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Authors

Nordmeyer, Trent
Wang, Weihong
Ragains, Mark L
[et al.](#)

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Unique products of the reaction of isoprene with atomic chlorine: Potential markers of chlorine atom chemistry

Trent Nordmeyer, Weihong Wang, Mark L. Ragains, and Barbara J. Finlayson-Pitts

University of California, Irvine, Department of Chemistry, Irvine, California

Chet W. Spicer, Robert A. Plastridge

Atmospheric Science and Applied Technology Department, Battelle, Columbus, Ohio

Abstract. The contribution of atomic chlorine to the chemistry of marine regions as well as the Arctic at ground level at polar sunrise is the subject of a number of recent studies. However, identifying the specific chlorine atom precursors has proven difficult. One potential approach is the measurement of definitive products of chlorine atom reactions, for example with biogenic hydrocarbons. We report here product studies of the chlorine atom reaction with isoprene using ppm concentrations at one atmosphere air and 298 K in a NO_x -free system using atmospheric pressure ionization-mass spectrometry (API-MS) as well as GC-MS. 1-chloro-3-methyl-3-butene-2-one (CMBO) is identified as a unique product of this reaction, and there is evidence of the formation of three additional isomers of CMBO as well. Methyl vinyl ketone (MVK) is formed in small yields ($9 \pm 5\%$), consistent with earlier studies of this reaction in which an upper yield of 13% was reported. The stable product expected from allylic hydrogen atom abstraction (measured in earlier kinetic studies to be 15% of the total reaction), 2-methylene-3-butenal, is also tentatively identified using API-MS. Assuming that similar chemistry occurs at the ppb-ppt levels found in the atmosphere, identification of CMBO and/or its isomers in field studies could provide strong evidence of chlorine atom chemistry in low NO_x environments where there are also sources of isoprene.

Introduction

The role of sea salt particles in the chemistry of the troposphere has been recognized for a number of years [Cicerone, 1981]. More recently, the potential for generation of photochemically active chlorine-containing products which subsequently photolyze to generate chlorine atoms has been of great interest [Finlayson-Pitts, 1993; Graedel and Keene, 1995; Keene et al., 1996; Behnke et al., 1997].

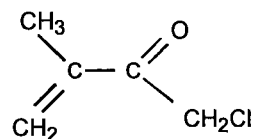
Observations in air to date provide evidence primarily for the existence of Cl_2 in marine areas. For example, Keene and coworkers [Keene et al., 1993; Pszenny et al., 1993] measured inorganic chlorine-containing compounds other than HCl using a mist chamber. While individual compounds were not identified, they were hypothesized to include Cl_2 and possibly other species such as HOCl. Recently, Spicer and coworkers (1996) specifically identified Cl_2 at concentrations up to 150 ppt for the first time in coastal marine areas using atmospheric pressure ionization mass spectrometry (API-MS). One or more photolyzable chlorine and bromine atom precursors whose

identity is not known have also been measured recently at ground level in the Arctic at polar sunrise [Impey et al., 1997]. The sources of these compounds are not known, but may include reactions of NaCl and NaBr as well as other sea salt components such as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [Langer et al., 1997] with various oxides of nitrogen and perhaps ozone, accompanied by a recycling mechanism [Barrie et al., 1988; McConnell et al., 1992; Fan and Jacob, 1992; Finlayson-Pitts, 1993; Graedel and Keene, 1995; LeBras and Platt, 1995; Mozurkewich, 1995; Tang and McConnell, 1996; Sander and Crutzen, 1996; Vogt, Crutzen and Sander, 1996].

Another potential approach to investigating chlorine atom production in the troposphere is to identify and measure any unique chlorine-containing products of its reactions with organics. For example, significant quantities of isoprene are produced by deciduous trees and shrubs in coastal areas [e.g. see Guenther et al., 1995]; in addition, there appears to be a source over the oceans since it has been shown to be generated by phytoplankton in seawater [Bonsang et al., 1992; Moore et al., 1994; Milne et al., 1995; McKay et al., 1996]. Isoprene emitted in coastal areas or in the marine boundary layer may be oxidized by O_3 , NO_3 (at night), OH (during the day) as well as Cl atoms at dawn. If the Cl-isoprene reaction gives unique chlorine-containing products, they could serve as "markers" for chlorine atom chemistry.

