

The Reactions of the Criegee Intermediate CH_3CHOO in the Gas-Phase Ozonolysis of 2-Butene Isomers

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ABSTRACT: Ozonolysis of *cis*- and *trans*-2-butene isomers were carried out in a 570 l spherical glass vessel in 730 torr synthetic air at 295 ± 3 K. The initial concentrations were 5 to 10 ppmv for the isomers and 2 to 5 ppmv for ozone. Quantitative yields were determined by FTIR spectroscopy for CH_3CHO , HCHO , CH_4 , CH_3OH , CO , and CO_2 . By means of computational subtraction of the spectral contribution of the identified products from the product spectra, residual spectra have been obtained. Formation of 2-butene ozonide, propene ozonide, and 1-hydroperoxyethyl formate $\text{CH}_3\text{CH}(\text{OOH})-\text{O}-\text{CH}(\text{O})$ have been identified in the residual spectra. These products have been shown to be formed in the reactions of the Criegee intermediate CH_3CHOO with CH_3CHO , HCHO , and HCOOH , respectively. Mechanistic implications and atmospheric relevance of these observations are discussed. ©1997 John Wiley & Sons, Inc. *Int J Chem Kinet* **29**: 461–468, 1997.

INTRODUCTION

Despite a wealth of gas-phase ozonolysis data [1–3 and references cited therein], only few studies have been devoted to quantitative product analysis [4–11]. In fact, no complete product data are available except for C_2H_4 . For this simplest alkene, we have been able to determine all the reaction products and their yields, with the carbon balance of more than 90% [11]. The pivotal finding which has led to the complete product

analysis in this system is that the transitory product is hydroperoxymethyl formate (hereafter HPMF), $\text{CH}_2(\text{OOH})-\text{O}-\text{CH}(\text{O})$, and is formed in the reaction of CH_2OO with HCOOH [11,12]. This compound had been assumed to be hydroxymethyl formate, $\text{CH}_2(\text{OH})-\text{O}-\text{CH}(\text{O})$, being composed of the stabilized Criegee intermediate CH_2OO and HCHO [4–6,9]. Following the observation of HPMF formation in the C_2H_4 ozonolysis [11], we found further that not only HCOOH but also CH_3COOH and CH_3OH react with CH_2OO to yield products with a general formula $\text{CH}_2(\text{OOH})-\text{O}-\text{R}$ where $\text{R} = \text{CH}(\text{O})$, $\text{CH}_3\text{C}(\text{O})$, and CH_3 , respectively, for HCOOH , CH_3COOH , and CH_3OH [13]. These results have indicated that there is a close connection be-

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tween the gas-phase and solution-phase ozonolysis reactions with respect to the Criegee intermediates [14,15].

Beyond CH_2OO , reactions of the stabilized Criegee intermediates have been studied very little [16]. In the ozonolysis of *trans*-2-butene using matrix-isolation FTIR spectroscopy, Horie and Moortgat [9] have observed formation of a product which was not assignable to known compounds. Since the yield of this product increased with the addition of HCHO, they [9] assigned hydroxyethyl formate, $\text{CH}_3\text{CH}(\text{OH})\text{—O—CH}(\text{O})$, to this product which is formed between CH_3CHOO intermediate and HCHO: analogous to now incorrectly assigned compound hydroxymethyl formate in the ethene ozonolysis.

In order to obtain quantitative product data relevant under atmospheric conditions, we carried out ozonolysis of *trans* and *cis*-2-butene in the low ppmv concentration range, using long-path FTIR spectroscopy [10] (hereafter referred to as HNM94). We observed, after subtracting computationally spectral contributions of identified products, formation of two products, a “carbonyl compound” and a “non-carbonyl compound”, and assigned tentatively hydroxyethyl formate, to the former and 2-butene ozonide to the latter. We were not able, however, to positively identify the formation of propene ozonide in the presence of added HCHO. Niki et al. [17] on the other hand have demonstrated the propene ozonide formation in the *cis*-2-butene ozonolysis with the added HCHO.

