controversial, it is clear that under conditions where depletion of ground level O_3 is observed, oxidation of many organics by Cl predominates over that by OH.[3]

There is also increasing interest in the possibility that atomic chlorine could make a significant contribution globally to the oxidation of organics and of ozone in the marine boundary layer.[4−6] Rates of decay of organics in several recent field studies have been used to assess the relative contributions of Cl and OH, from which peak morning concentrations of atomic chlorine of $\sim 10^3 - 10^5$ atoms cm^{-3} have been estimated.[7,8] These values are consistent with the estimates of $10^4 - 10^5$ chlorine atoms cm^{-3} of Keene and co-workers,[9,10] who measured inorganic chlorine-containing compounds other than HCl using a mist chamber. While the individual compounds were not identified, they are believed to include Cl_2 and possibly other chlorine-containing species such as HOCl. Although there is evidence that chlorine atoms do not appear to compete with OH on a global scale for the oxidation of organics,[11,12] they are clearly important during early morning in the marine boundary layer. Hence, they determine in part the fraction of organics emitted at the ocean surface which reach the free troposphere.

Once formed, chlorine atoms can react either with O_3

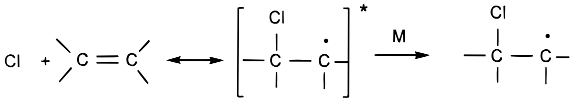
$$Cl + O_3 \rightarrow ClO + O_2 \tag{1}$$

or with organics such as alkanes:

$$Cl + RH \rightarrow HCl + R \tag{2}$$

The concentrations of organics and ozone are comparable in many regions of the troposphere. Since the room temperature rate constants for reaction 2[13,14] are on the order of 10^{-10} cm^3 $molecule^{-1}$ s^{-1} compared to 1.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for reaction 1,[14] the reaction with organics is expected to be the dominant pathway for chlorine atoms.

Past studies[15−25] of the reactions of chlorine atoms with simple alkenes have shown that the reaction is fast and occurs primarily via addition of chlorine atoms to the double bond:



(3)

However, abstraction of the allylic hydrogen can also occur; typical C−H bond strengths for allylic hydrogens are ∼80−85 kcal mol^{-1} compared to ∼100 kcal mol^{-1} for alkane C−H bonds.[26] For example, Lee and Rowland[16] estimated that a maximum of (14 ± 4)% of the Cl−propene reaction occurs via abstraction of the allylic hydrogen at 3000 Torr total pressure. Kaiser and Wallington[25] suggested that about 9% of the reaction of Cl atoms with propene proceeds by abstraction at 700 Torr, based on the relative yields of products characteristic of abstraction versus addition.

Recent studies[27−30] have shown that 2-methyl-1,3-butadiene (isoprene) is produced in seawater by phytoplankton. Hence, it is expected to be emitted into the marine boundary layer where it can be removed by reaction with Cl as well as with OH, O_3, and NO_3.[31] The rate constants for reaction of isoprene with OH, O_3, and NO_3 have been determined at 298 K and 1 atm to be 1.01×10^{-10}, 1.28×10^{-17}, and 6.78×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively.[32] While there have been a number of mechanistic studies of these reactions[32−46] and many of the reaction pathways elucidated, the chemistry is complex and not yet fully understood.

However, there have been no studies of the kinetics and mechanisms of the reaction of chlorine atoms with isoprene

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reported in the literature. This is of fundamental mechanistic and kinetics interest, since a number of different potential reaction paths are available. Not only are there four potential sites for addition of the chlorine atom to the carbon atoms of the two double bonds, but abstraction of the allylic hydrogen on the methyl group may also be important. In addition, understanding the kinetics and mechanisms is critical for assessing the sinks of both isoprene and atomic chlorine in the marine boundary layer. Finally, if unique chlorine-containing products are formed in this reaction, they may be used as "markers" of this chemistry in field studies.

We report here both kinetics and mechanistic studies of the reaction of atomic chlorine with isoprene at room temperature. The reactions of 1,3-butadiene and fully deuterated isoprene and 1,3-butadiene were also studied in order to assess the relative importance of addition and abstraction. It is shown that abstraction of the allylic methyl hydrogen is a significant pathway, but unlike the OH−isoprene reaction, production of methyl vinyl ketone and methacrolein is not. Formyl chloride is observed as a minor product. The implications of the kinetics and mechanisms for atmospheric chemistry are discussed.

Experimental Section

Product Studies. The formation of products from the reaction of isoprene with chlorine atoms at atmospheric pressure in air was followed using FTIR (Mattson Research Series) and a long path White cell[47] (base path, 1 m; total path, 40 m) housed in the external sampling compartment. The FTIR was equipped with a cooled MCT detector. A total of 64 scans at a resolution of 1 $\mathrm{cm^{-1}}$ was typically averaged for each spectrum. Reactants were introduced into the cell by direct expansion from a glass manifold system. Photolysis of Cl_2 to generate chlorine atoms was accomplished using eight Sylvania 350 Blacklights (30 W, F30T8/350BL) oriented longitudinally about the cylindrical cell.

Products were identified by matching spectral features with those of commercially available samples. The cell was calibrated for isoprene (991 $\mathrm{cm^{-1}}$), hydrogen chloride (2843 $\mathrm{cm^{-1}}$), carbon monoxide (2151 $\mathrm{cm^{-1}}$), methacrolein (934 $\mathrm{cm^{-1}}$), and methyl vinyl ketone (951 $\mathrm{cm^{-1}}$) using commercially available samples, where the particular peaks used to quantify the reactants and products are shown in parentheses. Calibration for the unstable formyl chloride at 738.6 $\mathrm{cm^{-1}}$ was carried out using the reaction of *trans*-1,2-dichloroethene [$(3.7-5.5) \times 10^{14}$ molecules $\mathrm{cm^{-3}}$] with chlorine atoms (initial [Cl_2] was $(1-2) \times 10^{14}$ molecules $\mathrm{cm^{-3}}$) at 1 atm in air. The loss of *trans*-1,2-dichloroethene and generation of formyl chloride and minor products such as phosgene (using the 857 $\mathrm{cm^{-1}}$ peak) were followed by FTIR after each 15 s interval of photolysis. The absorption cross section for formyl chloride was determined from its absorbance and mass balance considerations described below.

