

# Kinetic and Theoretical Investigation of the Gas-Phase Ozonolysis of Isoprene: Carbonyl Oxides as an Important Source for OH Radicals in the Atmosphere

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**Abstract:** Kinetic measurements as well as B3LYP/ and MP2/6-31G(d,p) calculations provide evidence that carbonyl oxides formed in the gas-phase ozonolysis of alkylated alkenes are an important source of OH radicals. In the gas-phase ozonolysis of propene, *cis*-2-butene, *trans*-2-butene, tetramethylethene, and isoprene, 18, 17, 24, 36, and 19% OH radicals (relative to reacted ozone, error margin  $\leq 4\%$ ) are measured using CO as a scavenger for OH. The quantum chemical calculations show that OH radical production depends on syn positioned methyl (alkyl) groups and their interaction with the terminal O atom of a carbonyl oxide. For example, in the gas-phase ozonolysis of ethene only 5% OH radicals are measured while for a carbonyl oxide with syn-positioned methyl (alkyl) group, a much larger amount of OH radicals is formed. This is due to the fact that 1,4 H migration and the formation of an intermediate hydroperoxy alkene, that is prone to undergo OO bond cleavage, is energetically more favorable than isomerization to dioxirane. In the case of *syn*-methyl, dimethyl, and isopropenyl carbonyl oxide calculated activation enthalpies at 298 K are 14.8, 14.4, and 15.5 kcal/mol compared to the corresponding dioxirane isomerization barriers of 23.8, 21.4, and 23.0 kcal/mol, respectively. The OO cleavage reactions of the hydroperoxy alkenes formed in these cases are just 11, 12.8, and 10.3 kcal/mol.

## 1. Introduction

Hydroxyl radicals play an important role in the chemistry of the atmosphere. They trigger the cyclic process that leads to the oxidation of NO<sub>x</sub> to NO<sub>2</sub>, which is one of the criteria pollutants of the atmosphere. The daytime atmospheric degradation of volatile organic compounds (VOC) is mainly initiated by their reaction with OH radicals, the generation of which in the unpolluted atmosphere is attributed to the reaction of photogenerated O(<sup>1</sup>D) atoms with water. A substantial part of the VOCs, especially alkenes, may also be degraded by reaction with ozone.<sup>1–3</sup> There exists increasing evidence that OH radicals are formed in the course of the ozonolysis.<sup>4–13</sup>

Identification and quantification of OH radicals generated from these sources are important to model the chemistry of the troposphere.

Several approaches have been adopted by the different groups that have worked in this field to estimate OH radical production in the course of the ozonolysis. Herron and Huie<sup>4</sup> as well as Martinez and Herron<sup>5,6</sup> measured product profiles in stopped flow studies of ozone–alkene reactions using photoionization mass spectroscopy for the product analysis. Computer simulation of their experimental results leads these authors to suggest ester, hydroperoxide, and O atom channels, respectively, to be operative in the reactions. Formation of OH radicals has been implied as possible step in the ester channel, however, without quantification. Niki and co-workers<sup>7</sup> observed in the ozonolysis of tetramethylethylene that the stoichiometric ratio  $r = \Delta[\text{alkene}]/\Delta[\text{O}_3]$  ( $\Delta$  is the difference between starting and final concentration, i.e.,  $\Delta$  gives the consumption of the compound in question) decreased from 1.7 to 1.0 when HCHO or CH<sub>3</sub>-CHO were added to the system. They proposed that an OH-initiated oxidation of the alkene was responsible for  $r > 1$ . Horie and co-workers<sup>8,9</sup> analyzed the product distribution in the ozonolysis of propene and *trans*- and *cis*-2-butene by FTIR technique and deduced OH formation yields of 14%, 24%, and 17%. Atkinson and co-workers<sup>10</sup> employed cyclohexane as OH radical scavenger in the ozonolysis of alkenes and terpenes. These authors reported a value of 27% for OH radicals generated in the ozonolysis of isoprene. Paulson and co-workers<sup>11</sup> evaluated OH formation yields in the ozonolysis of isoprene using methylcyclohexane as scavenger, reporting a value of  $68 \pm 15\%$ .

The most extended study on OH radical production in the gas-phase ozonolysis of alkenes under tropospheric conditions has been presented by Atkinson and Aschmann.<sup>12</sup> On the basis of the known chemistry in the system cyclohexane/OH/excess

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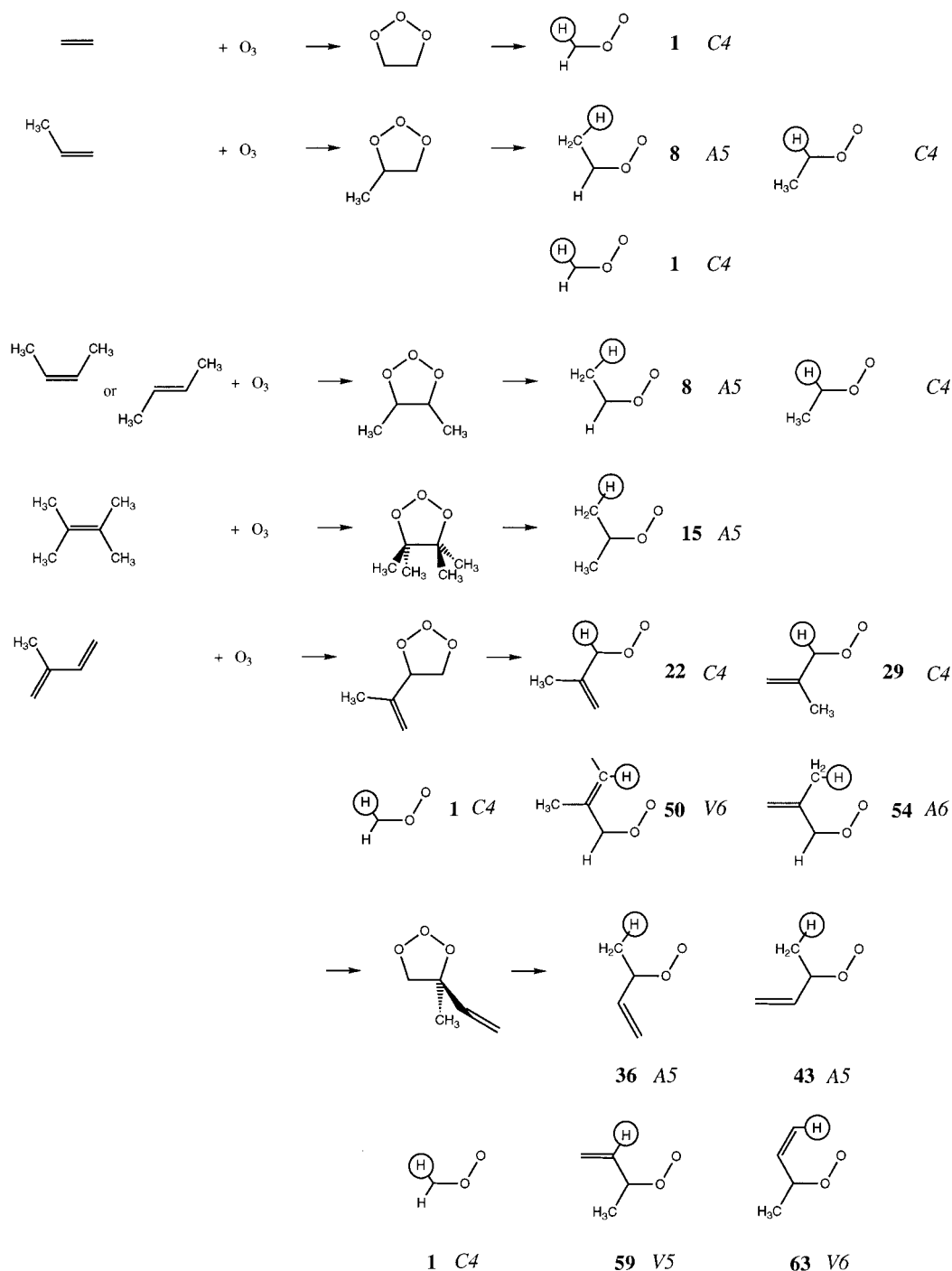
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## Scheme 1



$O_2$  and the experimentally determined cyclohexane/cyclohexanol formation yields, the production of OH radicals was derived with estimated overall uncertainties of a factor of 1.5. While the work by Atkinson and Aschmann contains a detailed discussion of the peroxy radical chemistry including the reaction between  $HO_2$  and  $O_3$ , possible interferences from reactions with other intermediates, especially with carbonyl oxides and/or dioxiranes are not addressed in ref 12. Expected sources for OH formation are only quoted (e.g., from refs 5 and 7) in ref 12; however, no attempt is made to quantify them.