This study was motivated by our new discoveries, that CH_3COOH , CH_3OH as well as HCOOH react with CH_2OO intermediate to form unique products in the ethene ozonolysis [11,13]. It was logical, therefore, to consider that the above conclusions be extended to higher homologues of Criegee intermediates. Specifically, the purpose of this study was (1) to obtain the residual spectra through computational spectral subtraction of the identified products, (2) to “isolate” possible individual products which are contained in the residual spectra via computer-assisted spectroscopic analysis, and (3) to achieve a better understanding of the reactions of the stabilized Criegee intermediate CH_3CHOO in the gas-phase ozonolysis of 2-butene isomers.

EXPERIMENTAL

Experiments were carried out in an evacuable, 570 l spherical glass vessel in 730 torr (1 torr = 133.322 Pa) synthetic air at 295 ± 3 K. Details of the apparatus

and procedure have been described in our previous publications [10,11,18], and no details will be given here. All runs were carried out in the excess of the alkene. The initial concentrations of the 2-butene isomers were 5 ppmv (1 ppmv = 2.39×10^{13} molecule cm^{-3} at 295 K and 730 torr) for *trans*, and 5 and 10 ppmv for *cis* isomer. Ozone was either 2 ppmv or 5 ppmv. For added compounds, the concentrations were 10 ppmv for HCHO, 10 and 100 ppmv CH_3CHO , and 2.3 ppmv HCOOH . Since under the experimental conditions, reaction was complete within 3 min, almost all spectral recordings (except for Run G, Table I) were made within about 10 min after the addition of the alkene to the reactor. No attempt was made to obtain time-resolved spectra.

The main analytical instrument used in this study was an FTIR spectrometer (Bruker IFS-28). Spectra were recorded with narrow-band MCT (700–2000 cm^{-1}) and InSb (2000–4000 cm^{-1}) detectors, with a resolution of 0.5 cm^{-1} , and 128 scans were co-added. The quantitative yields of the identified products were obtained by subtracting their spectral contributions from the product spectra by means of the reference spectra of the individual compounds. An estimate of the relative errors including calibration errors was as follows: $\text{O}_3 \pm 5\%$, $\text{C}_4\text{H}_8 \pm 20\%$, $\text{CH}_3\text{CHO} \pm 20\%$, $\text{HCHO} \pm 10\%$, $\text{CH}_4 \pm 10\%$, $\text{CH}_3\text{OH} \pm 10\%$, $\text{HCOOH} \pm 20\%$, $\text{CO} \pm 5\%$, and $\text{CO}_2 \pm 10\%$.

A reference spectrum of propene ozonide was prepared by means of spectral subtraction from a product spectrum of C_2H_4 ozonolysis in which 100 ppmv CH_3CHO was added to the reaction mixture with the initial concentrations of 16 ppmv C_2H_4 and 8 ppmv O_3 [19]. The spectrum was compared with a reference spectrum of synthesized propene ozonide (the reference spectrum was supplied by Dr. S. Hatakeyama, NIES), and was found to be identical with respect to the relative intensities and the positions of main absorption peaks. All chemicals and gases were of highest quality available commercially, and were used without further purification.

RESULTS AND DISCUSSION

Quantitative Yields of the Identified Products and the Spectral Features of the First-Generation Residual Spectra

Experimental conditions and the main results are summarized in Table I. The yield of a product and the butene conversion are expressed with respect to the converted ozone unless otherwise noted, and expressed as $Y(\text{compound})$ and $\Delta\text{Bu}/\Delta\text{O}_3$, respectively.

