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Gas-Phase Ozonolysis of Alkenes. Recent Advances in Mechanistic Investigations†

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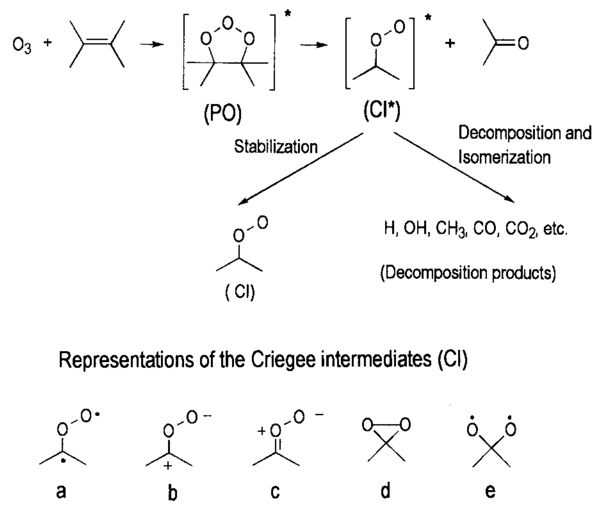
Introduction

The ozonolysis of alkenes in the gas phase has been a subject of intensive studies since the early 1960s. In recent years, research in this area has gained importance due primarily to its significant role in atmospheric chemistry.[1] The gas-phase ozonolysis of alkenes is an important sink for both O_3 and alkenes and has been recognized as a main source of organic acids[2] and organic hydroperoxides[3] in the atmosphere. The gas-phase ozonolysis of biogenic alkenes, typically terpenes, has been known to form particulate products which serve as the precursors to the secondary organic aerosols.[4] Also, vegetation surfaces exposed to O_3 have been shown to cause detrimental effects on the plant growth and to emit various compounds.[5]

The addition of O_3 to an alkenic double bond is the chemical activation process,[6] in which the adduct or its nascent dissociation intermediates are formed with sufficient excess energy for subsequent reactions such as unimolecular decomposition and isomerization or lose the excess energy by the collision with bath molecules and are eventually stabilized. While in the liquid phase the nascent intermediates are completely quenched, only a fraction (10−50%) is estimated to be stabilized in the gas phase under 1 atm at room temperature.[1d] The currently accepted mechanism for the gas-phase ozonolysis is essentially identical with the bare-bone Criegee mechanism developed for the liquid-phase ozonolysis[7−10] with a "slight" modification, as illustrated in Scheme 1.[1a,b] This slight modification, namely the presence of a significant fraction of the nascent intermediate (CI*, where * indicates vibrational excitation; often called "the energy-rich Criegee biradical" or "the excited Criegee intermediate") undergoing unimolecular decomposition, is the source of all the problems which studies on the gas-phase ozonolysis must suffer and which to this day hinders a complete understanding of the mechanism for the gas-phase ozonolysis of alkenes.

Scheme 1



Major problems in the laboratory studies of gas-phase ozonolysis, usually performed in the presence of O_2, are (1) the alkene conversions that are significantly larger than that of O_3 (up to a factor 2), (2) the persistently low carbon balance of the reaction (at most 70% except for the case of C_2H_4), and (3) the formation of large amounts of unidentified products (amounting at least ∼30% of the reacted alkenes, $\leq C_6$). The decomposition of the nascent intermediate produces stable molecules such as CO and CO_2 and free radicals such as H, OH, and CH_3 (Scheme 1), the latter of which interfere with the main ozonolysis reaction, rendering mechanistic interpretation ambiguous. Notably, if the OH radical is formed, it would react predominantly with the parent alkene under most experimental conditions and would result in the alkene consumption in excess of that of O_3, altering the product formation significantly. Under such conditions, it is difficult to examine mechanistic clues for the formation of various products, including the unidentified products.

What is required is to identify primary processes in the ozonolysis reactions and to "isolate" them from secondary processes which operate only under certain laboratory conditions. Specifically, if the OH radical is formed in a primary process (Scheme 1), the gas-phase ozonolysis in the atmosphere may be a potential source of OH radical[11]

Osamu Horie was born in 1937 in Tokyo, Japan, and received a B.Eng. and M.Eng. from Tohoku University in Sendai. His Ph.D. was obtained from the Johns Hopkins University in Chem. Eng. in 1968. After 10 years of research and teaching in the Faculty of Engineering, Tohoku University, he was engaged in research activities at the Max Planck Institute (MPI) for Strömungsforschung (Göttingen), Wuppertal University, and MPI for Strahlenchemie (Mülheim) in Germany. Since 1986 he has been employed at the MPI for Chemistry, where he is engaged in laboratory kinetic studies related to atmospheric chemistry, including ozonolysis, peroxy radical chemistry, and secondary organic aerosol formation.

Geert K. Moortgat was born in 1941 in Nieuwpoort, Belgium, where he graduated at the TH in Ghent with a degree in Chem. Eng. in 1964. He received M.Sc. and Ph.D. (1970) degrees in Physical Chemistry at the University of Detroit, Detroit, MI. After a Post-Doc at the National Center for Atmospheric Research in Boulder, CO, he joined in 1973 the Max Planck Institute for Chemistry in Mainz, Germany. His research interests are centered on the gas-phase kinetics, photochemistry, and mechanistic studies of atmospheric relevant trace species, especially focused on the role played by intermediates in the photooxidation of VOC, halogenated hydrocarbons, etc.

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[†] In memory of the late Hiromi Niki.

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that bypasses the solar-radiation-induced photolysis of O_3 in the presence of H_2O[12] and which can therefore take place at night. Numerous experimental data on the gas-phase alkene ozonolysis, qualitative as well as quantitative, have been accumulated,[1] which are sometimes difficult to interpret and have often created conflicting views on the mechanism. Nevertheless, significant advances in the mechanistic studies have been achieved in the past 20 years. This Account will describe the present state of our understanding of the mechanism for gas-phase ozonolysis with a close reference to the precedents in condensed-phase ozonolysis, summarize recent progress obtained in this laboratory as well as elsewhere, and point out some prospects for further studies.

