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Authors

Wang, Weihong
Finlayson-Pitts, Barbara J

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Unique markers of chlorine atom chemistry in coastal urban areas: The reaction with 1,3-butadiene in air at room temperature

Weihong Wang and Barbara J. Finlayson-Pitts

Department of Chemistry, University of California, Irvine, California

Abstract. Chlorine atoms are generated in the marine boundary layer, including coastal urban areas, through heterogeneous reactions of sea-salt particles. However, there are no measurements of tropospheric chlorine atoms, and few measurements of their precursors due to the difficulty in specifically identifying and measuring parts per trillion levels of these highly reactive species. We report here studies which suggest an alternate approach for elucidating the role of chlorine atoms in the chemistry of coastal urban areas: the identification and measurement of unique chlorine-containing products from the reactions of Cl with organics, in this case 1,3-butadiene, in air. The reaction of chlorine atoms with 1,3-butadiene (19 - 61 ppm), which is emitted by motor vehicles, was studied at 1 atm pressure in air at room temperature in both the absence and presence of NO (0 - 20 ppm). Cl₂ (4 - 16 ppm) was photolyzed to generate chlorine atoms, and the products were identified and measured using gas chromatography-mass spectrometry (GC-MS) and long path (40 m) Fourier transform infrared spectroscopy (FTIR). We identified 4-chlorocrotonaldehyde (CCA) as a unique chlorine-containing product from the Cl atom reaction with 1,3-butadiene in both the presence and absence of NO. The yield of CCA was (29 ± 7)% (2σ) in the absence of NO and (65 ± 20)% (2σ) in its presence. The yield of chloromethyl vinyl ketone (CMVK), another chlorine-containing compound from this reaction, was measured to be (19 ± 4)% (2σ) in the absence of NO; it was not observed in its presence. The reaction system was modeled using ACUCHEM to clarify the reaction paths and to allow extrapolation to ambient air conditions. These studies predict that CCA will be formed in coastal urban areas in the early morning hours at concentrations of ~ 100 ppt, which should be readily detectable by GC-MS and GC with electron capture detection (ECD). Some studies were also carried out on the isoprene reaction, and some potential unique products of its reaction with chlorine atoms are suggested as candidates for field investigations.

1. Introduction

In the lower troposphere, volatile organic compounds (VOC) emitted into the atmosphere undergo photochemical reactions in sunlight and in the presence of NO, eventually leading to ozone formation. The photochemical reactions are initiated by the attack on VOCs by OH radicals during the day, NO₃ radicals at night, and O₃ both day and night. There is also increasing evidence for a contribution by Cl atoms in coastal areas where they are generated from reactions of sea-salt particles to form photolyzable species such as Cl₂ [Finlayson-Pitts, 1993; Graedel and Keene, 1995; Keene *et al.*, 1996; Behnke *et al.*, 1997; Oum *et al.*, 1998; De Haan *et al.*, 1999; Knipping *et al.*, 2000]. The relative rates of decay of a series of hydrocarbons in the marine boundary layer suggest that they are oxidized in part by chlorine atoms as well as OH [Singh *et al.*, 1996; Wingenter *et al.*, 1996, 1999]. Chlorine atoms have also been shown to play a major role in the decay of alkanes in the Arctic at polar sunrise under conditions of ozone depletion [Jobson *et al.*, 1994; Solberg *et al.*, 1996;

Ariya *et al.*, 1998, 1999; Rudolph *et al.*, 1999; Ramacher *et al.*, 1999].

Once chlorine atoms are generated, they can react with ozone or with organics. The room temperature rate constants for reactions with most organics larger than C₂ are of the order of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, while that with O₃ is 1.2 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Thus reaction with organics will dominate at equal concentrations of the organics and O₃. At low organic concentrations which can be found in the remote marine boundary layer, ozone destruction by chlorine atoms is favored. However, at higher concentrations in coastal polluted areas, the reaction with organics is favored and in the presence of higher levels of NO_x characteristic of such areas will lead to ozone formation.

There have been several measurements of chlorine atom precursors in the troposphere. Keene, Pszenny, and coworkers measured inorganic chlorine compounds other than HCl in the range of 13 to 127 pptv (expressed as Cl₂^{*}) in a coastal site in Florida using a mist chamber technique [Keene *et al.*, 1993; Pszenny *et al.*, 1993]. Impey *et al.* [1997a, 1997b, 1999] measured total photolyzable chlorine compounds ranging from 9 to 100 pptv in the Arctic during the Polar Sunrise Experiment 1995 and 1997 by photolysis of the air sample and scavenging any Cl atoms generated by reaction with propene to form chloroacetone. The total photolyzable chlo-

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rine is hypothesized to include mainly Cl_2 and HOCl , but the individual compounds were not identified in either this study or mist chamber studies. A more specific approach by *Spicer et al.* [1998] involved measuring Cl_2 at concentrations up to 150 ppt directly for the first time in coastal marine areas using atmospheric pressure ionization-mass spectrometry (API-MS).

Despite such evidence for the presence of chlorine atom precursors in the lower troposphere, there is a paucity of data on such species, with respect to both geographical location and time. The lack of widespread and readily available techniques for measuring them has limited the extent of field studies directed toward elucidating the role of chlorine chemistry in the marine boundary layer. An alternate approach for investigating chlorine atom production in the troposphere is to identify and measure unique chlorine-containing products which would not otherwise be in the atmosphere except for Cl reactions with organics. If unique chlorine-containing products can be identified from the reaction of Cl with a particular organic, they could serve as "markers" for chlorine atom chemistry in the troposphere. Such products could be measured in the atmosphere using more conventional sampling and analysis techniques (such as gas chromatography-mass spectrometry (GC-MS) and gas chromatography with electron capture detection (GC-ECD)) and hence allow a more extensive search for chlorine atom chemistry in the lower atmosphere than has been possible to date.

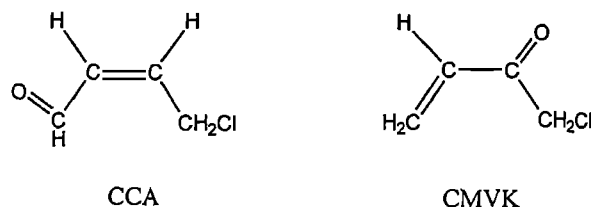
One such organic is 1,3-butadiene, which was specified as a "hazardous air pollutant" in the 1990 Clean Air Act and as a "toxic air contaminant" under California's air toxics program [California Air Resources Board, 1992; Kao, 1994; Kelly *et al.*, 1994]. It is widely used as a major component of synthetic rubber. Another major source of 1,3-butadiene is automobile exhaust [Ye *et al.*, 1997, 1998; Duffy *et al.*, 1998]. For example, in California, exhaust from motor vehicles is estimated to be ~96% of the annual emissions of 1,3-butadiene [California Air Resources Board, 1997]. The average concentration of 1,3-butadiene in the Los Angeles area is 2.2 ppb between 0600 and 0900 (E. M. Fujita and B. Zielinska, Desert Research Institute, personal communication, 2000).

One property of 1,3-butadiene is that it is highly reactive in the atmosphere. Once it is released into the air, it will react with OH radicals during the day, with NO_3 radicals at night, and with O_3 during both day and night [Atkinson, 1997, 2000]. It will also react with chlorine atoms if present [Atkinson and Aschmann, 1987; Wallington *et al.*, 1988; Finlayson-Pitts, 1993; Graedel and Keene, 1995; Bierbach *et al.*, 1996; Nordmeyer *et al.*, 1997; Ragains and Finlayson-Pitts, 1997; De Haan *et al.*, 1999].

While the kinetics of the reaction of chlorine atoms with 1,3-butadiene have been studied by several groups [Bierbach *et al.*, 1996; Ragains and Finlayson-Pitts, 1997; Notario *et al.*, 1997], studies of the mechanisms and products of the chlorine atom reaction with 1,3-butadiene have not been reported to date. The reactions of chlorine atoms with alkenes are thought to proceed mainly by initial addition to give chlorine-containing alkyl radicals [Lee and Rowland, 1977a, 1977b; Kaiser and Wallington, 1996a, 1996b; Ragains and Finlayson-Pitts, 1997; Stutz *et al.*, 1998; Finlayson-Pitts and Pitts, 2000]. In air the chloro-alkyl radicals will react with O_2 , followed by the self-reactions of the chlorine-containing alkyl peroxy radicals (in the absence of NO) or the reactions

of the chlorine-containing alkyl peroxy radicals with NO (in the presence of NO) to give chloro-alkoxy radicals. These should then decompose or react with O_2 to generate chloro-carbonyl compounds unique to these reactions.

The goals of this study were to elucidate, through laboratory studies, the mechanisms of the reaction of Cl atoms with 1,3-butadiene in sufficient detail to extrapolate to ambient air conditions. In particular, a search was made for unique chlorine-containing compounds which could serve as "markers" of chlorine atom chemistry in coastal urban areas. We show that there are two such products, 4-chlorocrotonaldehyde (CCA) and chloromethyl vinyl ketone (CMVK):



CCA is shown to be formed both in the presence and absence of NO, while the reaction paths forming CMVK are such that it is only generated in the absence of NO. These results are extrapolated to the Cl-isoprene reaction, and the implications for probing chlorine atom chemistry in polluted coastal areas are discussed.

2. Experimental Methods

Mechanisms and product studies were carried out using Fourier transform infrared spectroscopy (FTIR) and gas chromatography-mass spectrometry (GC-MS). The FTIR (Mattson, RS) has a long path (40 m) White cell [White, 1942] housed in the external sampling compartment and is equipped with a mercury cadmium telluride detector. Eight Sylvania 350 black lights (30 W, F30T8/350BL), oriented longitudinally about the cylindrical cell, provide UV radiation ($\lambda = 300\text{--}450$ nm with maximum intensity at 356 nm) to photolyze Cl_2 and generate chlorine atoms. Each spectrum consisted of 64 coadded scans at a resolution of 1 cm^{-1} . Cl_2 (5–16 ppm), 1,3-butadiene (19–61 ppm), and NO (0–20 ppm) were expanded into the evacuated long path cell directly from a glass manifold system attached to the cell, and air (Ultra-high purity (UHP) zero air, 99.99%, Oxygen Service Company) was added to a total pressure of 1 atm. Dark reactions between 1,3-butadiene and Cl_2 were not observed within these concentration ranges. The mixture was photolyzed for varying times, and the spectra were taken after the UV radiation was turned off.

For the GC-MS studies, 1,3-butadiene (20–40 ppm), Cl_2 (4–6 ppm) and NO (0–15 ppm) were mixed in a 50 L Teflon reaction chamber at 1 atm total pressure in air. The mixture was photolyzed by UV radiation for varying times using a set of black lamps (20 W, F20T12/350BL). After the UV radiation was off, the sample was preconcentrated in a liquid nitrogen trap before injecting onto the GC column. Because reactions between Cl_2 and 1,3-butadiene were observed in the dark as the trap was warmed, it was necessary to remove the excess Cl_2 prior to the cold trap. A filter coated with 1% weight/volume sodium carbonate, 1% vol/vol glycerol in 1:1 methanol/water solution was placed upstream of the liquid nitrogen trap to remove Cl_2 and eliminate these potential in-

interferences. The contents of the trap were then warmed, transferred to the gas sampling loop, and injected onto the GC column (Restek Corporation, RTX2330, 30 m x 0.20 mm, 0.25 μm ID) installed in a GC-MS (HP 5890 Series II, MS 5971A).

Most of the chlorine-containing products expected from the reaction of chlorine atoms with 1,3-butadiene are not commercially available and therefore had to be synthesized as standards for product studies. To synthesize 4-Chloro-crotonaldehyde (CCA), Cl_2 was added to 1-acetoxy-1,3-butadiene, followed by the hydrolysis of the intermediate compound [Berenguer *et al.*, 1971]. The structure was confirmed using ^1H NMR, δ 4.27 (d, 2H, $-\text{CH}_2\text{Cl}$), δ 6.34 (hex, 1H, $-\text{CH}=\text{}$), δ 6.85 (hex, 1H, $-\text{CH}=\text{}$), δ 9.62 (d, 1H, $-\text{CHO}$) and GC-MS (see below). Chloromethyl vinyl ketone (CMVK) was synthesized from the reaction of chloroacetyl chloride with ethylene following the procedure of Arbuzov and Korolev [1962]. The structure of CMVK was confirmed using ^1H NMR, δ 4.06 (s, 2H, $-\text{CH}_2\text{Cl}$), δ 5.82 and δ 6.22 (q, 2H, $=\text{CH}_2$), δ 6.40 (q, 1H, $-\text{CH}=\text{}$) and GC-MS (see below). The synthesis of 1-chloro-2-hydroxy-3-butene (CHB) was accomplished by the hypochlorination of 1,3-butadiene [Duescher and Elfarra, 1992]. CHB was characterized using GC-MS by comparing the mass spectrum to the published spectrum of CHB [Mass Spectrometry Data Centre, 1983]. The synthesis of 1-chloro-2-butene-4-ol (CBO) was carried out by the chlorination of 2-butene-1,4-diol [Ravikumar and Cheruvallath, 1996]. The structure of CBO was confirmed using ^1H NMR, δ 1.8 (broad, s, 1H, $-\text{OH}$), δ 4.2 (m, 4H, $-\text{CH}_2\text{Cl}$ and $-\text{CH}_2\text{O}$), δ 6.0 (m, 2H, $-\text{CH}=\text{CH}-$). There is no molecular ion in the mass spectrum, and the spectrum does not appear to have been reported in the literature; however, the fragmentation pattern is consistent with its structure [McLafferty, 1980], showing the largest fragment at $m/z = 76$ ($\text{C}_3\text{H}_5^{35}\text{Cl}$), with an associated ^{37}Cl peak at $m/z = 78$. For example, 1-butene-3-chloro-4-ol, similar to CBO, is reported to have a similar MS fragmentation pattern as CBO with the largest fragment at $m/z = 76$ ($\text{C}_3\text{H}_5^{35}\text{Cl}$) with its associated ^{37}Cl peak at $m/z = 78$ [Mass Spectrometry Data Centre, 1983].