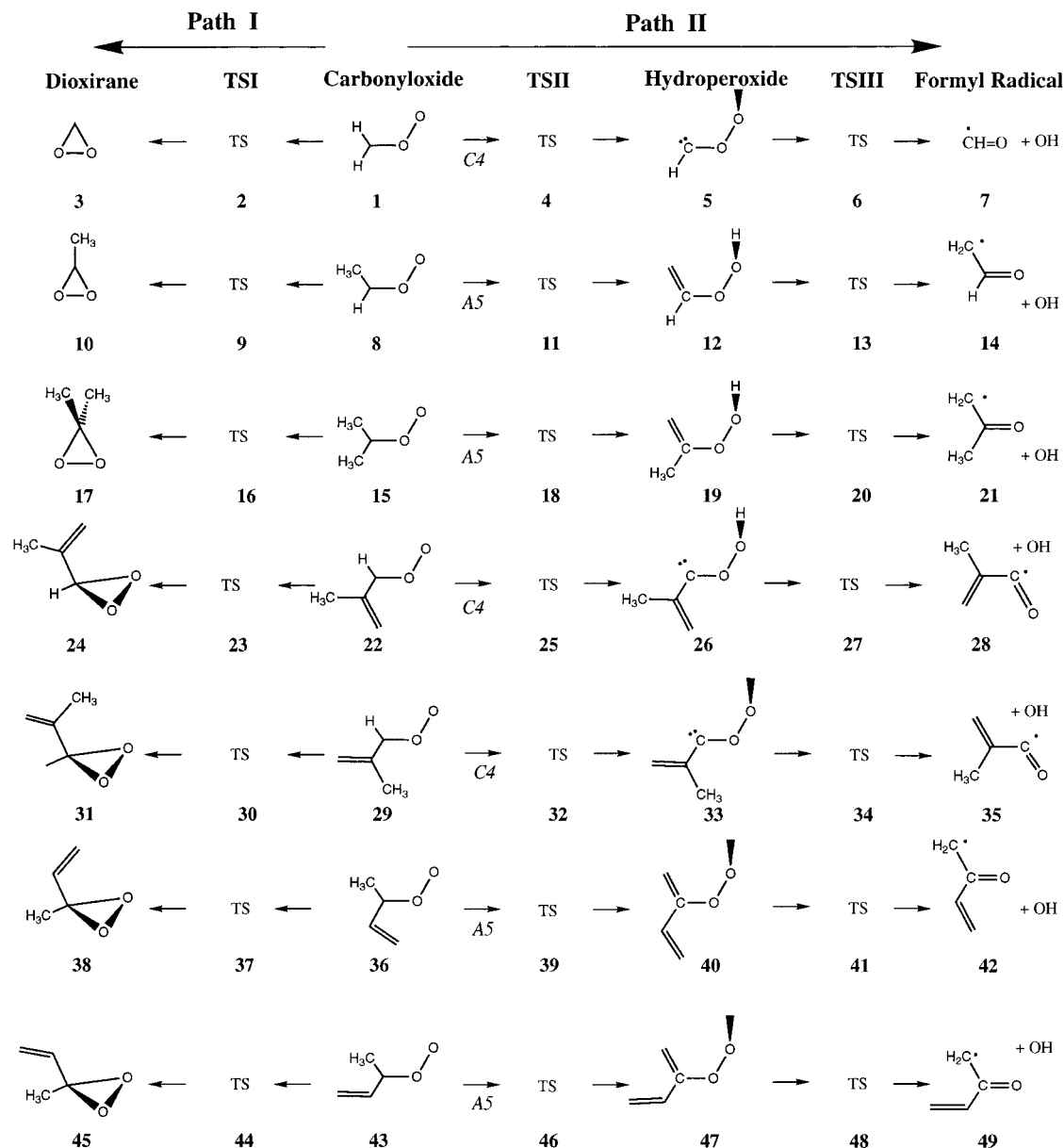
In view of the (partially contradictory) experimental observations made previously, a redetermination of the OH yields in the ozonolysis of alkenes and especially of isoprene by new methods appeared to be in order.

The accepted mechanism for the reaction of ozone with alkenes is the Criegee mechanism,<sup>3</sup> for which the first two steps

are shown in Scheme 1 for the alkenes investigated in this work. In the first step of the ozonolysis, ozone reacts with alkene by cycloaddition to yield in a highly exothermic reaction a 1,2,3-trioxolane, the so-called primary ozonide. Primary ozonide in turn decomposes into aldehyde and carbonyl oxide, the so-called Criegee zwitterion.<sup>3</sup> While primary ozonides have been isolated and characterized, there is only indirect evidence for the intermediary of carbonyl oxides in the course of the ozonolysis.<sup>3</sup> Carbonyl oxides are formed in these reactions with large amounts of internal energy and, therefore, it is likely that they can lead to the generation of OH radicals during the ozonolysis of alkenes.<sup>12</sup>

In recent theoretical work, we have investigated whether carbonyl oxides can directly decompose to yield OH radicals and whether such a decomposition reaction can compete with the rearrangement of carbonyl oxide to its more stable isomer

Scheme 2



dioxirane.<sup>13</sup> Using high level ab initio methods, we found that  $\text{CH}_2\text{OO}$  (**1**, Scheme 2) can decompose after H migration and intermediate formation of a carbene to OH and formyl radicals. However, the calculated activation enthalpy of this reaction (31 kcal/mol) is 13 kcal/mol higher than the activation enthalpy (18 kcal/mol) for the carbonyl oxide dioxirane isomerization (see **1–7** of paths I and II in Scheme 2). Under normal conditions, there should be a vanishingly small probability of generating OH radicals during the gas-phase ozonolysis of ethene.

The activation barrier for H migration becomes smaller than that for isomerization to dioxirane in the case of alkyl carbonyl oxides. Cremer<sup>14</sup> was the first to point out that *syn*-alkylcarbonyl oxides are internally stabilized by interactions between a H atom of an  $\alpha\text{-R}_2\text{CH}$  ( $\alpha\text{-RCH}_2$ ) group and the terminal O atom.



H<sub>2</sub>O interactions in the *syn* form should facilitate the migration of the H atom to the terminal O atom, which should

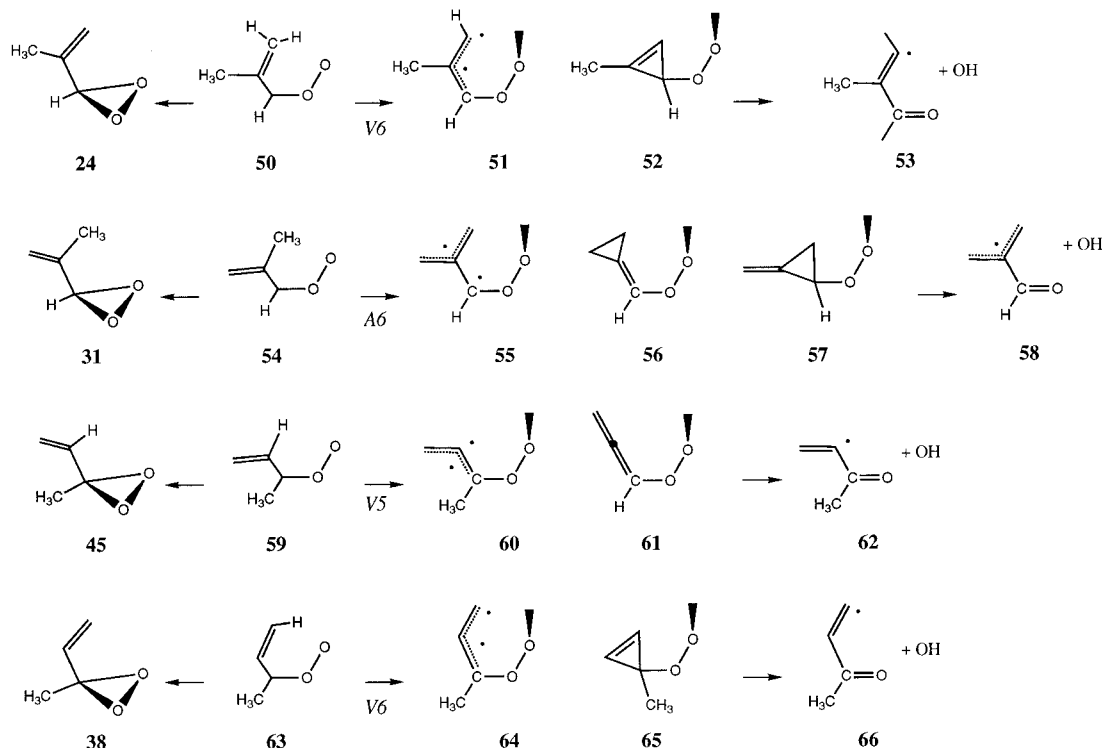
be followed by a subsequent decomposition of the intermediate hydroperoxide to OH and RCO radicals. Accordingly, OH generation becomes faster than isomerization of carbonyl oxide to dioxirane (see, e.g., **8–10** in Scheme 2).

In the present investigation, we provide evidence for the generation of OH radicals during the gas-phase degradation of alkenes by ozonolysis with carbonyl oxides being the primary source of OH radicals. Our evidence results from both experimental and quantum chemical investigations of the ozonolysis of ethene (ET), propene (PR), *trans*-2-butene (TB), *cis*-2-butene (CB), tetramethylethene (TME), and isoprene (ISP, Schemes 1 and 2). ISP is an important biogenic trace constituent of the atmosphere, being emitted by deciduous trees and other vegetation leading to concentrations of ~500 ppb within forest regions during the summer months.<sup>1,2</sup> In the presence of other pollutants, especially  $\text{NO}_x$  and  $\text{SO}_2$ , terpenes and ISP are involved in natural smog situations. Ozonolysis of simple alkenes and of ISP can act as a nighttime source of OH radicals as shall be described in the present work.

In section 2, we report on results of a kinetic investigation of the ozonolysis of PR, TB, CB, TME, and ISP and, in this connection, propose CO as probe to quantify OH radical

