The gas phase reaction of ozone with 1,3-butadiene: formation yields of some toxic products

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Abstract

The formation yields of acrolein, 1,2-epoxy-3-butene and OH radicals have been measured from reaction of ozone with 1,3-butadiene at room temperature and atmosphere pressure. 1,3,5-Trimethyl benzene was added to scavenge OH radicals in measurements of product yields. In separate experiments, small quantities of 1,3,5-trimethyl benzene were added as a tracer for OH. Formation yields of acrolein of (52 $\pm$ 7)\%, 1,2-epoxy-3-butene of (3.1 $\pm$ 0.5)\% and OH radicals of (13 $\pm$ 3)\% were observed. In addition, the rate coefficient of the gas-phase reaction of ozone with 1,2-epoxy-3-butene was measured both directly and relative to propene, finding an average of (1.6 $\pm$ 0.4) $\times$ 10\(^{-18}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively, at 296 $\pm$ 2 K. The results are briefly discussed in terms of the effect of atmospheric processing on the toxicity of 1,3-butadiene. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 1,2-Epoxy-3-butene; Ozone rate constant

1. Introduction

1,3-Butadiene is a common atmospheric pollutant that has been found to be carcinogenic due to its epoxide metabolites (Himmelstein et al., 1997). It was identified both as a Hazardous Air Pollutant in the 1990 Clean Air Act (US public law 101–549) and as a Toxic Air Contaminant under California’s air toxics program (AB 1807) in 1992. Butadiene is a very volatile and widely used industrial chemical as well as a product of the incomplete combustion of gasoline and diesel fuels, and is widely observed in ambient air at concentrations in the low ppt to low ppb range, with an average around 0.2 ppb (suburban air, (EPA, 1993; Schmitz et al., 1997). In-vehicle exposures are typically higher; around 1.3 ppb (EPA, 1993). It reacts in the atmosphere with OH, O\(_3\) and NO\(_3\) to produce a number of potentially toxic products. All three reactions produce acrolein and formaldehyde, which are also considered air toxics under the 1990 Clean Air Act. The ozone reaction also produces 1,2-epoxy-3-butene (Atkinson et al., 1994). Even though this epoxide is only formed in yields of a few percent, because of its mutagenic potential, the epoxide could contribute to the risk due to butadiene inhalation for human health in smoggy cities.

Ozone reacts with alkenes by adding across the double bond to form a primary ozonide which rapidly decomposes to a carbonyl compound and a vibrationally excited carbonyl oxide (see Scheme 1).

Butadiene also generates some 1,2-epoxy-3-butane, probably via pathway (R1c), (Atkinson et al., 1994). In the gas phase, carbonyl oxides can then be collisionally stabilized or undergo decomposition and/or isomerization (e.g., Herron and Huie, 1977; Su et al., 1980; Horie and Moortgat, 1991). For the C\(_1\) carbonyl oxide:

\[
[H_2COO]^\dagger \overset{M}{\rightarrow} H_2COO (\text{Thermalized}) + M (R2a) \\
HC(O)OH + M \quad (R2b) \\
\rightarrow 2H + CO_2 \\
H_2O + CO \quad (R2c) \\
CO_2 + H_2 \quad (R2d) \\
OH + HCO. \quad (R2f)
\]
Several recent studies have investigated OH formation from ozone–alkene reactions (e.g., Atkinson and Aschmann, 1993; Paulson et al., 1997; Gutbrod et al., 1997; Donahue et al., 1998). For many alkenes, OH yields are large and as such, these reactions are a significant source of the chain-initiating radicals that drive oxidizing photochemistry in urban and rural air (Paulson and Orlando, 1996).

The results of previous studies on the butadiene reaction with \( \text{O}_3 \) are summarized in Table 1. Using Fourier transform infrared spectroscopy (FTIR), Niki et al. (1983) observed acrolein, formaldehyde, \( \text{CO} \), and \( \text{CO}_2 \) together with small quantities of ethene, acetylene, and formic anhydride from the 1,3-butadiene ozone reaction, but did not use an OH scavenger. Atkinson et al. (1994) measured an 1,2-epoxy-3-butene yield (using an OH scavenger), and Atkinson and Aschmann (1993) estimated the OH formation yield. Recently, Liu et al. (1999) used a semi-quantitative derivatization technique to investigate formation of carbonyls, including multi-functional. In addition to the above carbonyls, they observed several (probably minor) products that are not observable with gas chromatography or FTIR.