To avoid potential problems of decomposition during sampling and analysis by GC, as has been observed in other studies of reactive organics [Tobias and Ziemann, 2000], the products were quantified *in situ* by long path FTIR. For 1,3-butadiene and the products measured here, linear correlations were observed between their concentrations and their IR absorbance in the CH stretching region (2600 – 3200 cm^{-1}). Therefore this region was used to fit the reference spectra to the product spectra using a fitting program MFC [Gomer *et al.*, 1995]. The fitted spectrum $f(\lambda)$ is defined by

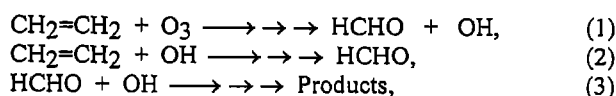
$$f(\lambda) = \sum_i a_i S_i(\lambda) + \text{constant},$$

where $S_i(\lambda)$ are reference spectra of known concentrations and a_i are scaling factors for the reference spectra from which the concentration of a compound (i) was obtained. After fitting, the residual was checked by subtracting the references from the product spectrum to ensure a good fit.

Reference spectra and calibrations for 1,3-butadiene, acrolein, CMVK, HCl, and NO_2 were obtained using authentic compounds. However, known concentrations of CCA in air could not be reliably generated due to a high wall loss. As a result, the calibration was obtained from FTIR spectra of solutions of CCA in CCl_4 . In order to assess whether this liquid

phase calibration could be quantitatively applied to the gas phase, calibrations were carried out for the related compound, crotonaldehyde, in both the liquid and gas phases. The integrated absorbance of the band at 2820 cm^{-1} in the gas phase was found to be 20% larger than that in the liquid phase for the same effective concentration. Therefore the CCA calibration in the liquid phase was corrected up by 20% for application to the gas phase.

The HCHO reference spectra were obtained from the reaction of ethylene with O_3 in the dark. Ozone was generated as a 3.5% mixture in O_2 (Air Liquide, ultrahigh purity, 99.999%) using a commercial ozonizer (Polymetrics, model T-816) and stored in a glass bulb. Ethylene (5–8 ppm, Matheson, 99.98%) and O_3 (1–2 ppm) were mixed together with air at 1 atm total pressure in the long path cell. The concentrations of ethylene were followed as a function of time by FTIR. The major reactions which form and destroy HCHO in this system can be represented by reactions (1)–(3),



where $k_2 = 8.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_3 = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [DeMore *et al.*, 1997]. The HCHO yield from the ethylene- O_3 reaction has been reported to be 1.03 [Grosjean and Grosjean, 1996] and the yield of OH radicals to be 0.12 [Atkinson *et al.*, 1992], respectively. The subsequent reaction of OH with ethylene in air generates the $\text{HOCH}_2\text{CH}_2\text{O}_2$ radical, which has been reported to form HCHO in 18–30% yield in the absence of NO [Jenkin and Cox, 1991; Barnes *et al.*, 1993]. We assumed a yield of 30% for this reaction (2); however, assuming an 18% yield would only change the predicted HCHO formed by 1%. The competition between reactions (2) and (3) is determined by the rate constants and the concentrations of ethylene and HCHO. Since the beginning concentration of HCHO was zero and the beginning concentration of ethylene was known, the concentrations of HCHO could be calculated from the measured loss of ethylene.

3. Results and Discussion

3.1. Reaction of Chlorine Atoms With 1,3-Butadiene in the Absence of NO

Figure 1 shows a typical chromatogram obtained after photolysis of the mixture of Cl_2 and 1,3-butadiene in 1 atm air at room temperature for 6 min in the absence of NO. As seen in Figure 1, the electron impact mass spectra (EI-MS) of peaks labeled A, B, and C in Figure 1a had the largest masses at 104/106, with the latter ratio approximately 3:1, as expected if these products contained chlorine. The peak labeled A has the same retention time and mass spectrum as CMVK, and peak C has the same retention time and mass spectrum as CCA. Peak B is tentatively assigned as 2-chloro-3-butenal based on the highest peak being at $m/z = 104$ and the fact that the mass spectrum is consistent with this structure with major fragments at $m/z = 39$ (loss of COH_2Cl) and at $m/z = 69$ (loss of Cl), similar to CCA. However, confirmation of the structure of the compound giving peak B was not possible due to the lack of availability of an authentic sample. Other chloro-alcohol compounds were also observed as products. From a comparison of the retention times and mass spectra of peaks

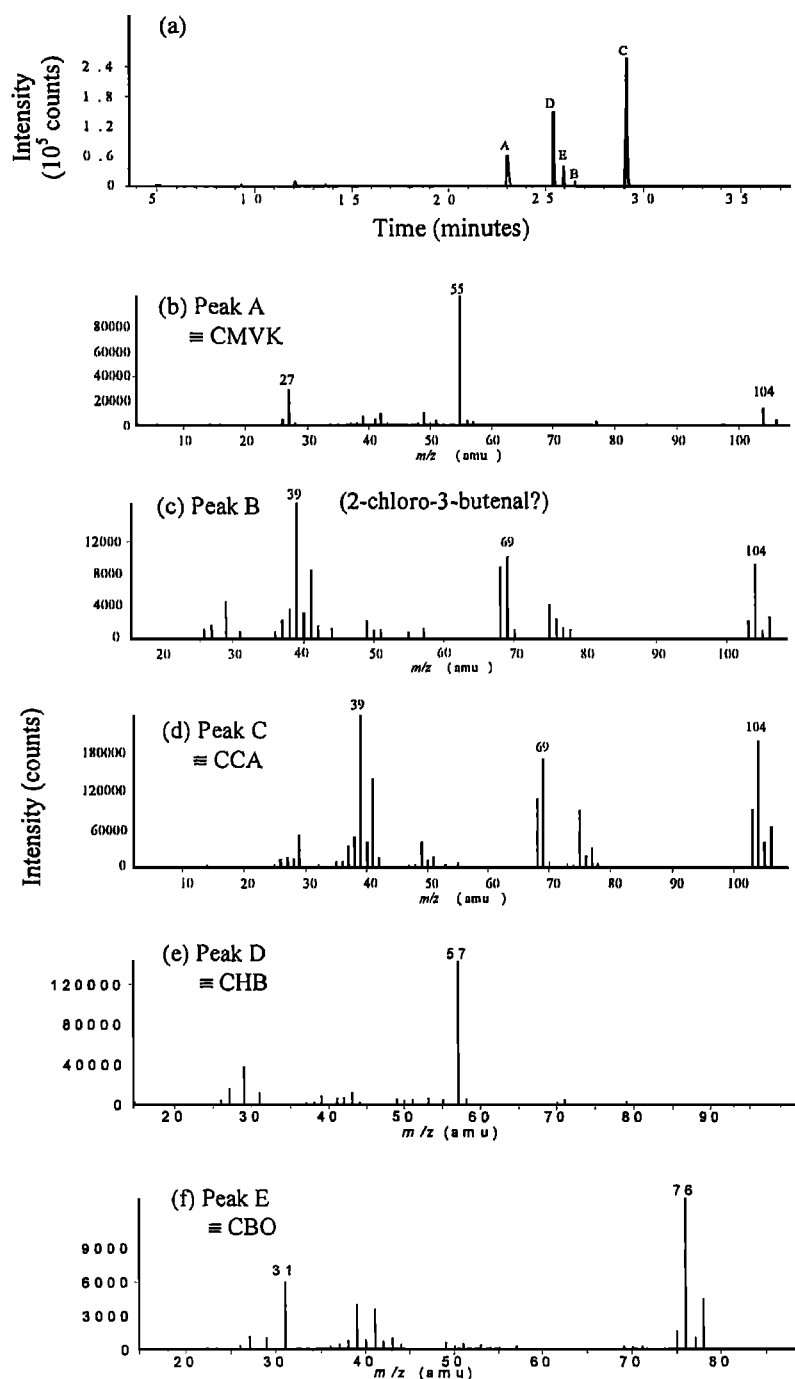
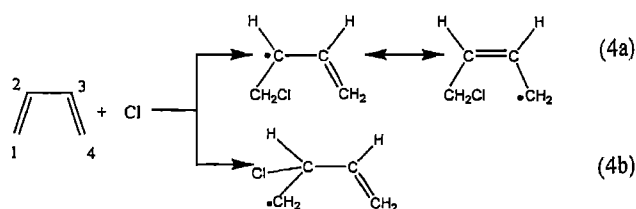


Figure 1. (a) Gas chromatogram of the reaction mixture of Cl_2 and 1,3-butadiene in the absence of NO after 6 min of photolysis in 1 atm air at room temperature, $[\text{butadiene}]_0 = 22$ ppm, $[\text{Cl}_2]_0 = 5$ ppm. (b – f) Electron impact mass spectra (EI-MS) of peaks A, B, C, D and E in Figure 1a.

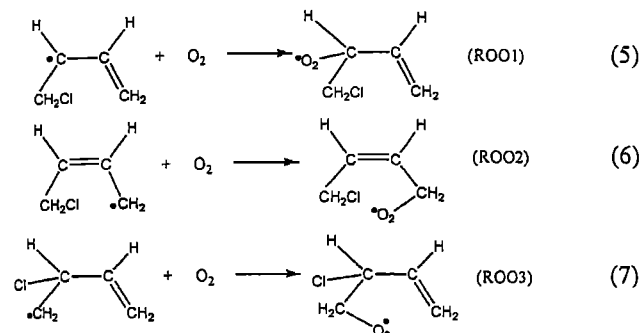
D and E, these were identified as 1-chloro-2-hydroxy-3-butene (CHB, peak D, Figure 1e) and 1-chloro-2-butene-4-ol (CBO, peak E, Figure 1f), respectively.

Previous kinetics studies of the Cl-butadiene reaction [Ragains and Finlayson-Pitts, 1997; Notario *et al.*, 1997; Fantechi *et al.*, 1998] showed that as expected, abstraction of vinyl hydrogens is small and addition to the double bond is the major reaction path. There are two possible positions where chlorine atoms can add, C1 (or C4), and C2 (or C3):

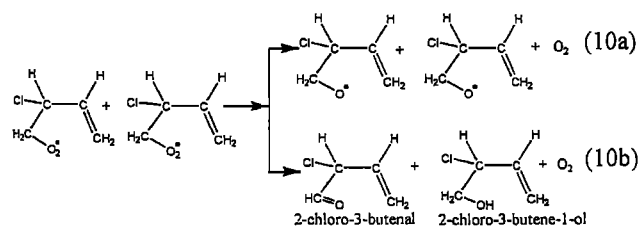
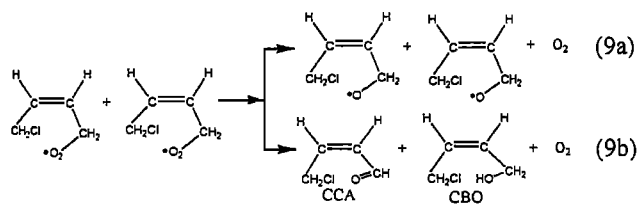
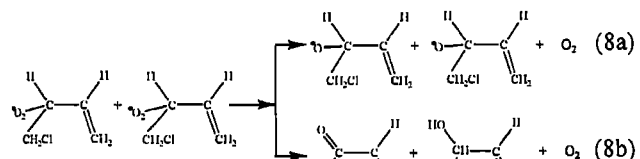


Path (4a) generates allyl radicals that are more stable than the primary alkyl radicals. For example, the enthalpies of forma-

