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Formation of Secondary Ozonides in the Gas-Phase Ozonolysis of Simple Alkenes

Peter Neeb, Osamu Horie* and Geert K. Moortgat

Max Planck Institute for Chemistry, Division of Atmospheric Chemistry
Postfach 3060, D-55020 Mainz, Germany

Abstract: Secondary propene ozonide and isobutene ozonide were formed in the gas-phase ozonolysis of ethene with added acetaldehyde and acetone, respectively. Combined with the formation of hydroperoxymethyl formate and methoxymethyl hydroperoxide in the ethene-ozone reaction system in the presence of HCOOH and CH_3OH, respectively, formation of the secondary ozonides reveals a close similarity between the gas-phase and the liquid-phase ozonolysis of alkenes.

Gas-phase ozonolysis of alkenes is an active area of research not only for the mechanistic interest but also due to its importance in atmospheric chemistry[1]. While the liquid-phase mechanism established by Criegee[2,3] is widely accepted to interpret the gas-phase ozonolysis data, there still remain uncertainties about the reactions of stabilised Criegee intermediates[4]. The initially-formed, vibrationally excited intermediate $R^1R^2COO^*$ partly decomposes to various products, (2a) and partly becomes collisionally deactivated to form the stabilised Criegee intermediate, R^1R^2COO, (2b)[1,4]. (R^1 - R^4 = H, alkyl, or alkenyl groups).

$$O_3 + R^1R^2C{=}CR^3R^4 \rightarrow R^1R^2COO^* + R^3R^4C{=}O \qquad (1)$$

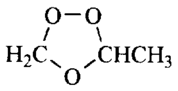
$$R^1R^2COO^* \rightarrow \text{decomposition products} \qquad (2a)$$

$$R^1R^2COO^* \rightarrow \text{stabilisation} \rightarrow R^1R^2COO \qquad (2b)$$

In a recent contribution, Fajgar *et al.*[5] have confirmed our observation of the secondary 2-butene ozonide formation in the gas-phase ozonolysis of 2-butene isomers[6]. The ozonolysis of ethene in the liquid phase has been known to produce the secondary ozonide with high yields[7,8] accompanied by minor formation of HCHO and HCOOH. In the gas phase, the ozone-ethene reaction has been shown to yield HCHO, CO, CO_2, HCOOH, formic acid anhydride $(HCO)_2O$, and hydroperoxymethyl formate $HOO\text{-}CH_2\text{-}O\text{-}CHO$, with a carbon balance of > 90%[9]. In the absence of carbonyl compounds, no formation of the secondary ozonide has been observed. This is partly due to a high degree of excitation of the initially formed Criegee intermediate CH_2OO, associated with large yields of products due to the decomposition of the excited CH_2OO^* intermediate, consistent with recent theoretical studies[10,11].

In this communication, we report formation of propene ozonide **1** and isobutene ozonide **2** in the ethene ozonolysis in air with added CH_3CHO and CH_3COCH_3, respectively, and show a close similarity between the gas-phase and liquid-phase ozonolysis exists with respect to the reactions of the Criegee intermediates.

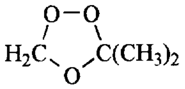
$CH_2OO + CH_3CHO \rightarrow$



1

(3)

$CH_2OO + CH_3COCH_3 \rightarrow$



(4)

2

Ozonolysis was carried out in an evacuable, 570 *l* spherical glass vessel in 730±3 Torr (1 Torr = 133.3224 Pa) synthetic air at 295±2 K[6,9]. Ozone was generated with a Hg Pen-ray lamp mounted on the bottom plate of the reactor. Dilute alkene/N_2 mixtures prepared in a 1.38 *l* transfer cylinder was flushed into the reactor with N_2 carrier gas stream. The alkenes used were ethene and *cis*-2-butene. The dilute mixtures in N_2 of added compounds, CH_3COCH_3, CH_3CHO, HCHO, and HCOOH, were added in a similar way. The concentrations of ozone, alkenes, and added compounds were in low ppmv (parts-per-million by volume, 1 ppmv = 2.4×10^{13} molecule cm^{-3} at the above temperature and pressure). The reaction was initiated by adding the alkene/N_2 mixture to an O_3-alkene(-added compound)-synthetic air mixture. A long-path (43.2 m path-length) FTIR (Bruker IFS28) spectroscopy with a resolution of 0.5 cm^{-1} was used to analyse the reaction products.