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## Scheme 3



**Table 1.** Reactions Considered in the Ozonolysis of Alkenes in the Presence of Excess CO to Scavenge OH<sup>a</sup>

reaction no.	reaction	<i>k</i>
(1a)	ET + O <sub>3</sub> → products	1.75 × 10 <sup>-18</sup>
(1b)	PR + O <sub>3</sub> → products	1.3 × 10 <sup>-17</sup>
(1c)	CB + O <sub>3</sub> → products	1.28 × 10 <sup>-16</sup>
(1d)	TB + O <sub>3</sub> → products	2.2 × 10 <sup>-16</sup>
(1e)	TME + O <sub>3</sub> → products	1.6 × 10 <sup>-15</sup>
(1f)	ISP + O <sub>3</sub> → products	1.43 × 10 <sup>-17</sup>
(2)	CO + OH → CO <sub>2</sub> + H	2.3 × 10 <sup>-13</sup>
(3)	CO + HO <sub>2</sub> → OH + CO <sub>2</sub>	1.14 × 10 <sup>-27</sup>
(4)	CO + O <sub>3</sub> → products	1.0 × 10 <sup>-21</sup>
(5a)	OH + ET → products	8.2 × 10 <sup>-12</sup>
(5b)	OH + PR → products	3.0 × 10 <sup>-11</sup>
(5c)	OH + CB → products	5.6 × 10 <sup>-11</sup>
(5d)	OH + TB → products	6.4 × 10 <sup>-11</sup>
(5e)	OH + TME → products	1.1 × 10 <sup>-10</sup>
(5f)	OH + ISP → products	1.0 × 10 <sup>-10</sup>
(6)	OH + aldehydes → products	(1.1–1.6) × 10 <sup>-11</sup>
(7)	OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	6.8 × 10 <sup>-14</sup>
(8)	H + O <sub>2</sub> + M → HO <sub>2</sub> + M	7.3 × 10 <sup>-13 b</sup>
(9)	H + O <sub>3</sub> → OH + O <sub>2</sub>	2.9 × 10 <sup>-11</sup>
(10)	H + alkene → products	~1.0 × 10 <sup>-12</sup>
(11)	R + O <sub>2</sub> + M → RO <sub>2</sub> + M	2 × 10 <sup>-12 b</sup>
(12)	R + O <sub>3</sub> → RO + O <sub>2</sub>	5 × 10 <sup>-12</sup>
(13)	HO <sub>2</sub> + O <sub>3</sub> → OH + 2 O <sub>2</sub>	2 × 10 <sup>-15</sup>
(14)	HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	2.9 × 10 <sup>-11</sup>
(15)	HO <sub>2</sub> + RO <sub>2</sub> → products	4 × 10 <sup>-12</sup>
(16)	HO <sub>2</sub> + OH → H <sub>2</sub> O + O <sub>2</sub>	1.11 × 10 <sup>-10</sup>
(17)	HO <sub>2</sub> + aldehydes → products	5 × 10 <sup>-15</sup>
(18)	O + O <sub>2</sub> + M → O <sub>3</sub> + M	8.4 × 10 <sup>-15</sup>
(19)	O + alkene → products	(2–4) × 10 <sup>-11</sup>

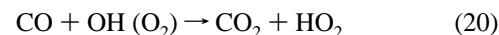
<sup>a</sup> Rate constants *k* (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) from ref 15. R denotes an alkyl substituent. <sup>b</sup> At 1 atm with 20 vol % O<sub>2</sub>.

production in ozonolysis reactions. In section 3, ab initio and DFT calculations on molecules and transition states **1–64** shown in Schemes 2 and 3 are presented. In section 4, the results of the quantum chemical investigations are used to rationalize the suggested generation of OH radicals in the ozonolysis of alkenes via a unimolecular dissociation of intermediate hydroperoxide. Finally, a brief account of existing discrepancies in reported experimental OH yields is given.

## 2. Experimental Investigation

The quantitative determination of OH radicals generated in the course of the ozonolysis requires a specific scavenger for OH that does not react measurably with any stable product or intermediate of the reaction where, as possible intermediates, H atoms, O atoms, peroxy radicals, and the Criegee zwitterion were considered. The scavenging should lead to a characteristic product that can directly be related to the reaction of the scavenger and can easily be quantified. Considering known rates of reactions 1–19 listed in Table 1, we concluded that carbon monoxide, CO, fulfills these requirements in the systems under investigation in a most satisfactory way.

CO is known to react with OH radicals to yield CO<sub>2</sub> with a rate constant of *k* = 2.3 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (reaction 2 of Table 1). In air at ambient conditions, the H atoms formed are immediately converted to HO<sub>2</sub> according to reaction 8 of Table 1. For this conversion at atmospheric conditions, a rate constant of *k* = 7.3 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was measured.<sup>15</sup> The overall scavenging reaction is thus governed by the process



i.e., CO<sub>2</sub> increase in the presence of CO indicates the amount of OH production due to carbonyl oxide decomposition. The hydroperoxy radicals generated hereby do not react measurably with CO to form CO<sub>2</sub> (cf., reaction 3, Table 1). They are removed predominantly by self-reaction and cross-reaction with other peroxy radicals present in the oxygen-rich system and also to a smaller extent by reactions with the aldehydes generated in the decomposition of the primary ozonides. A small fraction of the HO<sub>2</sub> radicals may also react with O<sub>3</sub> according to reaction 13 of Table 1 to regenerate OH. The significance of reaction 13 depends on the system studied. Model calculations show that for CB, TB, and TME an OH yield of <2% and for PR

(15) de More, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Nr. 10*; JPL Publication: Pasadena, 1994; p 92–20.

**Table 2.** Aldehyde and Ketone Yields Obtained in the Ozonolysis of Ethene (ET), Propene (PR), *cis*-Butene (CB), *trans*-Butene (TB), 2,3-Dimethyl-2-butene (TME), and Isoprene (ISP) in the Presence of 20 vol % O<sub>2</sub> with and without Addition of External CO

alkene	product	yields, % <sup>a</sup>	
		without CO	with CO
PR	formaldehyde	62	60
	acetaldehyde	46	43
CB	acetaldehyde	90	94
TB	acetaldehyde	94	95
TME	acetone	102	103
ISP	formaldehyde	54	55
	methacrolein	28	30
	methyl vinyl ketone	21	20

<sup>a</sup> With respect to reacted alkene.

and ISP an OH yield of <4% with respect to O<sub>3</sub> consumed can be expected. Hence, HO<sub>2</sub> and its reaction with O<sub>3</sub> do not affect the total OH yields significantly and the increase in CO<sub>2</sub> can be related to the primary OH, i.e., the OH radicals directly generated in the decomposition of the intermediate hydroperoxide.

Clearly, rate constants for the reactions of OH radicals with alkenes or aldehydes (reactions 5 and 6 of Table 1) are higher than that with CO. Hence, if OH radicals are produced in the course of the ozonolysis in the absence of a scavenger, they will produce hydroxy alkyl radicals, which will react with O<sub>2</sub> and decompose or stabilize in various ways. However, these initiation reactions of the OH radicals can largely be suppressed by adding an excess of CO. Whereas the concentrations of alkene and ozone in the present study were in the <25 ppm range, the scavenger CO was added up to 40 vol %.

CO does practically not react at all with any closed-shell species in the reaction systems investigated. For its reaction with O<sub>3</sub> (reaction 4, Table 1) e.g., the very low rate constant of  $k = 1.0 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  has been determined. Also its reactions with H atoms and O atoms may be neglected under present conditions. Both reactions are third order and are suppressed through steps 8–18 of Table 1.

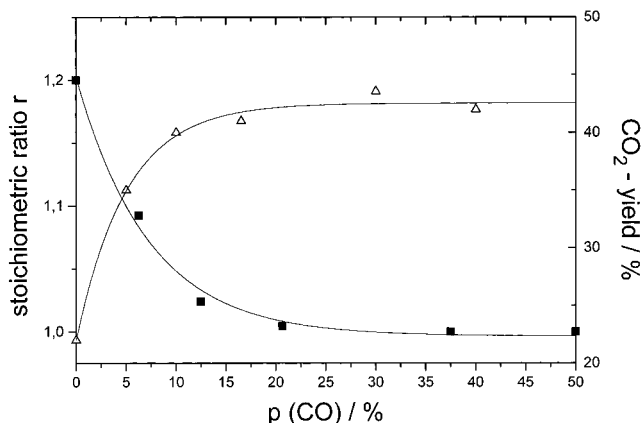
Most critical for the present discussion is the question whether carbonyl oxide might act as O transfer agent and, thereby, contribute to CO<sub>2</sub> generation via the formal reaction



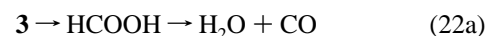
If this reaction were to occur the observed increase in CO<sub>2</sub> yield upon CO addition would not be related to OH scavenging alone and would require a correction. However, if reaction 21 would occur to a noticeable extent, the yield in R<sub>2</sub>CO would also have to increase. Results compiled in Table 2 clearly show that aldehyde/ketone yields with respect to alkene consumption do not increase upon addition of CO and, therefore, side reaction 21 cannot play a significant role in the reaction system. Furthermore, the consistency of these yields upon addition of excess CO must be taken as supporting evidence that these major products are formed directly in the unimolecular decomposition of the primary ozonides, which is considered to be not affected by the additive. No other information is available in the literature on products resulting from a reaction of the Criegee biradical with CO, except a brief statement by Moortgat and co-workers<sup>16</sup> that no formic anhydride is formed if H<sub>2</sub>COO is allowed to interact with excess CO.

In the gas-phase ozonolysis of alkenes, a considerable amount of intermediately formed carbonyl oxide may isomerize to the corresponding dioxirane, which can decompose to CO + HOH,

(16) Moortgat, G. K.; Neeb, P.; Horie, O.; Sauer, F.; Schäfer, C.; Winterhalter, R. *Ozonolysis of Alkenes: Recent Developments*; Air Pollution Research Report 57; MPI: Mainz, Germany, 1996; pp 279–286.

**Figure 1.** Decrease in stoichiometric ratio  $r$  (■) and increase in CO<sub>2</sub> yield ( $\Delta$ ) as function of CO added in the ozonolysis of isoprene. Data are indicated with symbols; solid lines show the simulation results.

CO<sub>2</sub> + H<sub>2</sub>, and CO<sub>2</sub> + 2H.<sup>17</sup> The corresponding reactions for the parent dioxirane **3** are the processes 22a–22c:



Hence, CO formed in the decomposition of dioxiranes would be available for a reaction with OH radicals formed in the decomposition of carbonyl oxides. Thus, it might be argued that CO<sub>2</sub> measured in the absence of external CO might also be due to the production of OH radicals. However, the reaction of OH with alkenes (reactions 5a–5f, Table 1) is so much faster than that with CO that reaction 2 will play only a role when a large excess of CO is added to the reaction system. The CO<sub>2</sub> generated without added scavenger will be formed in different reaction sequences.

Figure 1 gives the increase in CO<sub>2</sub> yields and decrease of the stoichiometric ratio  $r$  as a function of added CO measured for the system ISP/O<sub>3</sub>. Equivalent results were received for all alkenes studied. In each case, the stoichiometric ratio  $r = \Delta[\text{alkene}]/\Delta[\text{O}_3]$  was determined by in situ spectroscopic measurements. The concentration of reacted alkene was also measured by GC/MS analysis after complete O<sub>3</sub> consumption. Each point in the diagram is the average of at least three kinetic runs. The initial concentration  $[\text{alkene}]_0/[\text{O}_3]_0$  was 2.5 in all sets.<sup>18</sup> The solid lines were obtained by kinetic simulation of the chemical system with the rate constants compiled in Table 1. It is satisfying to see that the stoichiometric ratio  $r$  decreases from 1.2 without scavenger added to  $r = 1.0$ , which indicates that secondary ISP consumption by OH radicals is suppressed by added CO. In ozonolysis experiments in the absence of oxygen, it was established that O atoms are formed to only 4% and thus regeneration of O<sub>3</sub> according to reaction 18 of Table 1 can be excluded.