Table I Experimental Conditions and Main Results

Run	A	B	C	D	E	F	G	H
Isomer	<i>trans</i>	<i>trans</i>	<i>trans</i>	<i>cis</i>	<i>cis</i>	<i>cis</i>	<i>cis</i>	<i>trans</i>
[C ₄ H ₈] ₀ /ppmv	5.0	5.1	5.0	4.9	10.1	5.8	5.3	5.0
[O ₃] ₀ /ppmv	2.0	1.9	2.2	2.0	5.1	2.3	1.8	2.0
Added compd.	–	HCHO	HCOOH	–	HCHO	CH ₃ CHO	HCOOH	CH ₃ CHO
Concn./ppmv	–	5.2	2.3	–	10.3	10	2.4	98.3
[C ₄ H ₈]/ppmv	1.9	2.4	1.4	2.1	3.5	2.5	2.8	2.8
ΔBu/ΔO ₃	1.6	1.4	1.6	1.4	1.3	1.4	1.4	1.1
Product yield relative to the ozone consumption								
CH ₃ CHO	1.3	1.3	1.2	1.2	1.3	–	1.3	–
HCHO	0.28	–	0.24	0.18	–	0.33	0.16	0.60
CH ₄	0.15	0.16	0.16	0.22	0.22	0.21	0.20	0.15
CH ₃ OH	0.08	0.08	0.07	0.10	0.10	0.11	0.10	0.12
HCOOH	0	0	–0.41	0	0.06	0	–0.42	0
CO	0.30	0.34	0.25	0.20	^a	0.22	0.17	0.28
CO ₂	0.29	0.29	0.31	0.33	^a	0.45	0.29	0.50
Carbon balance/%	58	–	–	61	–	–	–	–

^a Not measured.

In the absence of the added compounds (Runs A and D, Table I), the product yields and ΔBu/ΔO₃ are similar to those of HNM94. Summing up, (a) ΔBu/ΔO₃ were ca. 1.6 and ca. 1.4 for *trans* and *cis* isomers, respectively, (b) Y(HCHO) and Y(CO) were larger in *trans* than in *cis* isomer, and (c) Y(CH₄) and Y(CH₃OH) were higher in *cis* than *trans* isomer. As previously noted (HNM94), HCOOH was absent in the product spectra. Trace amounts of glyoxal and ketene were detectable in the spectral range covered by the InSb detector (2000–4000 cm⁻¹). Also formation of small amount of 3-hydroxy-2-butanone (acetoin), CH₃C(O)CH(OH)CH₃, was observed by GC-FID in a separate experiment under similar conditions used here (C. Schäfer of this laboratory, unpublished results). Its yield was estimated to be below 2% of ΔO₃. The yield of these trace products was estimated to lie below 5% of ΔO₃. The carbon balance based on the product yields listed in Table I was about 60% for both isomers. The remainder of the reacted carbon is yet to be identified and probably to be sought in the residual products.

In the presence of added compounds, some interesting changes occurred. In Runs C and G with added HCOOH, about 40% (relative to the O₃ conversion) of the added HCOOH disappeared. Y(CO) appeared to be smaller than in other Runs, while the yields of other products remained unaffected. In Run F and H with added CH₃CHO, both Y(HCHO) and Y(CO₂) were higher than those in Runs D and A, respectively, which can be attributable to the reaction of the OH radical formed in the reaction [10,20]. Though not

listed in the table, formation of CH₃COOH and CH₃C(O)OOH, with approximate yields of 0.04 and 0.05, respectively, was observed in Run F. They are probably due to the reactions involving the CH₃C(O)O₂ radical formed in the reaction of OH with CH₃CHO in air [21].

From the product spectra of Runs A through H, “first-generation” residual spectra were obtained by subtracting the spectral contribution of the products listed in Table I. Six such spectra for Runs A through F are shown in Figure 1. Run E was carried out with the initial *cis*-2-butene concentration which was a factor 2 larger than the rest of the Runs. The product spectrum of Run E was therefore reduced to 1/2 in order to normalize the overall spectral intensity, and to achieve spectral subtraction on the same butene conversion basis with the rest. Results for Run G will be described in a later subsection.