In this study we report formation yields for acrolein, 1,2-epoxy-3-butene, the OH radical, and upper limits for the yields of several minor products of the ozone–butadiene reaction. The rate constant for the reaction of 1,2-epoxy-3-butene with \( \text{O}_3 \) was also measured using both absolute and relative rate techniques. Sufficient concentrations of 1,3,5-trimethylbenzene (TMB) or di-n-butylether (DBE) were added to scavenge OH in the product studies. The results are discussed in terms of the reaction mechanism and the effect of atmospheric processing on the toxicological potency of 1,3-butadiene.

### 2. Experimental description

Experiments were carried out in 250 l Teflon chambers at atmospheric pressure (760 ± 10 Torr) and 296 ± 2 K. Liquid compounds were evaporated into a stream of purified air (Thermo Environmental Model 111) as the
chamber was filled; gasses were added directly using graduated micro syringes. The quality of the zero air was checked periodically and concentrations of hydrocarbons, nitrogen oxides and ozone were always below the detection limits (about 15, 3 and 5 ppb, respectively). Once the gas mixture was prepared, the chamber was mixed by moving the walls and left to stand for at least 1 h to allow the reactant concentrations to stabilize. Several measurements of the organic compounds in the dark chamber were made to establish the initial concentrations before addition of ozone. All organic compounds (DBE, TMB, 1,3-butadiene, acrolein, and 1,2-epoxy-3-butene, Aldrich stated purity, 99, 98, 99, 96, and 98%, respectively), were used without further purification. Ozone was generated by flowing pure oxygen (150 ml/min) through a mercury lamp generator (JeLight, Model 600) and the ozone concentration inside the chamber was measured with UV absorption (Dasibi, Model 1003RS).

Experiments to investigate products of the 1,3-butadiene reaction with ozone are summarized in Fig. 3. TMB or DBE were added in sufficient excess to trap more than 95% of the OH radicals formed. Ozone was added every 30–60 min in aliquots, each resulting in 0.5 to 2 ppm O$_3$ inside the chamber. Analyses of the composition of the reacting mixture were made every 30 min just before addition of the next ozone aliquot. Identification of peaks was made both with authentic standards and with a gas chromatograph (GC)/mass spectrometer (Varian Saturn 2000 ion trap), with electron impact ionization (EI) and acetonitrile chemical ionization.

The small ratio relative-rate technique was used to measure OH formation (Paulson et al., 1999). Briefly, small quantities of a tracer (TMB) that reacts with OH but not O$_3$ was added to monitor OH formation. Initial tracer concentrations were less than 10% of the initial alkene concentrations (Table 2). Ozone was added in aliquots. To account for minor side-reactions such as loss of the tracer to the wall and reactions of OH with products, the data were analyzed numerically to derive an OH yield. It should be noted that it is evident from the rate constants that HO$_2$ formed in these experiments will primarily react with either itself or an RO$_2$ radical. Any other loss process for TMB (apart from a small amount of wall loss, < 1.5%) is unlikely. Rate constants show that H atoms rapidly combine with O$_2$, O(^1)D and O(^3)P rapidly react to form O$_3$, and while it is conceivable that the carboxyl oxides may react with TMB, the alkene is a far more likely target, as are water, organic acids and aldehydes. Relative loss of tracer pairs including TMB, di-n-butyl ether, m-xylene and several other tracers in the presence of ozone and alkenes have been studied by Paulson et al. (1997) and Marston et al. (1998); both studies are completely consistent with the tracers reacting with OH.