Experiments have been carried out with [CO] ranging from 10 to 30%. It was found that in all systems the stoichiometric ratio decreased to unity when up to 30% CO was used. In the TB and ISP systems, 20% CO were needed to reach  $r = 1$ . Further addition of CO did neither decrease the stoichiometric ratio below unity nor did it increase the CO<sub>2</sub> yield. The increase in the CO<sub>2</sub> yield is considered to represent the OH radical yield in the systems (see Table 3). Noteworthy is that the decrease

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(18) Gutbrod, R.; Meyer, S.; Rahman, M. M.; Schindler, R. N. *Int. J. Chem. Kinet.*, in press.

**Table 3.** Stoichiometric Ratio  $r = \Delta[\text{alkene}]/\Delta[\text{O}_3]$ , CO<sub>2</sub> Yields, and OH Yields (with Respect to Reacted O<sub>3</sub>) in the Ozonolysis of Propene (PR), *cis*-Butene (CB), *trans*-Butene (TB), 2,3-Dimethyl-2-butene (TME), and Isoprene (ISP) in the Presence of 20 vol % O<sub>2</sub><sup>a</sup>

alkene	$p_0(\text{CO})$	$r$	CO <sub>2</sub> yield, %	OH yield, %
PR	0	1.2	42	
	20	1.0	60	18 ± 4
CB	0	1.3	40	
	20	1.0	57	17 ± 2
TB	0	1.6	50	
	20	1.0	74	24 ± 2
TME	0	2.2	40	
	30	1.0	76	36 ± 2
ISP	0	1.2	22	
	20	1.0	41	19 ± 4

<sup>a</sup> The statistical error in the determination of  $r$  was ±0.01. The error in integrated CO<sub>2</sub> yields was estimated to be ±2%.

in stoichiometric ratio  $-\Delta r$  is within experimental uncertainty and in no case smaller than the increase in CO<sub>2</sub> production. For PR and ISP,  $-\Delta r \approx \Delta[\text{CO}_2]$ , for CB, TB, and TME; however,  $-\Delta r > \Delta[\text{CO}_2]$ . On the basis of the experimental findings reported in this work, no information can be deduced as to the additional alkene consumption (see also discussion in section 4). It is expected that statistical calculations describing the chemically activated systems employing the master equation approach will provide answers to this question. Preliminary results<sup>19</sup> indicate that OH yields of 100% reported by Atkinson and Aschmann<sup>12</sup> cannot be corroborated by statistical model calculations.

The OH yields given here are in good agreement with values for PR (17%), CB (14%), and TB (24%) reported by Horie and co-workers,<sup>9</sup> where it has to be stressed that the OH yield reported in ref 9 was based on a detailed product analysis by FTIR spectroscopy. On the other hand, the OH yields summarized in Table 3 are consistently lower than the values reported by Atkinson and Aschmann (PR, 33; CB, 41; TB, 64; TME, 100; ISP, 27%),<sup>12</sup> Niki and co-workers (TME, 70; ISP, 68 ± 15%),<sup>7</sup> and Paulson and co-workers,<sup>11</sup> which has to be considered when discussing the mechanism of OH formation (see Section 4).

While experimental results indicate a significant amount of OH radical production during ozonolysis, it was felt that independent confirmation for the formation of OH radicals in the reaction systems investigated needed to be obtained. Also a detailed computational assessment of previously implied pathways leading to OH formation in the ozonolysis of alkenes deemed to be in order. For this purpose, we carried out quantum chemical calculations, which are discussed in the next section.

### 3. Quantum Chemical Investigation

Our previous investigation<sup>13</sup> suggests that only those carbonyl oxides, which possess in *syn* position a CHR<sub>2</sub> or CH<sub>2</sub>R group, lead to formation of OH radicals because interactions of an H atom of CHR<sub>2</sub> (CH<sub>2</sub>R) with the terminal O atom of carbonyl oxide previously described by Cremer<sup>14</sup> in 1979 facilitate the rearrangement to a hydroperoxy compound which decomposes to yield OH radicals. In Scheme 1, all possible carbonyl oxides that can be generated upon decomposition of ET, PR, TB, CB, TME, and ISP primary ozonide are shown. For each of the carbonyl oxides of Scheme 1, there are two possible unimolecular rearrangement and decomposition paths I and II, which are shown in Schemes 2 and 3 (molecules and TSs 1–66). Path I corresponds to the isomerization reaction of carbonyl oxide to dioxirane via TSI (Scheme 2).<sup>3,17,20,21</sup> Dioxirane (3) has been

detected in the gas-phase ozonolysis of ET<sup>21</sup> and ample evidence for the generation of dioxiranes during the ozonolysis has been collected.<sup>17</sup> Hence, it is the general opinion that path I represents the preferred rearrangement route of carbonyl oxides.

Path II is characterized by the migration of a *syn* positioned H atom to the terminal O atom via TSII thus forming a hydroperoxide, which can decompose via TSIII to OH and formyl radicals. In the literature, there was early speculation that path II might represent an alternative rearrangement and decomposition route of carbonyl oxides in the gas phase.<sup>22</sup> In our recent *ab initio* investigation<sup>13</sup> we could clarify that for the parent carbonyl oxide 1, path II represents a high energy reaction with an activation enthalpy of 31 kcal/mol (CCSD(T)/6-31G-(d,p) calculations). The intermediate hydroperoxide 5, which as a carbene would be rather unstable, does not exist on the CCSD(T) potential energy surface. Instead, H migration leads directly to decomposition of 1 into the formyl and OH radicals 7 (Scheme 2).

In case of a *syn*-alkyl-substituted carbonyl oxide with an α-H atom such as in 8, an intermediate hydroperoxyalkene (see 12) rather than an unstable hydroperoxy carbene is formed, which in an endothermic process without energy barrier decomposes to OH and alkyl radicals such as 14. In the case of dimethyl carbonyl oxide 15, the activation enthalpy of path II is lower than that of path I and, therefore, path II should represent the preferred decomposition route.<sup>13</sup>

The question is, which of the carbonyl oxides of Scheme 1 prefer to follow path I or path II. To answer this question, we characterize each carbonyl oxide according to the nature of the migrating H atom and the number of atoms participating in the cyclic transition state (TS) of the H migration. As pointed out above, the *syn*-positioned H atom (encircled in Scheme 1) in the parent carbonyl oxide 1 does not migrate easily because (a) the intermediately formed hydroperoxy carbene is unstable and (b) the TS involves a four-atom cycle of considerable strain (C4-type H atom, carbonyl oxide H, 4-membered TS). In the case of carbonyl oxide 8, there is a *syn*-methyl H atom that can migrate via a five-membered cyclic TS of considerably less strain to the closed-shell system 12 (A5-type H atom: alkyl H atom, 5-membered TS; Scheme 2). The ozonolysis of PR, CB, and TB will involve *syn*- and *anti*-carbonyl oxides possessing either C4- or A5-type H atoms (Scheme 1), while the ozonolysis of TME exclusively leads to carbonyl oxide 15 with a A5-type H atom (Schemes 1 and 2).

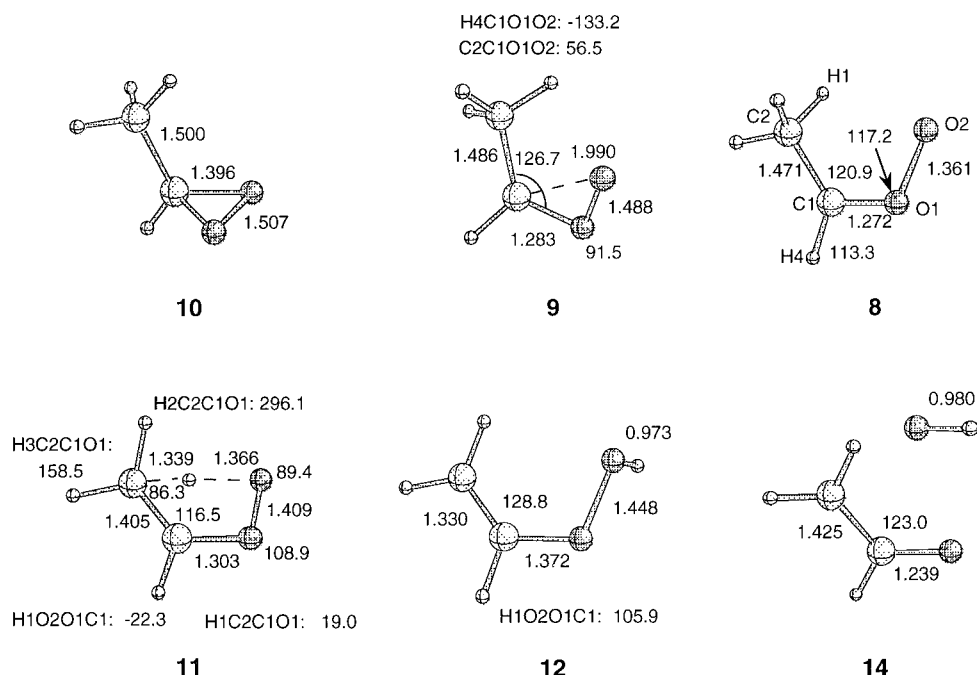
In the ozonolysis of ISP, the carbonyl oxides 1, 22, 29, 36, 43, 50, 54, 59, and 63 can be formed (Scheme 1). Of these, 1, 22, and 29 possess C4-type H atoms and, therefore, should not decompose easily to yield OH radicals. However, carbonyl oxides 36 and 43 have A5 H atoms, which should make them prone to follow path II. Migration of a methyl H in 54 will lead to a 6-membered TS and, accordingly, the H atom can be denoted as A6. It has to be checked whether 54 can also lead to an intermediate hydroperoxy alkene and, thereby, to a preference of OH production rather than dioxirane formation. Carbonyl oxides 50, 59, and 63 possess a vinyl H atom that might migrate to the terminal O atom via a 5- (V5-) or 6-membered TS (V6-type H atom, Scheme 1) and it has to be clarified whether V5 or V6 H atoms can as easy migrate as A5 H atoms.