Relative Rate Measurements. Rate constants were determined using the relative rate method.[31] Briefly, mixtures of Cl_2 and isoprene or 1,3-butadiene with *n*-butane as the reference compound were photolyzed for varying times and the decay of the two organics was followed using gas chromatography with flame ionization detection (GC-FID). The ratio of the rate constants, k_4/k_5,

$$\mathrm{Cl} + \text{isoprene (or 1,3-butadiene)} \xrightarrow{k_4} \text{products} \tag{4}$$

$$\mathrm{Cl} + n\text{-butane} \xrightarrow{k_5} \mathrm{HCl} + \mathrm{C_4H_9} \tag{5}$$

was determined from their relative rates of decay using eq I,

$$\ln\{[\text{isoprene}]_0/[\text{isoprene}]_t\} = (k_4/k_5)\ln\{[n\text{-butane}]_0/[n\text{-butane}]_t\} \quad \text{(I)}$$

where $[\text{isoprene}]_0$ and $[n\text{-butane}]_0$ are the initial concentrations before reaction and $[\text{isoprene}]_t$ and $[n\text{-butane}]_t$ are the concentrations after varying reaction/photolysis times. The slope of plots of $\ln\{[\text{isoprene}]_0/[\text{isoprene}]_t\}$ versus $\ln\{[n\text{-butane}]_0/[n\text{-butane}]_t\}$ used to obtain the ratio k_4/k_5 was calculated using a method described in detail elsewhere,[48] which takes into account errors in both $\ln\{[\text{isoprene}]_0/[\text{isoprene}]_t\}$ and $\ln\{[n\text{-butane}]_0/[n\text{-butane}]_t\}$, determined from the reproducibility of repeated injections before reaction.

Experiments conducted at atmospheric pressure were carried out in two types of reaction vessels. Most experiments were performed in collapsible Teflon reaction chambers fitted with a single Teflon septum port (Alltech Associates Inc.). Reactant at a measured pressure was flushed from a 497 $\mathrm{cm^3}$ transfer bulb into the reaction chamber through a calibrated rotameter (Omega Engineering Inc., Model FL4213-V) using the carrier gas. The walls of the chamber were constructed of 5 mil Teflon−FEP and the fully inflated reaction chamber had a volume of 50 L. A 6 L Pyrex bulb was used for similar experiments at reduced pressure. Introducing reactants into the Pyrex vessel was accomplished by direct expansion from a 366 $\mathrm{cm^3}$ glass manifold system.

The reaction vessel was located in the center of a rectangular lamp cage and was flanked by two sets of seven Sylvania 350 Blacklights (20 Watt, F20T12/350BL), which provide UV radiation in the region 300−450 nm, with a maximum intensity at approximately 360 nm. Before proceeding with the kinetics measurements, the full range of reaction mixtures was tested for dark reactions on the time scale of a typical experiment. At higher concentrations of reactants, $>1 \times 10^{15}$ molecules $\mathrm{cm^{-3}}$ of each, Cl_2 underwent a dark reaction with isoprene. A similar reaction in the liquid phase has been reported.[49] Concentrations of reactants were kept below those observed to react in the dark over the time scale of our experiments; that is, no change in isoprene in the mixture was observed in the dark within the typical 2% standard deviation associated with repeated injections of isoprene alone. The decay of organics upon photolysis was monitored by injecting samples into a gas chromatograph (Hewlett-Packard 5890) equipped with a room temperature 6-port gas sampling valve (Valco Instruments Co. Inc.). A 60 m Cyclodex-B column (J & W Scientific) was used for the isoprene studies. The oven was temperature programmed from 20 to 100 °C at 7°/min and held at 100 °C for an additional 10 min. For the butadiene experiments, a 30 ft × 1/8'' stainless steel packed column, 23% SP-1700 on 80/100 Chromosorb PAW (Supelco) was used; it was temperature programmed to run from 50−100 °C at 10°/min, with a final 10 min at 100 °C.

Concentrations of isoprene, 1,3-butadiene, and *n*-butane varied from $(0.64-10) \times 10^{14}$ molecules $\mathrm{cm^{-3}}$ and Cl_2 from $(0.64-9.8) \times 10^{14}$ molecules $\mathrm{cm^{-3}}$. Pressure measurements were carried out using a capacitance manometer (Datametrics Barocel Model 600) with digital readout (Datametrics Model 1500). In all cases, Ultra High purity air (Liquid Carbonic, Ultra Zero air, impurities: $H_2O < 2$ ppm, $CO < 1$ ppm, $CO_2 < 1$ ppm, $NO < 0.1$ ppm, total hydrocarbons <0.1 ppm) was added to achieve the desired total pressure or volume for the reaction mixture. Some runs were also carried out in nitrogen as the carrier gas to test for potential interferences due to the production and secondary reactions of OH.

Materials. Chemicals and their sources were as follows: chlorine (99.5%), *n*-butane (99.5%), hydrogen chloride (99.0%), carbon monoxide (99.5%), and phosgene (99.0%) were acquired from Matheson. 1,3-Butadiene (99.0% inhibited with 0.02 wt % *tert*-butylcatechol) was supplied by Phillips 66. Isoprene (99%; inhibited with 100 ppm *p*-*tert*-butylcatechol), methacrolein (95%), methyl vinyl ketone (99%), and *trans*-1,2-dichloroethene were obtained from Aldrich. Isoprene-d_8 (98%; inhibited with hydroquinone) and 1,3-butadiene-d_6 (98.0%) were procured from Cambridge Isotopes. Liquids were degassed using several freeze−pump−thaw cycles and distilled under vacuum into the gas phase. This removed the low volatility inhibitors which were not observed by FTIR, GC, or atmospheric pressure ionization mass spectrometry in the gaseous reactants. Gases were used as received. The nitrogen was Ultra High purity grade (Liquid Carbonic, >99.999%).

Results and Discussion

1. Reaction of *trans*-1,2-Dichloroethene with Chlorine Atoms. As discussed below, formyl chloride is a minor product of the reaction of chlorine atoms with isoprene. In order to quantify its yield, the absorption cross section at 738.6 cm^{-1} was determined by reacting *trans*-1,2-dichloroethene with atomic chlorine.[50] Figure 1 shows the infrared spectra before (Figure 1a) and after (Figure 1b) photolysis of *trans*-1,2-dichloroethene−Cl_2 mixtures. HCOCl is clearly the major product. Small amounts of phosgene are also observed, as are HCl and CO (not shown). This is consistent with the following chemistry:

$$\mathrm{ClHC{=}CHCl + Cl \rightarrow ClHC{-}CHCl_2} \tag{6}$$

$$\mathrm{ClHC{-}CHCl_2 + O_2 \rightarrow ClHC(OO){-}CHCl_2} \tag{7}$$

$$\mathrm{2ClHC(OO){-}CHCl_2 \rightarrow 2ClHC(O){-}CHCl_2 + O_2} \tag{8}$$

$$\mathrm{ClHC(O){-}CHCl_2 \rightarrow HCOCl + CHCl_2} \tag{9}$$

$$\mathrm{CHCl_2 + O_2 \rightarrow OOCHCl_2} \tag{10}$$

$$\mathrm{2OOCHCl_2 \rightarrow 2OCHCl_2 + O_2} \tag{11}$$

$$\mathrm{OCHCl_2 \rightarrow HCOCl + Cl} \tag{12}$$

$$\mathrm{OCHCl_2 + O_2 \rightarrow HO_2 + COCl_2} \tag{13}$$

$$\mathrm{HCOCl \rightarrow HCl + CO} \tag{14}$$

$$\mathrm{HCOCl} + h\nu \rightarrow \mathrm{HCl + CO} \tag{15a}$$

$$\mathrm{HCOCl} + h\nu \rightarrow \mathrm{HCO + Cl} \tag{15b}$$

$$\mathrm{Cl + HCOCl \rightarrow HCl + COCl} \tag{16}$$

$$\mathrm{COCl \rightarrow CO + Cl} \tag{17}$$

Niki and co-workers[51,52] have shown that in 700 Torr of air, the major fate of the alkoxy radical $OCHCl_2$ is decomposition to formyl chloride, reaction 12, rather than reaction with O_2 to form phosgene, reaction 13. This is consistent with the very small yields of $COCl_2$ observed in the Cl atom reaction with 1,2-dichloroethene (see below). The thermal decomposition of formyl chloride, reaction 14, has been observed in previous studies[53−56] and is believed to form HCl + CO. Finally, the reaction of Cl with HCOCl is known to proceed via reaction 16, and there is evidence that the COCl radical formed decomposes to CO + Cl, reaction 17.[54] This mechanism is similar to that for the OH reaction with 1,2-dichloroethene.[55]

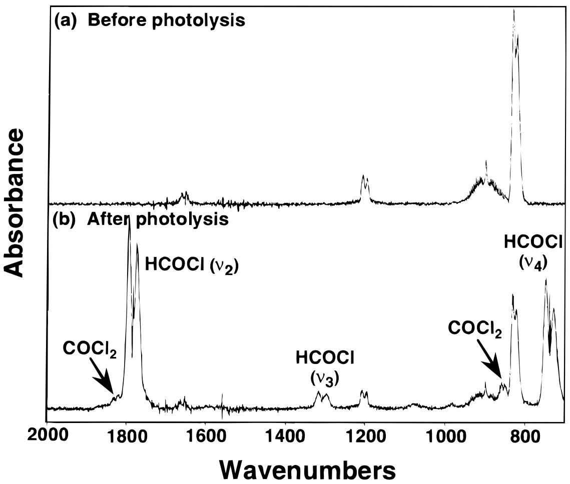


Figure 1. Infrared spectra of *trans*-1,2-dichloroethene (3.7×10^{14} molecules cm^{-3})−Cl_2 (2.0×10^{14} molecules cm^{-3}) mixtures in 1 atm of air at 298 K (a) before photolysis where all the bands are due to *trans*-1,2-dichloroethene and (b) after photolysis for 1.25 min, where bands due to the products formed in the reaction with atomic chlorine are as indicated.

On the basis of these reactions, concentrations of HCOCl were calculated from eq II.

$$[\mathrm{HCOCl}] = 2\Delta[\text{1,2-dichloroethene}] - [\mathrm{COCl_2}] - [\mathrm{HCl}] \tag{II}$$

In eq II, Δ[1,2-dichloroethene] is the amount of the reactant consumed at time *t* and [$COCl_2$] the concentration of phosgene formed, which reflects the small fraction of alkoxy radicals reacting via 13 rather than 12. The hydrogen chloride concentration formed at time *t*, [HCl], reflects the loss of HCOCl by its thermal decomposition, reaction with chlorine atoms or photolysis via 15a. Since the quantum yields for 15a and 15b have not been reported in the literature, loss via 15b was assumed to be negligible.

Figure 2 shows a typical time dependence for the loss of the *trans*-1,2-dichloroethene and the formation of HCOCl and $COCl_2$. As expected, HCOCl is the major product, $COCl_2$ is formed in small yields, and HCl is observed primarily at longer reaction times where decomposition of HCOCl becomes significant.

Three such runs were carried out to determine the relationship between the absorbance and concentrations of HCOCl using this approach. On the basis of absorbances below 0.4 where absorbance was linear with concentration, the absorption cross section (base *e*) for HCOCl at the Q-branch of the ν_4 C−Cl stretch at 738.6 cm^{-1} was calculated to be $\sigma = (\ln I_0/I)/Nl = (7.9 \pm 1.2) \times 10^{-19}$ cm^2 molecule^{-1} s^{-1} ($\pm 2\sigma$). This is in reasonably good agreement with the value of 6.6×10^{-19} cm^2 molecule^{-1} of Libuda et al.[56] Our value for the absorption cross section was then used to determine the yield of HCOCl in the isoprene reactions.

2. Product Studies of the Cl + Isoprene Reaction. Figure 3 shows infrared spectra of typical isoprene−Cl_2 mixtures (a) before photolysis, (b) after photolysis, and (c) the difference spectrum b − a. Because isoprene is consumed in the reaction, its absorption in the difference spectrum appears as negative peaks. Products observed at less than ∼35% consumption of isoprene are HCl, HCOCl (formyl chloride), and CO. In addition, the formation of carbonyl compounds is indicated by a strong peak at 1710 cm^{-1}. Peaks due to unidentified organic product(s) are also observed at ∼1100, 1263, 1340, and 2820 cm^{-1}.

An absorption band at 1710 cm^{-1} is characteristic of α,*β*-unsaturated aldehydes and ketones, while those at 2820, 1340, and 1263 cm^{-1} are in the regions for the C−H stretch, C−H deformation, and C−C stretch, respectively.[57,58] The band at 1100 cm^{-1} is in the region expected for a peroxide or epoxide

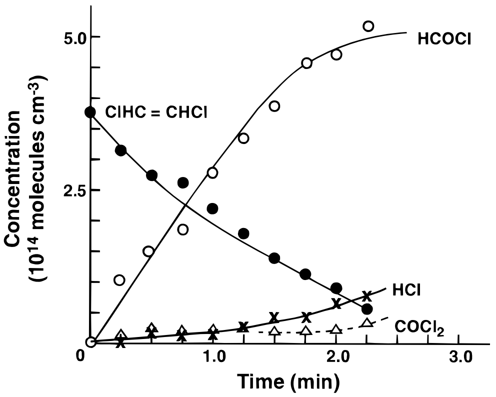


Figure 2. Typical loss of *trans*-1,2-dichloroethene (initial concentration was 3.7 × 10^{14} molecules cm^{-3}) and formation of products during the photolysis of Cl_2 (2.0 × 10^{14} molecules cm^{-3}) at 1 atm in air.