Different representations of the intermediate are illustrated at the bottom of Scheme 1.[10,13−15] Throughout this article, the intermediate is called “Criegee intermediate” and represented typically as the peroxymethylene biradical (**a**). In the liquid phase, the intermediate is often called the carbonyl *O*-oxide or simply carbonyl oxide, represented by the zwitterionic structures (**b** and **c**).[8] To facilitate comparison between the liquid-phase and gas-phase ozonolysis phenomena, however, the term Criegee intermediate (hereafter CI when appropriate) used in this article includes both ionic and biradical structures (**a**−**c**). It should be noted, however, that representation with different structures does not mean the existence of separate structural isomers of CI; they represent different resonance contributions to a CI. More appropriately, the electronic structure of CI can be represented by a superposition of biradical and zwitterionic states.[10] Two other structural isomers of CI, dioxiranes (**d**) and to a lesser extent methylenebis(oxy) (**e**), have appeared as possible intermediates in the gas-phase ozonolysis literature.[1a,15,16] However, in most cases they have been given only a cursory interest in the mechanistic studies as a precursor to the unimolecular decomposition products, although we have seen a surge of recent advances in the chemistry of dioxiranes in the liquid phase.[17,18]

Ozonolysis of Ethene: Toward a Complete Understanding

Ethene has been extensively subjected to gas-phase ozonolysis studies. The reaction produces HCHO and CH_2OO^*; about 50% of the latter stabilizes to the CH_2OO intermediate under 1 atm at room temperature.[1d] A most intriguing observation was the formation of a transitory product “compound X”.[16,19] Formation of this compound was discovered through successive subtraction of the spectral contributions of known products and reactants from FTIR spectra of reaction mixtures. Su et al.[16a] observed that (i) formation of X increased with addition of HCHO, (ii) X gradually decomposed to formic acid anhydride, and (iii) addition of SO_2 completely eliminated formation of X. From these observations, they tentatively assigned the structure hydroxymethyl formate, $CH_2(OH)-O-CH(O)$ **1**, to X and postulated its formation via the reaction of CH_2OO with HCHO, the main product of the ozonolysis reaction R1. This assignment was supported

$$CH_2OO + HCHO \rightarrow \underset{\mathbf{1}}{CH_2(OH)-O-CH(O)}\ (\text{compound X}) \qquad (R1)$$

$$CH_2(OH)-O-CH(O) \rightarrow (HCO)_2O + H_2 \qquad (R2)$$

by Niki et al.,[19] who identified the presence of an OH group through a detailed FTIR spectroscopic study. The decomposition of X to formic acid anhydride was supposed to accompany the release of H_2 via (R2).

There were however some experimental and thermochemical problems in assuming that reaction R1 occurs. (a) The increase in the formation of X was not so significant as could be expected from (R1) with the HCHO addition.[16] (b) Occurrence of (R1) assumes that the HCHO yield relative to the C_2H_4 conversion is lower than unity. Although the data of Su et al.[16] and of Niki et al.[19] seem to be consistent with this presumption, recent data of Horie et al.[20] indicated that the HCHO yield was close to unity. (c) Reaction R2 is calculated to be 77 kJ mol^{-1} endothermic, based on $\Delta H_f = -540$ kJ mol^{-1} for X.[21] Even if (R2) may involve heterogeneous processes,[19] it is unlikely that the reaction proceeds with measurable speed at room temperature.

A breakthrough to this problem was achieved by Neeb et al.[22] They performed the C_2H_4 ozonolysis in a 570 L spherical-glass reactor in 730 Torr (1 Torr = 133.3 Pa) synthetic air at room temperature, with the reactant concentrations in the range of low parts-per-million by volume (ppmv) (1 ppmv $\sim 2.4 \times 10^{13}$ molecule cm^{-3} at 730 Torr and 295 K). Ozone was generated by photolyzing O_2 or synthetic air with a low-pressure Hg lamp and hence free of NO_x contamination. They found that (a) the HCHO yield was close to unity as observed by Horie et al.,[20] (b) the sum of X and formic acid anhydride (the total X) yields increased linearly with the C_2H_4 conversion (~20% yield), while the yield of X itself tended to decrease toward high C_2H_4 conversions, (c) HCOOH yield was only ~4%, (d) the yield of the total X decreased, though slightly, with the addition of HCHO, and, most unexpectedly, (e) the yield of total X increased to ~50% yield with the addition of an excess of HCOOH.

From these results, it was concluded[22] that X was formed between CH_2OO and HCOOH (eq R3) and had a

$$CH_2OO + HCOOH \rightarrow \underset{\mathbf{2}}{CH_2(OOH)-O-CH(O)} \qquad (R3)$$

$$CH_2(OOH)-O-CH(O) \rightarrow (HCO)_2O + H_2O \qquad (R4)$$

$$\Delta H = -235 \text{ kJ mol}^{-1}$$

probable structure of hydro*peroxy*methyl formate, $CH_2(OOH)-O-CH(O)$, **2** (Scheme 2). Consequently, decomposition of X which is now **2** to formic acid anhydride was expressed as an exothermic reaction (with $\Delta H_f = -470$ kJ mol^{-1} for **2**) (eq R4), where H_2O instead of H_2 was eliminated. With these assignments, it was possible to account for almost all the carbon-containing products, attaining a carbon balance of more than 90%. It is necessary to emphasize that (in the absence of the added HCOOH), the yield of **2** far exceeded the HCOOH yield as mentioned above. These results were confirmed by Thamm et al.,[23] who demonstrated that **2** was readily synthesized by the ozonolysis of ethyl vinyl ether in solution at low temperature in the presence of HCOOH, reaction R5

$$O_3 + CH_2{=}CH{-}O{-}C_2H_5 \rightarrow CH_2OO + C_2H_5OCH(O) \quad \text{(R5)}$$

followed by (R3). They characterized the properties of **2** by means of HPLC, GC-MS, and ^1H NMR. This important study has established that **2**, which had existed only on paper, can be synthesized in the test tube. These studies[22,23] have opened an interesting area of study of the reactions of CI but simultaneously forced us to reconsider the mechanism of the gas-phase alkene ozonolysis.