Characteristic features are as follows. (a) All spectra have carbonyl absorption; (b) the carbonyl absorption is larger in *trans* (1A) than *cis* (1D) isomer; (c) in both isomers the addition of HCHO increased the carbonyl absorption, though its effect is larger in *cis* (1E) than *trans* isomer (1B), and additional absorption bands appear at the both sides of the strong absorption at ca. 1120 cm⁻¹, and at ca. 850 cm⁻¹ ((1B) and (1E)); (d) the residual spectrum changes its appearance significantly with the addition of only 2.3 ppmv HCOOH, (1C) (The effects that were observed with added HCHO are markedly enhanced, suggesting that these spectral features belong to one compound); and finally (e) spectrum (1F) resembles very

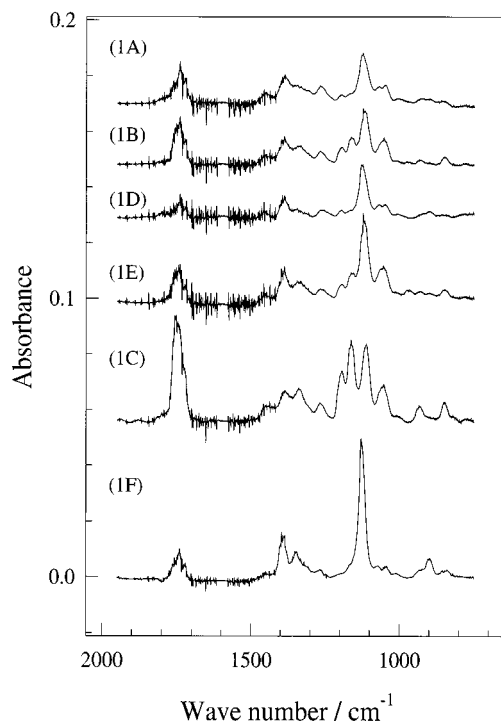


Figure 1 First-generation residual spectra. The experimental conditions of each spectrum correspond to those of Table I. From the original product spectra, contributions of the products quantified in Table I were subtracted.

closely to 2-butene ozonide except for the carbonyl absorption. Though not illustrated in Figure 1, the first-generation residual spectrum obtained from Run H shows similar characteristic features of (1F). In summary, it is apparent that the residual spectra contain at least two products, whose yields vary with the addition of HCHO and/or HCOOH, or with the isomers.

Further Spectral Subtraction Among the First-Generation Residual Spectra: Identification of Residual Products

By taking advantage of the difference in the features among the spectra obtained under different conditions (Figures (1A)–(1F)), further spectral subtraction was performed to identify individual products. The spectral subtraction was guided by the following available results: (a) 2-butene ozonide is formed in the ozonolysis of 2-butene isomers (HNM94); (b) propene ozonide is formed in the ethene ozonolysis with added CH_3CHO [19] (see Experimental Section); and (c) HCOOH reacts with CH_2OO to form hydroperoxymethyl formate $\text{CH}_2(\text{OOH})\text{OCH}(\text{O})$ [11], and hence formation of its homologue 1-hydroperoxy-

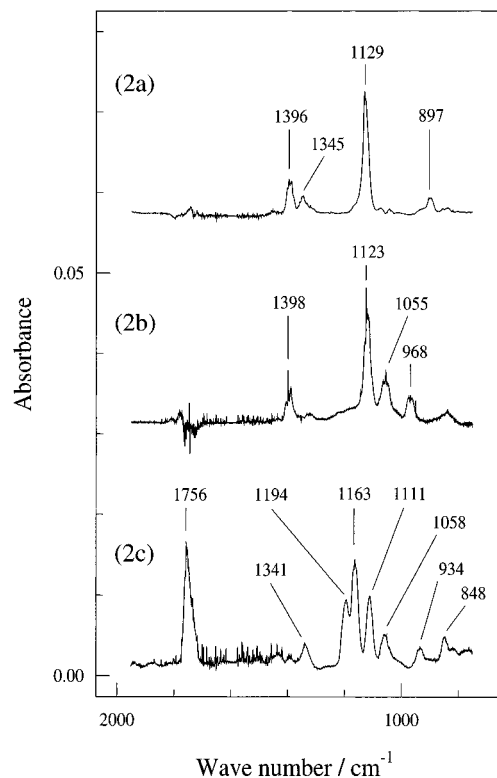


Figure 2 Spectra of the identified products. (2a) 2-butene ozonide, (2b) propene ozonide, and (2c) 1-hydroperoxyethyl formate (HPEF).

ethyl formate $\text{CH}_3\text{CH}(\text{OOH})-\text{O}-\text{CH}(\text{O})$ is expected in the reaction of HCOOH with CH_3CHO .