C−O stretch. The formation of organic peroxides R_1OOR_2 in this NO_x-free system is expected since a minor channel in the $R_1O_2 + R_2O_2$ reaction forms $R_1OOR_2 + O_2$.[59,60]

Figure 4 shows typical concentration−time profiles for the loss of isoprene and the formation of HCl, HCOCl, CO, and the 1710 cm^{-1} band obtained using the unsubtracted spectra. Initially HCl, HCOCl, and the 1710 cm^{-1} carbonyl peaks increase linearly with time, while there is an induction period for the formation of CO. (HCl formation does not extrapolate to zero because of the presence of small amounts of HCl initially present in the Cl_2). The concentration of HCOCl does not continue to increase along with HCl and the 1710 cm^{-1} band because of its removal by thermal decomposition and other secondary reactions. These time dependencies are consistent with the direct formation of HCl, HCOCl, and the carbonyl compound(s) in the primary reaction, while CO is generated in part at least by secondary reactions of HCOCl.

At larger extents of reaction than shown in Figure 4, the 1710 cm^{-1} peak decreases as expected for a carbonyl compound, which photolyzes and/or reacts with chlorine atoms. The ratio of the 1263 and 1340 cm^{-1} peak heights to that at 1710 cm^{-1} does not vary significantly with the extent of reaction, while the ratio of peak heights at 1100 and 2820 cm^{-1} to the 1710 cm^{-1} peak increases at longer reaction times. This suggests that the 1263 and 1340 cm^{-1} peaks are associated with the carbonyl product responsible for the 1710 cm^{-1}, while those at 1100 and 2820 cm^{-1} are not.

This combination of organic and inorganic products is consistent with two reaction paths, abstraction of an allylic hydrogen from the methyl group, or addition to one of the double bonds:

$$\mathrm{Cl} + \text{isoprene} \xrightarrow{\text{abstraction}} \mathrm{HCl} + \mathrm{C_5H_7} \qquad (18)$$

$$\mathrm{Cl} + \text{isoprene} \xrightarrow{\text{addition}} \mathrm{C_5H_8Cl} \qquad (19)$$

(It should be noted, however, that as discussed below the abstraction may not be a simple bimolecular reaction, but may involve complex formation followed by an intramolecular elimination of HCl.)

The initial rate of HCl formation, before the decomposition of HCOCl becomes important, should reflect abstraction of the allylic hydrogen, reaction 18. The fraction of the overall reaction which proceeds by abstraction can therefore be calculated from the initial rate of HCl formation compared to the loss of isoprene. As discussed below, the kinetics data also provide some insight into the relative importance of abstraction versus addition.

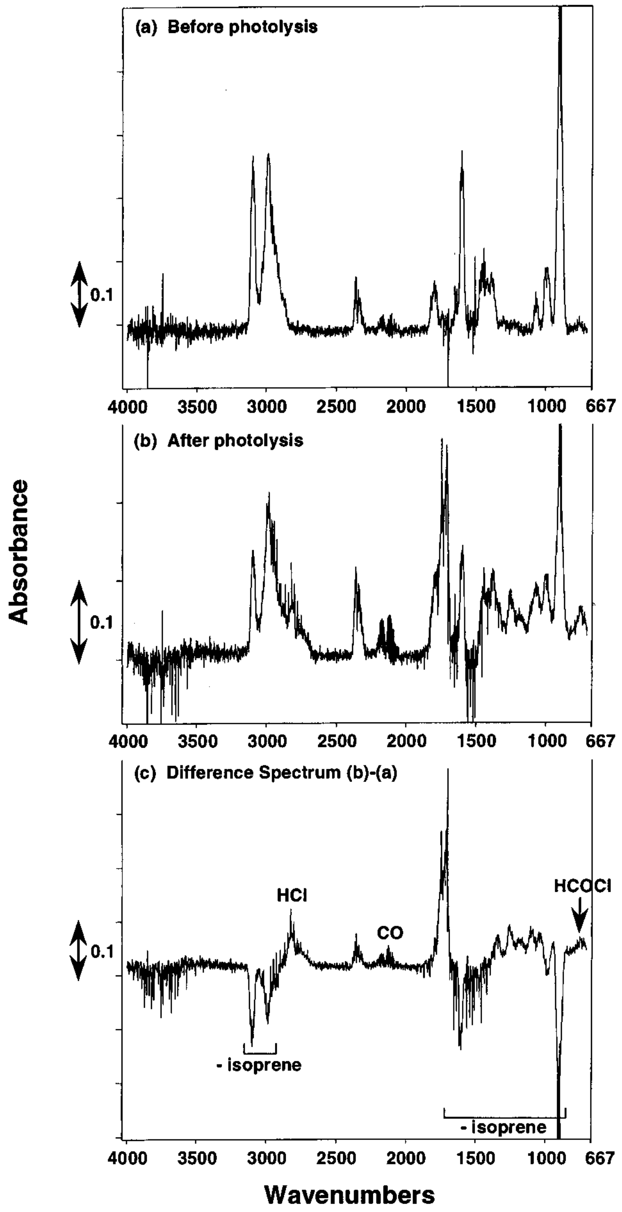


Figure 3. Infrared spectra of isoprene (8.0 × 10^{14} molecules cm^{-3})−Cl_2 (4.0 × 10^{14} molecules cm^{-3}) mixtures in 1 atm of air at 298 K (a) before photolysis and (b) after photolysis for 14 min. (c) The difference spectrum of b−a. The increased CO_2 is due to a change in the sample compartment purge during the run.

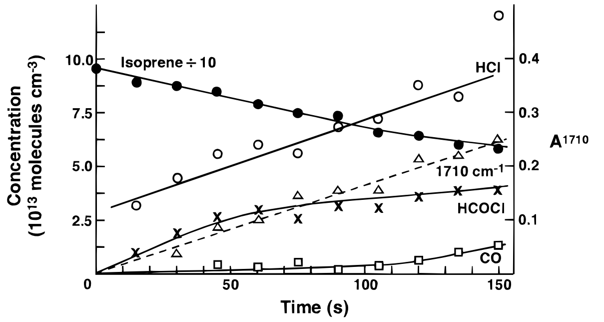


Figure 4. Typical loss of isoprene (initial concentration was 9.5 × 10^{14} molecules cm^{-3}) and formation of products during the photolysis in the presence of Cl_2 (8.1 × 10^{14} molecules cm^{-3}) at 1 atm in air. ●, isoprene; ○, HCl; X, HCOCl; □, CO; △, absorbance at 1710 cm^{-1}.