In liquid-phase ozonolysis, the reactions of CI with participating (protic, nucleophilic) solvents are well-known, where α-alkoxy alkyl hydroperoxides in alcohol solvents have been formed often with high yields.[8] The formation of α-acyloxy- and α-hydroxyalkyl hydroperoxides in carboxylic acid and aqueous solvents, respectively, on the other hand has been much less recorded. This is attributed to difficulties in isolating the unstable compounds.[8]

Studies on the CI reactions with hydroxy compounds such as CH_3COOH, CH_3OH, and H_2O in the gas-phase ozonolysis have been further pursued following the above observations[22,23] and also motivated by the earlier observation of the formation of hydroxymethyl hydroperoxide $HOCH_2OOH$ (**5**) in the ozonolysis of naturally occurring alkenes in humidified air.[24] The results for CH_2OO are summarized in Scheme 2.[25] Similar observations have recently been reported by Wolff et al.[26] Reaction R8 has an important atmospheric relevance concerning the formation of a phytotoxic compound **5**[5b] and its eventual precursor role for the HCOOH formation.[27] The well-known reaction of CI with carbonyl compounds forming secondary ozonides in condensed-phase ozonolysis has been replicated in the gas phase. Specifically, CH_2OO has been observed to react with carbonyl compounds CH_3CHO,[16a,28] CH_3COCH_3,[28] and CF_3COCF_3[29] to form the corresponding ozonides **6**−**8**, respectively (Scheme 2). These results established a clear link between the reactions of CI in the liquid-phase and gas-phase ozonolysis.

Formation of **2** in the gas-phase ozonolysis was initially observed in the absence of HCOOH.[16a,19,22,25] Under these conditions, the HCOOH yield was only ~$^1/_5$ of the yield of **2**, as mentioned above. In this case, HCOOH is believed to be produced in a unimolecular isomerization of the energy-rich CI* (cf. Scheme 1).[15,16] Then, where does the HCOOH that is necessary in (R3) come from? This question was answered by performing C_2H_4 ozonolysis with the addition of large excess of $H^{13}CHO$[30] under experimental conditions similar to those used before.[22] Typical results of $H^{13}CHO$ addition are illustrated in Figure 1. It was found,[30] under the conditions of Figure 1, that (a) formic acid produced consisted of $H^{12}COOH$ (with the yield of ~15%) and $H^{13}COOH$, (b) $H^{12}CHO$ yield was ~120% of the C_2H_4 conversion, and (c) ^{13}CO was formed with a significant yield.

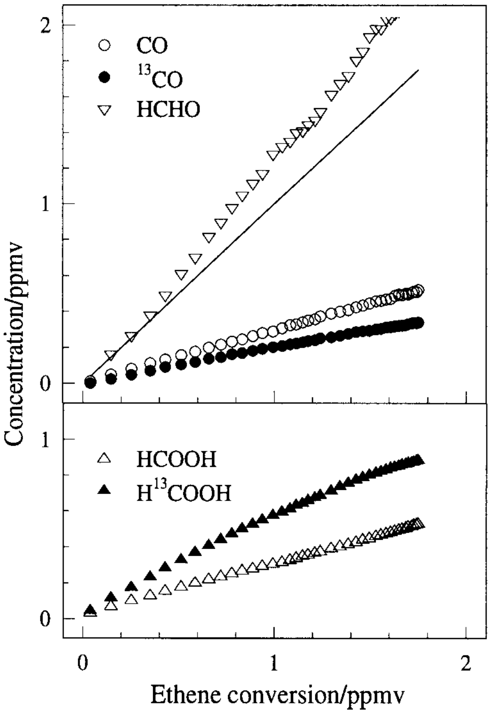
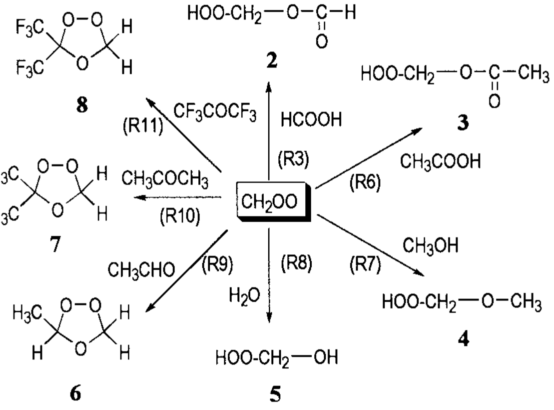


FIGURE 1. Effect of the addition of 50 ppmv of $H^{13}CHO$ on the ozonolysis of C_2H_4, with $[C_2H_4]_0 = 4.0$ ppmv and $[O_3]_0 = 2.3$ ppmv. The straight line represents the stoichiometric yield of HCHO.

Scheme 2



Since the only source of ^{12}C atoms available for the bimolecular reaction with the $H^{13}CHO$ present in a large excess is CH_2OO, the large yield of $H^{12}COOH$ must be due to the reaction of CH_2OO with $H^{13}CHO$ (eq R12).

$$CH_2OO + H^{13}CHO \rightarrow H^{12}COOH + H^{13}CHO \quad \text{(R12)}$$

The increase in the $H^{12}CHO$ formation exceeding the stoichiometric yield of 100% must also be due to the reaction of CH_2OO with $H^{13}CHO$. Likely reactions are (R13a) and (R13b), which are also consistent with the significant formation of ^{13}CO.

$$CH_2OO + H^{13}CHO \rightarrow H^{12}CHO + H^{13}CO + OH \quad (R13a)$$

$$CH_2OO + H^{13}CHO \rightarrow H^{12}CHO + {}^{13}CO + H_2O \quad (R13b)$$

It is known that HCHO oxidation produces a large amount of secondary HCOOH, which is explained by a chain cycle involving the HO_2 radical and HCHO.[31] Since the HO_2 radical is known to be formed in C_2H_4 ozonolysis,[16,32,33] $H^{13}COOH$ formation with added $H^{13}CHO$ observed above is probably attributable to this HO_2-HCHO cycle. Thus, the HCOOH increase in the presence of HCHO is shown to be due to at least two sources: (R12) and the HO_2-HCHO cycle. Therefore, the previous conclusion that the HCOOH increase was completely due to the HO_2-HCHO cycle[33] has to be modified.