The kinetics and mechanism of reaction of chlorine atoms with isoprene have been studied recently [Ragains and Finlayson-Pitts, 1997]. As expected for a di-unsaturated alkene, the reaction is fast, with a rate constant of $(4.6 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ) at 298 K and one atmosphere pressure. A small but significant fraction, $15 \pm 4\%$ (2σ), of the overall reaction proceeds by abstraction of an allylic hydrogen, which is expected to lead to the formation of 2-methylene-3-butenal as a stable product in air. The remaining 85% of the reaction must proceed via the initial addition of the chlorine atom to one of the double bonds, followed by reaction of the resulting alkyl radical with O_2 . This suggests the potential for formation of unique chlorine-containing products characteristic of this reaction.

We report here laboratory studies identifying 1-chloro-3-methyl-3-butene-2-one (CMBO):



and three of its isomers as unique products of the gas phase chlorine atom reaction with isoprene in air at room temperature. In addition, we have tentatively identified the expected abstraction product, 2-methylene-3-butenal.

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Experimental

Isoprene (Aldrich, 99%, stabilized with 100 ppm *p*-*tert*-butylcatechol) and isoprene- d_8 (Cambridge Isotope Laboratories, Inc., 98%, stabilized with hydroquinone) were first degassed using three freeze-pump-thaw cycles. The isoprene was then vacuum distilled into the gas phase, and aliquots were stored in a 5 L bulb. As expected, the low volatility inhibitors were not present in the gaseous isoprene at levels which could be detected by FTIR, GC-FID or API-MS. Cl_2 (Matheson, 99.5%) was trapped at liquid nitrogen temperature before use and stored as a gas in a 5 L bulb prior to use. The isoprene and Cl_2 gases were swept separately from a calibrated volume into a 50 L Teflon reaction chamber (Alltech) using ultra high purity air (Liquid Carbonic, Ultra Zero air), giving final concentrations in the range of 12–58 ppm isoprene and 4–19 ppm Cl_2 , respectively at one atmosphere total pressure. The mixture was photolyzed using eight Sylvania 350 Blacklights (30 Watt, F30T8/350BL) which provide UV radiation in the 300–450 nm region with a maximum intensity at ~360 nm. Total photolysis times were typically 10 minutes, resulting in an 18% loss of isoprene. All runs were carried out at room temperature.

The loss of isoprene was followed using GC-FID (Hewlett Packard Model 5890 with a Carle gas sampling valve) using a 80/120 Carbopack B/3%/SP-1500, 10 ft x 1/8 in packed column (Supelco) temperature programmed from 20 - 110° C at a rate of 6° C/min. Some API-MS studies were also carried out at shorter reaction times to confirm that the products observed at 10 minutes were also observed at lower extents of reaction.

Reaction products were analyzed by API-MS in the positive ion mode (Perkin Elmer Sciex, Model 300). This instrument consists of two sets of quadrupoles in series, separated by a collision cell. Ionization in the positive ion mode involves chemical ionization primarily by hydrogen ion transfer from protonated water clusters, $H^+(H_2O)_n$ which are formed by a corona discharge. After ionization, the sample moves through a stream of dry N_2 "curtain gas", which strips the water clusters from the ion to give a protonated parent at $m/z = (M+1)$ as well as some fragments. The use of only the first set of quadrupoles (Q1 scan) produces conventional mass spectra. Alternatively, selected ions exiting Q1 can be fragmented using collisionally activated dissociation (CAD) with N_2 to yield a unique fragmentation pattern. These fragments are then analyzed using the second set of quadrupoles to produce an MS/MS spectrum.

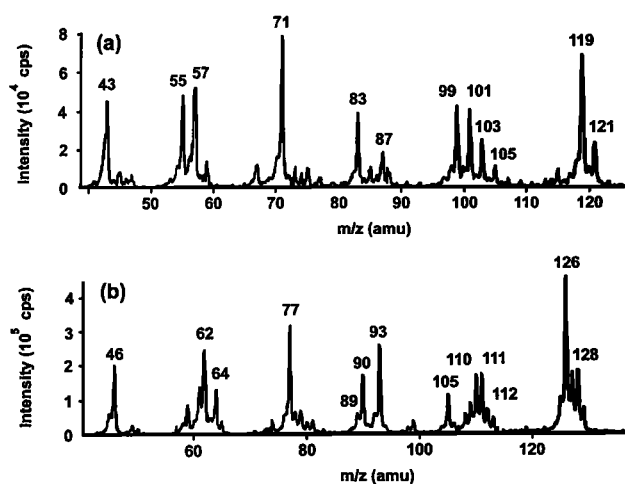


Figure 1. Q1 mass spectra of the products formed from the photolysis of Cl_2 in the presence of isoprene in 1 atm. air at 298 K (a) $[C_5H_8]_0 = 12$ ppm and $[Cl_2]_0 = 4$ ppm; (b) $[C_5D_8]_0 = 58$ ppm, $[Cl_2]_0 = 19$ ppm.