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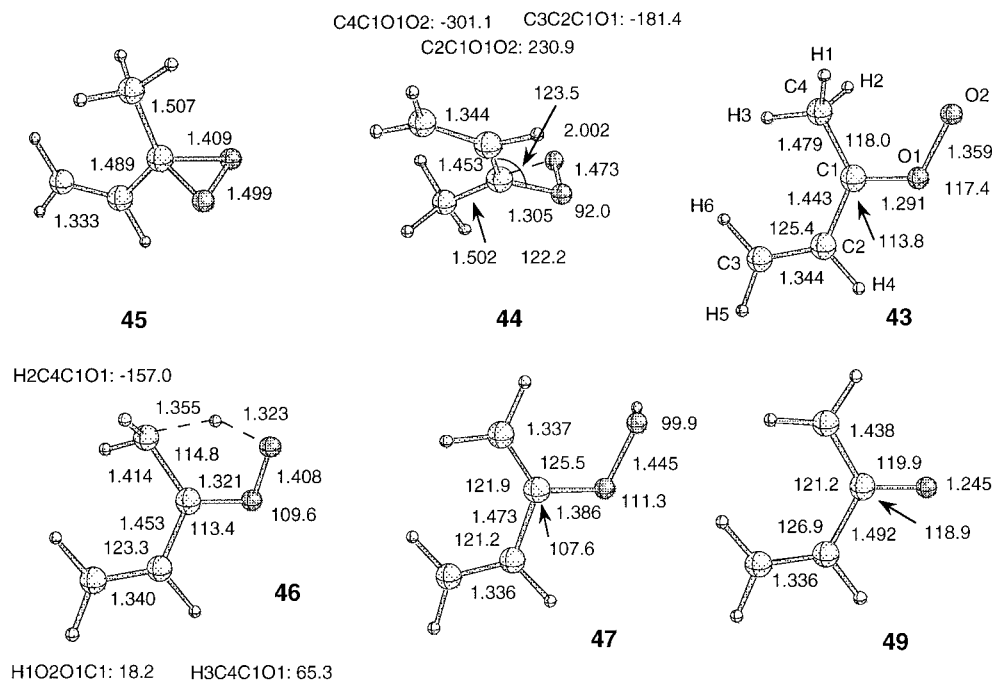
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**Figure 2.** B3LYP/6-31G(d,p) geometries for molecules and TSs **8–14**. (Distances are in Å; angles, in deg.)



**Figure 3.** B3LYP/6-31G(d,p) geometries for molecules and TSs **43–49**. (Distances are in Å; angles, in deg.)

We have investigated molecules and TSs **1–66** with ab initio MP2 (second-order Møller–Plesset perturbation theory)<sup>23</sup> and density functional theory (DFT) using the hybrid functional B3LYP<sup>24</sup> and the 6-31G(d,p) basis set.<sup>25</sup> The relative stability of ISP carbonyl oxides and some of their isomers is compared in Table 4. Calculated reaction energies, energy barriers, zero-point energy (ZPE) corrections, reaction and activation enthalpies at 298 K, and  $\Delta\Delta H_f^\circ(298)$  are listed in Table 5. Some selected geometries of **1–66** are shown in Figures 2 and 3 while a complete set of calculated geometries is given in the

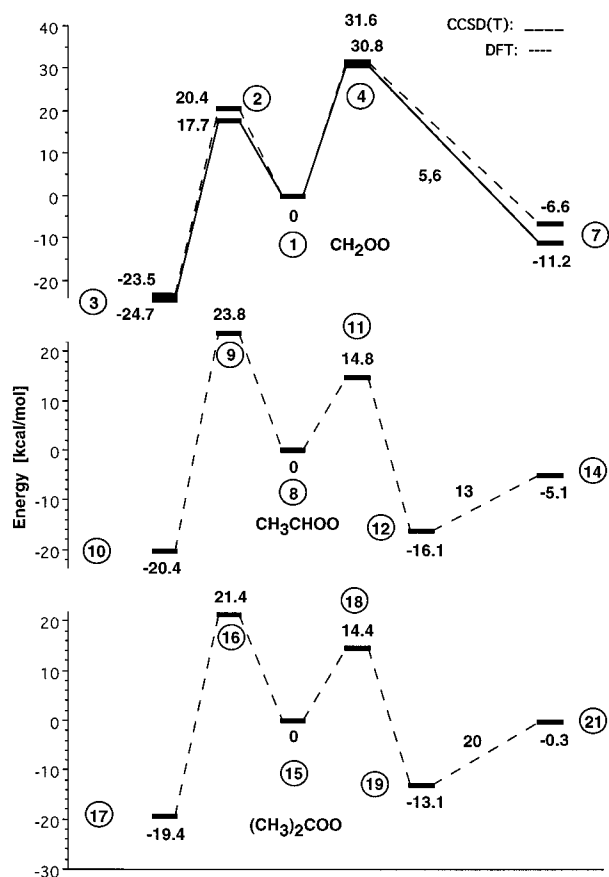
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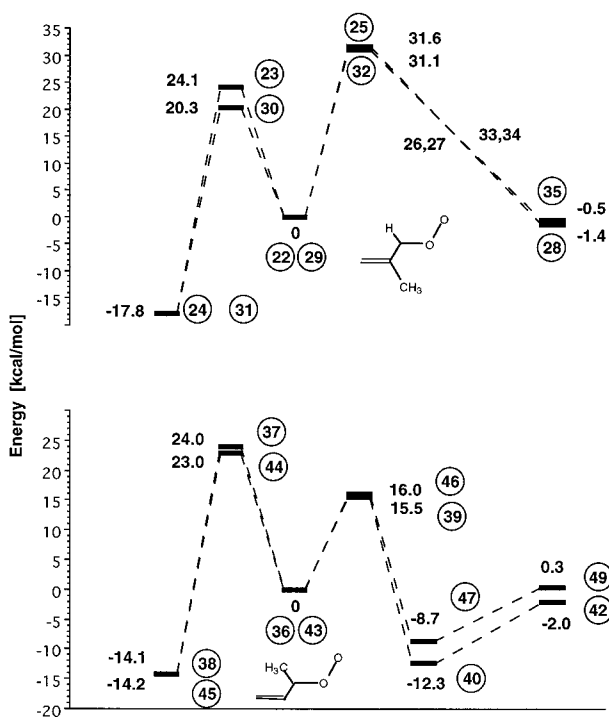
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Supporting Information. Relevant  $\Delta\Delta H_f^\circ(298)$  values calculated for path I and path II are compared in Figures 4 and 5.

**Geometries.** Cremer and co-workers<sup>20</sup> have shown that the most critical geometrical feature of a carbonyl oxide is the ratio of OO and CO bond length. While this is largely overestimated by HF and semiempirical MO methods, low order electron correlation methods tend to underestimate it.<sup>13,20</sup> Reliable values of the geometrical parameters of carbonyl oxides are obtained by CCSD(T)/TZ+2P calculations (**1**, OO, 1.355; CO, 1.276 Å), the results of which are surprisingly well reproduced at the DFT-B3LYP/6-31G(d,p) level of theory (**1**, OO, 1.343; CO, 1.266 Å<sup>13</sup>). It has been shown<sup>13,20</sup> that MP2/6-31G(d,p) (**1**, OO, 1.293; CO, 1.298 Å) only provides reasonable starting values for CCSD(T) or B3LYP geometry optimizations, and, therefore, we will refer in the following exclusively to B3LYP/6-31G(d,p) geometries and energies.



**Figure 4.** B3LYP/6-31G(d,p) reaction and activation enthalpies  $\Delta\Delta H_f^\circ(298)$  for reaction paths I and II in the case of carbonyl oxide (**1**), *syn*-methylcarbonyl oxide (**8**), and dimethylcarbonyl oxide (**15**). Encircled numbers correspond to the molecules and TSs shown in Scheme 2.



**Figure 5.** B3LYP/6-31G(d,p) reaction and activation enthalpies  $\Delta\Delta H_f^\circ(298)$  for reaction paths I and II in the case of ISP carbonyl oxides **22**, **29**, **36**, and **43**. Encircled numbers correspond to the molecules and TSs shown in Scheme 2.

Methyl substitution as in **8** (one CH<sub>3</sub>) or **15** (two CH<sub>3</sub> groups) increases the OO/CO bond length ratio from 1.343:1.266 (**1**) to

**Table 4.** Relative Energies (kcal/mol) of ISP Carbonyl Oxides and the Corresponding Hydroperoxides (B3LYP/6-31G(d,p) Calculations, Compare with Schemes 2 and 3)

ISP carbonyl oxides					ISP hydroperoxides			
no.	substituent	s/a <sup>a</sup>	Me at <sup>b</sup>	vinyl <sup>c</sup>	$\Delta E^d$	no.	$\Delta E^e$	$\Delta E^f$
<b>22</b>	2-propenyl	a	DB	c	9.1	<b>26</b>	14.0	34.2
<b>29</b>	2-propenyl	a	DB	t	5.9	<b>33</b>	14.3	31.3
<b>36</b>	Methyl,vinyl	s	COO	c	1.5	<b>40</b>	-12.6	0
<b>43</b>	Methyl,vinyl	s	COO	t	0	<b>47</b>	-8.8	2.3
<b>50</b>	2-propenyl	s	DB	c	6.4	<b>52</b>	$\geq 20$	$\geq 38$
<b>54</b>	2-propenyl	s	DB	t	7.9	<b>56</b>	6.3	25.3
<b>59</b>	Methyl,vinyl	a	COO	t	2.2	<b>61</b>	0.5	13.8
<b>63</b>	Methyl,vinyl	a	COO	c	1.9	<b>65</b>	$\geq 20$	$\geq 33$

<sup>a</sup> Syn (s) or anti (a) position of 2-propenyl or methyl substituent with regard to COO unit. <sup>b</sup> Position of methyl group at CC double bond (DB) or COO unit. <sup>c</sup> Cis (s) or trans (t) position of vinyl group with regard to COO unit. <sup>d</sup> Relative to most stable ISP carbonyl oxide. <sup>e</sup> Relative to corresponding ISP carbonyl oxide. <sup>f</sup> Relative to most stable ISP hydroperoxide.