First, a reference spectrum of 2-butene ozonide was obtained by subtracting spectrum (1D) from spectrum (1F) to eliminate carbonyl absorption. The results are shown in Figure (2a). Next, in order to find out the effect of the HCOOH addition (Run C), spectrum (1A) was subtracted from spectrum (1C), since the only difference in the product data (Table I) between Runs A and C was the decrease in the added HCOOH. The result, after adjusting for the decreased amount of HCOOH by spectral addition, spectrum Figure (2c), is obtained. The compound having this spectrum is assigned to 1-hydroperoxyethyl formate (HPEF) $\text{CH}_3\text{CH}(\text{OOH})-\text{O}-\text{CH}(\text{O})$. This assignment was validated in another experiment as will be described later.

By making use of the reference spectra of 2-butene ozonide Figure (2a), propene ozonide whose spectrum is shown in Figure (2b), and 1-hydroperoxyethyl formate Figure (2c), the effect of the HCHO addition (Runs B and E) was then examined. It was found that the effect of the addition of HCHO was two-fold: propene ozonide formation and HPEF formation. Further, comparison with the 2-butene

Table II The identified Products and their Relative Concentrations

Spectra Isomer Added compd.	1A <i>trans</i> –	1B <i>trans</i> HCHO	1C <i>trans</i> HCOOH	1D <i>cis</i> –	1E <i>cis</i> HCHO	1F <i>cis</i> CH ₃ CHO	4A <i>cis</i> HCOOH	H ^a <i>trans</i> CH ₃ CHO
2a (2-Butene ozonide) ^b	0.2	0	0	0.4	0	1.0	0	0.6
2b (Propene ozonide) ^c	0	0.1	0	0	0.2	0	0	0
2c (HPEF) ^d	0	0.3	1.0	0	0.3	0	0.9	0

^a The first-generation residual spectra from Run H are not illustrated in Figure 1. HPEF = 1-Hydroperoxyethyl formate. The relative concentrations are compared with respect to the values (unity) given in bold face.

^b Spectrum 2a (2-butene ozonide) has been reduced to $\frac{1}{3}$ of the spectrum obtained by the subtraction procedure (see text). The relative concentrations are based on the original spectrum.

^c The propene ozonide spectrum (2b) has been reduced to $\frac{1}{8}$ of the original spectrum which was obtained by spectral subtraction from a product spectrum of the C₂H₄ ozonolysis with added CH₃CHO (see Experimental section). The initial reactant concentrations were [C₂H₄]₀ = 16 ppmv, [O₃]₀ = 8 ppmv, and [CH₃CHO]₀ = 100 ppmv. The concentration of the resulting propene ozonide was estimated to be ca. 2.7 ppmv. The relative concentrations are based on the original propene ozonide spectrum with ca. 2.7 ppmv concentration. Thus, for (1B), it is ca. 0.27 ppmv and for (1E), it is ca. 0.54 ppmv.

^d Spectrum 2c has been reduced to $\frac{1}{2}$ of the spectrum obtained by the subtraction procedure (see text). The relative concentrations are based on the original spectrum.

ozonide spectrum showed that 2-butene ozonide is not formed under these conditions. It was then possible to make a rough estimate of the (relative) yields of these three products in various runs, based on the amount of the spectral subtraction of these compounds from the first-generation residual spectra of Figure 1. The results are summarized in Table II. After these procedures, it was found that there still remained certain residual spectra in all runs. All these spectra had identical spectral characteristics about the positions of major absorption bands and their relative intensities. Two examples of the remaining spectra are illustrated in Figures 3 (3A) and (3D) for *trans* and *cis* isomers, respectively.

