Products and Mechanisms of the Reactions of 1,3-Butadiene with Chlorine Atoms In Air

Weihong Wang and Barbara J. Finlayson-Pitts

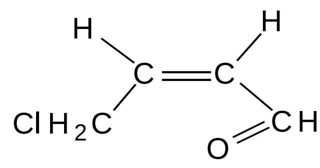
Department of Chemistry
University of California, Irvine

Introduction

Chlorine atoms may be generated by reactions of sea salt particles transported inland with air masses. Chlorine atom precursors have been measured at coastal sites and in the Arctic at polar sunrise (Keene *et al.*, 1993; Pszenny *et al.*, 1993; Impey *et al.*, 1997a, b; Spicer *et al.*, 1998). Once chlorine atoms are generated, they can react with ozone, with a rate constant of 2.9 x 10^{-11} cm^{-3} $molecule^{-1}$ s^{-1}, or organics, with rate constants at ~10^{-10} cm^{-3} $molecule^{-1}$ s^{-1}, in air. The Cl-organic reactions will eventually lead to ozone formation in the presence of NO_x. Thus chlorine atoms will have impacts on ozone level either way.

The reactions of chlorine atoms with organics proceed in a similar way as hydroxyl radicals (OH). For Cl reactions with alkenes, Cl would add to the double bond and form some unique chloro-carbonyl compounds, which would not otherwise be in the atmosphere, except for these kinds of reactions. A potential approach to investigate chlorine atom production in the troposphere is to identify and measure unique chlorine-containing products of the reactions of Cl with organics, such as 1,3-butadiene, in air. 1,3-Butadiene was classified as a hazardous air pollutant under 1990 Clean Air Act and is emitted from motor vehicles. If any unique chlorine-containing products can be determined from the reaction of Cl with 1,3-butadiene, they could serve as “markers” for chlorine atom chemistry in urban coastal areas where there are both sources of Cl atoms and 1,3-butadiene.

We present here studies of mechanism and formation of 4-chlorocrotonaldehyde (CCA),



CCA

a unique chlorine-containing compound, from the reaction of atomic chlorine with 1,3-butadiene in air at room temperature.

Experimental

Product studies of the Cl-butadiene reaction were carried out by GC-MS (Fig. 1) and FTIR (Fig. 2).