1.361:1.272 (**8**, Figure 2) to 1.370:1.276 (**15**), indicating that the hyperconjugative and steric effects of the methyl group(s) support more the zwitterionic form of carbonyl oxides. In the case of **8**, the *syn* form is more stable than the *anti* form which has been discussed by Cremer.<sup>14</sup> Extension of the  $4\pi$  system of **1** by a vinyl group as in the ISP carbonyl oxides **22**, **29**, **36**, **43**, **50**, **54**, **59**, and **63** (Scheme 1) leads to a planar  $6\pi$  electronic system characterized by a typical decrease of the OO/CO bond length ratio (**43** in Figure 3, 1.359:1.291) and a short C1C2 bond (1.443 Å, Figure 3). The geometry of a ISP carbonyl oxide is also influenced by the hyperconjugative effect of the methyl group where this effect is stronger when the methyl group is located at the COO unit rather than at the double bond.

Electronic and steric effects of methyl or vinyl group are also reflected by the calculated TSI and dioxirane geometries. Since basic features of the geometry of dioxiranes and TSI have been discussed elsewhere,<sup>14,20,26,27</sup> we refrain from a detailed discussion of calculated geometrical features and instead refer to Figures 2 and 3 as well as the Supporting Information. As for TSII, Figures 2 and 3 reveal that the migrating H atom takes a position above the heavy atom plane typical of the TS of a 1,4-sigmatropic H shift, i.e., almost in the middle between the C atom of the methyl group and the terminal O atom. In the case of TS **11**, calculated distances H1C2 and H1O2 are 1.339 and 1.366 Å while the corresponding parameters for **46** are 1.355 and 1.323, respectively. In TS **11**, the CC bond is reduced from 1.471 to 1.405 Å while the CO and OO bond lengths increase from 1.272 and 1.361 to 1.303 and 1.409 Å. Similar changes are calculated for **46**, i.e., the geometrical features of the hydroperoxide can already be recognized in TSII, namely the establishment of a CC double bond and a formal C(sp<sup>2</sup>)O single bond. After the migration atom H1 keeps its position above the heavy-atom plane since hydroperoxides prefer the *gauche* conformation because this facilitates lone pair delocalization into the OO bond.<sup>28,29</sup>

**Relative Stability of ISP Carbonyl Oxides.** In Table 4, the relative energies of ISP carbonyl oxides **22**, **29**, **36**, **43**, **50**, **54**, **59**, **63**, and some of their isomers are given. They can be understood in terms of conjugative, hyperconjugative, H bonding and steric interactions. Considering the two resonance formulas **a** and **b**, it becomes clear that an alkyl group at the COO unit has a stabilizing hyperconjugative effect, which explains the

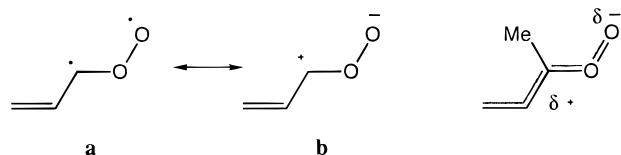
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larger stability of **36**, **43**, **59**, and **63**. Attractive interactions between a positively charged H atom and the negatively charged terminal O atom add to the stability of **36**, **43**, **50**, **54**, **59**, and **63** where the closer approach of H and O atom explains the higher stability of **50** compared to **54** and **63** compared to **59**. Finally, 4-electron destabilizing effects are responsible for the lower stability of **22** compared to **29** and **36** compared to **43** (Table 4). Hence, **43** is the most stable of all carbonyl oxides possibly generated in the ozonolysis of ISP because it has (a) a methyl group located at the COO carbon (hyperconjugative stabilization of resonance structure **a**), (b) the methyl group is in syn position so that steric attraction between two of the CH<sub>3</sub> H atoms and the terminal O atom becomes possible, and (c) the vinyl group is in trans position thus avoiding steric repulsion with the CO bond.

Clearly, attractive interactions between a methyl or vinyl H atom and the terminal O atom facilitate the migration of H and the formation of a hydroperoxide. However, it plays also an important role whether the hydroperoxide to be formed represents a closed- or open-shell electron system. In the case of ISP carbonyl oxides **22** and **29**, the unstable singlet carbenes are formed thus leading to relatively high lying TSI. For ISP carbonyl oxides **50**, **54**, **59**, and **63**, H migration leads to the singlet biradicals **51**, **55**, **60**, and **64**, respectively (Scheme 3), which are difficult to calculate, but all of which should represent high-energy forms (Table 4). We have checked this by calculating the isomeric forms **52**, **56**, **57**, **61**, and **65**, which contain either a highly strained cyclopropyl ring or the allene unit. Formation of **56** or **57** out of carbonyl oxide **54** is endothermic by 6.3 and 7.1 kcal/mol, respectively, and the corresponding TS energies are >34 kcal/mol, which excludes H migration as an important mechanistic factor in these cases. The situation is even worse in the case of **52** and **65**, which contain the highly strained cyclopropene ring<sup>30</sup> [strain energies 40.9 (left) and 55.2 kcal/mol (right)]:



Even in the case of the allene **61**, the barrier for H migration is too high to have a significant amount of **63** following path II rather than path I (dioxirane formation, Scheme 3). Hence, for the ISP carbonyl oxides **50**, **54**, **59**, and **63** (Scheme 3) it was sufficient to investigate just the path I.

**Reaction Barriers and Energetics.** The energy data collected in Table 5 reveal that carbonyl oxides with a C4-type H atom will prefer isomerization to dioxirane (path I) rather than H migration and decomposition (path II, Scheme 2). Calculated activation enthalpies for carbonyl oxides **1**, **22**, and **29** are close to 31 kcal/mol while the activation enthalpies for path I are just 20.4 (CCSD(T) calculations: 17.7 kcal/mol<sup>20</sup>), 24.1, and 20.3 kcal/mol, respectively (Table 5, Figures 4 and 5). In none of these cases could calculational proof for the existence of an intermediate hydroperoxycarbene be obtained. An artificial local minimum is only found at the UMP2 and UDFT levels of theory because in these cases the calculated energies for TSIII and formyl + OH radical are too high because of spin contamination (Table 5). If spin contamination errors are

corrected by using projected UMP2,<sup>31</sup> then the artificial minima **5**, **26**, and **33** vanish (Table 5).

In the case of the two methyl-substituted carbonyl oxides **8** and **15**, the activation enthalpies for H migration are 14.8 and 14.4 kcal/mol, respectively, which is 9 and 7 kcal/mol lower than the corresponding activation enthalpy for dioxirane formation (**9**, 23.8; **16**, 21.4 kcal/mol, Table 5 and Figure 4). A second methyl group has little effect on H migration while it stabilizes TSI (21.4 compared to 23.8 kcal/mol). The intermediate hydroperoxy alkenes **12** and **19** are about 4 and 6 kcal/mol higher in energy than the corresponding dioxiranes, which means that they are also rather unstable species. The decomposition of **12** and **19** (Figure 4) is an endothermic process without a barrier and with a reaction enthalpy of just 11.0 and 12.8 kcal/mol, respectively.

In the case of carbonyl oxides **36** and **43**, the activation enthalpy for H migration (15.5 and 16 kcal/mol) is 7 and 8.5 kcal/mol smaller than the activation enthalpy for isomerization to dioxirane (23 and 24 kcal/mol, Table 5, Figure 5) depending on whether one considers the conformation with the vinyl group in cis or trans position to the CO group. The trans form **40** of the two possible hydroperoxybutadienes **40** and **47** is more stable by 3.6 kcal/mol than the cis form, which reflects the conformational stability of *trans*- and *cis*-butadiene and suggests that both **36** and **43** rearrange to **40**. Hydroperoxybutadiene **40** and dioxirane **45** possess about the same relative stabilities (−12.3 and −14.2 kcal/mol, Figure 5). Decomposition of **40** to yield **42** requires 10.3 kcal/mol thus indicating that the OO bond of the hydroperoxide is even weaker as in the case of **12** (11.0 kcal/mol) and **19** (12.8 kcal/mol, Figure 4). We note that in cases such as **47** or **49** rapid rotation into the more stable forms **40** and **42** is most likely. However, in the present context, determination of the most stable hydroperoxide or aldehyde form is not of relevance.

#### 4. Discussion

On the basis of the results of the quantum chemical calculations we can predict that carbonyl oxides with a A5-type H atom prefer to rearrange to hydroperoxyalkenes followed by OO bond cleavage to yield OH radicals (path II) rather than to dioxiranes (path I). This is in qualitative agreement with the experimental observation (see Table 3) that the OH yield increases with the number of methyl substituents providing H atoms that can interact with the terminal O atom of carbonyl oxide via an A5-type arrangement of bonds. Although there were early speculations in the literature that path II might play a role in carbonyl oxide reactions,<sup>22</sup> we provide in this work the first evidence that path II is indeed the preferred decomposition path. It is also a novel finding that the OO bond of a hydroperoxy alkene is so extremely labile that when possessing an excess energy of just 10–12 kcal/mol, it immediately cleaves. These results explain a number of experimental findings, which so far were not well understood:

(1) In the gas-phase ozonolysis, so far only dioxirane **3** has been observed.<sup>21</sup> Our calculations suggest that dioxirane formation is preferred in the case of the ET ozonolysis, however not necessary, in the case of the ozonolysis of higher alkenes.

(2) In the ozonolysis of higher alkenes, dioxiranes were never observed.<sup>3,17</sup> This was always considered as a result of the fact that aldehyde–carbonyl oxide recombination to yield final ozonides is much faster than dioxirane formation. We note that hydroperoxide formation with subsequent reactions at the CC double bond or OO bond cleavage is probably more likely than dioxirane formation in most cases.