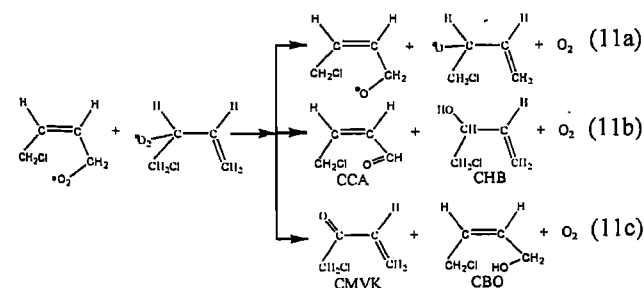
tion of the radicals formed in (4a) were estimated using the group additivity method [Benson, 1976] to be 24 kcal mol⁻¹ compared to 36 kcal mol⁻¹ for the radical formed in (4b). The chloro-alkyl radicals will react rapidly with O₂ to form chloro-alkyl peroxy radicals [Finlayson-Pitts and Pitts, 2000]:



In the absence of NO, alkyl peroxy radicals self-react [Lightfoot et al., 1992; Wallington et al., 1992; Finlayson-Pitts and Pitts, 2000]:

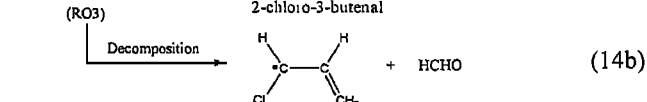
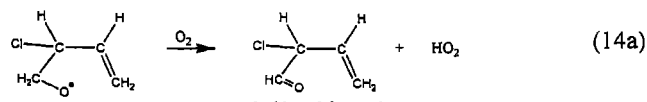
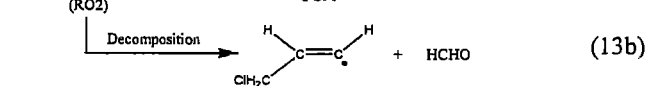
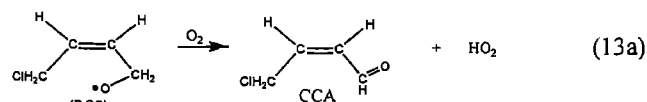
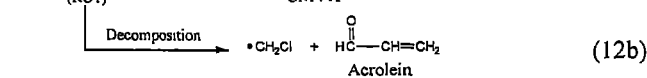
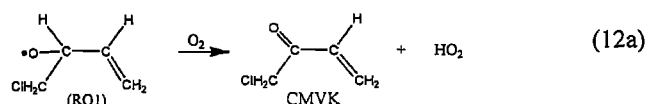


Alternatively, they can cross-react, for example,

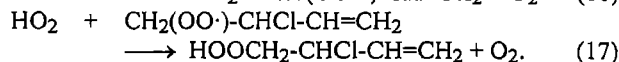
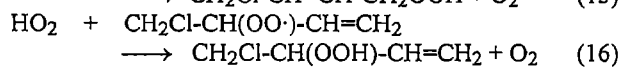
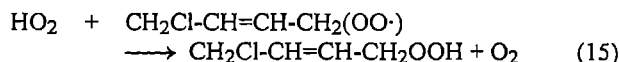


The branching ratio for the path which generates peroxides is normally small [Lightfoot et al., 1992; Wallington et al., 1992].

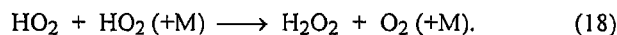
The chloro-alkoxy radicals from reactions (8a), (9a), (10a), and (11a) can, in principle, decompose or react with O₂:



(As discussed below, reaction (13b) is unlikely). Reaction of the chloro-alkyl peroxy radicals with HO₂ to form hydroperoxides may also occur:



In addition to reactions with RO₂, HO₂ undergoes a self reaction [DeMore et al., 1997]:



In short, the identification of CCA, CBO, CMVK, CHB, and possibly 2-chloro-3-butenal as products by GC-MS is consistent with known organic free radical chemistry in the gas phase. CMVK, CCA, CHB and CBO all originate from the allyl radicals formed in reaction (4a), while 2-chloro-3-butenal originates from the radicals formed in reaction (4b). As seen in Figure 1a, the peaks due to CMVK (peak A), CCA (peak C), CHB (peak D) and CBO (peak E) are all much larger than peak B, which has been tentatively assigned to 2-chloro-3-butenal. The higher yields of stable products originating from addition to the terminal carbon of 1,3-butadiene (path (4a)) are consistent with the higher stability of the allyl radicals relative to primary alkyl radicals [Benson, 1976].

Figure 2a shows the FTIR spectrum of the products of the Cl-butadiene reaction in the absence of NO after 2 min of photolysis in 1 atm air at room temperature. The spectrum at *t* = 0 has been subtracted so that the negative peaks reflect the loss of 1,3-butadiene. Strong absorptions around 1720 cm⁻¹, typical of carbonyls, are evident. For comparison, reference spectra of CCA (Figure 2b), CMVK (Figure 2c), acrolein (Figure 2d) and 1,3-butadiene (Figure 2e) are also shown. (Peaks at around 2350 cm⁻¹ and fine rotational structure at the 1600 cm⁻¹ region are absorptions of CO₂ and H₂O in room air

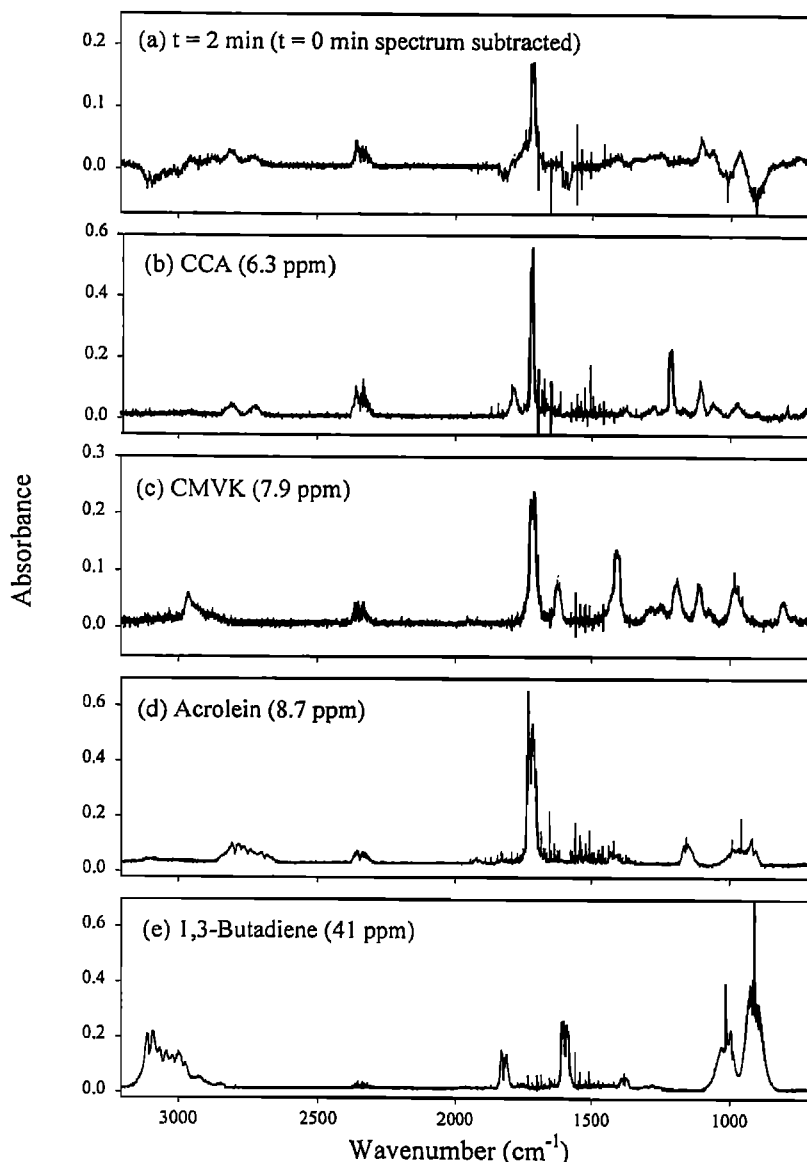


Figure 2. Fourier transform infrared (FTIR) spectra of (a) products of the Cl-butadiene reaction in the absence of NO after 2 min of photolysis in 1 atm air at room temperature, $[\text{butadiene}]_0 = 41$ ppm, $[\text{Cl}_2]_0 = 14$ ppm, $t = 0$ spectrum subtracted; (b) 4-chlorocrotonaldehyde (CCA) reference, $[\text{CCA}] = 6.3$ ppm; (c) chloromethyl vinyl ketone (CMVK) reference, $[\text{CMVK}] = 7.9$ ppm; (d) acrolein reference, $[\text{acrolein}] = 8.7$ ppm; and (e) 1,3-butadiene reference, $[\text{1,3-butadiene}] = 41$ ppm. All spectra were taken in 1 atm air at room temperature.

due to a changing purge of the external optics during the run.)

FTIR was used to measure the product yields of CCA, CMVK, and acrolein based on peaks in the 2700–3000 cm^{-1} C-H stretching region. The product spectra were fit using a fitting program MFC [Gomer *et al.*, 1995] with a linear combination of reference spectra for 1,3-butadiene, CCA, CMVK, and acrolein. After fitting, the residual was checked by subtracting the references from the product spectrum. Figure 3a shows a product spectrum after reference spectra of butadiene and a small amount of acrolein were subtracted. Figures 3b and 3c show reference spectra for CCA and CMVK, respectively, and Figure 3d shows a combination of CCA and CMVK chosen to fit the product spectra in Figure 3a. While three of the peaks in Figure 3a can be attributed to CCA and CMVK, there is an additional weak peak at ~ 2880 cm^{-1} which may be due to one of the minor products.

Figure 4 shows typical time-concentration profiles for 1,3-butadiene, CCA, and CMVK. A linear fit to the product formation was made for $< 20\%$ loss of 1,3-butadiene (within 2 min of photolysis), and the product yields (uncorrected for secondary reactions) were calculated from the slopes of the lines:

$$\text{Product yield} = \frac{d[\text{product}]/dt}{-d[\text{1,3-butadiene}]/dt}$$

The product yields were measured to be $(27 \pm 7)\%$ (2σ) for CCA and $(18 \pm 4)\%$ (2σ) for CMVK, respectively (Table 1). Small yields of acrolein were also observed and are summarized in Table 1. The losses of CCA and CMVK due to secondary reactions with chlorine atoms were small. The meas-

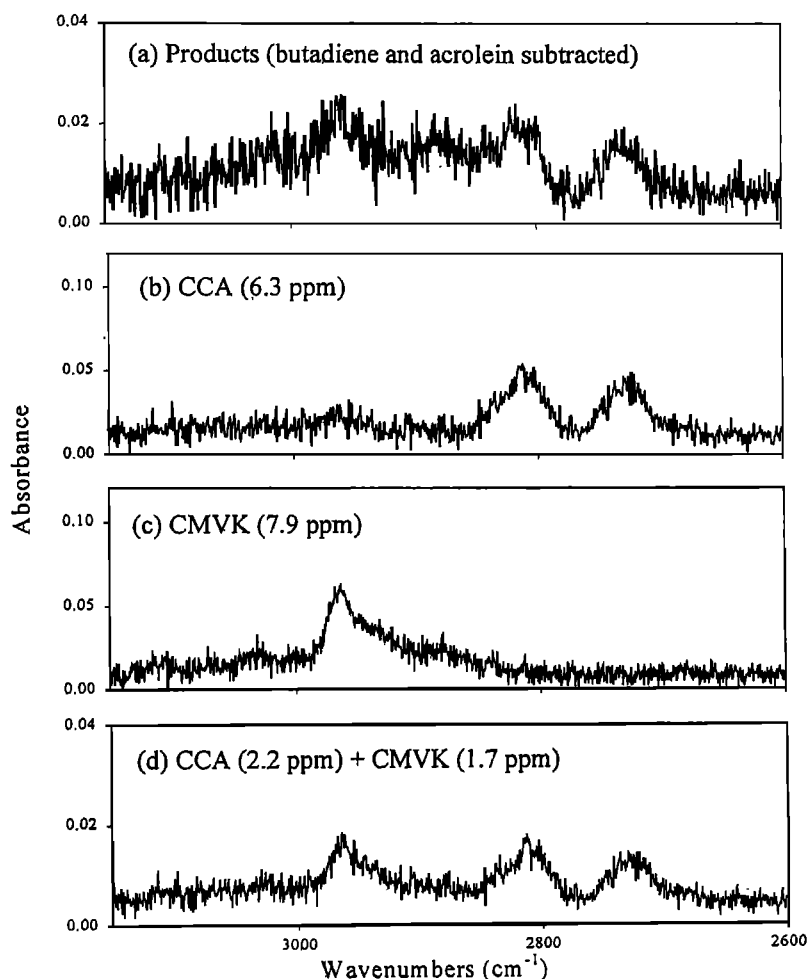


Figure 3. FTIR spectra of (a) products of the Cl-butadiene reaction under same conditions as Figure 2, reference spectra of butadiene and acrolein subtracted; (b) CCA reference, [CCA] = 6.3 ppm; (c) CMVK reference, [CMVK] = 7.9 ppm; (d) 0.35 of Figure 3b + 0.22 of Figure 3c.