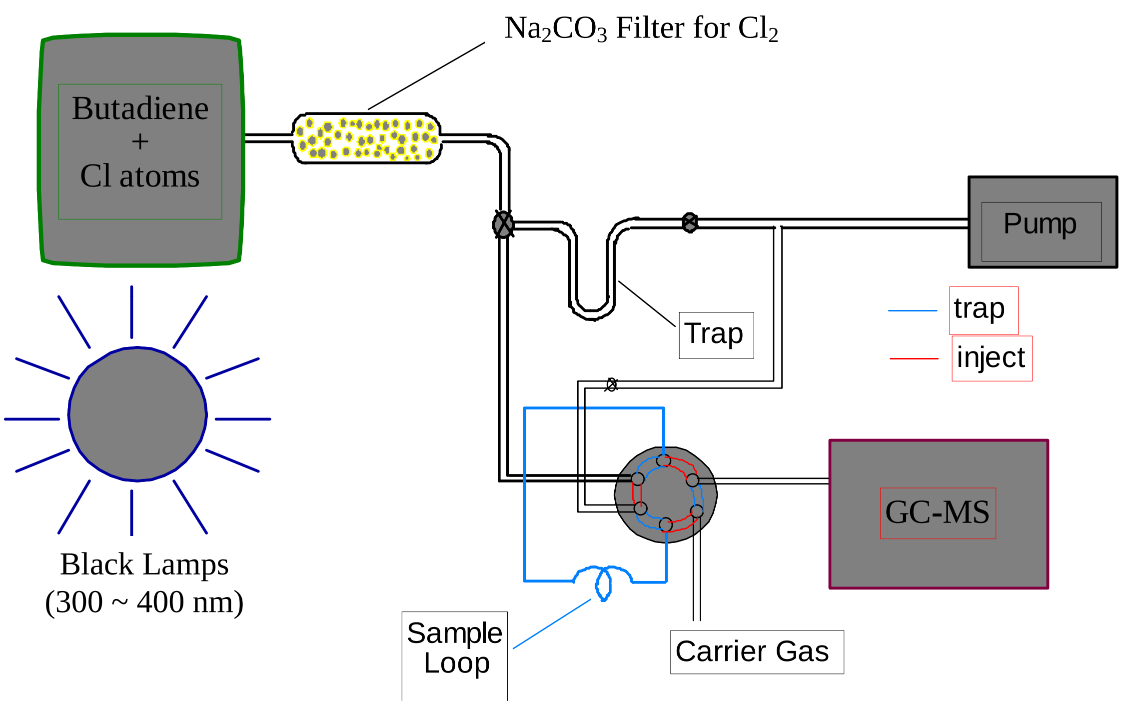


Figure1. GC-MS experimental apparatus

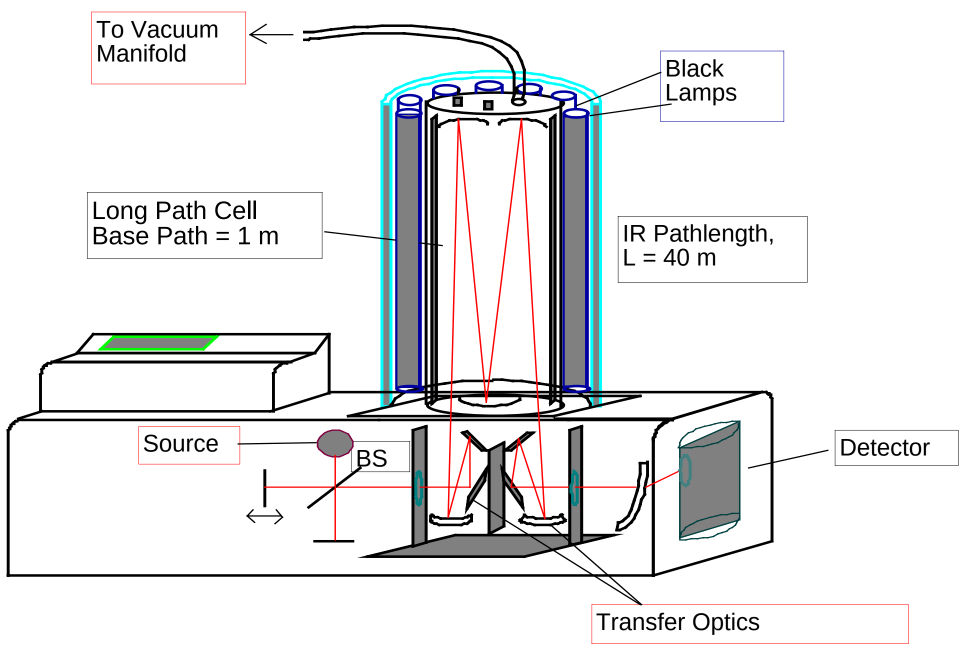


Figure 2. FTIR experimental apparatus

Results and Discussion

GC-MS studies show that many products are formed in the reaction of chlorine atoms with 1,3-butadiene (Fig. 3), including 4-chlorocrotonaldehyde (CCA), a unique chlorine-containing compound.