Typical results are illustrated in Fig. 1. The spectra of **1** and **2** were generated by computationally subtracting contributions of the identified products and remaining reactants from the FTIR spectrum of product mixtures. These spectra were compared with the reference spectra of synthesised ozonides and authenticity confirmed[12]. Figure 1 clearly shows that with sufficient excess of CH_3CHO and CH_3COCH_3 addition, the stabilised Criegee intermediate CH_2OO reacts almost quantitatively with the added compounds and form **1** and **2**, respectively. Under these conditions, formation of hydroperoxymethyl formate (HPMF), HOO-CH_2-O-CHO **3** was found to be nearly completely suppressed. Since we know[9] that **3** is formed between HCOOH and CH_2OO, we can conclude that CH_3CHO and/or CH_3COCH_3 compete against HCOOH toward CH_2OO intermediate. This was confirmed in experiments where formation of **3** as well as the ozonides was observed with the addition of lower concentrations of CH_3CHO and/or CH_3COCH_3 than used in the experiments shown above.

$$CH_2OO + HCOOH \rightarrow HOO\text{-}CH_2\text{-}O\text{-}CHO\ (HPMF)\ \mathbf{3} \qquad (5)$$

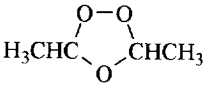
The same ozonides **1** and **2** are formed in the reaction systems *cis*-2-butene/O_3/HCHO and 2,3-dimethyl-2-butene/O_3/HCHO, respectively[13,14]. From these results, therefore, it can be concluded that in the gas-phase ozonolysis of alkenes, the stabilised Criegee intermediates react with added or foreign aldehydes or ketones to form secondary ozonides.

$$CH_3CHOO + HCHO \rightarrow \mathbf{1} \qquad (6)$$

$$(CH_3)_2COO + HCHO \rightarrow \mathbf{2} \qquad (7)$$

We find that the formation of the secondary ozonides is not restricted to the added or foreign aldehydes or ketones. Ozonolysis of *cis*-2-butene was performed with and without CH_3CHO addition. As before, spectral subtraction was performed to obtain the spectra of 2-butene ozonide **4** under these conditions. Formation of **4** was observed in the absence of the CH_3CHO addition, confirming our previous results[6]. The ozonide concentration was shown to increase with the CH_3CHO addition. The spectrum of **4** obtained under these conditions is illustrated in Fig. 1.

$CH_3CHOO + CH_3CHO \rightarrow$



(8)

4

When HCHO instead of CH_3CHO was added, the formation of propene ozonide **1** was clearly observable. In our previous study[6], it was not possible to positively identify the formation **1** with addition of HCHO[13], mainly due to higher noise levels and lower spectral resolution in that study.

Formation of a homologue of **3**, hydroperoxyethyl formate (HPEF), $HOO\text{-}CH(CH_3)\text{-}O\text{-}CHO$ **5** in 2-butene ozonolysis with added HCOOH is shown in Fig. 1, together with a spectrum of **3**[9]. Under these conditions, formation of **4** is completely suppressed: an almost exact replica of the case of ethene ozonolysis.

$$CH_3CHOO + HCOOH \rightarrow HOO\text{-}CH(CH_3)\text{-}O\text{-}CHO \text{ (HPEF) } \mathbf{5} \qquad (9)$$

It was found that **5** is formed also in the presence of added HCHO in the 2-butene ozonolysis (not shown). HCOOH in the reaction was probably formed in a reaction cycle involving HCHO and HO_2 radical[15]. Our unexpected finding, that HCOOH and not HCHO as previously assumed[15,16] react with the stabilised Criegee