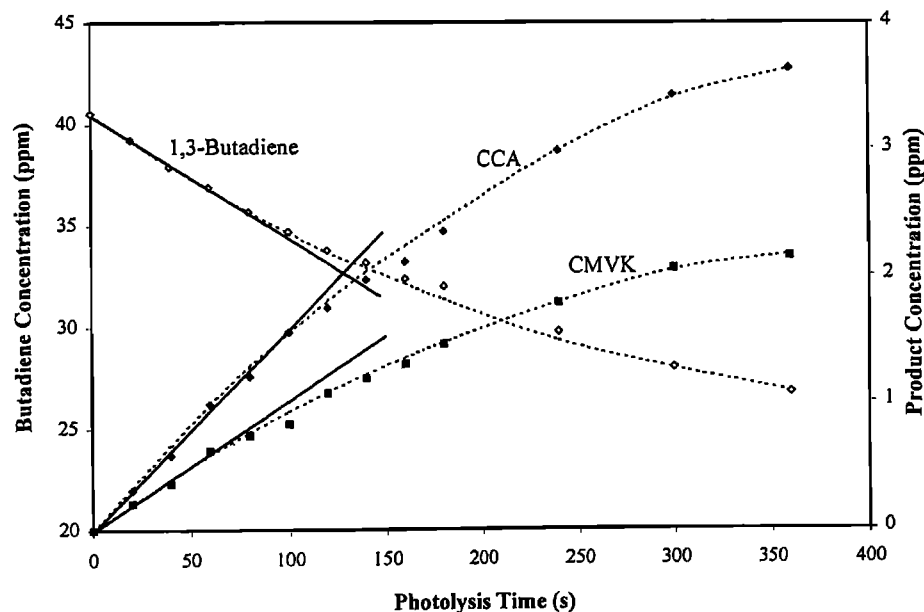


Figure 4. Typical time-concentration profile of the Cl-butadiene reaction products and 1,3-butadiene in the absence of NO. Open diamonds represent 1,3-butadiene. Solid diamonds represent CCA. Solid squares represent CMVK. The solid lines show the fits for the loss of butadiene and the increase of CCA and CMVK for first 2 min of photolysis which were used to obtain the product yields. The dotted lines are guides for the eye for the experimental data.

Table 1. Product Yields of the Cl-Butadiene Reaction in the Absence of NO in 1 atm Air at Room Temperature From FTIR Studies

Experiment	[Butadiene] ₀ , ppm	[Cl ₂] ₀ , ppm	Yields of CCA ^a , %	Yields of CMVK ^a , %	Yields of Acrolein, %
1	61	6	28	15	6
2	60	6	27	18	9
3	59	5	27	19	3
4	55	5	29	19	5
5	41	14	29	15	6
6	38	16	25	14	8
7	35	11	26	17	5
8	35	11	31	18	7
9	34	16	27	21	3
10	32	6	31	18	5
11	31	14	26	19	7
12	28	13	24	18	5
13	27	9	24	19	8
14	27	6	25	19	6
15	27	11	23	15	4
16	26	11	27	20	7
17	26	11	24	19	7
Average			27 ± 7 (2σ) ^b	18 ± 4 (2σ) ^b	6 ± 3 (2σ) ^b

^a CCA denotes 4-chlorocrotonaldehyde, and CMVK denotes chloromethyl vinyl ketone.

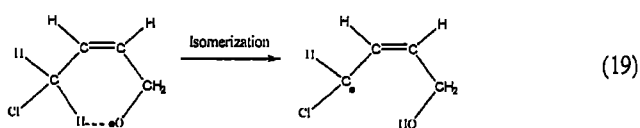
^b Errors are estimated from the standard deviation of the individual measurements and calibrations.

ured yields were corrected for these losses, giving initial yields for CCA and CMVK of (29 ± 7)% (2σ) and (19 ± 4)% (2σ), respectively.

Because CHB and CBO could not be clearly identified and measured using FTIR, their yields were estimated by comparing their peak areas in the GC-MS studies to those of CCA where the yield could be measured in an absolute manner *in situ* by FTIR. Based on a CCA yield of 27% and the GC-MS data such as those in Figure 1a, the yields of 1-chloro-2-hydroxy-3-butene (CHB) and 1-chloro-2-butene-4-ol (CBO) are estimated to be (17 ± 6)% (2σ) and (3 ± 3)% (2σ), respectively (Table 2). Assuming the rate constants for chlorine atom reactions with CHB and CBO are both 2 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, the yields of CHB and CBO corrected for secondary reactions with chlorine atoms are (18 ± 6)% (2σ) and (3 ± 3)% (2σ), respectively.

The yield of CHB is similar to that of CMVK, and both are much larger than that of CBO. CHB and CMVK originate from CH₂Cl-CH(OO·)-CH=CH₂, while CBO and CCA originate from CH₂Cl-CH=CH-CH₂(OO·). CMVK and CCA can be formed from both channels of the reactions of chloro-alkyl peroxy radicals (reactions (8) – (11)), that is, both from the path of reactions (8a), (9a), (10a), and (11a), which forms alkoxy radicals, and from the path of reactions (8b), (9b), (10b), (11b), which forms the aldehyde and alcohol (and O₂). CHB and CBO (chloro-alcohols), however, can only be generated from the second path of the self-reactions of chloro-alkyl peroxy radicals (reactions (8b) and (9b)), or the second and third paths of the cross reactions of chloro-alkyl peroxy radicals (for example, reactions (11b) and 11c)). The similarity in the yields of CMVK and CHB suggests that most of CMVK is generated in channel (8b) together with CHB. (As discussed below, reaction (12a) of the alkoxy radical with O₂ does not appear to be a major source of CMVK in this system.) That channel (8b) is the major source of CMVK is also supported by the lack of observation of CMVK or CHB as products in the presence of NO; in this case the self-reaction of the peroxy radicals such as reaction (8) is negligible.

Most of the CCA must be generated through generation of the alkoxy radical in reaction (9a) followed by reaction (13a) of the alkoxy radical with O₂. Reaction (9b) cannot be the major source of CCA since CBO would be formed in comparable yields; however, CBO was found to be only a minor product. The alkoxy radicals formed in reaction (9a) can not only react with O₂ to form CCA, but can also, in principle, decompose or isomerize. Decomposition is unlikely since decomposition of CH₂Cl-CH=CH-CH₂(O·) will generate vinyl radicals which are not energetically favored. Intramolecular isomerization of the alkoxy radical in the *cis* configuration is, however, possible since it can proceed via a six-membered ring:



The alkyl radical formed will then react with O₂, generating another chloroperoxy alkyl radical:

The total carbon mass accounted for in the Cl-butadiene reaction in the absence of NO in 1 atm air at room temperature is 74% (corrected for secondary reactions). Computer kinetics modeling using ACUCHEM (discussed in detail below) predicts that total hydroperoxides from reactions of HO₂ with chloroperoxy alkyl radicals account for 21% of the loss of 1,3-butadiene. We were not able to measure hydroperoxides since they have a weak infrared absorbance. They would likely not be observable in the GC-MS studies since they may be removed by the Cl₂ filter and/or decompose during sampling and GC analysis [e.g., Tobias and Ziemann, 2000]. The hydroperoxides formed in reactions (15), (16), and (17) would be expected to decompose to form CMVK, CCA, and 2-chloro-3-butenal, respectively. Thus the measured yields of these three compounds may be overestimated, since they may include a contribution from the decomposition of hydroperoxides. However, the fact that the yields of these products do

Table 2. Product Yields of the Cl-Butadiene Reaction in the Absence of NO in 1 atm Air at Room Temperature Estimated From GC- MS Studies

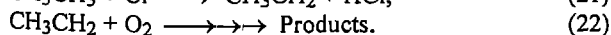
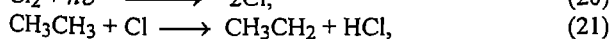
Experiment	[Butadiene] ₀ , ppm	[Cl ₂] ₀ , ppm	Yields of CHB ^a , %	Yields of CBO ^a , %
1	22	5.5	17	1
2	22	5.5	15	2
3	22	5.5	20	2
4	22	5.5	19	2
5	22	5.5	22	2
6	22	5.5	16	6
7	22	5.5	21	4
8	22	5.5	13	3
9	22	5.5	13	3
10	22	5.5	14	3
11	22	5.5	17	3
12	22	5.5	14	1
13	22	5.5	17	1
14	22	5.5	16	1
15	22	5.5	20	0
16	22	5.5	16	1
17	22	5.5	19	3
18	22	5.5	14	1
19	22	5.5	14	2
20	22	5.5	14	1
21	22	5.5	17	1
22	22	5.5	21	1
23	22	5.5	23	1
24	22	5.5	19	2
25	22	4	22	6
26	20	4	19	6
27	22	4	19	6
28	20	4	13	5
29	20	4	14	4
30	20	4	13	2
31	20	4	14	3
32	20	4	18	
33	20	4	16	
34	20	4	19	
35	20	4	13	
36	40	4	16	
37	40	4	15	
38	40	4	15	
Average			17 ± 6 (2σ) ^b	3 ± 3 (2σ) ^b

^a CHB denotes 1-chloro-2-hydroxy-3-butene, and CBO denotes 1-chloro-2-butene-4-ol.

^b Errors are estimated from the standard deviation of the individual measurements.

not add up to 100% and that the missing carbon is approximately that predicted by the model to be in the form of hydroperoxides suggests that removal by the Cl₂ filter is most likely.

In order to elucidate the branching ratios of the various paths, the reaction scheme shown in Table 3 was used as input into the ACUCHEM model [Braun *et al.*, 1988]. The photolysis rate constant for Cl₂ (first reaction in Table 3) was determined experimentally by measuring the formation of HCl from the reaction of chlorine atoms with ethane in 1 atm air at room temperature. The reaction mechanism for this system can be represented by reactions (20) - (22):



HCl was followed as a function of time. This allowed the concentrations of Cl₂ to be calculated as a function of time using the known initial concentration of Cl₂ and the relation-

ship $[\text{Cl}_2]_t = [\text{Cl}_2]_0 - [\text{HCl}]_t/2$. The photolysis rate constant, k_p , was then calculated from a plot of $\ln [\text{Cl}_2]_t$ against photolysis time, giving $k_p = (2.0 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$ (2σ). A value of $2.5 \times 10^{-3} \text{ s}^{-1}$ gave the best fit to the loss of butadiene and hence was used in the model.

In order to match the yields of CCA and CMVK, the branching ratios for the Cl + butadiene reactions in Table 3, the first of which leads to CMVK and the second of which leads to CCA were adjusted to provide a best fit to the experimentally determined yields of these compounds. Figure 5 shows the match to the experimental data obtained using a branching ratio of 0.40 for the first Cl + butadiene reaction, 0.55 for the second reaction and 0.05 for the third reaction. The branching ratio for the third reaction, which represents addition of Cl to an internal carbon, was chosen to reflect the small yield of 2-chloro-3-butenal, which must originate from this channel. Rate constants and branching ratios shown in Table 3 for the RO₂ + RO₂ self-reaction and cross reactions were initially chosen based on those reported by Jenkin *et al.* [1998] for similar hydroxy-substituted peroxy radicals. Rate

Table 3. Reactions and Rate Constants for Modeling the Cl-Butadiene Reaction in the Absence of NO