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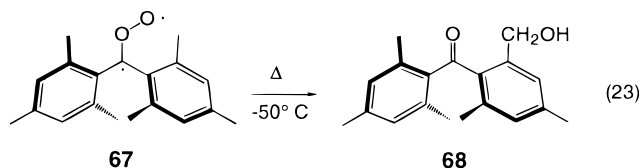
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**Table 5.** Calculated Absolute and Relative Energies for Path I and II Reactions<sup>a</sup>

method/basis set	energy	carbonyl oxide	TSI	dioxirane	TSII	hydroperoxide	TSIII	radical + OH
<b>reaction of 1</b>								
MP2/6-31G(d,p)	$\Delta E$	-189.068 65	25.0	-34.6	33.7	10.0	8.3 <sup>b</sup>	-11.1 <sup>b</sup>
	ZPE	18.4	17.8	19.5	15.8	17.7	16.9	13.0
	$\Delta\Delta H_f^\circ(298)$	0	24.3	-33.7	31.0	9.5	7.8	-14.5
DFT/6-31G(d,p)	$\Delta E$	-189.579 89	21.5	-24.1	34.9	10.8	12.1	-0.2
	ZPE	18.9	17.9	19.7	15.7	17.7	16.4	13.0
	$\Delta\Delta H_f^\circ(298)$	0	20.4	-23.5	31.6	9.9	<9.9	6.6
CCSD(T)/[5s3p2d/3s2p]	$\Delta E$	-189.320 44	19.2	-25.6	34.0			-7.8
	$\Delta\Delta H_f^\circ(298)$	0	17.7	-24.7	30.8			-11.2
<b>reaction of 8</b>								
MP2/6-31G(d,p)	$\Delta E$	-228.272 97	28.0	-32.6	16.5	-22.0		2.1 <sup>b</sup>
	ZPE	35.6	35.1	36.4	33.8	35.5		30.9
	$\Delta\Delta H_f^\circ(298)$	0	27.2	-31.8	14.0	-21.9		-2.0
DFT/6-31G(d,p)	$\Delta E$	-228.916 04	24.9	-21.0	17.5	-16.4		7.3
	ZPE	35.9	35.1	36.7	33.8	36.1		30.8
	$\Delta\Delta H_f^\circ(298)$	0	23.8	-20.4	14.8	-16.1		-5.1
<b>reaction of 15</b>								
MP2/6-31G(d,p)	$\Delta E$	-267.471 85	24.7	-33.3	15.7	-20.4		3.3 <sup>b</sup>
	ZPE	52.5	51.9	53.1	50.5	52.4		47.8
	$\Delta\Delta H_f^\circ(298)$	0	23.8	-32.9	13.2	-20.3		0.3
DFT/6-31G(d,p)	$\Delta E$	-268.245 86	22.5	-19.8	17.0	-13.6		9.5
	ZPE	52.8	52.0	53.4	50.6	53.1		47.7
	$\Delta\Delta H_f^\circ(298)$	0	21.4	-19.4	14.4	-13.1		-0.3
<b>reaction of 22</b>								
MP2/6-31G(d,p)	$\Delta E$	-305.428 45	26.8	-32.4		10.4	11.9	
	ZPE	55.2	54.8	56.0	54.5	54.7	54.5	
	$\Delta\Delta H_f^\circ(298)$	0	26.1	-31.7		10.0	10.9	
DFT/6-31G(d,p)	$\Delta E$	-306.316 39	25.2	-18.1	34.9	14.0	15.3	2.4
	ZPE	56.2	55.4	56.7	53.0	55.2	54.2	51.6
	$\Delta\Delta H_f^\circ(298)$	0	24.1	-17.8	31.6	13.3	13.5	-1.4
<b>reaction of 29</b>								
MP2/6-31G(d,p)	$\Delta E$	-305.433 94	23.4	-32.1	31.0	10.7	10.0	
	ZPE	55.4	55.1	56.1	52.9	54.9	55.9	
	$\Delta\Delta H_f^\circ(298)$	0	22.8	-31.5	28.3	10.4	10.6	
DFT/6-31G(d,p)	$\Delta E$	-306.321 46	21.4	-18.1	34.3	14.3	15.9	3.2
	ZPE	56.3	55.5	56.8	53.3	55.4	54.3	51.9
	$\Delta\Delta H_f^\circ(298)$	0	20.3	-17.8	31.1	13.6	-11.4	-0.5
<b>reaction of 36</b>								
MP2/6-31G(d,p)	$\Delta E$	-305.439 51	26.8	-29.8		-20.4		7.3 <sup>b</sup>
	ZPE	55.3	54.7	55.8	54.7	55.1		52.8
	$\Delta\Delta H_f^\circ(298)$	0	25.8	-29.5		-20.4		5.5
DFT/6-31G(d,p)	$\Delta E$	-306.328 43	25.3	-14.2	18.3	-12.6		10.5
	ZPE	56.1	55.2	56.4	53.9	56.3		51.2
	$\Delta\Delta H_f^\circ(298)$	0	24.0	-14.1	15.5	-12.3		-2.0
<b>reaction of 43</b>								
MP2/6-31G(d,p)	$\Delta E$	-305.443 04	26.1	-28.7	17.0	-16.9		10.3 <sup>b</sup>
	ZPE	55.5	55.1	55.9	53.5	55.1		52.7
	$\Delta\Delta H_f^\circ(298)$	0	25.4	-28.4	14.4	-17.0		8.3
DFT/6-31G(d,p)	$\Delta E$	-306.330 86	24.1	-14.3	18.9	-8.8		13.3
	ZPE	56.3	55.6	56.5	54.0	56.2		51.1
	$\Delta\Delta H_f^\circ(298)$	0	23.0	-14.2	16.0	-8.7		0.3

<sup>a</sup> Absolute energies in hartree, relative energies in kcal/mol. DFT/B3LYP calculations. CCSD(T) energies from ref 13. <sup>b</sup> Values are obtained with PMP2/6-31G(d,p)//UMP2/6-31G(d,p). The relative UMP2/6-31G(d,p) energies are 31.2, -8.7, -3.6 (reaction of 1); 10.1, 6.0, 2.9 (reaction of 8); 10.0, 7.0, 6.4 (reaction of 15); 35.8, 36.4, 14.2 (reaction of 29); 15.4, 6.1 (reaction of 36); 18.8, 8.8 (reaction of 43).

(3) Sander and co-workers<sup>32</sup> have recently reported the formation of dimesitylcarbonyl oxide **67** in  $\text{CFCl}_3/\text{BrF}_2\text{CCF}_2\text{-Br}$  at  $-70^\circ\text{C}$  as the first carbonyl oxide in solution. Upon raising the temperature to  $-50^\circ\text{C}$  the alcohol **68** is formed as an unexpected rearrangement product (reaction 23).



Kraka and co-workers<sup>33</sup> have shown on the basis of B3LYP

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calculations that in its equilibrium geometry **67** possesses one methyl H atom close to the terminal O atom and, accordingly, formation of an intermediate hydroperoxy derivative  $\text{RR}'\text{COOH}$  with some biradical character via path II is likely. Decomposition of  $\text{RR}'\text{COOH}$  into ketone  $\text{RR}'\text{C}=\text{O}$  and OH radical in the solvent cage and recapture of OH by the  $\text{RR}'\text{C}=\text{O}$  radical would lead directly to the observed product **68**.

(4) The formation of addition products of carbonyl oxides in the presence of protic nucleophiles could involve an internally formed hydroperoxide since nucleophilic attack at the carbonyl oxide C atom probably causes a proton to migrate and, thereby, facilitates formation of a hydroperoxide. Addition reactions at the double bond could explain a number of byproducts of the ozonolysis.<sup>3</sup>

As for the generation of OH radicals, three factors have to be considered: (a) The ratio of the activation energies for path I and path II as calculated in this work, (b) The amount of excess

energy produced when carbonyl oxides are formed in the course of the gas phase ozonolysis, and (c) dissipation mechanisms of the excess energy during the gas-phase ozonolysis.

Apart from this one has to consider which carbonyl oxides will preferentially be formed upon primary ozonide decomposition. Cremer<sup>34</sup> has predicted that in the ozonolysis of CB more anti will be produced; however, in the ozonolysis of TB more syn methyl carbonyl oxide is formed. This is insofar confirmed as the OH radical yield in the TB ozonolysis (Table 3) is significantly higher than in the CB ozonolysis. Similar differences in OH yields have been reported before;<sup>9,12</sup> however, no explanation has been offered to account for this observation. In the case of the ISP ozonolysis ozone can attack at the methyl-substituted double bond or the unsubstituted double bond. From rate comparisons,<sup>3</sup> one knows that ozone attack at a methyl-substituted double bond is always faster, which has to do with the fact that electron-rich double bonds (double bonds with a higher  $\pi$ -HOMO) form a stronger  $\pi$ -complex with ozone and, therefore, are more prone to undergo the cycloaddition reaction to primary ozonide. Hence, in the ISP ozonolysis carbonyl oxides **36**, **43**, **59**, and **63** should preferentially be formed where **36** and **43** will lead to more OH production and **59** and **63** to more dioxirane production.

During the gas-phase ozonolysis of ET, primary ozonide is formed with an excess enthalpy of 59 kcal/mol (B3LYP/6-31G-(d,p)) measured relative to the enthalpy of the TS of the ozone-ET cycloaddition reaction.<sup>34,35</sup> Decomposition of ET primary ozonide is endothermic by 6.6 kcal/mol, which means that both **1** and formaldehyde are formed with an excess enthalpy of about 52 kcal/mol. Since methyl substitution enhances the stability of both carbonyl oxide and aldehyde, the amount of excess energy increases with the number of methyl groups attached to the alkene double bond. In the case of the TME ozonolysis, the excess enthalpy of acetone and carbonyl oxide **15** is 82 kcal/mol, which reflects the fact that the decomposition of TME primary ozonide is an exothermic step ( $\Delta\Delta H_f^\circ -20.6$  kcal/mol).<sup>35</sup>

One can conclude that for the ozonolysis of both PR, CB, TB, TME, and ISP the excess enthalpy is so large that, despite their different stability, all carbonyl oxides shown in Scheme 1 can be formed in the form of hot molecules. The more vibrational degrees of freedom a carbonyl oxide possesses the higher should be its chance to stabilize before a subsequent reaction and the higher the chance of stabilization the more the difference between path I and path II barriers will matter since carbonyl oxide will become more selective.