Table 1 summarizes experiments carried out during the initial loss of ~35% of the isoprene where the formation of HCl and HCOCl were followed. The slope of plots of HCl versus

TABLE 1: Summary of FTIR Product Studies of the Reaction of Cl Atoms with Isoprene at 298 K and One Atmosphere Pressure in Air

expt. no.	initial isoprene concn (10^{14} molecule cm^{-3})	initial Cl_2 concn (10^{14} molecule cm^{-3})	% yield of HCl[a] ($\pm 2\sigma$)	% yield of HCOCl[b] ($\pm 2\sigma$)
1	10.4	4.1	9.4 ± 4.2	7.3 ± 0.7
2	9.9	4.1	13.6 ± 3.2	3.6 ± 0.9
3	4.7	4.1	16.9 ± 4.8	8.3 ± 2.1
4	9.5	8.1	15.8 ± 6.2	11.4 ± 2.1
5	4.3	2.0	12.4 ± 9.2	6.7 ± 1.6
6	8.0	4.0	10.5 ± 2.6	11.1 ± 3.6
		average =	13.1 ± 5.8[c]	8.1 ± 5.8[c]

[a] Calculated from the slope of plots of HCl versus Δ[isoprene]. [b] Calculated from the slope of plots of Δ[HCOCl]/Δ[isoprene] forced through the origin. [c] Average $\pm 2\sigma$.

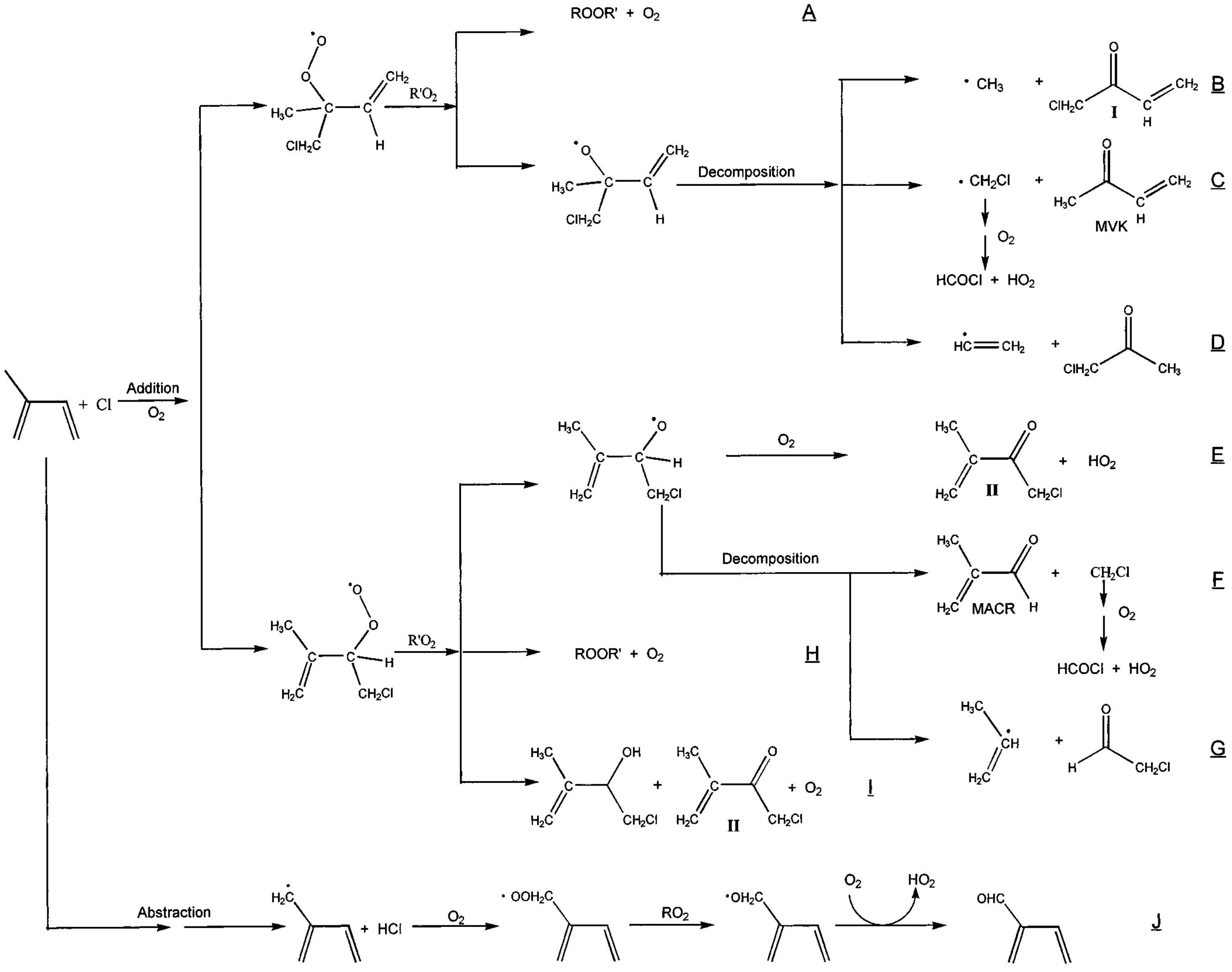


Figure 5. Reaction scheme for the reaction of atomic chlorine with isoprene in air. For simplicity, only addition to the terminal carbon atoms is shown. Addition to the central carbon atoms and isomerization of the double bond to the C2−C3 position are also possible (see text).

Δ[isoprene] was used to estimate the percentage of the Cl + isoprene reaction which proceeds by abstraction. The value obtained from these HCl yields is (13.1 ± 5.8)% (where the error cited is $\pm 2\sigma$). The error is relatively large for several reasons. Because of HCl is a relatively weak absorber in the infrared, the absorbances at 2843 cm^{-1} were always less than 0.1, even at the largest extent of reaction used. In addition, there was a small amount of HCl present before photolysis due to an ~3% impurity in the Cl_2. This was reflected as an intercept in the plots of [HCl] against Δ[isoprene], where the slope of these plots gives the HCl yield.

Table 1 also summarizes the HCOCl formation. Although it is formed in the initial stages of the reaction, the concentrations and the associated absorbances are weak, ≤0.05 under the conditions of the experiments in Table 1. The average yield is calculated to be (8 ± 6)% ($\pm 2\sigma$).