The rate coefficient of the reaction between 1,2-epoxy-3-butene and ozone was measured both directly and relative to propene (Table 3). All experiments had added excess TMB to scavenge OH. For the relative measurements, ozone was added in three aliquots of about 2 ppm each. In the direct measurements, O$_3$ was added once and analyses of the hydrocarbon and ozone concentrations were made every half hour during the 4–5 h experiments.

Samples of organic compounds were drawn through a heated Teflon line and analyzed with GC/flame ionization detection (Hewlett-Packard 5890) equipped with a 30 m DB-1 column (J&W, ID 0.32 mm, 1 μm film). The GC was calibrated daily using a 20.2 ± 0.4 ppm n-hexane standard (Scott Specialty Gases). Calibration standards for TMB, DBE and propene (Scott Specialty Gases, all certified ± 2%) were run periodically and the per-carbon peak areas were compared to the n-hexane standard. For TMB and propene, the agreement was better than ± 4%. Because of the oxygen atom in DBE, a peak area equivalent to 7.3 carbons was observed. The concentration of butadiene was calculated relative to the n-hexane standard assuming a per-carbon peak area. This approach is very reliable for compounds containing only carbon and hydrogen (± 4%). In order to calculate concentrations for oxygenated products, the FID peak areas were measured by two independent methods.

First, in a set of four experiments, mixtures of acrolein and 1,2-epoxy-3-butene and n-hexane (as an internal standard) in the 2–10 ppm range were generated in Teflon bags by injection of the liquids into a known volume

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1,3-Butadiene initial concentration (ppb)</th>
<th>TMB initial concentration (ppb)</th>
<th>Concentration ratio TMB/1,3-butadiene</th>
<th>Calculated OH formation yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2350</td>
<td>161</td>
<td>0.07</td>
<td>13</td>
</tr>
<tr>
<td>10</td>
<td>2700</td>
<td>242</td>
<td>0.09</td>
<td>15</td>
</tr>
<tr>
<td>11</td>
<td>3190</td>
<td>224</td>
<td>0.07</td>
<td>16</td>
</tr>
<tr>
<td>12</td>
<td>4260</td>
<td>225</td>
<td>0.05</td>
<td>13</td>
</tr>
</tbody>
</table>
of zero air. The reproducibility of these experiments was better than \( \pm 3\% \). The resulting \( \text{C}_6\text{H}_{14} \) was within 10% or better of the calculated value, but was lower in all cases. Using the internal standard to calculate the measured \( \text{C}_6\text{H}_{13} \) concentration, concentrations of \( \text{C}_6\text{H}_{13} \) and \( \text{C}_2\text{H}_{4} \) resulted in FID peak areas equivalent to \( 1.9 \pm 0.2 \) and \( 2.9 \pm 0.3 \) carbons, respectively. Second, we measured the peak area/ppmv of \( \text{C}_6\text{H}_{13} \) directly using an instrument developed to measure total non-methane organic carbon (Paulson et al., 1996) by oxidizing \( \text{C}_6\text{H}_{13} \) samples to \( \text{CO}_2 \), reducing to \( \text{CH}_4 \), and comparing the FID peak area/ppmv to measurements of unaltered samples. The FID peak area for \( \text{C}_6\text{H}_{13} \) measured this way was equivalent to \( 2.1 \pm 0.2 \) carbons. To calculate \( \text{C}_6\text{H}_{13} \) yields in this study we have used 2.0 as the FID response. Wall losses are very minor for all compounds involved in this study (Kramp and Paulson, 1998), but were nevertheless included in each analysis used to derive the product yields. An upper limit for 1,3-butadiene wall loss rate of about \( 2 \times 10^{-7} \text{ s}^{-1} \) was measured.