Reactions	Rate Constants ^a
$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$	$2.5\text{E-}3^b$
$\text{Cl} + \text{butadiene} \rightarrow \text{CH}_2\text{Cl-CH=CH=CH}_2$ (R1)	$1.68\text{E-}10^c$
$\text{Cl} + \text{butadiene} \rightarrow \text{CH}_2\text{Cl-CH=CH-CH}_2$ (R2)	$2.31\text{E-}10^c$
$\text{Cl} + \text{butadiene} \rightarrow \text{CH}_2\text{-CHCl-CH=CH}_2$ (R3)	$2.1\text{E-}11^c$
$\text{R1} + \text{O}_2 \rightarrow \text{ROO1}$	$1\text{E-}11^d$
$\text{R2} + \text{O}_2 \rightarrow \text{ROO2}$	$1\text{E-}11^d$
$\text{R3} + \text{O}_2 \rightarrow \text{ROO3}$	$1\text{E-}11^d$
$\text{ROO1} + \text{ROO1} \rightarrow \text{RO1} + \text{RO1} + \text{O}_2$	$3\text{E-}13^e$
$\text{ROO1} + \text{ROO1} \rightarrow \text{CHB} + \text{CMVK} + \text{O}_2$	$7\text{E-}13^e$
$\text{ROO2} + \text{ROO2} \rightarrow \text{RO2} + \text{RO2} + \text{O}_2$	$7\text{E-}13^e$
$\text{ROO2} + \text{ROO2} \rightarrow \text{CBO} + \text{CCA} + \text{O}_2$	$3\text{E-}13^e$
$\text{ROO3} + \text{ROO3} \rightarrow \text{RO3} + \text{RO3} + \text{O}_2$	$5\text{E-}13^e$
$\text{ROO3} + \text{ROO3} \rightarrow \text{C}_4\text{ClH}_4\text{O} + \text{C}_4\text{ClH}_6\text{O} + \text{O}_2$	$5\text{E-}13^e$
$\text{ROO1} + \text{ROO2} \rightarrow \text{RO1} + \text{RO2} + \text{O}_2$	$2.5\text{E-}13^e$
$\text{ROO1} + \text{ROO2} \rightarrow \text{CHB} + \text{CCA} + \text{O}_2$	$5\text{E-}13^e$
$\text{ROO1} + \text{ROO2} \rightarrow \text{CBO} + \text{CMVK} + \text{O}_2$	$2.5\text{E-}13^e$
$\text{RO1} + \text{O}_2 \rightarrow \text{CMVK} + \text{HO}_2$	$8\text{E-}15^d$
$\text{RO1} \rightarrow \text{acrolein} + \text{CH}_2\text{Cl}$	$2\text{E+}4^d$
$\text{RO2} + \text{O}_2 \rightarrow \text{CCA} + \text{HO}_2$	$9.5\text{E-}15^d$
$\text{RO2} + \text{M} \rightarrow \text{ISOR2} + \text{M}$	$4\text{E-}16^f$
$\text{RO3} + \text{O}_2 \rightarrow \text{C}_4\text{ClH}_4\text{O} + \text{HO}_2$	$9.5\text{E-}15^d$
$\text{RO3} \rightarrow \text{HCHO} + \text{CH}_2=\text{CHCHCl}$	$1\text{E+}4^d$
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.7\text{E-}12^g$
$\text{HO}_2 + \text{ROO1} \rightarrow \text{ROOH1} + \text{O}_2$	$1.5\text{E-}11^d$
$\text{HO}_2 + \text{ROO2} \rightarrow \text{ROOH2} + \text{O}_2$	$1.5\text{E-}11^d$
$\text{HO}_2 + \text{ROO3} \rightarrow \text{ROOH3} + \text{O}_2$	$1.5\text{E-}11^d$
$\text{CH}_2\text{Cl} + \text{O}_2 \rightarrow \text{CH}_2\text{ClO}_2$	$8.6\text{E-}13^g$
$\text{CH}_2\text{ClO}_2 + \text{CH}_2\text{ClO}_2 \rightarrow \text{CH}_2\text{ClO} + \text{CH}_2\text{ClO}$	$3.7\text{E-}12^h$
$\text{CH}_2\text{ClO} + \text{O}_2 \rightarrow \text{HCOCl} + \text{HO}_2$	$6\text{E-}14^g$
$\text{HO}_2 + \text{CH}_2\text{ClO}_2 \rightarrow \text{CH}_2\text{ClOOH} + \text{O}_2$	$1.4\text{E-}12^i$
$\text{HO}_2 + \text{CH}_2\text{ClO}_2 \rightarrow \text{HCOCl} + (\text{O}_2 + \text{H}_2\text{O})$	$3.8\text{E-}12^i$
$\text{CCA} + \text{Cl} \rightarrow \text{CCACl}$	$3.1\text{E-}10^j$
$\text{CMVK} + \text{Cl} \rightarrow \text{CMVKCl}$	$2\text{E-}10^k$
$\text{HCOCl} + \text{Cl} \rightarrow \text{products}$	$7.6\text{E-}13^l$
$\text{Acrolein} + \text{Cl} \rightarrow \text{products}$	$2.9\text{E-}10^m$
$\text{CHB} + \text{Cl} \rightarrow \text{products}$	$3.1\text{E-}10^k$
$\text{CBO} + \text{Cl} \rightarrow \text{products}$	$2\text{E-}10^j$
$\text{CCA} + h\nu \rightarrow \text{products}^n$	
$\text{Acrolein} + h\nu \rightarrow \text{products}^n$	
$\text{HCHO} + h\nu \rightarrow \text{products}^n$	
$\text{HCOCl} + h\nu \rightarrow \text{products}^n$	

^a Units are s^{-1} for first order reactions and $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ for second order reactions, respectively. Read $2.5\text{E-}3$ as 2.5×10^{-3} .

^b Based on measured HCl formation from the Cl-ethane reaction as described in text.

^c Rate constant of the Cl-butadiene reaction is from *Ragains and Finlayson-Pitts* [1997]; the branching ratios are estimated using the experimental data.

^d Estimated using typical rate constants [*Finlayson-Pitts and Pitts*, 2000].

^e These are the rate constants for similar hydroxyl-peroxy radicals [*Jenkin et al.*, 1998], assuming they have similar rate constants. Branching ratios are estimated using experimental data.

^f Estimated based on experimental data.

^g *DeMore et al.* [1997].

^h *Wallington et al.* [1992].

ⁱ *Wallington et al.* [1996a].

^j This is the rate constant for crotonaldehyde + Cl (unpublished data), assuming they have similar rate constants.

^k This is the rate constant for methyl vinyl ketone + Cl [*Finlayson-Pitts et al.*, 1999], assuming they have similar rate constants.

^l *Bilde et al.* [1999].

^m Unpublished data.

ⁿ Less than 1% of photolysis rate for Cl_2 .

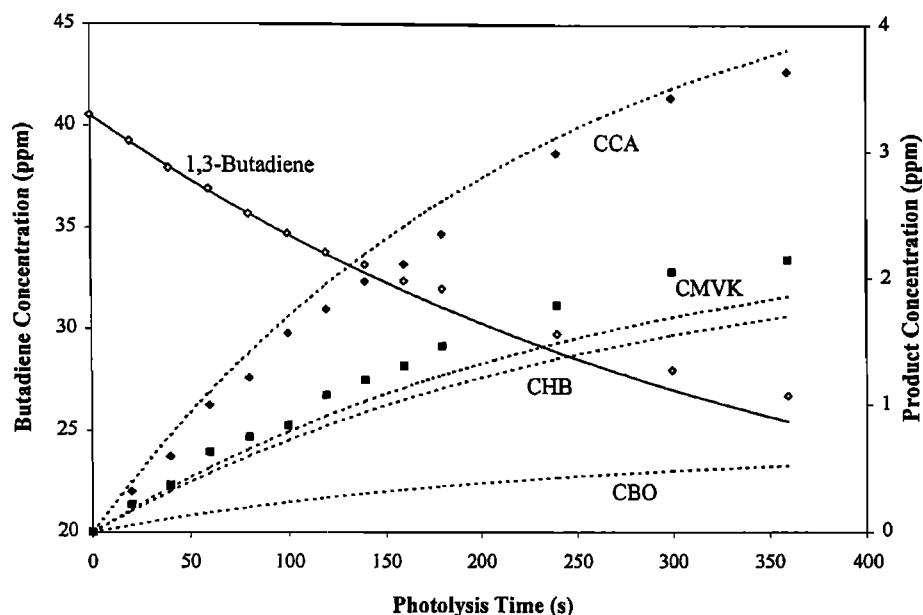


Figure 5. A comparison of results from the ACUCHEM model (lines) and the FTIR data (symbols) from the Cl-butadiene reaction in the absence of NO. Open diamonds represent butadiene. Solid diamonds represent CCA. Solid squares represent CMVK. Experimental data for CHB and CBO are not shown because they could not be measured by FTIR (see text).

constants for decomposition, isomerization, and reaction with O_2 of the alkoxy radicals were chosen based on those for alkoxy radicals of similar structure [Finlayson-Pitts and Pitts, 2000]. The branching ratios were adjusted to give the best fits to the experimentally measured product yields, as dis-

cussed above. It is seen that the match to the experimentally determined formation of CMVK and CCA is excellent.

Figure 6 summarizes the major reaction pathways in the reaction of 1,3-butadiene with chlorine atoms in the absence of NO.

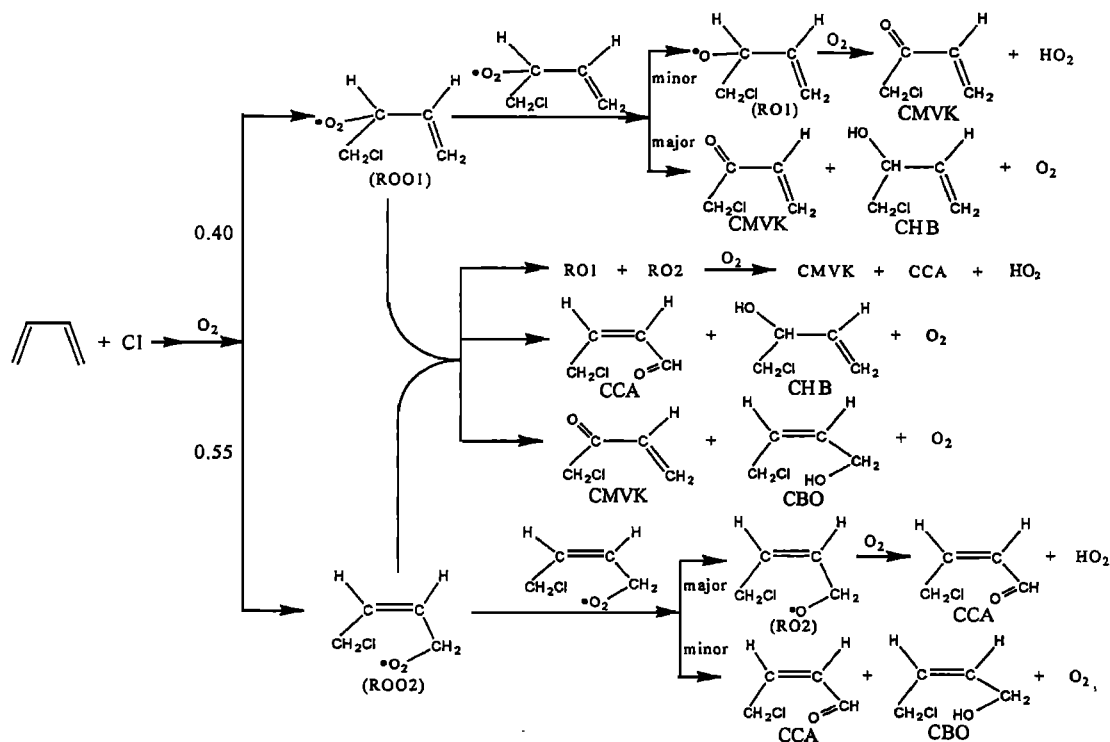


Figure 6. Major pathways for the Cl-butadiene reaction in the absence of NO in 1 atm air at room temperature.

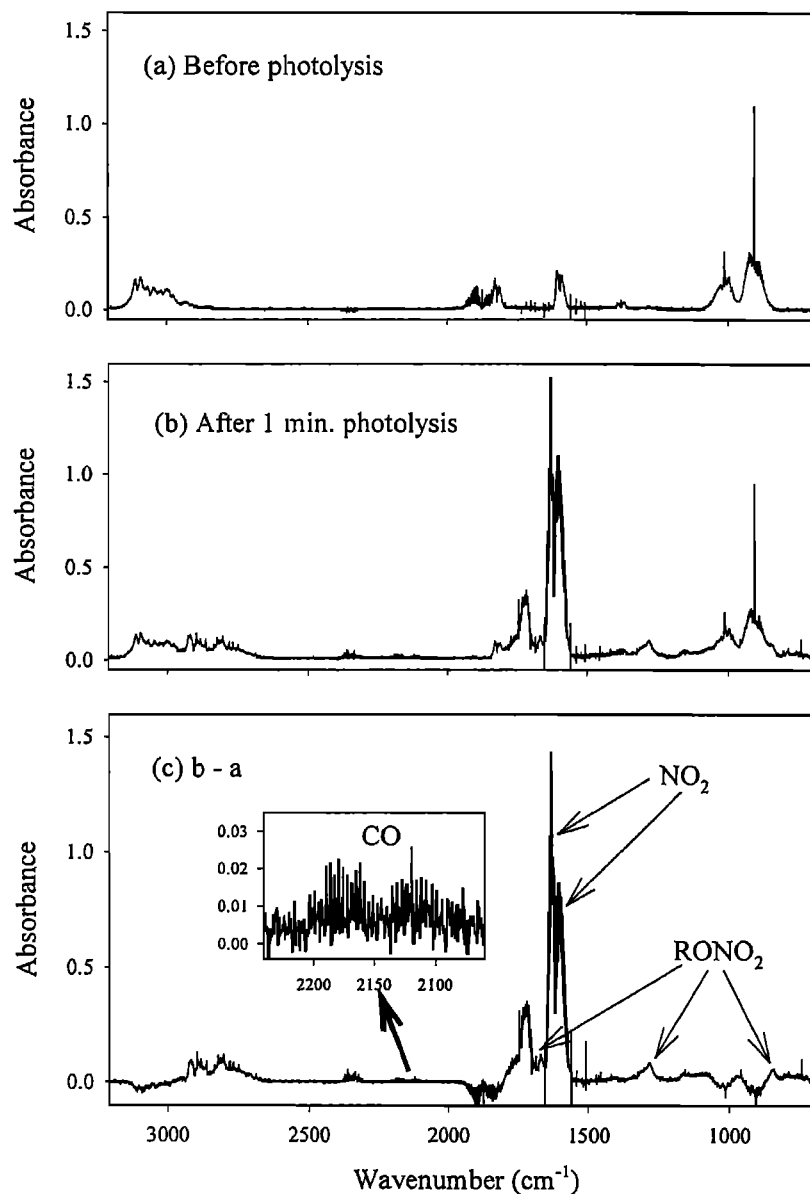
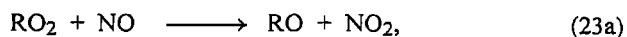


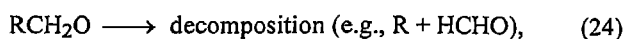
Figure 7. FTIR spectra of 1,3-butadiene and Cl_2 in the presence of NO in 1 atm air at room temperature, $[\text{butadiene}]_0 = 33$ ppm, $[\text{Cl}_2]_0 = 9$ ppm, $[\text{NO}]_0 = 20$ ppm (a) before photolysis; (b) after photolysis for 1 min; and (c) the difference between them (Figure 7b spectrum minus Figure 7a spectrum). The loss of butadiene was 23%.