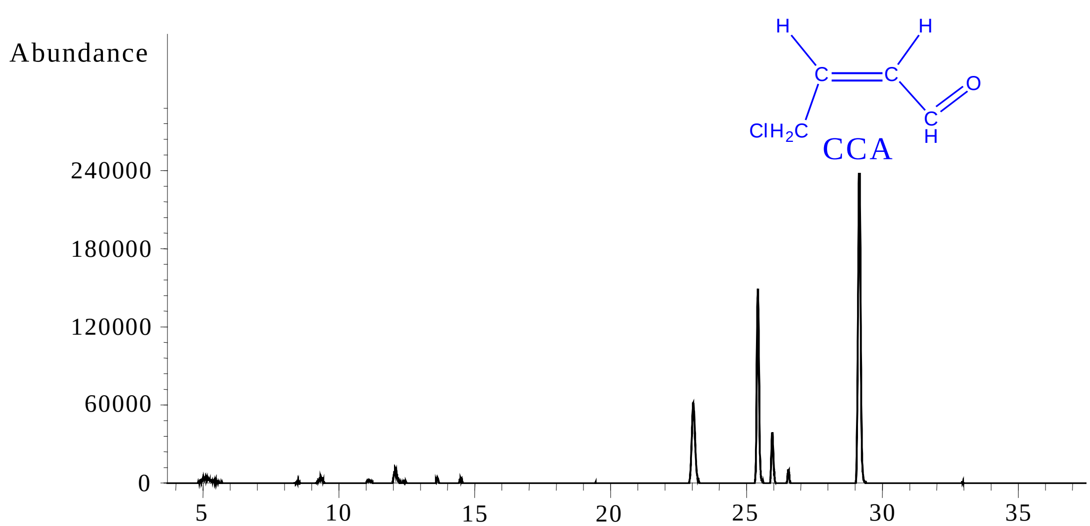


Figure 3. Gas chromatogram of the Cl-butadiene reaction products.

FTIR studies show that the yield of CCA is (35 ± 7)% (2σ) independent of the presence of NO (Fig. 4).

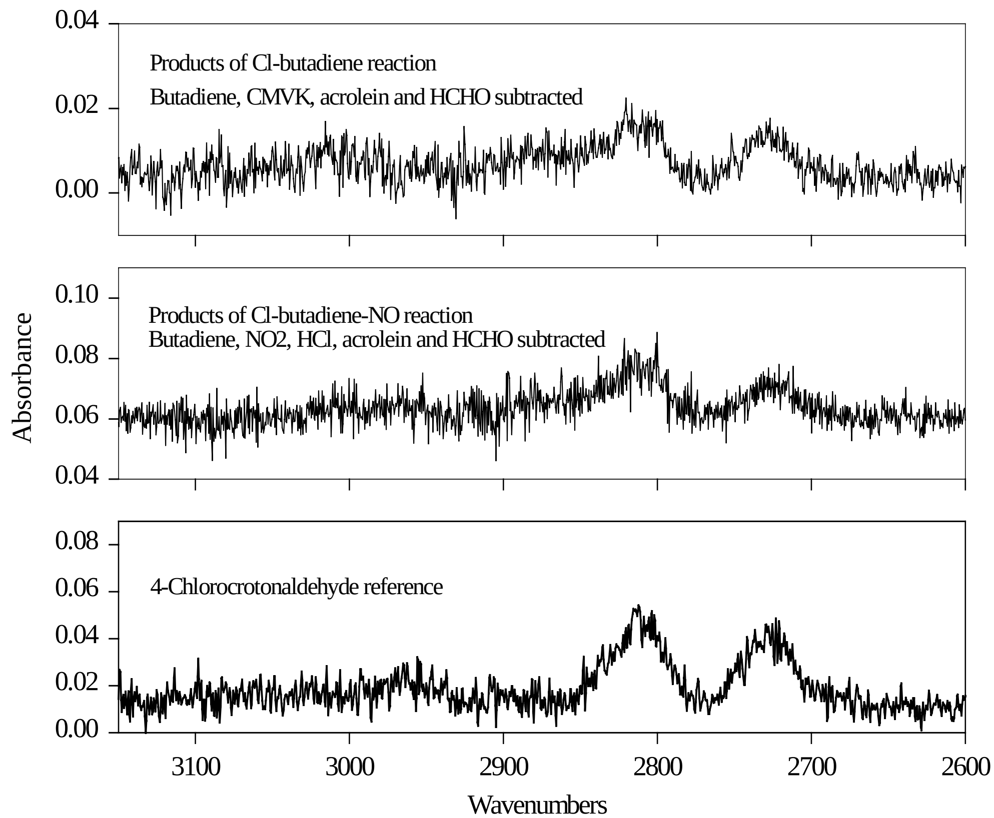


Figure 4. FTIR spectra of the Cl-butadiene reaction products and CCA reference.

4-Chlorocrotonaldehyde (CCA) has been identified as a unique chlorine-containing product from the reaction of 1,3-butadiene with chlorine atoms in the presence or absence of NO in air. CCA could therefore serve as a marker for Cl chemistry in coastal urban areas.

References

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