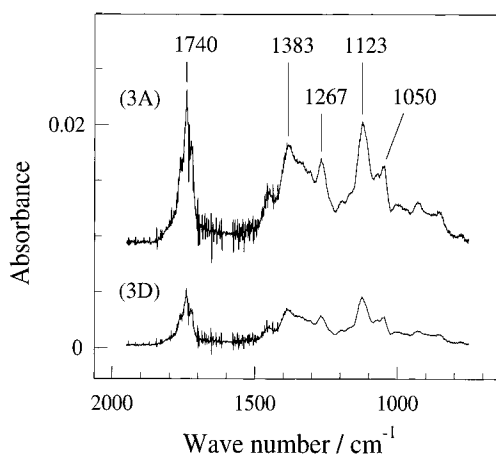


Figure 3 Spectra indicating formation of unidentified product(s). Spectra (3A) and (3D) were obtained from the experiment with *trans* isomer (Run A, Table I) and *cis* isomer (Run D, Table I), respectively.

Transitory Nature of 1-Hydroperoxyethyl Formate

In Run G where HCOOH was added in the ozonolysis of *cis*-2-butene, spectral change was followed for more than 1250 min. Two product spectra at the reaction time of 18 min (initial stage) and ca. 1240 min (final stage) were selected for spectral subtraction. The residual spectra for the initial and the final stages are shown in Figures (4a) and (4b), respectively. To obtain the residual spectra, the same amounts of the product spectra listed in Table I were subtracted except HCOOH. A slightly larger amount of HCOOH, [HCOOH]/ΔO₃ = 0.50 was subtracted for spectrum (4b). The increased amount is probably due to a slow heterogeneous loss of HCOOH on the reactor walls. The two spectra (4a) and (4b) look similar except that spectrum (4b) is reduced in overall intensity, and shows some additional features in the carbonyl absorption region. Exploiting the spectrum (3A) (obtained from the first-generation spectrum (1A) after subtracting the spectral contribution of 2-butene ozonide), further spectral subtraction was carried out. The results are shown in Figure (4c) and (4d), for the initial and the final stages, respectively. Comparison between spectrum (4c) and that of HPEF, (2c), reveals that both are the same.

Spectrum (4d) is seen to contain not only HPEF but also another compound. In order to find out the nature of still remaining product at the final stage, 60% of spectrum (4c) was subtracted from spectrum (4d). The result is spectrum (4e). Comparison with a reference spectrum of formic acetic anhydride, HC(O)—O—C(O)CH₃, shown as spectrum (FAC), most features of the residual spectrum (4e) agree with

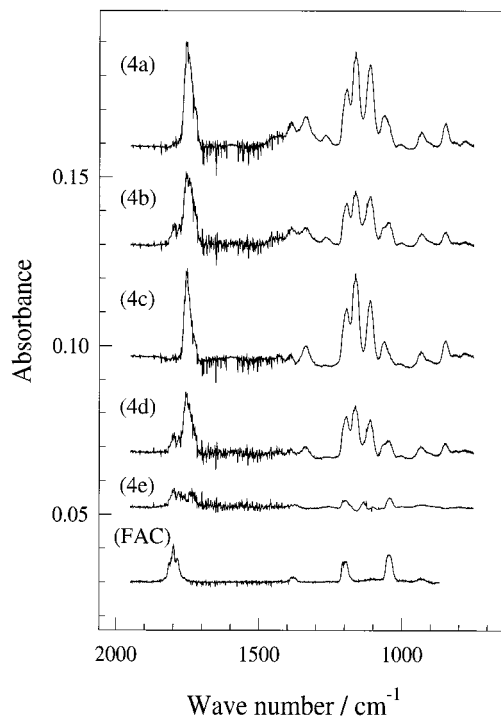
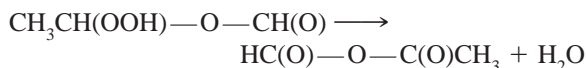
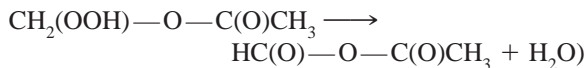


Figure 4 Residual spectra in the ozonolysis of *cis*-2-butene in the presence of the added HCOOH (Run G). Spectra (4c) and (4d) were obtained by subtracting 80% and 50% of spectrum (2A) from spectra (4a) and (4b), respectively. Spectrum (4e) was obtained by subtracting 60% of spectrum (4c) from spectrum (4d). The reference spectrum of formic acetic anhydride, (FAC), corresponds to the concentration of about 0.1 ppmv.

that of the reference. Although the residual spectrum has additional absorbances in the carbonyl region and around 1130 cm^{-1} , these could have been the result of so many subtractions. Thus, it is quite likely that HPEF undergoes degradation to formic acetic anhydride and H_2O .