Figure 5 shows some of the potential reaction paths for the chlorine atom−isoprene reaction. For simplicity, only the addition to the terminal carbon atoms is shown. As discussed elsewhere[32−46] with respect to addition of OH to double bonds in isoprene, two other possibilities also exist: addition of the atom to the central C2 and C3 carbon atoms or isomerization of the double bond in the initial adduct to the central position between C2 and C3. Figure 5 shows that methyl vinyl ketone (MVK) and methacrolein (MACR) are potential products from addition of chlorine to C1 or C4, respectively. Both of these paths would also generate the CH_2Cl radical. Once CH_2Cl is formed in the presence of air, it will add O_2 to form the alkyl peroxy radical $OOCH_2Cl$, which reacts further to generate OCH_2Cl. Niki and co-workers[51] have shown that this alkoxy radical preferentially reacts with O_2 to form formyl chloride

$$OCH_2Cl + O_2 \rightarrow HCOCl + HO_2 \qquad (20)$$

rather than dissociating as is the case for $OCHCl_2$ formed in the *trans*-1,2-dichloroethene reaction.

The scheme shown in Figure 5 suggests that MVK ($CH_3COCH{=}CH_2$) or MACR ($CH_2{=}C(CH_3)CHO$) should be formed simultaneously with HCOCl if the chlorine atom adds to a terminal carbon atom. A search for these products was made by FTIR. MVK has a strong peak at 1711 cm^{-1} and a peak approximately half this intensity at 951 cm^{-1}. In addition, there are several smaller peaks between these two. If the strong product peak at 1710 cm^{-1} in our system was due to MVK, the yield would be very high, about 50%. However, no peak at 951 cm^{-1} was observed, ruling out MVK as being major carbonyl product. Using a peak-to-peak signal-to-noise ratio of 1 to estimate the upper limit for MVK, we calculate an upper limit for the net yield of MVK in the runs shown in Table 1 of 10% of the isoprene loss.

While MACR also has a strong absorption in the 1710−1726 cm^{-1} region, the peak positions and shapes do not match those observed in the chlorine atom−isoprene reaction. Hence, this product can also be ruled out as contributing significantly to the carbonyl product. Using the peak at 934 cm^{-1} and a peak-to-peak signal-to-noise ratio of 2 to take into account the fact that the 934 cm^{-1} MACR peak is overlapped by the shoulder of an isoprene band, an upper limit to the net formation of MACR is also estimated to be 10% of the isoprene loss.

These product studies were generally restricted to the loss of the first ∼35% of isoprene in order to minimize the contribution of secondary reactions. However, many of the potential products, including MVK and MACR, are also expected to undergo fast secondary reactions with chlorine atoms. The measured upper limits of 10% for the percentage of the isoprene reacted which appears as MVK and MACR do not take into account the potential removal by such secondary reactions.

To estimate the potential loss of these products by reaction with chlorine atoms, the ACUCHEM model[61] was applied to a simplified reaction scheme for this system. It was assumed that 32% of the reaction of chlorine atoms with isoprene gives MVK and 23% gives MACR as is the case for the OH−isoprene reaction,[46] and that MVK and MACR react with chlorine atoms with the same rate constant as for the Cl−isoprene reaction. This is likely an extreme assumption since the corresponding OH rate constants with MACR and MVK are a factor of 3−5 smaller than the OH−isoprene reaction.[32] Under typical reaction conditions such as those shown in Figure 4, if MVK and MACR reacted with chlorine atoms, the yields of the measured final products would be low by 30%. Taking this into account, upper limits for the yields of MVK and MACR are 13%, much smaller than observed in the OH−isoprene reaction.[46]

The absence of MVK and MACR as products is consistent with the kinetics runs carried out using GC (see below). No peaks due to these two compounds were observed during the runs carried out under conditions similar to those used in the FTIR studies.

In summary, the small initial yields of HCOCl and the lack of detection of methyl vinyl ketone or methacrolein suggest that paths C and F in Figure 5 are not the major reaction paths for the chlorine atom−isoprene reaction. The sum of the abstraction path to form HCl and the paths C and F using HCOCl to estimate the latter only accounts for ∼20−25% of the total reaction. The carbonyl compound responsible for the peak at 1710 cm^{-1} (and likely those at 1340 and 1263 cm^{-1} as well) appears to be the major organic product. In addition, organic peroxides are formed, likely from $RO_2 + R'O_2$ reactions.

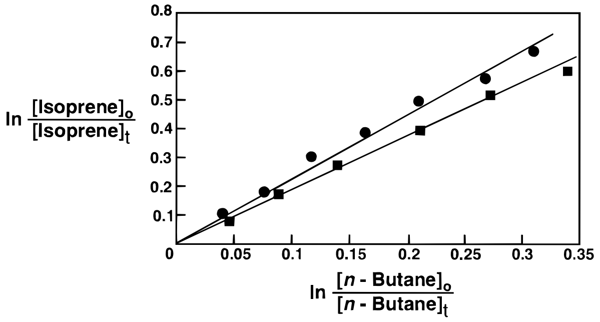


Figure 6. Decays of isoprene and isoprene-d_8 relative to *n*-butane at 1 atm in air at 298 K during one typical run for each compound. ●, isoprene; ■, isoprene-d_8.

The major carbonyl product remains unidentified. Compounds such as I, $ClCH_2C(O)CH{=}CH_2$, and II, $CH_2{=}C(CH_3){-}C(O)CH_2Cl$, in Figure 5 are possibilities. If I is produced, HCHO should also be formed from the subsequent oxidation of the methyl radical generated simultaneously; no peak was observed at 2778 cm^{-1} as expected for HCHO. Other compounds from chlorine atom addition to C2 or C3 such as $CH_2{=}CH{-}C(CH_3)ClCHO$ or $CH_2{=}C(CH_3)CHClCHO$ are also potential candidates. Unfortunately, authentic samples of these compounds are not commercially available for comparison.

3. Kinetics of the Cl−Isoprene and Isoprene-d_8 Reactions at 1 atm. Figure 6 shows decays of isoprene and isoprene-d_8 relative to *n*-butane at 1 atm in one typical experiment for each compound. The decay of the organics, plotted to be consistent with eq I, is linear with an intercept of zero as expected. The kinetics data are summarized in Table 2.

Kaiser and Wallington[24] reported that the rate constant measured for ethene increased in air at total pressures below 100 Torr and attributed the increase to a contribution from OH formed by secondary reactions involving O_2. To test for such an effect in the isoprene and 1,3-butadiene reactions, two experiments were carried out in N_2 for each compound at a total pressure of 1 atm. There was no increase in the relative rate constants for the isoprene and isoprene-d_8 reactions carried out in air compared to nitrogen, confirming that generation and secondary reactions of OH are negligible.