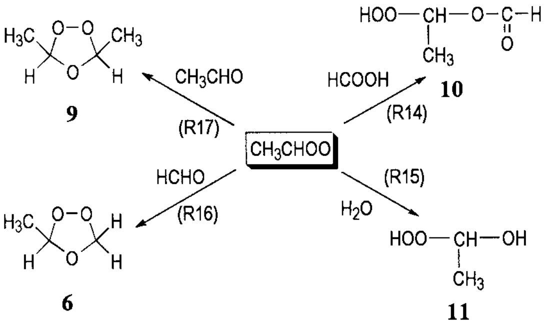
Ozonolysis of 2-Butene Isomers: Why Is the Carbon Balance So Low?

Beyond C_2H_4, no clear-cut mechanistic interpretation is available for the experimental ozonolysis data, as will be shown for the case of 2-butene isomers.[33−41] The ozonolysis of 2-butenes produces CH_3CHO and CH_3CHOO^*; 20−40% of the latter is considered to stabilize the CH_3CHOO intermediate in the gas phase under 1 atm at room temperature. In a matrix-isolation FTIR spectroscopic study of 2-C_4H_8 ozonolysis, Horie and Moortgat[33,34] determined quantitatively the reaction products which were attributable to the decomposition of the excited CH_3CHOO^* and noted that the carbon balance obtained by summing up the identified products was ~60%. They observed formation of a new transitory product and assigned it tentatively (but incorrectly; see later) as hydroxyethyl formate, $CH_3(OH)CH-O-CH(O)$, based on the effect of the added HCHO.

In the ozonolysis of 2-butene isomers using a long-path FTIR spectroscopy in low ppmv concentration ranges, Horie et al.[38] found that (a) the conversions of C_4H_8 relative to that of O_3, defined as the stoichiometry ratio, $\Delta C_4H_8/\Delta O_3$, were ~1.6 and ~1.4 for trans and cis isomers, respectively, and the stoichiometry ratio decreased in the presence of the added HCHO or CH_3CHO, (b) the carbon balance was ~60% for the both isomers, similarly low as observed earlier,[33,34] and (c) a considerable fraction of the product spectra remained unassigned. These "residual spectra" are the likely cause of the low carbon balance.

A further study[39] resolved some aspects of the residual spectra: (a) Formation of 2-butene ozonide (**9**) was observed in the absence of the added CH_3CHO, whose addition increased the yield of the ozonide significantly. (b) Formation of propene ozonide (**6**) with the added HCHO was positively identified.[35] (c) Formation of a transitory product, hydro*peroxy*ethyl formate $CH_3(OOH)CH-O-CHO$ (**10**), was observed with the added HCOOH (Scheme 3). It should be mentioned that little formation of CH_3COOH was observed in the presence or absence of the added CH_3CHO. The formation of α-hydroxyethyl hydroperoxide (**11**) in the presence of H_2O vapor[20] (eq R15) is analogous to (R8) in the case of the CH_2OO reaction[27] (Scheme 2). The previously observed transitory product, which had been assigned as hydroxyethyl formate,[33,34] turned out to be **10**. The HCOOH that was needed for the formation of **10** in the presence of HCHO[34] was probably due to reaction of HO_2 with HCHO.[31] It is interesting to note that Niki et al.,[35] after identifying formation of propene ozonide in the *cis*-2-butene ozonolysis with the added HCHO, mentioned the presence of still unidentified IR absorption bands. Horie et al.[39] were able to show that a part of these unidentified bands belonged to **10**.

Scheme 3



The ozonides **6** and **9** and the compound **10** which had previously been contained in the residual spectra[38] are in fact formed in well-defined reactions of the CH_3CHOO with added HCHO, CH_3CHO, and HCOOH, respectively.[39] Unlike in the condensed-phase ozonolysis,[7−10] formation of the secondary ozonides in the gas phase has scarcely been studied, and discussion about stereochemistry of CI and of the ozonide formation has been practically nonexistent. This is in part due to complicated secondary chemistry involved[33−40] and in part probably due to generally low yields of CI in the gas-phase ozonolysis.[1d]

It was further observed,[39] after subtracting spectral contributions of all the identified products including **6**, **9**, and **10** (Scheme 3), that there still remained considerable IR absorption bands which may account for as much as ~30% of the carbon balance. A typical example of a spectrum for the trans isomer[29,39] is illustrated in Figure 2. It is quite likely that such residual spectra contain two or more compounds, summarily called "the residual products" here, although their precursor(s) may be the same. The residual products were observed[39] to be (a) formed under all the experimental conditions, (b) roughly twice for the trans isomer than for the cis isomer, (c) weakly sensitive to variations in the experimental conditions, and (d) formed in the absence as well as presence of O_2 (Horie et al., unpublished data). Their formation was suppressed significantly when a very large excess of CH_3CHO was present. Before discussing their nature further, we will point out another problem about the reaction mechanism.