This is analogous to the degradation of hydroperoxymethyl acetate $\text{CH}_2(\text{OOH})-\text{O}-\text{C}(\text{O})\text{CH}_3$ formed in the ethene ozonolysis with added CH_3COOH into $\text{HC}(\text{O})-\text{O}-\text{C}(\text{O})\text{CH}_3$ and H_2O [13].



The above observation has shown that the identity of

the compound represented by spectrum (2c) is consistent with HPEF.

Comparison with the Previous Results

A main difference between the present results and the previous data (HNM94) is the interpretation of the effect of HCHO addition. This is largely due to the finding of the formation of HPEF with added HCOOH. In HNM94, the residual spectra from the ozonolysis of *cis* isomer with and without the added HCHO were employed to isolate computationally the carbonyl and noncarbonyl products. As seen above, this procedure would lead to a mixed spectrum of propene ozonide and HPEF, and hence would not yield individual product spectra.

The formation of HPEF with the added HCHO (Runs B and E) is probably due to HCOOH which is produced in secondary reactions involving HCHO and HO_2 radicals formed in the reaction [10,21]. Thus, the net effect of HCHO addition is the formation of propene ozonide. In fact, Run E was carried out under the conditions that are nearly identical to those of Niki et al. [17], including that of the added HCHO (the reason for using a factor 2 larger initial concentration of *cis*-2-butene than the rest of the runs). The residual spectrum (1E) should therefore correspond to the residual spectrum (2) of Figure 1 in their article. After identifying propene ozonide formation, they mentioned that several weak bands, notably one near 1200 cm^{-1} , remained unassigned. We have been able to show that the spectrum (2) of Niki et al. [17] as well as spectrum (1E) contain at least HPEF as an additional product.

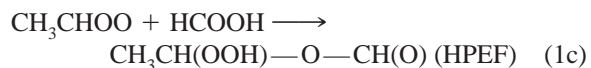
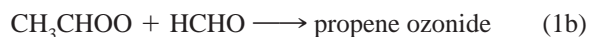
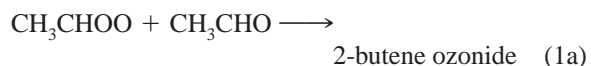
Another difference from the previous data (HNM94) is about the remaining spectra obtained after subtracting all the identified products including 2-butene ozonide, propene ozonide and HPEF, as typically illustrated in Figure 3. We assign tentatively a name CBC to this unidentified product spectrum. The presence of CBC was not apparent in HNM94. This is mainly due to a lower spectral resolution and larger noise levels of HNM94. It was found in this work that CBC is formed under all the experimental conditions. As seen from Figure 3, the magnitude of CBC in *trans* isomer (3A) is roughly twice as that in *cis* isomer (3D). It was further found that change in the absorption intensity is insensitive to the variation of the experimental conditions, except in Run H where the intensity decreased to about 60% of spectrum (3A).

The nature of CBC is at present not well defined. The overall feature of the CBC absorption (Fig. 2) indicates that CBC may be a composite of two or more

components. It is possible that products of the reaction of the OH radical with 2-butene isomers represent a fraction of CBC. The consumption of the butene isomers with respect to the O₃ conversion, $\Delta\text{Bu}/\Delta\text{O}_3$ (Table I) are always larger than unity, indicating formation of the OH radical in the ozonolysis [1–3,10]. The OH radical reacts predominantly with the butene isomers under the experimental conditions. Acetaldehyde seems to represent a major fraction of the reaction products (HNM94), as can be seen from its larger-than-unity yield (Table I). Beside CH₃CHO, the OH reaction with 2-butenes has been known to produce acetoin [22], which has been detected as a minor product as mentioned above. Comparison of a reference spectrum of acetoin with CBC spectra indicated that acetoin may be contained in the CBC but it was found that still a considerable fraction remain unaccounted for. One expected product of the OH reaction is a hydroperoxide CH₃CH(OH)CH(OOH)CH₃, to be formed between HO₂ and the peroxy radical CH₃CH(OH)CH(OO)CH₃. Although a reference spectrum of this compound is not available, it is not possible to exclude this compound from the components of CBC.