3. Results

3.1. Reaction of ozone with 1,2 epoxy-3-butene

The rate coefficient for the ozone reaction with 1,2-epoxy-3-butene was determined in direct and relative-rate experiments (Table 3). A linear least-squares regression (Fig. 1) of two experiments using \( \text{C}_2\text{H}_{4} \) as the reference compound \((k_{\text{O}_3 + \text{C}_2\text{H}_{4}} = (1.01 \pm 0.25) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \) Atkinson, 1994) resulted in a value of \((1.4 \pm 0.4) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for the 1,2-epoxy-3-butene–ozone reaction. Data from three direct experiments are shown in Fig. 2 and lead to a slightly larger rate coefficient of \((1.7 \pm 0.3) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). There are several potential sources of the difference between the direct and relative-rate measurements, including (probably small) errors from the \( \text{C}_2\text{H}_{4} \) reaction rate constant, mixing (which tends to underestimate the more slowly reacting compound; R. Atkinson, pers. communication), and errors in the initial concentrations of \( \text{O}_3 \) or the hydrocarbons. In the calculations of 1,2-epoxy-3-butene yields below, we have used \( 38 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).
3.2. Product yields for the reaction of butadiene with ozone

The major products of the reaction between ozone and 1,3-butadiene are acrolein, formaldehyde (HCHO) and the carbonyl oxides [H₂COO] and [CH₂ = CH–CHOO] (R1, Scheme 2). In Fig. 3, acrolein, 1,2-epoxy-3-butene are plotted versus 1,3-butadiene reacted. This data was obtained from eight experiments conducted with different initial 1,3-butadiene concentrations and turnover rates. Linear least-squares regression of the entire data set results in yields of (50 ± 2) and (2.4 ± 0.2)% for acrolein and 1,2-epoxy-3-butene, respectively. Identification of these compounds was confirmed with authentic standards and GC/MS. With the ion trap, EI spectra agreed well with the National Institutes of Standards and Technology (1992) mass spectral libraries for all compounds (including 1,3-butadiene, di-n-butyl ether and their oxidation products) except acrolein. Chemical ionization with CH₃CN provided clean M + 1 spectra for 1,2-epoxy-3-butene, di-n-butylether, butanal and butyric acid-butylester but produced some fragmentation or larger ions for acrolein and 1,3-butadiene.

Both observed yields need to be corrected for their losses due to reaction with ozone. For this, the set of ordinary differential equations describing the reactions in these experiments (including O₃ and products) was solved numerically (Carter and Atkinson, 1988) to account for secondary reactions in the derivation of the...
product yields. The reaction of ozone with acrolein ((2.9 ± 1.0) × 10⁻¹⁹ cm³ molecule⁻¹ s⁻¹; Atkinson, 1994) is about 20 times slower than its reaction with 1,3-butadiene ((6.3 ± 1.9) × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹; Atkinson, 1997) and thus has a small effect; the resulting acrolein yield is 52%. The effect of the secondary consumption of 1,2-epoxy-3-butene is more significant; its corrected yield was 3.1%. Inclusion of uncertainties in FID peak area/ppm, rate coefficients, and random errors results in yields of (52 ± 7)% and (3.1 ± 0.5)% for acrolein and 1,2-epoxy-3-butadiene, respectively.

Several small peaks appear on the chromatogram as the butadiene is reacted away. Efforts to identify these products were unsuccessful. Possible minor products, 2,5-dihydrofuran, β-propiolactone, ethylene and acetylene all remained below detection limits, indicating upper limits for their formation yields are 1%. Since this study was performed, Liu et al. (1999) have identified or found molecular weights for several possible additional products (Table 1).

3.3. OH formation yield

The calculated OH yields for each tracer in four experiments, together with the initial conditions, are summarized in Table 2; data and calculations are shown in Fig. 4. The predicted behavior of TMB and butadiene assuming OH yields of 13 and 16% are shown; 13% provides the best fit for experiments 9 and 12, while experiments 10 and 11, where less than 4% of the TMB was reacted, are best fit with slightly higher OH yields. A weighted average of these data combined with the uncertainties in the TMB rate constant and other minor sources of systematic uncertainty results in an OH yield of 13 ± 3%.