3.2. Reaction of Chlorine Atoms With 1,3-Butadiene in the Presence of NO

The addition of NO to the system replaces the self-reactions and cross reactions of the chloroperoxy alkyl radicals with the reaction with NO:



Potential fates of the chloroalkoxy radicals formed in reaction (23a) include decomposition,

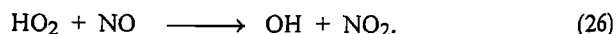


or reaction with O_2 to form a carbonyl compound and HO_2 :



In addition, intramolecular isomerization can occur if a six-membered ring can be formed in the transition state, as shown above in reaction (19).

Any HO_2 generated in the system reacts rapidly with NO to form OH:



Because of the high reactivity of OH with organics, including 1,3-butadiene, the chemistry rapidly becomes dominated by OH, and this must be taken into account in interpreting the loss of reactant and formation of products.

Figure 7 shows typical infrared spectra for the Cl-butadiene reaction at 1 atm in air in the presence of NO be-

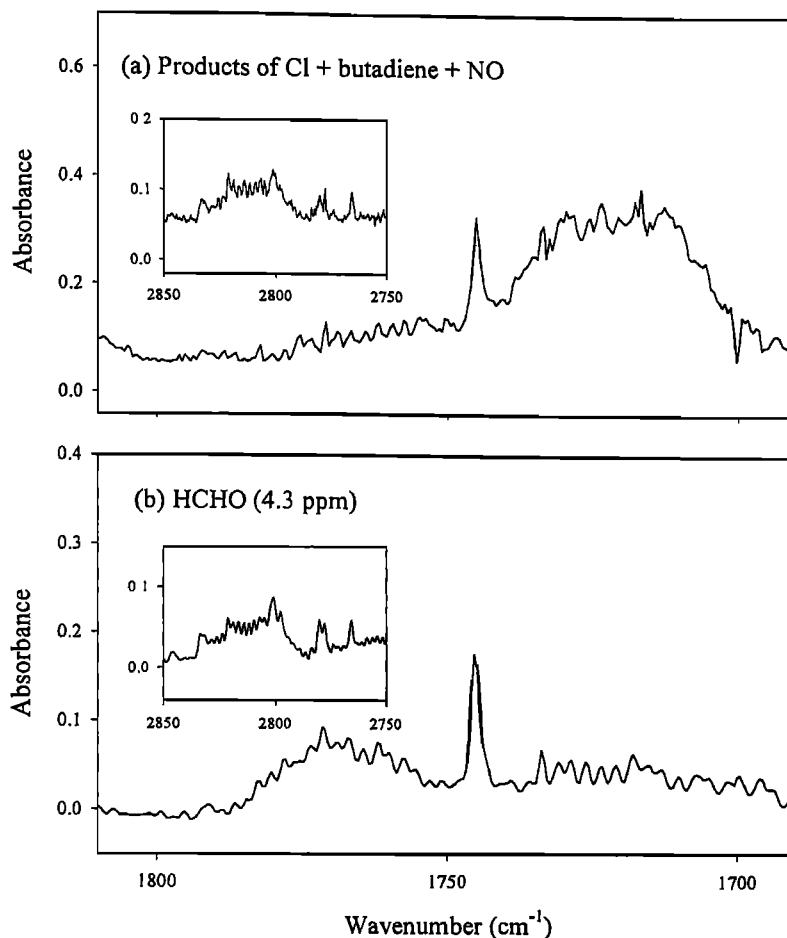


Figure 8. FTIR spectra of (a) products of the Cl-butadiene reaction in the presence of NO under same conditions as Figure 7b; and (b) HCHO reference, [HCHO] = 4.3 ppm in 1 atm air at room temperature.

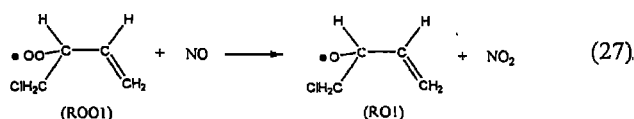
fore photolysis (Figure 7a), after photolysis for 1 min (Figure 7b), and the difference spectrum (Figure 7c, obtained by subtracting Figure 7a from Figure 7b). Because 1,3-butadiene and NO decrease during the reaction, their absorptions in the difference spectrum appear as negative bands. There are significant differences between the product spectrum in the presence of NO (Figure 7c) compared to that in its absence (Figure 2a). In the presence of NO, NO₂ is generated (~2906 and 1617 cm⁻¹) and there are absorptions due to CO (2140 cm⁻¹) and organic nitrates (1668, 1286 and 850 cm⁻¹). Because authentic samples of the chloro-organic nitrates were not available, they were identified by the typical organic nitrate strong absorptions around 1630 and 1280 cm⁻¹ for N=O stretching and 860 cm⁻¹ for O-N stretching [Lin-Vien *et al.*, 1991]. For comparison, a spectrum of isobutyl nitrate was measured in our system; absorptions at 1659, 1284, and 856 cm⁻¹ due to the -ONO₂ group, similar to those observed in Figure 7c, were seen. The calibration for isobutyl nitrate was used to quantify the organic nitrates.

The absorptions in the carbonyl region around 1700 cm⁻¹ and in the CH 2700 - 3100 cm⁻¹ region are also different from those in the absence of NO. As seen in Figure 8a, there is a sharp peak at 1745 cm⁻¹ and a broad absorption from 1740 to 1690 cm⁻¹. By comparison to a spectrum of HCHO (Figure 8b), the 1745 cm⁻¹ peak and the doublet around 2780 cm⁻¹ can be assigned to HCHO. Clearly, other carbonyl com-

pounds contribute to the broad absorption at the 1700 cm⁻¹ region as well; as discussed below, these include acrolein and CCA.

In the CH stretching region (2700 - 3100 cm⁻¹), absorptions from 1,3-butadiene, NO₂, and HCHO dominate. The residual spectrum after subtracting out the absorptions from HCHO, 1,3-butadiene, NO₂, acrolein, and a small amount of HCl is shown in Figure 9a. By comparison to a reference spectrum of CCA (Figure 9b), these two peaks can be assigned to CCA. CMVK was not observed in the presence of NO.

Thus CCA is formed from the Cl-butadiene reaction in the absence or presence of NO, while CMVK is only formed in its absence. This is consistent with the source of CMVK being the self-reactions or cross reactions of the chloroperoxy alkyl radicals, which are negligible in the presence of NO. In the presence of NO, the alkyl peroxy radicals (ROO1 in Tables 3 and 4) are converted primarily to alkoxy radicals (RO1) (with a small fraction (<10%) expected to form a stable nitrate):



As shown by reactions (12a) and (12b), the alkoxy radical

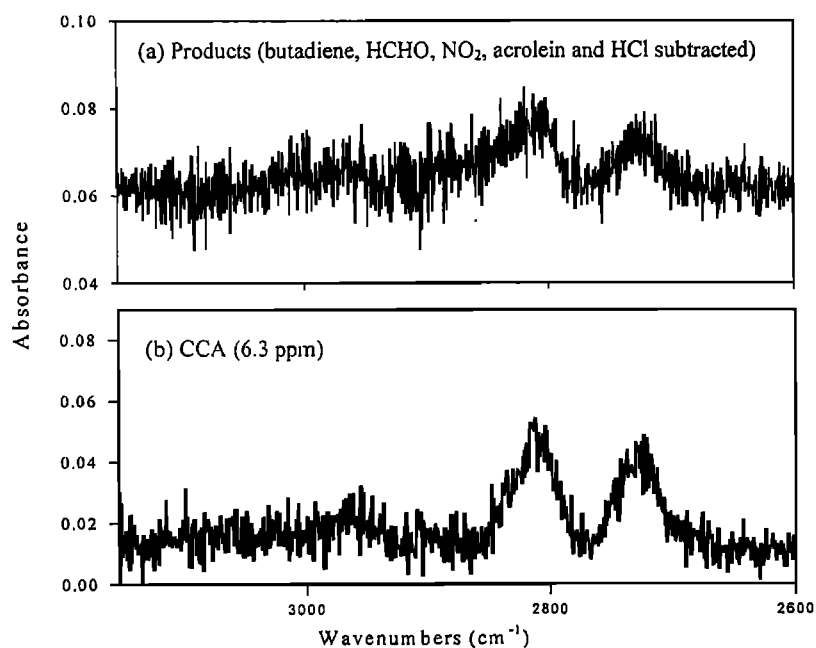


Figure 9. FTIR spectra of (a) mixture of 1,3-butadiene, Cl₂, and NO under same conditions as Figure 7b, with reference spectra of 1,3-butadiene, NO₂, HCHO, acrolein and HCl subtracted; and (b) CCA reference, [CCA] = 6.3 ppm in 1 atm air at room temperature.

can either react with O₂ to form CMVK or decompose to ·CH₂Cl and acrolein. The fact that CMVK is not observed as a product in the presence of NO and that the yield of acrolein increases shows that decomposition dominates over reaction with O₂. The decomposition rate depends on the internal energy in the radical. Alkoxy radicals formed in the RO₂ + RO₂ self-reactions or cross reactions are thermalized because the reactions are approximately thermoneutral. Those formed from RO₂ + NO contain excess internal energy due to the exothermicity of the reaction, typically ~ 12 kcal mol⁻¹ [e.g. *Orlando et al.*, 1998]. Depending on the barrier for C-C bond cleavage, this may be sufficient to increase the rate of decomposition so that it predominates [Wallington *et al.*, 1996b; *Orlando et al.*, 1998; *Bilde et al.*, 1999]. For example, the activation barrier for decomposition of HOCH₂CH₂O·, formed in the reaction of OH with ethylene, is ~10-11 kcal mol⁻¹, so that a significant fraction of the radicals formed in the reaction of HOCH₂CH₂O₂· with NO have sufficient energy to decompose; on the other hand, the activation barrier for the decomposition of the analogous species formed from the addition of chlorine atoms to ethylene, ClCH₂CH₂O·, is estimated to be ~15-17 kcal mol⁻¹ [Orlando *et al.*, 1998]. As a result, ClCH₂CH₂O· reacts in air predominantly with O₂ rather than decomposing, and ClCH₂CHO is the major product [Orlando *et al.*, 1998].

Our experimental observation that CMVK is not formed in the presence of NO while the yield of acrolein increases suggests that the barrier to decomposition for the radical CH₂CICH(O·)CH=CH₂ formed in the RO₂ + NO reaction is sufficiently low that decomposition predominates. The same has been proposed to be the case for the analogous alkoxy radical formed in the reaction of OH with 1,3-butadiene [Tuazon *et al.*, 1999].

CCA, however, is formed from the alkoxy radical CH₂CICH=CHCH₂O·. Because decomposition of this spe-

cies would generate a vinyl radical, which is not energetically favorable, reaction (13a) with O₂ to generate CCA continues, even when the alkoxy radical is formed in the RO₂ + NO reaction. Thus the enthalpy of formation of vinyl radicals is about 40 kcal mol⁻¹ higher than that for alkyl radicals; for example, ΔH⁰_f (298 K) = 71 kcal mol⁻¹ for ·C₂H₃ and ΔH⁰_f (298 K) = 28 kcal mol⁻¹ for ·C₂H₅ [DeMore *et al.*, 1997]. The "energy cost" for decomposition is too large to be overcome by the exothermicity of ~10-12 kcal mol⁻¹ of the RO₂ + NO reaction.