If we assume that CH_3CHOO is formed in the yield of 20−40%,[1d,38,39,41] we should expect the yield of the ozonide **9** to be in the same range of the CH_3CHOO yield in the absence of added carbonyl compounds (by analogy with the liquid-phase ozonolysis), which was not observed. The increase in the yield of **9** with the CH_3CHO addi-

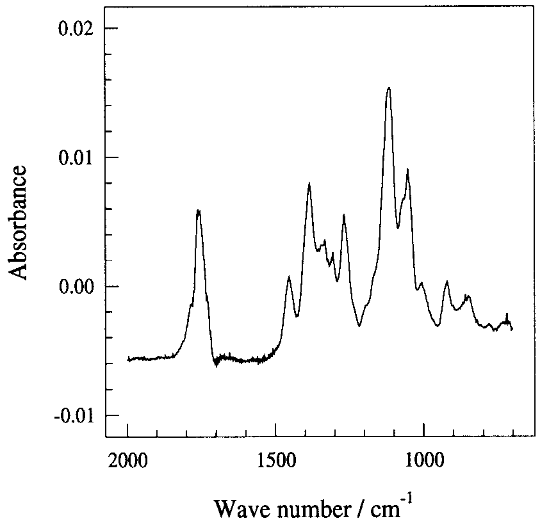


FIGURE 2. FTIR spectrum of the residual products in the ozonolysis of *trans*-2-C_4H_8, obtained by computationally subtracting the spectral contribution of identified products and reactants. The initial reactant concentrations were $[C_4H_8]_0 = 7.5$ ppmv and $[O_3]_0 = 3.3$ ppmv.

tion[28,39] therefore suggests that, in the absence of additives, CH_3CHOO is consumed in certain reactions which compete with the reaction forming the ozonide. One such possibility is the reaction with the parent C_4H_8.[42] This hypothesis is consistent with the observation that the stoichiometry ratio was significantly larger than unity.[39] The commonly accepted explanation of this observation has been, however, to assume the OH radical formation and its predominant reaction with the parent alkenes under the experimental conditions.[43] A detailed discussion will be made in the next section.

Ozonolysis of 2,3-Dimethyl-2-butene (DMB): Is OH Formed in the Ozonolysis?

The ozonolysis of DMB ($(CH_3)_2C{=}C(CH_3)_2$) is characterized by a very large rate constant $k_{298} = 1.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1},[44] compared to $k_{298} = 1.8 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for C_2H_4 ozonolysis.[45] The ozonolysis produces CH_3COCH_3 and $(CH_3)_2COO^*$ as the initial products. Niki et al.[43] performed a detailed FTIR spectroscopic study on DMB ozonolysis in 700 Torr synthetic air with the reactant concentrations in the range of 1−7 ppmv. They found that the stoichiometry ratio $\Delta DMB/\Delta O_3$ was ~1.7, which decreased to ~1.0 with the addition of sufficient excess of CH_3CHO and HCHO. In the presence of added HCHO, formation of isobutene ozonide (**7**) was observed, whose concentration increased with the HCHO concentration up to ~30% yield, which was taken as the degree of the stabilization of the energy-rich biradical, producing $(CH_3)_2COO$. They observed also that the stoichiometry ratio was reduced to ~1.0 in the absence of O_2.

The reported values of the stoichiometry ratio in the gas-phase ozonolysis of alkenes in the presence of O_2 are larger than unity and vary significantly with the alkene.[38,39,43,46,47] Addition of a large excess of aldehydes[38,39,43] such as CH_3CHO or HCHO, alkanes such as cyclohexane,[11] or CO[48] reduces the values of the stoichiometry ratio close to unity. For an alkene, the stoichiometry ratio varies not only with the concentrations of the reactants but also with the reactant ratio.[38,47] In the absence of O_2, the stoichiometry ratio becomes close to or less than unity.[43,46,47] It is worth noting that, in the absence of O_2, the rate of conversion of both alkene and O_3 is accelerated significantly.[47]

These experimental data indicate the formation of at least one reactive species that reacts with either or both reactants, affects the stoichiometry ratio as well as the rate of reaction under various conditions, and competes with the added compounds (often called scavengers) for the reactions. The most likely candidate has been the OH radical.[11,43] The OH radical is assumed to be produced in the unimolecular decomposition of the excited CI.[11,14b,43] The OH formation in the primary reaction is important in atmospheric chemistry[11] as well as from a mechanistic point of view.[14b] Experimental data which support the OH formation, such as observation of cyclohexanol and cyclohexanone in the ozonolysis with the added scavenger cyclohexane[11,49] or 2-butanone in the presence of 2-butanol,[50] are all consistent with, but provide no compelling evidence for, primary OH formation. The OH formation yield determined by the scavenger methods[11,48−50] is in addition difficult to explain in terms of the unimolecular decomposition of the excited CI. Given a fixed amount of excess energy for decomposition, the larger the CI (or the internal degrees of freedom), the larger the extent of stabilization, yielding less OH radical from statistical mechanical point of view.[6] The OH yield data trends[1d,11] are in the opposite direction.

Schäfer et al.[42] adopted a different approach to assess OH radical formation, in which the relative rates of consumption of a pair of alkanes that are added to selected alkene/O_3 systems were measured. The results were compared with OH-initiated relative removal (via H_2O_2 photolysis) and with expected relative rates based on literature data.[51] Typical results for DMB are illustrated in Figure 3.[42] The relative consumption of cyclohexane to isobutane in the ozonolysis was clearly different from the results obtained in the H_2O_2 photolysis, which agreed well with the literature data for the OH reaction.[51] The data indicate that the relative consumption of isobutane in the ozonolysis is significantly greater than in the case of the H_2O_2 photolysis. Similar results were obtained for *trans*-2-butene and isobutene. Although these data do not preclude a small role of the OH radical, the data are inconsistent with the assumption that OH is solely responsible for the excess consumption of the alkenes during their ozonolysis.