4. Discussion

A summary of product yields for the 1,3-butadiene reaction with ozone is shown in Table 1. The values for acrolein, 1,2-epoxy-3-butene and OH are all in agreement with previous values within mutual uncertainties. In the case of acrolein, the agreement may be fortuitous. In the study where OH scavengers were not employed (Niki et al., 1983) about 11% of the butadiene was presumably consumed by OH, but since the products of the butadiene reaction with OH in the absence of NOₓ are expected to include acrolein, formaldehyde, and hydroperoxides, not much effect on the observed yield of acrolein is expected. Our yield of the epoxide was identical to that of Atkinson et al. (1994) prior to correction for reaction with O₃, which they did not include. This correction produces a yield that is about 35% higher. More striking is the discrepancy between Niki et al.’s observation of ethene and acetylene, which we could not corroborate. Our OH yield is about 60% higher than that measured by Atkinson and Aschmann, 1993, although both are again within the mutual uncertainties. This difference may arise from the unknown amount of HO₂ that forms — the method used by Atkinson and Aschmann, 1993 in that study is sensitive to HO₂ formation. Formation of OH from HO₂ + O₃ is likely very small with either method, but the cyclohexanol/cyclohexanone method measures formation of those products from the disproportionation reaction of the RO₂ radical that results from the OH reaction with cyclohexane. RO₂–RO₂ reactions compete with RO₂–HO₂ reactions; the latter reactions are faster. The cyclohexanol/cyclohexanone method is based on a typical yield of those compounds from reacted cyclohexane (a 55% yield, derived from experiments with α-pinene and Δ⁸-carene (Atkinson et al., 1992), and is the source of the uncertainty that is attached by Atkinson and co-workers. Clearly, one explanation for the cyclohexane method to result in a lower OH yield is for the HO₂ yield to be higher than typical.

The initial O₃–butadiene reaction produces formaldehyde and a C₃ carbonyl oxide (R1a), acrolein and a C₁ carbonyl oxide (R1b), or 1,2-epoxy-3-butene and O₂ (R1c). A 52% yield of acrolein indicates that the primary ozone decompose with more regard to statistics than to thermochemistry; consistent with other unbranched alkenes (Grosjean and Grosjean, 1997 #515). The 65% formaldehyde yield reported by Niki et al. (1983) is reasonably consistent with this split; additional formaldehyde can be formed via a number of secondary pathways. Epoxide formation (R1c) is a minor
channel that has also been observed from isoprene, which produces a similar yield of \( \sim 5\% \) (Paulson et al., 1992; Atkinson et al., 1994). Several reaction pathways for the C\(_3\) carbonyl oxides from the butadiene reaction with ozone are shown in Scheme 2. Syn- and anti-carbonyl oxides probably do not equilibrate efficiently (Scheme 2a) due to a \( \sim 28 \) kcal/mol activation barrier for isomerization (Kuwata et al., unpublished work). The possible formation channels for acetylene, ethene and \( \beta\)-propiolactone (Scheme 2e–g) appear to be inoperative, consistent with isoprene, which does not form an analogous lactone or methyl acetylene. Isoprene does, however, produce about 5% propene (Paulson et al., 1992; Carter and Atkinson, 1996), presumably through the pathway analogous to Scheme 1.

Butadiene’s OH formation yield is reasonable compared to ethene, which has a yield of 0.18 ± 0.06 (Paulson et al., 1998). Quantum chemical calculations have led to the idea that ethene decomposes via a four-membered ring to produce OH (Gutbrod et al., 1997; Donahue et al., 1998), although this mechanism (shown for the C\(_3\) carbonyl oxide, Scheme 1b) predicts OH yields that are much lower than observed. Presumably, the same mechanism operative for ethene is at work for 1,3-butadiene, through both the C\(_1\) carbonyl oxide and the anti-C\(_3\) carbonyl oxide. The C\(_3\) syn-carbonyl oxide cannot rearrange this way due to lack of an available H atom for abstraction. 1,3-butadiene might be expected to produce about 75% of the OH from ethene, exactly as observed.

The rate constant for the O\(_3\) reaction with 1,2-epoxy-3-butene, \( 1.6 \pm 0.4 \times 10^{-18} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), is, as far as we know, the first measurement of the O\(_3\) reaction rate for an unsaturated epoxide. Relatively few rate constants for O\(_3\) reactions with oxygenates have been measured. In contrast to OH–alkene reactions, the rate constants for ozone–alkene reactions are generally quite sensitive to substituents around the double bond. The rate constants for the similar reactions between O\(_3\) and 1-butene, methylvinylketone, and acrolein are 10, 5 and 0.7 \( \times 10^{-18} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively (Atkinson and Carter, 1984). The effect of an epoxide oxygen appears to fall in the range suggested by acrolein and methylvinylketone.