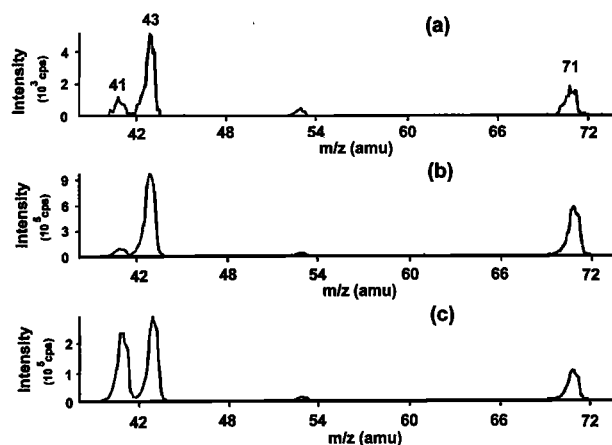


Figure 2. MS/MS spectra of $m/z = 71$ for (a) $Cl +$ isoprene reaction product under same conditions as Fig. 1a; (b) methyl vinyl ketone (direct introduction of vapor) and (c) methacrolein (direct introduction of vapor).

Analysis of photolysis products was also carried out by trapping the contents of the reaction chamber in a sampling loop at 77 K, and then warming the loop to 298 K to transfer its contents to the head of a GC column (Restek Corp., RTX2330, 30 m x 0.20 mm, 0.25 μm ID) installed in a GC-MS (Hewlett Packard Model 5890 Series II, mass selective detector 5971A). The column was held at 0° C for 10 minutes, heated at 10° C/min to 20° C where it was held for 10 minutes, heated at 10° C/min to 80° C, held for 5 minutes and then heated to 150° C at 20° C/min.

Reference spectra for API-MS and GC-MS were obtained for methyl vinyl ketone (Aldrich, 99%, stabilized with 0.1% acetic acid and 0.05% hydroquinone), methacrolein (Aldrich, 95%, stabilized with 0.1% monomethyl ether hydroquinone), and 1-chloro-3-methyl-3-butene-2-one (CMBO) with the same instrumental parameters as used in the isoprene studies. CMBO was synthesized from the reaction of chloroacetyl chloride with cyclopropane following the procedure of Hart and coworkers [Hart and Curtis, 1957; Hart and Levitt, 1959]. This gave a mixture of products, including CMBO. GC-MS analysis of the product mixture revealed several peaks; however, only one compound (approximately 49% of the total area) had parent peaks at $m/z = 118/120$. The fragmentation pattern of this peak and the retention time were used as a reference for comparison to the products formed in the reaction of chlorine atoms with isoprene. The proton NMR spectrum was also consistent with a mixture containing predominantly CMBO.

Results and Discussion

Figure 1a shows a typical Q1 scan obtained after photolysis of Cl_2 in the presence of isoprene for 10 minutes. Figure 1b shows the analogous spectrum after reaction with isoprene- d_8 .

Products responsible for $m/z = 71$ and 119 (with its associated ^{37}Cl isotope peak at 121) in Fig. 1a were probed using reference compounds. Figure 2a compares the MS/MS for $m/z = 71$ for the product obtained from the photolysis experiment to those from methyl vinyl ketone (Fig. 2b) and methacrolein (Fig. 2c) which are products of the OH-isoprene reaction [Carter and Atkinson, 1996] and are potential products of the $Cl +$ isoprene reaction [Ragains and Finlayson-Pitts, 1997]. The lack of a strong fragment peak at $m/z = 41$ supports identification of this product as methyl vinyl ketone, although a small contribution from methacrolein cannot be ruled out. A yield of $9 \pm 5\%$ was estimated for methyl vinyl ketone product from independent calibrations of the API-MS using the authentic compound.