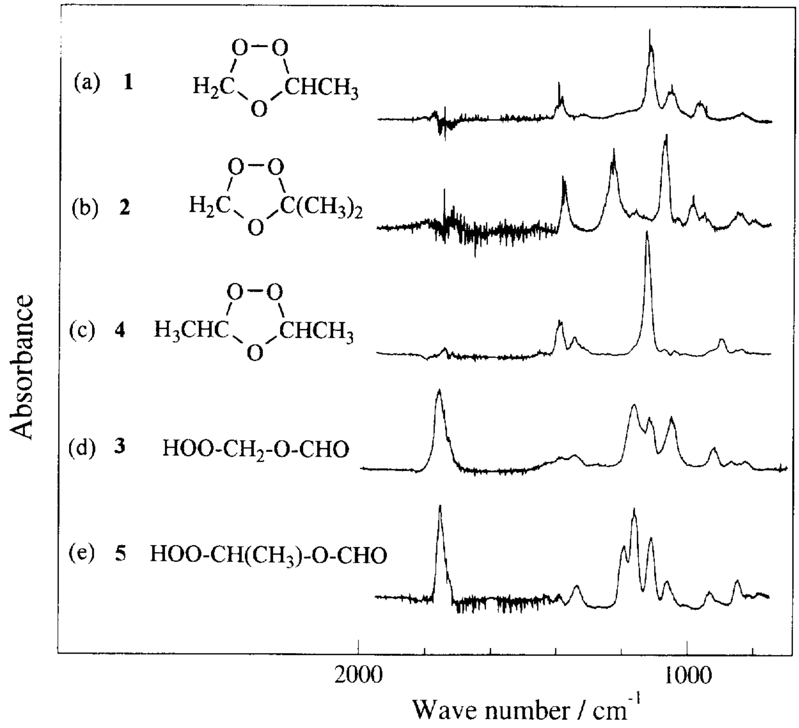


Fig. 1. FTIR spectra of the reaction systems ethene-O_3 and *cis*-2-butene-O_3.
(a) Propene ozonide, **1**. Experimental conditions were as follows. $[C_2H_4]_0$ = 16 ppmv, $[O_3]_0$ = 8 ppmv, and $[CH_3CHO]_0$ = 100 ppmv. No HPMF formation was observed under these conditions. The propene ozonide yield is about 0.4 relative to the converted C_2H_4. (b) Isobutene ozonide, **2**. Experimental conditions were: $[C_2H_4]_0$ = 4.0 ppmv, $[O_3]_0$ = 2.9 ppmv, and $[CH_3COCH_3]_0$ = 51 ppmv. The sum of the yields of FAN and HPMF relative to the converted C_2H_4 is about 0.07, as contrasted to ca. 0.5 with added HCOOH[7]. (c) 2-butene ozonide, **4**. Experimental conditions were: $[C_4H_8]_0$ = ca. 5 ppmv, $[O_3]_0$ = 2 ppmv, and $[CH_3CHO]_0$ = 10 ppmv. (d) Hydroperoxymethyl formate (HPMF), **3**. Taken from ref. 9. Experimental conditions were: $[C_2H_4]_0$ = 16 ppmv, and $[O_3]_0$ = 9.5 ppmv. (e) Hydroperoxyethyl formate (HPEF), **5**. The spectrum was obtained under the conditions of $[C_4H_8]_0$ = 5 ppmv, $[O_3]_0$ = 2 ppmv and $[HCOOH]_0$ = 2.4 ppmv. Under these conditions, no formation of 2-butene ozonide was observable.

intermediates to form transitory products in the gas-phase alkene ozonolysis[9,17], has made it necessary to revise our previous interpretation[6] on the formation of hydroxyethyl formate, HO-CH(CH_3)-O-CHO **6**, in the 2-butene ozonolysis. The residual spectrum containing a carbonyl group obtained with added HCHO[6] that had been assigned to **6**, has turned out to consist of **5** and another residual product whose identity is still being studied.

$$CH_3CHOO + HCHO \xrightarrow{X} HO\text{-}CH(CH_3)\text{-}O\text{-}CHO \quad \mathbf{6} \qquad (10)$$

Following our finding of the formation of **3** in ethene ozonolysis[9], it has been shown that other hydroxy compounds such as CH_3OH, $CH_3C(O)OH$ and H_2O react with CH_2OO to form corresponding hydroperoxy compounds, HOO-CH_2-OR where R = CH_3, $CH_3C(O)$, and H, respectively[17].

$$CH_2OO + RO\text{-}H \rightarrow HOO\text{-}CH_2\text{-}OR \qquad (11)$$

These reactions as well as the formation of secondary ozonides are reactions which are observed typically in the liquid-phase ozonolysis[2,3], manifesting the Criegee mechanism in the liquid-phase ozonation. Present results, combined with those of our previous studies[6,9,17], show clearly that there is a close relationship between the gas-phase and the liquid-phase ozonolysis with respect to the reaction mechanism. Formation of **4** in N_2 observed by Fajgar *et al.*[5] indicates that the same mechanism is operative in the absence or presence of O_2. The failures to observe secondary ozonides in the gas-phase ozonolysis as pointed out by Fajgar *et al.*[5] are therefore not due to the involvement of oxygen in the reaction but due to our inability yet to fully identify the ozonolysis products. In fact, ethene-O_3 system is the only case where a complete identification of all the reaction products has been achieved[9]. Further details of the gas-phase ozonolysis of 2-butene isomers will be published elsewhere[18].

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