Table 5 summarizes the product yields measured using FTIR at about 20% loss of 1,3-butadiene. The major products are CCA with a yield of (26 ± 8)%, acrolein at (43 ± 7)%, and HCHO with a yield of (42 ± 6)% (all errors are 2σ). These yields have not been corrected for secondary reactions of the products with OH radicals and chlorine atoms, and for the loss of 1,3-butadiene by reaction with OH radicals, which contribute significantly in the presence of NO. Model studies discussed in more detail below show that ~ 40% of the observed loss of 1,3-butadiene is due to the reaction with Cl atoms and about 60% to reaction with OH. Table 5 also shows the product yields corrected for the loss of 1,3-butadiene due to its reaction with OH radicals, which increases the yield of CCA due to the chlorine atom reaction to (65 ± 20%). The yield of CCA in Table 5 has not been corrected for loss due to reactions with OH and Cl since these are estimated to be less than 1%. The corrected yields of HCl and CO are each 28%.

Correcting the yields of acrolein and HCHO is more complex because both are also formed in the OH-butadiene reaction. The yields of acrolein and HCHO from the OH-butadiene reaction have been reported to be (58 ± 4)% (2σ) and (62 ± 5)% (2σ), respectively [Tuazon *et al.*, 1999]. Correcting for the contribution of OH chemistry to the formation of acrolein and HCHO, the yields of these products from the Cl-butadiene reaction are calculated to be (21 ± 3)% (2σ) and

Table 4. Reactions and Rate Constants for Modeling the Cl-Butadiene Reaction in the Presence of NO

Reactions	Rate Constants ^a
$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$	$2.5\text{E}-3^b$
$\text{Cl} + \text{butadiene} \rightarrow \text{CH}_2\text{Cl}-\text{CH}=\text{CH}_2$ (R1)	$1.68\text{E}-10^c$
$\text{Cl} + \text{butadiene} \rightarrow \text{CH}_2\text{Cl}-\text{CH}=\text{CH}-\text{CH}_2$ (R2)	$2.31\text{E}-10^c$
$\text{Cl} + \text{butadiene} \rightarrow \text{CH}_2-\text{CHCl}-\text{CH}=\text{CH}_2$ (R3)	$2.1\text{E}-11^c$
$\text{R1} + \text{O}_2 \rightarrow \text{ROO1}$	$1\text{E}-11^d$
$\text{R2} + \text{O}_2 \rightarrow \text{ROO2}$	$1\text{E}-11^d$
$\text{R3} + \text{O}_2 \rightarrow \text{ROO3}$	$1\text{E}-11^d$
$\text{ROO1} + \text{NO} \rightarrow \text{RO1}^* + \text{NO}_2$	$9\text{E}-12^d$
$\text{ROO1} + \text{NO} \rightarrow \text{RONO}_2$	$5\text{E}-13^d$
$\text{ROO2} + \text{NO} \rightarrow \text{RO2}^* + \text{NO}_2$	$9\text{E}-12^d$
$\text{ROO2} + \text{NO} \rightarrow \text{RONO}_2$	$5\text{E}-13^d$
$\text{ROO3} + \text{NO} \rightarrow \text{RO3}^* + \text{NO}_2$	$9\text{E}-12^d$
$\text{ROO3} + \text{NO} \rightarrow \text{RONO}_2$	$5\text{E}-13^d$
$\text{RO1}^* + \text{M} \rightarrow \text{RO1} + \text{M}$	$4\text{E}-15^e$
$\text{RO1}^* \rightarrow \text{CH}_2\text{Cl} + \text{acrolein}$	$2\text{E}+6^e$
$\text{RO2}^* + \text{M} \rightarrow \text{RO2} + \text{M}$	$4\text{E}-15^e$
$\text{RO3}^* + \text{M} \rightarrow \text{RO3} + \text{M}$	$4\text{E}-15^e$
$\text{RO3}^* \rightarrow \text{HCHO} + \text{CHClCHCH}_2$	$2\text{E}+6^e$
$\text{RO1} \rightarrow \text{CH}_2\text{Cl} + \text{acrolein}$	$2\text{E}+4^d$
$\text{RO1} + \text{O}_2 \rightarrow \text{CMVK} + \text{HO}_2$	$8\text{E}-15^d$
$\text{RO2} + \text{O}_2 \rightarrow \text{CCA} + \text{HO}_2$	$9.5\text{E}-15^d$
$\text{RO2} + \text{M} \rightarrow \text{ISOR2} + \text{M}$	$4\text{E}-16^f$
$\text{RO3} \rightarrow \text{HCHO} + \text{CHClCHCH}_2$	$1\text{E}+4^d$
$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	$8.1\text{E}-12^h$
$\text{CHClCHCH}_2 + \text{O}_2 \rightarrow \text{C}_3\text{ClH}_4\text{O}_2$	$1\text{E}-11^d$
$\text{C}_3\text{ClH}_4\text{O}_2 + \text{NO} \rightarrow \text{C}_3\text{ClH}_4\text{O} + \text{NO}_2$	$9\text{E}-12^d$
$\text{C}_3\text{ClH}_4\text{O} + \text{O}_2 \rightarrow \text{C}_3\text{ClH}_3\text{O} + \text{HO}_2$	$1\text{E}-11^d$
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$	$6.5\text{E}-3^g$
$\text{CH}_2\text{Cl} + \text{O}_2 \rightarrow \text{CH}_2\text{ClO}_2$	$1\text{E}-15^h$
$\text{CH}_2\text{ClO}_2 + \text{NO} \rightarrow \text{CH}_2\text{ClO}^* + \text{NO}_2$	$1.9\text{E}-11^i$
$\text{CH}_2\text{ClO}^* \rightarrow \text{HCO} + \text{HCl}$	$1\text{E}+5^f$
$\text{CH}_2\text{ClO}^* \rightarrow \text{HCHO} + \text{Cl}$	$8\text{E}+5^f$
$\text{CH}_2\text{ClO}^* \rightarrow \text{CH}_2\text{ClO}$	$1\text{E}+5^f$
$\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$	$5.5\text{E}-12^h$
$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$	$2.4\text{E}-13^h$
$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	$1.2\text{E}-12^h$
$\text{CH}_2\text{ClO} \rightarrow \text{HCO} + \text{HCl}$	$2.6\text{E}+3^i$
$\text{CH}_2\text{ClO} + \text{O}_2 \rightarrow \text{HCOC1} + \text{HO}_2$	$1\text{E}-14^i$
$\text{CH}_2\text{ClO} + \text{NO} \rightarrow \text{HCOC1} + \text{HNO}$	$7\text{E}-12^i$
$\text{CH}_2\text{ClO} + \text{NO} \rightarrow \text{HCHO} + \text{NOCl}$	$9\text{E}-12^i$
$\text{HCOC1} \rightarrow \text{CO} + \text{HCl}$	$1\text{E}-2^i$
$\text{HCOC1} + \text{Cl} \rightarrow \text{COCl} + \text{HCl}$	$7.6\text{E}-13^i$
$\text{COCl} \rightarrow \text{CO} + \text{Cl}$	$1\text{E}+1^i$
$\text{HCOC1} + \text{OH} \rightarrow \text{COCl} + \text{H}_2\text{O}$	$1\text{E}-13^i$
$\text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	$1\text{E}-11^h$
$\text{HCHO} + \text{Cl} \rightarrow \text{HCO} + \text{HCl}$	$7.3\text{E}-11^h$
$\text{Butadiene} + \text{OH} \rightarrow \text{ROH1}$	$3.86\text{E}-11^j$
$\text{Butadiene} + \text{OH} \rightarrow \text{ROH2}$	$2.8\text{E}-11^j$
$\text{ROH1} + \text{O}_2 \rightarrow \text{ROHOO1}$	$1\text{E}-11^d$
$\text{ROHOO1} + \text{NO} \rightarrow \text{ROHO1} + \text{NO}_2$	$9\text{E}-12^d$
$\text{ROHO1} \rightarrow \text{HCHO} + \text{acrolein}$	$2\text{E}+4^d$
$\text{ROH2} + \text{O}_2 \rightarrow \text{ROHOO2}$	$1\text{E}-11^d$
$\text{ROHOO2} + \text{NO} \rightarrow \text{ROHO2} + \text{NO}_2$	$9\text{E}-12^d$
$\text{ROHO2} + \text{O}_2 \rightarrow \text{BUOH} + \text{HO}_2$	$9.5\text{E}-15^d$
$\text{Acrolein} + \text{OH} \rightarrow \text{ACROOH}$	$2\text{E}-11^k$
$\text{Acrolein} + \text{Cl} \rightarrow \text{ACROCl}$	$2.9\text{E}-10^l$
$\text{CCA} + \text{OH} \rightarrow \text{CCA OH}$	$3.6\text{E}-11^m$
$\text{CCA} + \text{Cl} \rightarrow \text{CCACl}$	$3.3\text{E}-10^n$
$\text{CMVK} + \text{OH} \rightarrow \text{CMVKOH}$	$1.8\text{E}-11^o$
$\text{CMVK} + \text{Cl} \rightarrow \text{CMVKCl}$	$2\text{E}-10^p$
$\text{HCl} + \text{OH} = \text{H}_2\text{O} + \text{Cl}$	$8\text{E}-13^h$
$\text{CCA} + h\nu \rightarrow \text{products}^q$	
$\text{Acrolein} + h\nu \rightarrow \text{products}^q$	
$\text{HCHO} + h\nu \rightarrow \text{products}^q$	

Table 4. (continued)

Reactions	Rate Constants ^a
HCOCl + $h\nu \rightarrow$ products^a	
^a Units are s^{-1} for first order reactions and $cm^3 \text{ molecule}^{-1} s^{-1}$ for second order reactions, respectively.	
^b Based on measured HCl formation from the Cl-ethane reaction as described in text.	
^c Rate constant for the Cl-butadiene reaction is from <i>Ragains and Finlayson-Pitts</i> [1997], the branching ratios are estimated using the experimental data.	
^d Estimated using typical rate constants [<i>Finlayson-Pitts and Pitts</i> , 2000]. Self-reactions and cross reactions of peroxy radicals are negligible.	
^e Estimated for excited alkoxy radicals.	
^f Estimated using experimental data.	
^g Measured for photolysis of NO_2 in N_2 as described in text.	
^h <i>DeMore et al.</i> [1997].	
ⁱ <i>Bilde et al.</i> [1999].	
^j <i>Tuazon et al.</i> [1999].	
^k <i>Atkinson</i> [1990].	
^l Unpublished data.	
^m This is the rate constant for $CA + OH$ [<i>Atkinson</i> , 1990], assuming they have similar rate constants.	
ⁿ This is the rate constant for $CA + Cl$ (unpublished data), assuming they have similar rate constants.	
^o This is the rate constant for $MVK + OH$ [<i>Atkinson</i> , 1990], assuming they have similar rate constants.	
^p This is the rate constant for $MVK + Cl$ [<i>Finlayson-Pitts et al.</i> , 1999], assuming they have similar rate constants.	
^q Less than 1% of photolysis rate for Cl_2 .	

(12 ± 2)% (2σ), respectively. Small yields (4 ± 1)% (2σ) of organic nitrates were also observed, which can be accounted for by the OH-butadiene reaction alone [*Tuazon et al.*, 1999]. While small yields of nitrates are expected from the minor path in the chloroperoxy alkyl radical reaction (23b) as well, the small amounts formed precluded an accurate estimate of their yields from the chlorine atom reactions alone. The total carbon mass balance accounted for the Cl-butadiene reaction in the presence of NO is (91 ± 21)%.

The reaction scheme shown in Table 4 was developed for the system in the presence of NO. In this case the self-reactions and cross reactions of RO_2 and HO_2 can be ignored. The photolysis rate constant for Cl_2 was measured as described earlier. That for NO_2 was measured using the method described by *Holmes et al.* [1973]; briefly, NO_2 is photolyzed in the long path cell in 1 atm N_2 at room temperature and the loss of NO_2 is followed with time using FTIR. As described by Holmes and coworkers, the photolysis rate constant for

Table 5. Product Yields of the Cl-Butadiene Reaction in the Presence of NO in 1 atm Air at Room Temperature From FTIR Studies^a

Experiment	[Butadiene] ₀ , ppm	[Cl ₂] ₀ , ppm	[NO] ₀ , ppm	Yields of CCA, %	Yields of Acrolein, %	Yields of HCHO, %	Yields of HCl, %	Yields of CO, %	Yields of Total Organic-Nitrate ^b , %
1	61	5	8	25	48	41	13	10	3
2	59	5	8	28	43	40	20	15	4
3	34	9	20	28	47	38	10	11	4
4	33	9	20	29	42	44	5	10	4
5	33	9	20	32	44	45	12	12	4
6	30	10	20	30	42	42	17	12	3
7	30	10	20	24	46	39	10	15	4
8	30	10	20	24	40	38	11	9	4
9	30	10	20	27	46	44	20	12	4
10	27	8	16	23	37	44	9	9	4
11	27	8	16	29	44	45	8	12	3
12	27	8	16	30	48	43	11	12	3
13	23	7	14	24	40	44	8	5	3
14	23	7	14	21	36	41	12	8	2
15	20	5	8	23	45	49	5	12	3
16	19	5	8	24	47	41	13	11	3
Measured average ^c				26 ± 8 (2σ) ^d	43 ± 7 (2σ) ^d	42 ± 6 (2σ) ^d	11 ± 9 (2σ) ^d	11 ± 5 (2σ) ^d	4 ± 1 (2σ) ^d
Corrected average ^e				65 ± 20 (2σ)	21 ± 3 (2σ) ^f	12 ± 2 (2σ) ^f	28 ± 23 (2σ)	28 ± 13 (2σ)	0 ^g

^a Yield = $\Delta[\text{product}]/\Delta[1,3\text{-butadiene}]$, where the loss of butadiene was typically 20%.