These results were interpreted by assuming CI as the reactive species that reacts with both alkenes and alkanes,[42] as mentioned earlier briefly. This hypothesis is supported by the high reactivity of CI toward nucleophilic agents (alcohols, carboxylic acids, water), carbonyl compounds, alkenes, and alkanes in the liquid phase, where both the photodecomposition of diazo compounds in O_2 and the ozonolysis have been used as the CI sources.[10]

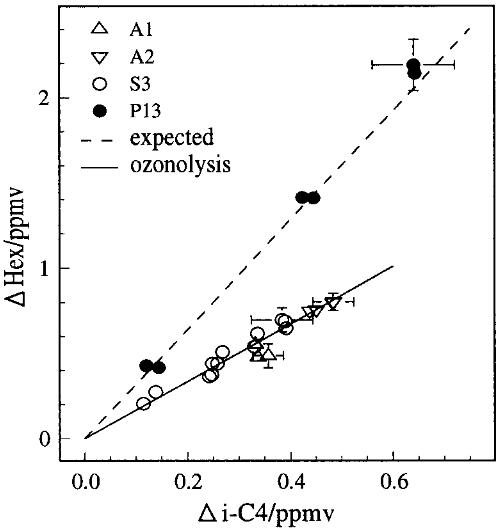


FIGURE 3. Consumption of cyclohexane (ΔHex) and isobutane (Δ*i*-C4) in the ozonolysis of DMB (A1, A2, S3) and in the photolysis of H_2O_2 (P13). The broken line is based on the literature value for the OH reactions. The solid line represents a linear regression analysis for the ozonolysis data. For each run, an equimolar mixture of cyclohexane and isobutane (either 20 or 15 ppmv each) was used. Other conditions were as follows (concentrations in ppmv): A1, $[DMB]_0 = 2.5$ and $[O_3]_0 = 1.1$; A2, $[DMB]_0 = 2.5$ and $[O_3]_0 = 5.5$; S3, $[DMB]_0 = 4.0$; O_3 generated in situ with a Pen-ray Hg lamp; P13, $[DMB]_0 = 3.1$; H_2O_2 used as the photolytic OH precursor with a 1000 W Xe lamp.

Reactions that are relevant to the above experimental results[42] are the reactions of CI with alkenes to undergo cycloadditions in certain cases (enol ethers),[52] to undergo O-atom transfer including epoxidation, or to produce cognate carbonyl compounds.[53] The formation of cyclohexanol and cyclohexanone in the photodecomposition of diazo compounds in oxygen-saturated cyclohexane [53,54] was explained in terms of the H-atom abstraction by CI (eq R18) and subsequent reactions of free radicals in solution.[54] If the liquid-phase reactions in alkane solutions are assumed to occur in gas-phase ozonolysis, the intermediate R^1R^2COOH may undergo further reactions, including decomposition to various molecular and radical products (eq R19).[42]

$$R^1R^2COO + RH \rightarrow R^1R^2COOH + R \qquad (R18)$$

$$R^1R^2COOH \rightarrow R^1R^2CO + OH \qquad (R19)$$

Another way of interpreting the relative rate data[42] is to invoke dioxiranes as a possible intermediate in the gas-phase ozonolysis,[55] not as a mere precursor to the decomposition products as mentioned earlier[15,16] but as a species undergoing isomerization and various bimolecular reactions as in the liquid-phase chemistry.[17,18] It has been established that dioxiranes are a versatile epoxidation agent which are much more efficient than carbonyl oxides. Also, dioxiranes are known to undergo O-atom insertion to the alkanoic C−H bonds yielding alcohols and ketones quite efficiently.[17,18,56] The enhanced relative consumption of isobutane in the ozonolysis compared to that in the OH reaction shown in Figure 3[42] appears to be more consistent with the O-atom insertion data observed in the dioxirane reactions[56] than the H-abstraction by OH radical.[57]

The intermediacy of dioxiranes in the gas-phase ozonolysis requires that CI must isomerize rapidly to dioxiranes in competition with the bimolecular reaction of CI with the product aldehyde forming ozonides and other products. Dioxiranes are calculated to be ~120 kJ mol^{-1} more stable than CI,[14a,18b] but the activation energy for the isomerization is considerable (~80 kJ mol^{-1}). While this is a rather high energy barrier in the liquid phase,[58,59] it may be reasonable to assume that a fraction of the initially formed, energy-rich CI* isomerizes to dioxiranes in the gas phase.[15,55] In the presence of sufficient concentrations of added aldehydes, dioxiranes would not be formed due to the competition. In the absence of additives, dioxiranes would react with both the parent alkene and the aldehyde formed in the reaction. In the liquid phase, the reaction of dioxiranes with aldehydes is known to produce carboxylic acids and not ozonides.[17] If this applies to the gas-phase ozonolysis, dioxiranes must react predominantly with the parent alkene, since formation of the corresponding carboxylic acids was not observed. So far, there appears to have been no relevant experimental data which justify further discussion.

Criegee Intermediates in the Gas Phase: An Alternative to the OH Radical?

As we saw in the reactions with hydroxy compounds, CH_2OO is a highly reactive species. Thus, the results of C_2H_4 ozonolysis in the presence of $H^{13}CHO$[30] mentioned above (Figure 1) can alternatively be interpreted in terms of the high reactivity of CH_2OO. An overall picture is illustrated in Scheme 4. The formation of $H^{12}CHO$, which was expressed as a one-step reaction (eq R13), can be explained instead by a two-step process, where CH_2OO is assumed to abstract H atom from $H^{13}CHO$ producing $H^{13}CO$ and CH_2OOH radicals; the latter then decomposes to yield $H^{12}CHO$ and the OH radical (eq R20), followed by (R21). In Scheme 4, ^{13}C atom is depicted by **C** (H**C**HO, H**C**O, **C**O) and $H^{12}CHO$ formed in the initial reaction and in (R21) (both originating from a C_2H_4 molecule) is enclosed in rectangles for easy identification. The radical CH_2OOH is known to be produced in the reaction of CH_3OOH with OH and to give HCHO and OH (eq R21) with a decomposition lifetime of ~20 μs.[60]

$$CH_2OO + H^{13}CHO \rightarrow CH_2OOH + H^{13}CO \quad (R20)$$

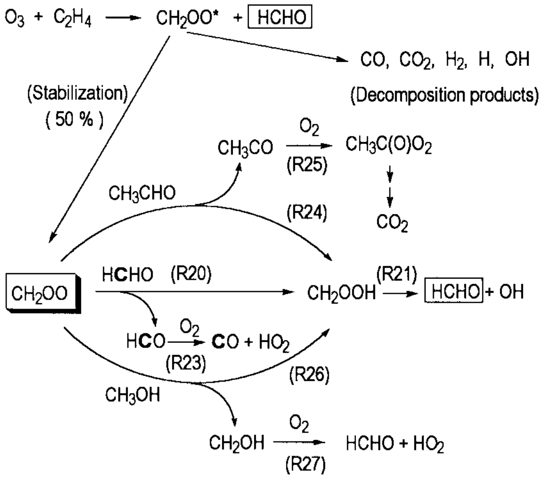
$$CH_2OOH \rightarrow H^{12}CHO + OH \qquad (R21)$$