5. Human exposure

1,3-Butadiene is considered an air toxic because of its potential carcinogenic effects based primarily on rat and mice studies (Himmelstein et al., 1997). The active compounds appear to be butadiene metabolites 1,2-epoxy-3-butene and 1,2 : 3,4-diepoxybutane; the latter is about 100 times more potent (Kallioniemi et al., 1992; Cochran and Skopec, 1994; Himmelstein et al., 1997). As butadiene reacts in the atmosphere with OH and O\(_3\), it is converted primarily to acrolein and formaldehyde. Formaldehyde is a ubiquitous pollutant that is both directly emitted and a product of numerous photochemical reactions, such that butadiene photooxidation contributes only a tiny fraction of ambient formaldehyde. Butadiene can be a major precursor to acrolein, however. Acrolein is considered an air toxic because of its acute toxicity; exposure to concentrations of 10 ppm can be fatal, and upper respiratory tract irritation may result from concentrations as low as 170 ppb (ATSDR, 1989; Hazardous Substances Data Bank, 1993). Away from strong sources, oxidation of 1,3-butadiene will clearly not result in acrolein concentrations that are high enough to produce acute toxicity effects. The question remains if the 1,2-epoxy-3-butene and 1,2 : 3,4-diepoxybutane, both of which are more carcinogenic than butadiene itself, formed in the atmospheric reaction of 1,3-butadiene with O\(_3\) preserves or increases the human health risk posed by butadiene. In urban air, the ratio of O\(_3\) to OH generally fall in the range from \( 1 \times 10^5 \) to \( 2 \times 10^6 \) (Seinfeld and Pandis, 1997). Given the rate constants for reaction of 1,3-butadiene with OH and O\(_3\) of \( 6.7 \times 10^{-11} \) and \( 7.5 \times 10^{-15} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively, the amount of 1,2-epoxy-3-butene produced as butadiene is oxidized in the atmosphere should be from 0.03 to 0.7%. We estimate a reaction rate for the OH reaction with 1,2-epoxy-3-butene of \( 3 \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) based on structure–activity relationships (Kwok and Atkinson, 1995). As such, in urban air, the O\(_3\) reaction consumes at most 10% of the epoxide; the remainder is consumed by OH. If we then assume that the 1,2 : 3,4-diepoxy has a yield that is the same as that for O\(_3\) reacting with butadiene, then the yield of 1,2 : 3,4-diepoxy is not more than 0.005% of the reacted 1,3-butadiene.

Pharmacokinetic modeling of 1,3-butadiene inhalation and metabolism indicates that roughly 20% of the 1,3-butadiene inhaled is absorbed and converted to 1,2-epoxy-3-butene (Himmelstein et al., 1997). The inhalation uptake efficiency of 1,2-epoxy-3-butene and 1,2 : 3,4-diepoxybutane are at least 30 times greater than 1,3-butadiene (Weast, 1986; Sweeney et al., 1997). Even so, the toxicity of inhaled 1,2-epoxy-3-butene is not more than five times that of 1,3-butadiene. Likewise, 1,2 : 3,4-diepoxybutane has a maximum toxicity that is about 500 times greater than that of 1,3-butadiene. As 1,3-butadiene reacts, therefore, on balance its toxicity based on carcinogenicity is reduced; the production of carcinogenic epoxide products replaces from less than 1 up to about 5% of its initial toxicity. It should be emphasized that the products atmospheric reactions of 1,3-butadiene with NO\(_3\), which are expected to include carbonyl nitrates (Barnes et al., 1990), some of the unknown products of the ozone reaction with butadiene, as well as some of the products of the OH radical chemistry (e.g., malonaldehyde recently discovered by Liu et al., 1999) may also be quite toxic.
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