The relative rate constant at 1 atm is substantially smaller for the fully deuterated compound, and a *t*-test shows that the difference is significant at the 95% confidence level. As shown below, the reaction is in the high-pressure limit at 1 atm. Thus, the measured rate constant, k_{obs}, is the sum of the individual rate constants for abstraction, k_{abs}, and for addition to the double bond, k_{add},

$$k_{obs}\,(\text{isoprene}) = k_{abs}\,(\text{isoprene}) + k_{add}\,(\text{isoprene}) \qquad (III)$$

Assuming that the addition reaction has a negligible isotope effect, the difference between the atmospheric pressure rate constants for isoprene and isoprene-d_8 gives the difference between their rate constants for hydrogen abstraction:

$$k_{obs}\,(\text{isoprene}) - k_{obs}\,(\text{isoprene-}d_8) = k_{abs}\,(\text{isoprene}) - k_{abs}\,(\text{isoprene-}d_8) \qquad (IV)$$

In the extreme limit where deuteration slows the abstraction to negligible levels, this difference can be used to calculate the contribution of abstraction to the total reaction. If abstraction still contributes significantly to the measured rate constant for

TABLE 2: Summary of Relative Rate Experiments for the Reaction of Cl with Isoprene, Isoprene-d_8, 1,3-Butadiene, and 1,3-Butadiene-d_6 Relative to *n*-Butane at 298 K and One Atmosphere Total Pressure

compd	range of organic concns (10^{14} cm^{-3})	range of *n*-butane concns (10^{14} cm^{-3})	range of Cl_2 concns (10^{14} cm^{-3})	relative rate[a] ($\pm 2\sigma$)	absolute rate constant[b] k_4(10^{-10} cm^3 molecule^{-1} s^{-1}) ($\pm 2\sigma$)
isoprene	0.64−3.7	0.64−3.7	0.66−7.4	2.16 ± 0.17(23)	4.6 ± 0.5
isoprene-d_8	1.2−4.9	2.5−4.9	6.2−7.4	1.79 ± 0.22(9)	3.8 ± 0.6
1,3-butadiene	1.2−4.9	1.2−3.7	4.9−8.6	2.01 ± 0.11(8)	4.2 ± 0.4
1,3-butadiene-d_6	2.5−4.9	1.2−4.9	4.9−8.6	1.85 ± 0.10(10)	3.9 ± 0.4

[a] Number of experiments given in parentheses. [b] Using $k_5 = (2.11 \pm 0.18) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} ($\pm 2\sigma$) for the Cl + *n*-butane reaction at 298 K;[13] the errors cited include those in the relative rate measurements and that in the absolute rate constant for *n*-butane.

the isoprene-d_8 reaction, this difference between the observed rate constants provides a lower limit to the fraction of the isoprene reaction which is due to abstraction.

Assuming that abstraction is negligible for isoprene-d_8, i.e., that k_{abs} (isoprene-d_8) in eq IV is zero, the percent of the total reaction of chlorine atoms with isoprene at 1 atm in air which is due to abstraction is calculated to be 17.3 ± 13.1% ($\pm 2\sigma$), consistent with the HCl yields within the wide error bars.

The assumption that abstraction becomes negligible for the fully deuterated compound is reasonable. The maximum kinetic isotope effect expected for abstraction of a hydrogen from a C−H bond when deuterium is substituted can be calculated assuming a very loose transition state. If the force constants of the breaking C−H and C−D bonds approach zero in the transition state, the zero point energies of C−H and C−D also both become zero in the transition state. The difference in the activation energies for breaking the C−H versus the C−D bonds is then given by the difference in zero point energies in the reactants. Taking the force constant for a C−H or C−D bond to be 480 N m^{-1}, and assuming that the pre-exponential factor does not change upon deuteration, the maximum kinetic isotope effect for breaking of a C−H versus a C−D bond is calculated to be 7.5. Given that the HCl yields from the FTIR studies suggest that abstraction accounts for 13% of the isoprene reaction, the maximum kinetic isotope effect would predict that only 1.7% of the overall isoprene-d_8 reaction proceeds by abstraction.

4. Kinetics of Reaction of Cl with 1,3-Butadiene and 1,3-Butadiene-d_6. A third approach to clarifying the relative importance of abstraction of allylic hydrogen versus addition is to compare the reaction kinetics for isoprene and isoprene-d_8 with those for 1,3-butadiene and 1,3-butadiene-d_6 where there are no abstractable allylic hydrogen atoms. Table 2 also summarizes the relative rate constants determined for the butadiene reactions. Again, the kinetics at 1 atm were the same in air or in N_2 for both butadiene and its deuterated analog.

If the deuteration of isoprene reduces the probability of abstraction of an allylic hydrogen to negligible levels compared to addition, the rate constants for isoprene-d_8 and butadiene-d_6 should be the same. As seen from the data in Table 2, this is indeed the case. The relative rate for the 1,3-butadiene reaction appears to be slightly faster, however, than for the 1,3-butadiene-d_6 reaction. A *t*-test confirms that the difference in the rate constants for butadiene and butadiene-d_6 is statistically significant at the 95% confidence level, while that between butadiene-d_6 and isoprene-d_8 is not. This suggests that there is a small kinetic isotope effect for the Cl + 1,3-butadiene reaction, perhaps associated with some abstraction of a vinyl hydrogen. Hence, the rate constant for the 1,3-butadiene-d_6, where abstraction appears to be negligible, was used for comparison to the isoprene kinetics. Comparing the 1,3-butadiene-d_6 relative rate constant of 1.85 ± 0.10 to that for isoprene, 2.16 ± 0.17, one obtains an estimate for abstraction of allylic hydrogen from isoprene of 14.3 ± 9.0% ($\pm 2\sigma$). This assumes that the methyl group in isoprene has insignificant steric or inductive effects on the addition to the double bonds. Although the error is large, the estimate based on this approach is comparable to those using the other approaches discussed above.