In the presence of a large excess of $H^{13}CHO$, the OH radical formed in (R21) reacts with $H^{13}CHO$ (eq R22) and produces ^{13}CO, (eq R23). Under these conditions, it is

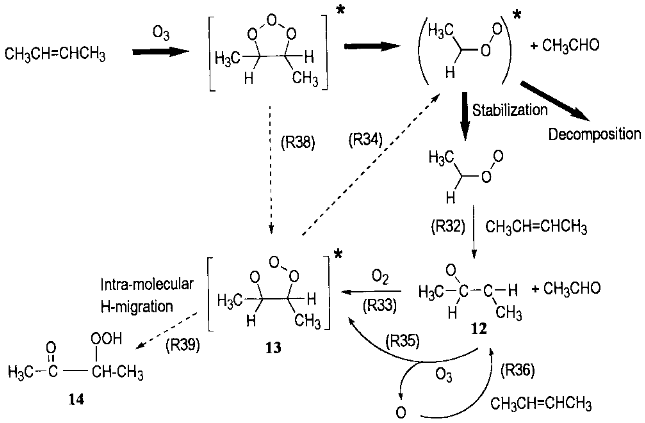
$$OH + H^{13}CHO \rightarrow H_2O + H^{13}CO \qquad (R22)$$

$$H^{13}CO + O_2 \rightarrow {}^{13}CO + HO_2 \qquad (R23)$$

Scheme 4



Scheme 5



apparent from Scheme 4 that the yield of $H^{12}CHO$ exceeds the maximum stoichiometric value of 100%, consistent with the data shown in Figure 1. Also, a large increase (>20%) in the CO_2 yield accompanied with the formation of **6** in the presence of added CH_3CHO[29,30] and the formation of **4** together with a significant (~20%) increase in the HCHO yield with the added CH_3OH,[25] can both be interpreted by the H-abstraction by CH_2OO, eqs R24 and R26, respectively, and the subsequent reactions R25 and R27 (Scheme 4).

In summary, the above interpretation, where CH_2OO may act as H-atom abstraction agent in the presence of added compounds thereby liberating OH radical (Scheme 4), provides a consistent picture of the active role of CH_2OO in C_2H_4 ozonolysis.

Though not a priori, the above argument may be extended to CH_3CHOO in C_4H_8 ozonolysis.[38,39] In this case, the CH_3CHOO reactions equivalent to the CH_2OO reactions R20 and R24 are (R28) and (R29), respectively,

$$CH_3CHOO + HCHO \rightarrow CH_3CHOOH + HCO \quad (R28)$$

$$CH_3CHOO + CH_3CHO \rightarrow CH_3CHOOH + CH_3CO \quad (R29)$$

$$CH_3CHOOH \rightarrow CH_3CHO + OH \quad (R30)$$

where the ensuing radical CH_3CHOOH is assumed to undergo dissociation to liberate the OH radical (eq R30). Under these assumptions, OH is formed only when suitable OH scavengers such as aldehydes or alkanes are added to the reaction. Such a secondary OH radical is relevant only under certain experimental conditions.

The larger-than-unity stoichiometry ratio in the absence of the additives, and increases in the formation of CO_2 with added CH_3CHO or CO with added HCHO,[38,39] have been usually explained by the primary OH formation from the excited CI, for example (R31).[37b,38]

$$CH_3CHOO^* \rightarrow CH_3 + CO + OH \quad (R31)$$

However, the data can be alternatively interpreted by assuming CH_3CHOO to be a reactive O-atom transfer agent, as illustrated in Scheme 5. The main reaction channels (Criegee mechanism) are depicted in thick arrows. In this postulate, CH_3CHOO is assumed to react with C_4H_8 via the O-atom transfer, forming a biradical **12** (eq R32). The subsequent O_2 addition to **12** (eq R33) will produce a biradical, **13**. This biradical **13** may be vibrationally excited and undergo dissociation. One such decomposition channel (eq R34) produces CH_3CHOO^* and CH_3CHO as in the Criegee channels (Scheme 1). It is evident that (R32) is the cause of the larger-than-unity stoichiometry ratios in this mechanism.

In the absence of O_2, the radical **12** is assumed to react rapidly with O_3 in an exothermic reaction (eq R35) with $\Delta H = -114$ kJ mol^{-1} and produce O atoms, which in turn would react with the parent alkene ($k_{296} \sim 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1})[45] and regenerate **12** (eq R36) (Note in (R36), CH_3CHO is not formed unlike in (R32)). The O-atom reaction with O_3 (eq R37) cannot compete (k_{296}

$$O + O_3 \rightarrow 2O_2 \quad (R37)$$

$\sim 8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1})[45] with (R36) under these conditions. As a result, the conversions of the both reactants would be accelerated. When O_2 is present, (R35) would be overridden by (R33) and eventually the acceleration would cease. As noted above briefly, the rate of gas-phase ozonolysis has been found to be significantly accelerated in the absence of O_2.[47] A typical example of such data for isobutene ozonolysis (Grossmann et al., unpublished data from this laboratory) is illustrated in Figure 4. These results are consistent with the above hypothesis in which the O-atom transfer reaction of CI with the parent alkene, (eq R32) plays a decisive role. Needless to say, the validity of this hypothesis must be examined in further studies. The O-atom formation from the decomposition of the excited CI on the other hand could occur irrespective of the O_2 presence but has been estimated to be of minor importance.[43,61]