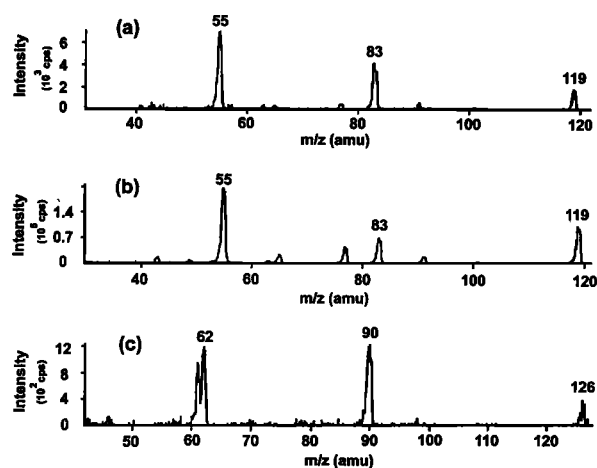
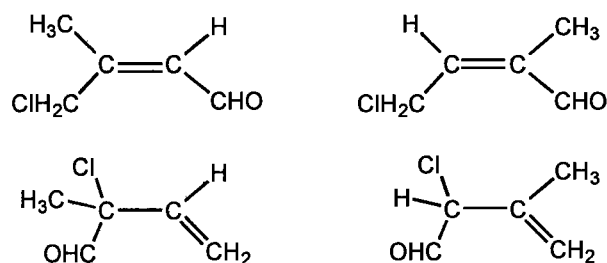


Figure 3. MS/MS spectra of $m/z = 119$ for (a) Cl + isoprene reaction product under same conditions as Fig. 1a; (b) synthesized sample of CMBO; (c) Cl + isoprene- d_8 reaction under same conditions as Fig. 1b.

Figures 3a and 3b show the MS/MS for $(M+1) = 119$ for the product formed in the Cl-isoprene reaction as well as for the CMBO reference. Although there are substantial impurities in the synthesized CMBO as determined from GC-MS, none showed peaks at $m/z = 118$ and 120. The MS/MS fragmentation patterns of the reaction product and the synthesized compound are similar, with major fragments at $m/z = 83$ and 55 which correspond to loss of HCl ($m/z = 83$) and loss of both HCl and CO from the parent ion ($m/z = 55$). The products of the isoprene- d_8 reaction with chlorine atoms have a peak at $m/z = 126$ in the Q1 scan, which would be expected for fully deuterated analogs of the $m/z = 119$ products (Fig. 3c). The MS/MS of this peak has major fragments at $m/z = 90$ and 62, again corresponding to the loss of HCl and then CO from the parent ion, where the source of H is the ionizing water cluster. The peak at $m/z = 61$ may be due to H-D exchange during ionization.

There are four possible unsaturated carbon atoms to which chlorine atoms can add, and isomerization of the double bond to the C2-C3 position can also occur, yielding isomers of CMBO such as the following:



To assess the possible formation of such isomers, GC-MS studies were also performed. The chromatogram of the products from the chlorine atom-isoprene reaction shows a number of product peaks (Fig. 4a). The peak labeled *A* in Fig. 4a is at the same retention time and has the same electron impact mass spectrum (EI-MS) as CMBO, providing further confirmation of CMBO as a product of the chlorine atom-isoprene reaction. However, at least three other peaks (labeled *B*, *C*, and *D* in Fig. 4a) had EI-MS showing the highest masses at 118/120 (Fig. 4c-e) indicating that indeed, more than one isomer is formed. (The small peak between *A* and *B* in Fig. 4a is the addition product of

the dark reaction of isoprene with Cl_2 , likely formed during condensation of the product mixture in the sampling loop [Hatch and Ijam, 1975].

Because purified, authentic samples of all isomers in addition to CMBO are not available, the product yields have not yet been quantified. However, the four peaks showing 118/120 as the highest masses comprised an average of $77 \pm 3\%$ (2σ) of the total peak area of all the reaction products (excluding the product of the dark reaction), suggesting these are major products of the reaction. Of the total area of the isomers *A*, *B*, *C* and *D*, CMBO (peak *A*) comprises $28 \pm 12\%$ (2σ).

The Q1 scan of the chlorine atom-isoprene reaction (Fig. 1), contains a peak at $m/z = 83$ which is much larger than can be attributed to fragmentation of the $M+1$ ion of CMBO. This peak is consistent with the expected product of the abstraction pathway, 2-methylene-3-butenal (C_5H_6O), which earlier studies [Ragains and Finlayson-Pitts, 1997] have shown accounts for $15 \pm 4\%$ (2σ) of the overall reaction. The MS/MS of $m/z = 83$ showed a single major fragment at $m/z = 55$, corresponding to the loss of CO from the parent ion. Synthesis of this compound is needed to confirm this tentative identification. The corresponding $(M+1)$ peak for the C_5D_6O product from the deuterated experiment is not observed, since the kinetic isotope effect decreases the abstraction to negligible levels [Ragains and Finlayson-Pitts, 1997].