Mechanistic and Atmospheric Implications

The three “residual” products, 2-butene ozonide, propene ozonide and 1-hydroperoxyethyl formate (HPEF), are formed in well-defined reactions of the stabilized Criegee intermediate CH₃CHOO with CH₃CHO, HCHO and HCOOH, respectively, as represented below.



Since these reactions are competing, addition of either of the reactants results in the preferred formation of the corresponding products (see Table II). Previously (HNM94), the dipole complex was introduced to interpret the experimental results. The dipole complex was assumed to form the excited 2-butene ozonide from which CH₃CHOO plus CH₃CHO as well as the 2-butene ozonide resulted. Consequently, the 2-butene ozonide yield was held unaffected by the addition of HCHO. As this study has shown, however, the formation of 2-butene ozonide is replaced by propene ozonide by the addition of HCHO.

It is possible to estimate the concentration of 2-butene ozonide formed in Run H based on the comparison between the propene ozonide reference spectrum (Fig. 2b) and the 2-butene ozonide spectrum (Fig. 2a). Assuming the same absorption cross section of the bands centered at 1396 cm⁻¹ and at 1398 cm⁻¹ for 2-butene ozonide and propene ozonide, respectively, and knowing the approximate concentration of the latter to be 2.7 ppmv (Fig. 2b), the 2-butene ozonide concentration was estimated to be roughly 0.8 ppmv. This corresponds to the yield of 35% with respect to the converted *trans*-2-butene isomer. If we assume that most (> 90%) of the stabilized CH₃CHOO intermediate reacted with CH₃CHO to form the ozonide, it follows that the degree of the stabilization of the initially formed, excited CH₃CHOO* intermediate to be ca. 35%. This value is consistent with our previous results [9,10] but significantly higher than the value (18.5% for *trans* isomer) obtained by Hatakeyama et al. [23]. They based the determination on the yield of H₂SO₄ which is formed in the reaction of CH₃CHOO with SO₂ added in excess to the reaction system.

Formation of HPEF in the 2-butene ozonolysis with added HCOOH has demonstrated once again the high reactivity of HCOOH toward the Criegee intermediates [11–13]. Combined with the formation of the ozonides with/without added aldehydes, the analogy between the gas-phase and liquid-phase ozonolysis on the reactions of the Criegee intermediates [13–15] has clearly been shown in this study. These observations, initiated by our finding of the formation of hydroperoxymethyl formate in the ethene ozonolysis [11], should shed further light in understanding still remaining mechanistic problems (see below) in the gas-phase ozonolysis.

Under atmospheric conditions, the most important bimolecular reaction of the Criegee intermediates is with water vapor (due to the large atmospheric concentration) and possibly with NO_x (this reaction has not been studied experimentally). As our recent study [24] has shown, the intermediate CH₂OO formed from various terminal alkenes including isoprene reacts with H₂O vapor to form hydroxymethyl hydroperoxide HOCH₂OOH. This hydroperoxide was found to dissociate into HCOOH and H₂O under the laboratory conditions. It is expected that similar reaction of CH₃CHOO intermediate with H₂O vapor leads to formation of 1-hydroxyethyl hydroperoxide CH₃CH(OH)OOH which then may dissociate into CH₃COOH and H₂O [18].

Atmospheric relevance of the unidentified product(s) as summarily represented by CBC is not clear at present. If CBC is formed as a result of unimolecu-

lar rearrangement of certain yet unknown reaction intermediate, it has some interesting atmospheric consequence. Above all, its reaction with H₂O vapor would be worth considering. Clearly, further studies are needed.

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