TABLE 3: Summary of Pressure Dependence of Relative Rate Constants for the Reaction of Chlorine Atoms with Isoprene and Isoprene-d_8

compd	total pressure (Torr)	relative rate constant ratio ($\pm 2\sigma$)[a]	absolute rate constant (10^{-10} cm^3 molecule^{-1} s^{-1})[b] ($\pm 2\sigma$)
isoprene	5.0	1.90 ± 0.11(1)[c]	4.01 ± 0.42
	0.58	1.64 ± 0.13(3)	3.46 ± 0.40
	0.20	1.36 ± 0.19(5)[d]	2.87 ± 0.47
	0.16	1.25 ± 0.06(2)	2.64 ± 0.26
isoprene-d_8	5.0	1.72 ± 0.26(2)	3.63 ± 0.63
	0.58	1.60 ± 0.16(2)	3.38 ± 0.44
	0.20	1.38 ± 0.08(2)	2.91 ± 0.30
	0.16	1.42 ± 0.18(4)[d]	3.00 ± 0.46

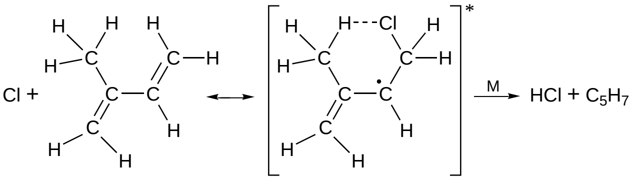
[a] Relative to *n*-butane; number of runs shown in parentheses. [b] Using $k(n\text{-butane}) = (2.11 \pm 0.18) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K;[13] errors include both those in the rate constant ratio and that associated with the *n*-butane rate constant. [c] Error for single run is 2σ for that run; for the remaining experiments it is twice the standard deviation of the mean of the individual experiments. [d] Two runs carried out in N_2.

In summary, abstraction of an allylic hydrogen is a small, but significant, pathway in the chlorine atom reaction with isoprene. The three approaches used here, HCl yields by FTIR, kinetics of the isoprene compared to the isoprene-d_8 reaction, and the kinetics of isoprene relative to the butadiene reactions gives an average of 15 ± 4% ($\pm 2\sigma$) of the overall reaction, which proceeds by abstraction.

5. Pressure Dependence of the Isoprene and Isoprene-d_8 Reactions. The relative rate constants were measured as a function of total pressure. They decrease slowly as the total pressure is reduced from 760 Torr, and then slightly more rapidly below ~1 Torr. Table 3 summarizes the rate constants for chlorine atoms reacting with isoprene and isoprene-d_8 at pressures from 5 to 0.16 Torr. Since the reaction of chlorine atoms with alkanes is known to be pressure independent, the pressure dependence can be attributed entirely to the isoprene reactions.

The data in Table 3 indicate that the lowest pressures accessible in these experiments are still at the high-pressure end of the fall-off region and well above the low pressure, termolecular regime. Hence, obtaining values of the low-pressure limiting rate constant (k_0) is not feasible with these data. However, comparison to the reaction of chlorine atoms with ethene and propene[24,25] indicates that k_0 for the isoprene reaction must be significantly larger, consistent with the increased number of degrees of freedom in this larger molecule.

Surprisingly, the rate constants for isoprene and isoprene-d_8 coincide over this pressure range within the relatively large error bars for these low-pressure measurements. This is unexpected, given that there is a significant difference at 760 Torr which, as discussed above, is attributable to abstraction to form HCl. One might therefore have anticipated that the rate constants for isoprene would be consistently greater than those for isoprene-d_8 by a constant amount representing the additional, pressure independent, abstraction pathway available for the isoprene reaction. A possible explanation is that the formation of HCl is not a direct, bimolecular abstraction, but rather involves addition followed by elimination of HCl, e.g.,



If this path has a different pressure dependence than adduct formation, reaction 3, it could be important at 1 atm but decrease sufficiently rapidly so as to be negligible at pressures of ~1 Torr or less. In this case, the absolute rate constants and the pressure dependence for the reaction of chlorine atoms with both isoprene and isoprene-d_8 in the fall-off region where this HCl elimination is negligible should be the same, as is observed.

6. Atmospheric Implications. Isoprene emitted into the marine boundary layer by phytoplankton can react with Cl and OH during the day, with NO_3 at night, and with O_3 during both the day and the night.[31] Chlorine atom concentrations are expected to peak in the early morning hours, while OH typically peaks around noon. Taking a peak morning chlorine atom concentration of 10^5 atoms cm^{-3} and OH radical concentration of 10^5-10^6 radicals cm^{-3}, the lifetime of isoprene is 6 h with respect to reaction with Cl and 2.8−28 h with respect to reaction with OH. These can be compared to lifetimes of about 29 h with respect to reaction with 30 ppb O_3 and 17−1.7 h with respect to reaction with 1−10 ppt NO_3. Hence Cl, OH, and NO_3 may all contribute to the loss of isoprene in the early morning hours.

Unlike the OH reaction,[46] MVK and MACR are not major products in the chlorine atom−isoprene reaction, with their yields each being less than 13%. This is consistent with the small yield of HCOCl, (8 ± 6)% ($\pm 2\sigma$), which is expected to be produced simultaneously. However, the fraction of the reaction which produces HCOCl and photolyzes to form chlorine atoms leads to regeneration of atomic chlorine, rather than acting as a chlorine atom sink.

The major organic product(s) remain unidentified but are most likely α,β-unsaturated chlorine-containing carbonyl compounds, different from MVK and MACR produced in the OH−isoprene reaction. While these unidentified products should also be highly reactive in the marine boundary layer, their lifetimes are expected to be longer than the rapidly photolyzed chlorine atom precursors such as Cl_2 whose lifetime is only about 50 min at a solar zenith angle of 78°. Hence, once they are identified, they may be useful markers of chlorine atom chemistry for field studies in the marine boundary layer. Attempts are underway to synthesize and characterize some of the chlorine atom-containing compounds.

7. Conclusions. Chlorine atoms react at essentially the collision-controlled rate with isoprene at 298 K and 1 atm total pressure, $k = (4.6 \pm 0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} ($\pm 2\sigma$). Rate constants for the reactions of chlorine atoms with isoprene-d_8, 1,3-butadiene, and 1,3-butadiene-d_6 at 298 K and 1 atm were determined to be (3.8 ± 0.6), (4.2 ± 0.4), and (3.9 ± 0.40) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} ($\pm 2\sigma$). The percentage of the total reaction proceeding by abstraction based on three different approaches in the chlorine atom reaction with isoprene is 15 ± 4% ($\pm 2\sigma$). Studies of the pressure dependence of the rate constants for the reactions of isoprene and isoprene-d_8 suggest that HCl is not formed by direct abstraction but from intramolecular HCl elimination in a pressure dependent process. Formyl chloride is formed in small yields, 8 ± 6% ($\pm 2\sigma$), and upper limits to the yields of vinyl ketone and MACR, expected to be formed simultaneously, were calculated to be 13%. The major organic products appear to be unsaturated chlorine-containing carbonyl compounds which remain unidentified.

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