In addition to the peaks at $m/z = 119$, 83 and 71, a number of other peaks were observed in the Q1 scan (Fig. 1a). Plausible molecular formulae corresponding to $m/z = 87$, 99, 101, 103 and 105 are: $87-C_4H_6O_2$, $99-C_5H_6O_2$, $101-C_5H_8O_2$, and $103/105-C_5H_7Cl$. However, identification of the products responsible for

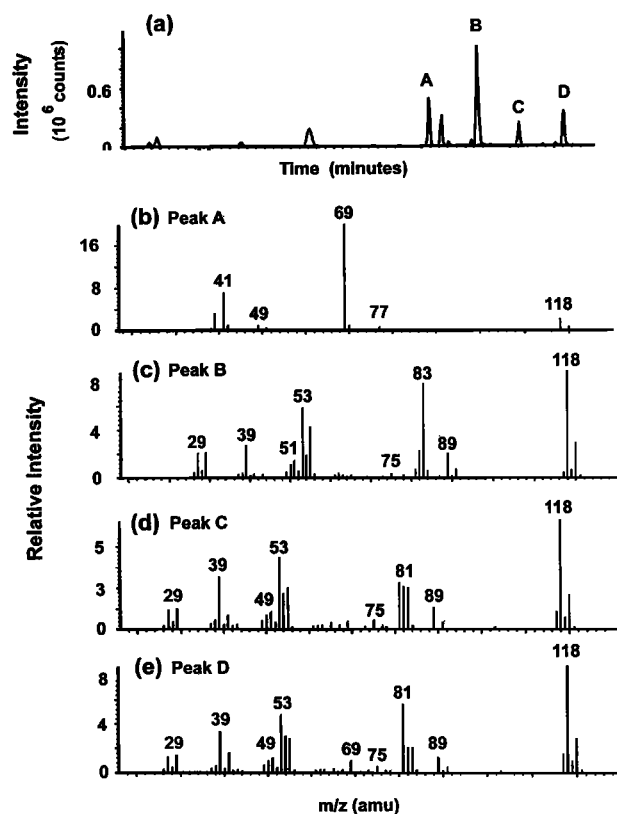


Figure 4. GC-MS analysis of products of Cl + isoprene under same conditions as Fig. 1a; (a) chromatogram of reaction mixture; (b) - (e) EI-MS of peaks marked *A*, *B*, *C* and *D* in Fig. 1a. The peak marked *A* is identified as CMBO using the retention time and EI-MS.

these peaks will require synthesis and purification of isomers corresponding to these species.

These reactions were carried out without the addition of NO_x and hence are applicable to low NO_x environments. Initial experiments using 2.5 ppm isoprene and 1.25 ppm Cl₂ indicate that the addition of 1.0 ppm NO leads to an induction time of ~3 minutes and lower peak intensities for the formation of *m/z* = 119/121. Preliminary FTIR and modeling studies indicate that under these conditions, the chemistry becomes very complex, with rapid conversion of NO to NO₂ and significant production of organic peroxy nitrates at the ppm concentrations required in these studies. Under these conditions, significant generation of OH is predicted, which then also reacts rapidly with both isoprene and its reaction products. Further work is underway to explore this complex system in more detail.

Conclusions

A unique chlorine-containing reaction product, 1-chloro-3-methyl-3-butene-2-one (CMBO), has been identified in the reaction of ppm concentrations of isoprene with atomic chlorine at atmospheric pressure and 298 K in NO_x-free air. Isoprene is ubiquitous in the troposphere, and chlorine atoms are formed by photolysis of the halogenated products of reactions of NaCl and other chlorides in sea salt particles. Hence, assuming similar chemistry occurs at the lower concentrations found in the troposphere, CMBO and its isomers may serve as unique markers for chlorine atom chemistry in future field studies of low NO_x coastal regions and the marine boundary layer.

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T. Nordmeyer, W. Wang, M. L. Ragains, and B. J. Finlayson-Pitts, Department of Chemistry, University of California, Irvine, CA 92717-2025. (e-mail: bjfinlay@uci.edu)

C. M. Spicer, R. A. Plastringe, Atmospheric Science and Applied Technology Department, Battelle, Columbus, OH 43201. (e-mail: spicer@battelle.org)

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