We now discuss the nature of the residual products mentioned earlier. The question is whether their formation could provide mechanistic clues or if they have any atmospheric relevance. Probably, formation of the residual products does not involve CH_3CHOO, since they are formed irrespective of the presence or absence of

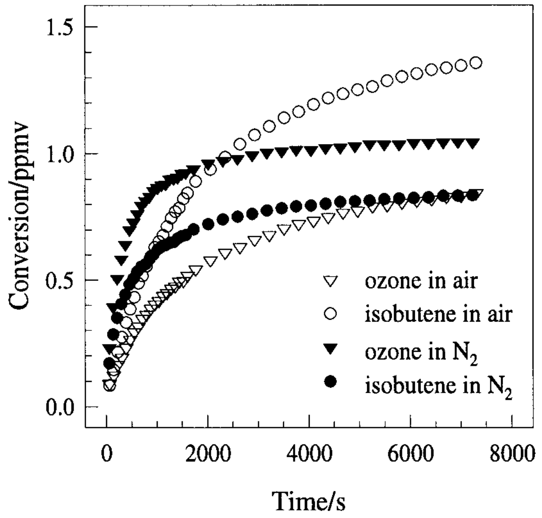


FIGURE 4. Temporal profiles of the conversions of O_3 and isobutene in air and in N_2. $[i\text{-}C_4H_8]_0 = 2$ ppmv and $[O_3]_0 = 1$ ppmv for both runs. Note that the stoichiometry ratio $= \Delta i\text{-}C_4H_8/\Delta O_3 \sim 1.6$ in air and ~ 0.8 in N_2.

HCOOH which is an efficient CI scavenger, as seen above.[39] Formation of the residual products in the ozonolysis of *trans*-2-C_4H_8 and DMB was observed to be undisturbed in the presence of an efficient CI scavenger CF_3COCF_3.[29] Also, their formation irrespective of the presence of O_2 suggests that a major fraction of the residual products may bypass the OH-initiated oxidation reaction of C_4H_8, as speculated by Niki et al.[43] in the case of DMB. A mechanism which is consistent with the above results is to assume that the residual products are formed directly from the primary ozonide. An example of the mechanism leading to one such possible product in 2-C_4H_8 is illustrated in Scheme 5, (R38) followed by (R39). The structure of the compound, 3-hydroperoxy butan-2-one (**14**) is consistent with the characteristic FTIR absorption of the residual spectra shown in Figure 3. They contain absorptions assignable to carbonyl, C−H stretch, and the OH (or OOH) group.

The above assumption is based on the ozonolysis mechanism proposed by O'Neal and Blumstein.[62] The essence of their mechanism consists of the formation of a biradical from an O−O splitting of the energy-rich primary ozonide (eq R38), followed by various reactions of the biradical, represented by dashed arrows in Scheme 5. On the other hand, the same species **13** may be produced in the O-atom transfer from CI to C_4H_8 (eq R32) followed either by O_2 addition (eq R33) or in the reaction with O_3 (eq R35). Therefore, formation of the residual products in the presence or absence of O_2 can be explained without assuming the mechanism of O'Neal and Blumstein.[62] However, if the residual products are formed according to O'Neal−Blumstein mechanism, it is a primary process, albeit minor, and will need careful attention for their atmospheric relevance. In either way, it is worth noting that the postulate presented in Scheme 5 which operates without the intermediacy of OH radical is capable of yielding the same product distributions irrespective of the presence of O_2.

It is evident that the role of CI in Scheme 5 can be substituted by the high reactivity of dioxiranes to varying degrees. It is rather curious that there have been very few ozonolysis studies where dioxiranes have been considered as an intermediate with a comparable importance as CI, despite the fact that the simplest dioxirane was identified as a transitory product first in the gas-phase C_2H_4 ozonolysis at low temperature.[63] It is also somewhat strange that no further experimental observations of the dioxirane homologues in the gas phase seem to have been made.

The formation of dioxiranes as reaction intermediates in the liquid-phase ozonolysis, though apparently discussed also scantily,[64,65] has an interesting consequence with respect to the gas-phase mechanism. In the ozonolysis of DMB in hexane and methylene chloride, Murray et al.[65] observed formation of the DMB epoxide and 3-hydroperoxy-2,3-dimethyl-1-butene. They postulated that the energy-rich acetone oxide can be partially converted to dimethyldioxirane, which then reacted with the parent alkene to form the epoxide. Also, the hydroperoxide was explained to be formed without consuming extra O_3. These results indicate that the excess alkene consumption, or the larger-than-unity stoichiometry ratios observed in the gas phase, could be a phenomenon common to the ozonolysis in both phases and might be due to the same mechanism.

Conclusion: A Perspective on the Gas-Phase Ozonolysis Studies

We have discussed recent progress in our understanding of the mechanism of the gas-phase ozonolysis from the viewpoint of the Criegee mechanism and summarized to what extent the gas-phase ozonolysis emulates the liquid-phase phenomena. The most outstanding deviation from the liquid-phase ozonolysis is the larger-than-unity stoichiometry ratio in the presence of O_2 and associated observations, such as low carbon balance coupled with the formation of the residual products or very low ozonide yields in the absence of added carbonyl compounds. The currently prevailing explanation for these results is to assume that OH radical is formed from the decomposition of the initially formed, energy-rich CI*. Although several indirect observations are consistent with this assumption, they provide no compelling or direct evidence for primary OH formation.

The above postulate was therefore developed, in the absence of convincing evidence for the primary OH formation, as an alternative interpretation of gas-phase ozonolysis data, in terms of the high reactivity of CI and dioxiranes observed in the liquid phase with a slight extension. If direct evidence for the primary OH formation will be obtained, numerous observations of the gas-phase ozonolysis must be interpreted consistently, which should lead to quantitative descriptions of the mechanism suitable for incorporating into atmospheric modeling, our final goal. It is hoped that this Account serves to clarify some of problems likely to be encountered during the course of further studies.

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