^b Using absorption band at $\sim 850 \text{ cm}^{-1}$ calibrated using isobutyl nitrate.

^c Not corrected for secondary reactions.

^d Errors are estimated from the standard deviation of the individual measurements and calibrations.

^e Corrected for 60% loss of 1,3-butadiene due to its reaction with OH radicals; errors reflect only those in our measurements.

^f Corrected for the formation from the OH radicals reactions with 1,3-butadiene [*Tuazon et al.*, 1999].

^g All the nitrates can be accounted for by the OH-butadiene reaction.

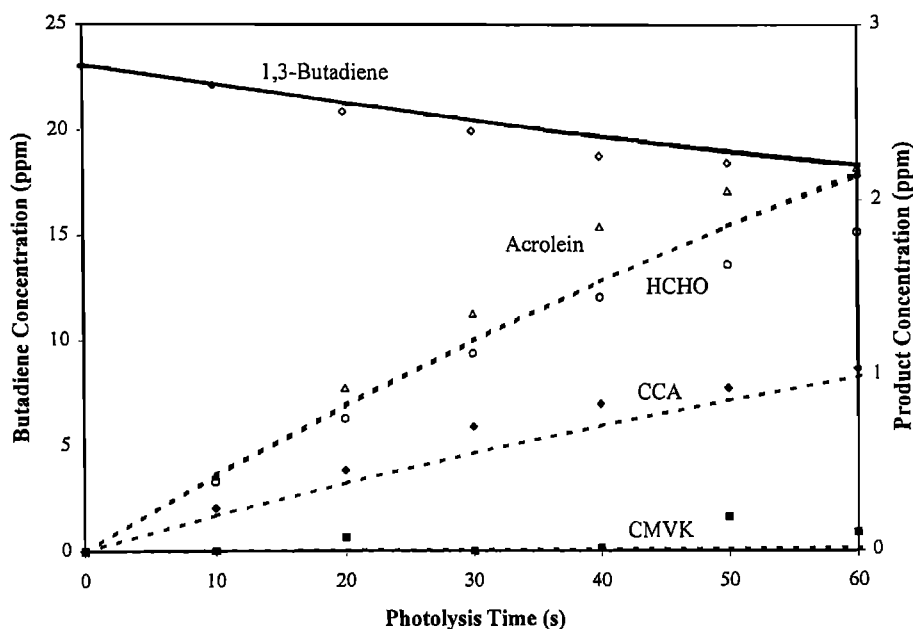


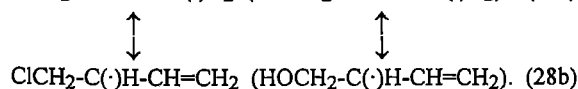
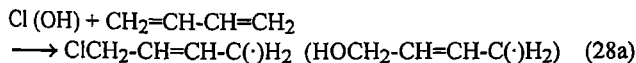
Figure 10. A comparison of results from the ACUCHEM model (lines) and the experimental data (symbols) of the Cl-butadiene reaction in the presence of NO. Open diamonds represent butadiene. Open triangles represent acrolein. Open circles represent HCHO. Solid diamonds represent CCA. Solid squares represent CMVK.

NO₂ can be extracted from the time dependence of NO₂ using the known chemistry. Using this technique, k_p for NO₂ was measured to be $(6.5 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ (2σ).

Figure 10 shows the model-predicted loss of butadiene and the formation of acrolein, HCHO, CCA, and CMVK obtained using the same branching ratios for the initial addition of chlorine atoms to the double bonds as was found to be the best match in the absence of NO. However, it is assumed that the alkoxy radicals $\text{CH}_2\text{ClCH}(\text{O}\cdot)\text{CH}=\text{CH}_2$ formed in the $\text{CH}_2\text{ClCH}(\text{OO}\cdot)\text{CH}=\text{CH}_2 + \text{NO}$ reaction have sufficient energy to decompose, rather than being thermalized and then reacting with O₂. It is seen that the model predictions and the experimental data are in very good agreement.

Figure 11 summarizes the major reaction paths for the Cl-butadiene reaction in the presence of NO.

The mechanism of the reaction of chlorine atoms with butadiene might be expected to be similar to that of the OH reaction. When Cl (or OH) adds to C1 or C4 carbon of 1,3-butadiene, both primary (from reaction (28a)) and secondary (from reaction (28b)) alkyl radicals are generated:



Acrolein originates from the secondary radical and $\text{ClCH}_2\text{-CH}=\text{CH}-\text{CHO}$ (CCA) (or $\text{HOCH}_2\text{-CH}=\text{CH}-\text{CHO}$ (HCA) in the case of the OH reaction) from the primary radical, respectively. The acrolein yield in the chlorine atom reaction is about half that in the OH reaction, while the yield of CCA is about twice that of the corresponding product (HCA) of the OH reaction reported by Tuazon *et al.* [1999]. This suggests that the addition of chlorine to the terminal carbon stabilizes

the primary radical more than the addition of OH. Theoretical studies of these Cl- and OH-radical intermediates would help to clarify the reasons for this difference.

3.3. Atmospheric Implications

Because sources of butadiene are anthropogenic, it is likely that NO_x will be present simultaneously. Thus CCA should be the most appropriate chlorine-containing product which could be used as a marker for chlorine atom chemistry in coastal urban areas. CCA will be removed from air by reactions with OH radicals and Cl atoms, as well as by photolysis. Assuming the rate constants for the OH and Cl atom reactions are the same as those with crotonaldehyde, the lifetimes of CCA under early morning conditions can be calculated to be about 15 hours with respect to removal by reaction with OH radicals at $5 \times 10^5 \text{ radical cm}^{-3}$ (using $k_{\text{OH} + \text{CA}} = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Atkinson, 1990]), and about 17 hours with respect to Cl atoms at $5 \times 10^4 \text{ atom cm}^{-3}$ (using $k_{\text{Cl} + \text{CA}} = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

The ACUCHEM model was used to estimate the potential concentrations of CCA formed in the early morning under typical conditions in a coastal urban area. The average concentration of 1,3-butadiene in the LA area is 2.2 ppb between 0600 and 0900 (E. M. Fujita and B. Zielinska, Desert Research Institute, personal communication, 2000). A constant source of 1,3-butadiene was added into the model to keep the concentration of 1,3-butadiene in the parts per billion level during the 3 hours modeling time. The concentrations of NO and NO₂ used in the model were 0.05 ppm and 0.04 ppm, respectively. These are the average data between 0600 and 0900 in July in the Los Angeles area (<http://www.arb.ca.gov/adam>). The concentration of chlorine atoms is assumed to be of the order of $10^4 \text{ atom cm}^{-3}$ in the early morning hours and that of OH radicals of the order of $10^5 \text{ radical cm}^{-3}$. NO, NO₂, Cl, and OH were held constant

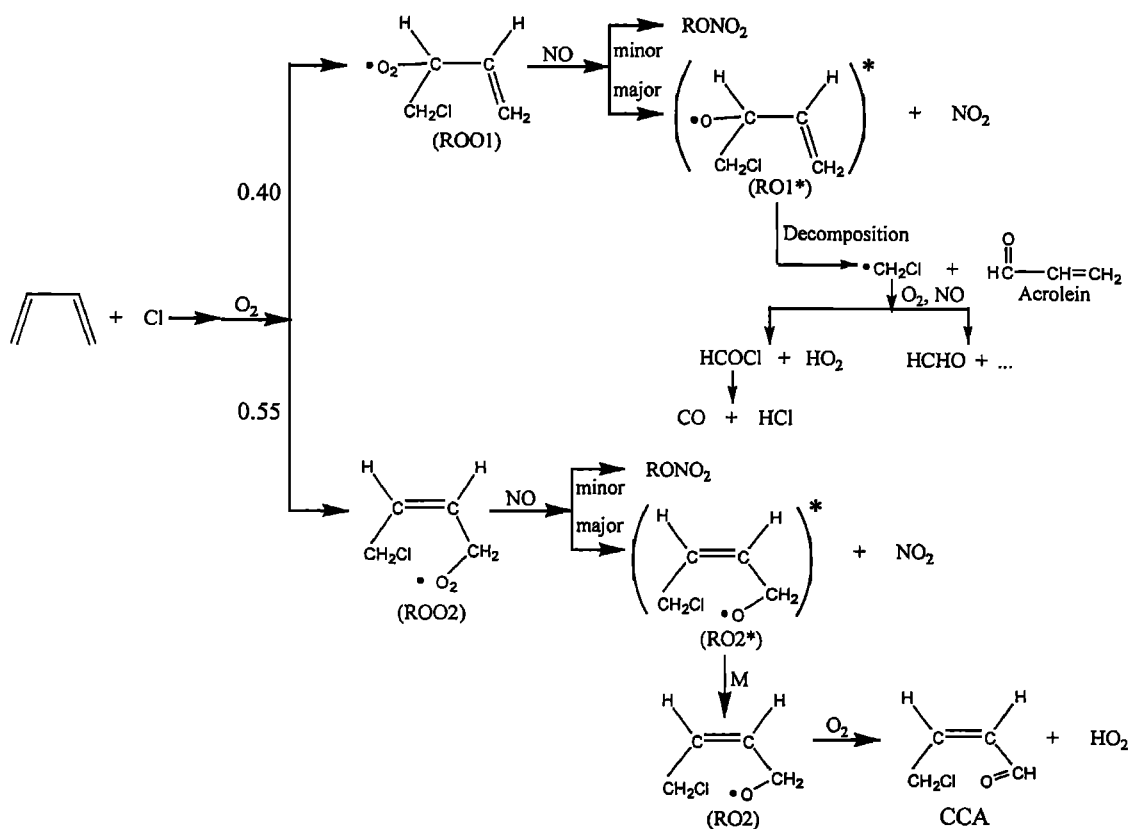


Figure 11. Major pathways for the Cl-butadiene reaction in the presence of NO in 1 atm air at room temperature.

during the run. The reaction of 1,3-butadiene with ozone (at a rate constant of $6.3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Atkinson, 1997]) was also added to the model, with ozone at 20 ppb [http://www.arb.ca.gov/adam]. The model included removal of CCA by reactions with OH and Cl. The modeling results predict that the concentration of CCA will be approximately 0.1 ppb after 1 hour, which should be easily detectable by GC, GC-ECD, and GC-MS. Indeed, CCA has been detected recently in several air samples collected in southern California near the coast (J. Low and R. J. Cicerone, personal communication, 2000).

Isoprene, which is a major component of biogenic emissions globally [Guenther *et al.*, 1995] is similar in structure to 1,3-butadiene. If the mechanism of the chlorine atom reaction is analogous to that for 1,3-butadiene, similar unique chlorine-containing organics should be formed. One would therefore predict the formation of 1-chloro-3-methyl-3-butene-2-one (CMBO) at low NO concentrations, and 4-chloro-3-methyl-2-butenal and 4-chloro-2-methyl-2-butenal formation irrespective of NO. CMBO was identified in earlier laboratory studies of the isoprene reaction with Cl atoms in the absence of NO [Nordmeyer *et al.*, 1997]. Our present work suggests that a search for 4-chloro-3-methyl-2-butenal and 4-chloro-2-methyl-2-butenal as well as CMBO would also be useful.

4. Conclusions

The reaction of chlorine atoms with 1,3-butadiene in 1 atm. air generates 4-chlorocrotonaldehyde (CCA) in both the presence and absence of NO, with yields (relative to the loss of

butadiene) of 65% and 29%, respectively. Chloromethyl vinyl ketone (CMVK) was observed with a yield of 19% only in the absence of NO. Box modeling suggests that approximately 0.1 ppb h⁻¹ of CCA could be formed during the morning hours in coastal urban regions where there are sources of butadiene from motor vehicle exhaust and chlorine atoms from sea-salt reactions. Thus CCA should be a unique marker of chlorine atom chemistry in such regions and be generated in sufficient concentrations to be measurable by conventional techniques such as GC-MS and GC-ECD. These studies also suggest that characteristic products of the reaction of the biogenic hydrocarbon isoprene with chlorine atoms should include 4-chloro-3-methyl-2-butenal and 4-chloro-2-methyl-2-butenal in the presence or absence of NO, and 1-chloro-3-methyl-3-butene-2-one (CMBO) at very small NO concentrations. A search for such products in a variety of locations would provide the data to help to assess the importance of chlorine atom chemistry in coastal continental regions.

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B. J. Finlayson-Pitts and W. Wang, Department of Chemistry, University of California, Irvine, 516 Physical Sciences, Irvine, CA 92697-2025. (bjfinlay@uci.edu; wangw@uci.edu)

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