From these considerations, we conclude that the largest amount of OH radicals should be generated in the ozonolysis of TME, which is in agreement with the experimental observation. In the TME ozonolysis, just carbonyl oxide **15** is formed, which has a larger chance of stabilization than either **8** or **1**. Hence, **15** is more selective than **8** or **1** and will preferentially follow path II that leads to the formation of hydroxyl radicals. Statistical calculations describing the chemically activated systems employing the master equations suggest that at 1013 mbar 20% stabilized carbonyl oxide can be expected in the case of the ET ozonolysis; however, ~40% can be expected in the case of the TME ozonolysis.<sup>19</sup> Furthermore, calculations predict only a small amount of **1** to lead to OH formation; however, about 40% of **15** do so, which may be considered as a verification of the qualitative arguments concerning energy dissipation in molecules with a relatively large excess energy. On the other hand, one has to note that also vibrationally excited **15** largely prefers path II because of the lower barrier.<sup>19</sup>

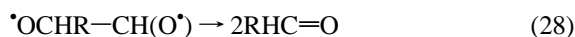
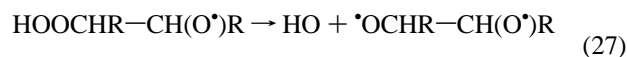
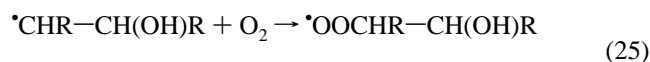
There is also the possibility that carbonyl oxide is formed in an electronically excited state where the lowest is just about 20 kcal/mol above the ground state and corresponds to a triplet state.<sup>36</sup> In this state, carbonyl oxide can easily decompose to aldehyde and O(<sup>3</sup>P), which would represent an alternative reaction path provided spin-orbit coupling and the chance of intersystem crossing would be large. However, calculations suggest that probably less than 5% carbonyl oxide follows this reaction path.<sup>36</sup> Apart from the unimolecular reactions of carbonyl oxide there is also, according to our calculations, the chance of a bimolecular reaction with O<sub>2</sub>, which adds at the C atom of the carbonyl oxide thus forming the triplet biradical O<sub>2</sub>CH<sub>2</sub>OO. The biradical can rearrange to dioxirane and O<sub>2</sub> providing in this way another route to the typical dioxirane oxidation products CO<sub>2</sub>, CO, etc. Although the addition of O<sub>2</sub> to carbonyl oxide involves a (calculated) barrier of just 0.7 kcal/mol, rate calculations reveal that the bimolecular reaction cannot compete with the unimolecular decomposition routes of carbonyl oxide.<sup>19</sup>

In the case of the ozonolysis of PR, CB, TB, or ISP, about equal amounts of carbonyl oxides that prefer to rearrange to dioxirane or to decompose to yield OH radicals should be formed. If one expects about 36% of the latter to follow path II as found in the case of the ozonolysis of TME, a OH yield close to 20% should be expected for the ozonolysis of these alkenes as is found in the kinetic investigation.

It should be pointed out that the predominant goal of the quantum chemical calculations presented here is to firmly establish that carbonyl oxides generated in the primary steps of the alkene ozonolysis are the most important source of OH radicals. It is suggested to label them as primary OH radicals. Depending on the experimental techniques applied, secondary OH radicals can also be encountered in an ozonolysis experiment. At least two sources for secondary OH radicals have to be considered:

(i) In the decomposition of intermediate hydroperoxides **12**, **19**, **40**, and **47** (Scheme 2) vinyloxy-type radicals are formed, which are calculated to be primarily C centered. These radicals will readily react with O<sub>2</sub> as has been shown in the case of **14**.<sup>37</sup> Also, formation of OH radicals<sup>38,39</sup> as well as of glyoxal and formaldehyde<sup>37</sup> has been reported. No information is available for the methyl-substituted homologues; however, an increased efficiency for secondary OH formation can be predicted.

(ii) Stoichiometric ratios  $r > 1$  imply secondary alkene consumption through OH attack. In the case that no OH scavenger is present, the most likely reaction of OH is that with alkene according to reaction 24 thus forming a radical which can easily react with O<sub>2</sub> present in the reaction system (see reaction 25):



H migration (reaction 26) and decomposition of the hydroper-

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oxide thus formed (reaction 27) should be similar to the carbonyl oxide rearrangements investigated in this work. The total process  $\text{CHR}=\text{CHR} + \text{OH} \rightarrow 2\text{RHC}=\text{O}$  would be exothermic by  $\sim 30$  kcal/mol and would be characterized by the fact that primary OH starting the reaction sequence (reactions 24–28) would be replaced by secondary OH from reaction 27 thus initiating a chain reaction. The consumption of alkene would be larger than expected from the ozone–alkene reaction and, as a consequence, the OH yield measured relative to alkene consumption would increase.

Hence, experimentally determined OH yields using a scavenger may be larger than the true OH yield in the ozonolysis depending on the efficiency of the chain (reactions 24–27) relative to the efficiency of scavenging primary OH or any of the chain carriers.

Scavenging experiments have been carried out by Niki and co-workers using HCHO and  $\text{CH}_3\text{CHO}$ ,<sup>7</sup> by Atkins and co-workers using cyclohexane,<sup>10,12</sup> by Paulson and co-workers employing methylcyclohexane,<sup>14</sup> and in this work using a large excess of CO. Some experiments with HCHO and with CO, respectively, have also been reported by Horie and co-workers.<sup>9</sup> Although it is beyond the scope of the present investigation to rationalize differences in the action of these scavengers, it is safe to say that the additional chemistry introduced into the ozonolysis system by scavengers such as aldehyde<sup>7,9</sup> or CO (this work and ref 18) will be less complex than using cyclohexane or its methyl derivative. A comparison of reported OH yields as given by the different research groups is also hampered by the fact that some authors relate OH yields to alkene consumption<sup>10,12</sup> while others relate it to  $\text{O}_3$  consumption.<sup>7,9,18</sup> A direct comparison requires that secondary processes as outlined in ii can be neglected. For example, Horie and co-workers<sup>9</sup> pointed out that OH yields of 0.64 as reported by Atkinson and Aschmann<sup>12</sup> for the TB ozonolysis correspond to an overall OH formation yield and may contain contributions from secondary formation(s).

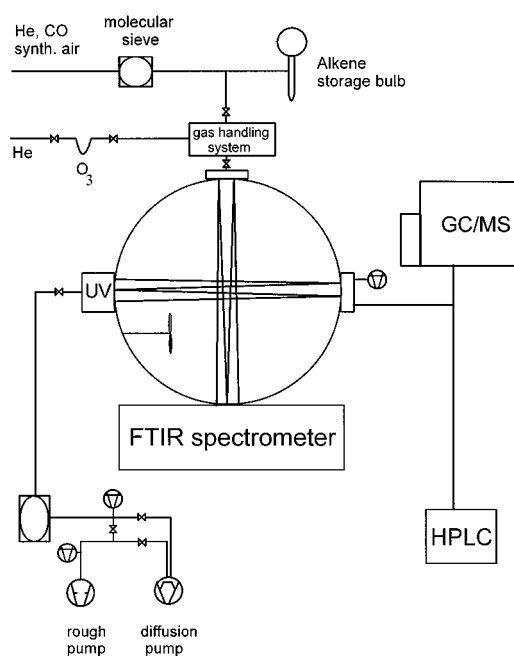
The OH yields reported here have been obtained in ozonolysis experiments, in which CO was present up to 50% (see Figure 1), i.e., CO acted as both a radical scavenger and effective collision partner suppressing secondary alkene consuming processes. The high concentrations of the additive were needed to secure that the stoichiometric ratio  $r = \Delta[\text{alkene}]/\Delta[\text{O}_3]$  had truly reached its limiting value of  $r = 1.00 \pm 0.02$ . Secondary reactions were precluded under these conditions.

## 5. Conclusions

In a two-pronged approach involving both kinetic measurements and quantum chemical calculations, we have shown that substituted carbonyl oxides with a A5-type H atom in syn position prefer to rearrange to hydroperoxy alkenes, which have a labile OO bond and, therefore, decompose to yield OH radicals. Using CO as scavenger for OH radicals in ozonolysis, we could detect 18, 17, 24, 36, and 19% OH radicals in the ozonolysis of PR, CB, TB, TME, and ISP. Since ISP is a trace constituent of the atmosphere with a concentration of about 500 ppb, the ozonolysis of this compound can be considered as an important nighttime source of OH radical production in the atmosphere. Future work has to clarify under which conditions OH radical production due to carbonyl oxide decomposition becomes particularly critical.

## 6. Experimental and Computational Details

**Experimental Details.** All reactions were carried out at atmospheric pressure in a 70 L duran glass reactor equipped



**Figure 6.** Schematic illustration of experimental setup used in the ozonolysis experiments.

with White mirror systems for in situ absorption measurements in the UV and in the IR, using optical path lengths of 8 m and of 40 m, respectively. The setup also permitted direct sampling for product analysis by HPLC or GC/MS as schematically outlined in Figure 6. As standard bath gas a 20%  $\text{O}_2/\text{He}$  mixture was used. Various amounts of the OH scavenger CO were added to the system while the  $\text{O}_2$  concentration was always kept at 20%. Ozone was prepared by microwave discharge in pure  $\text{O}_2$  at (20–30) mbar and collected in a cold trap over silica. It was transported into the reactor by a flow of bath gas. Its concentration in the reactor was determined by absorbance measurements at 254 nm using  $\epsilon(\text{O}_3) = 1155 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ .<sup>11</sup> The alkene was added as the last reactant to the gas mixture. It was transported into the reactor from calibrated volumes by He. To achieve rapid mixing an effective teflon stirrer was used during the filling operation. Concentrations used were  $[\text{O}_3]$  8.3–9.6 ppm and  $[\text{alkene}]$  20.8–24.1 ppm. He (purity >99.999 vol %),  $\text{O}_2$  (purity >99.998 vol %), and CO (purity >99.999 vol %) from Messer-Griesheim were used. He and CO were passed through a 7 m long molecular sieve  $13 \times$  column to remove traces of impurities in particular  $\text{CO}_2$ . ET, PR, CB, TB, TME, and ISP were reagent-grade chemicals from Aldrich. They were degassed and these vapors diluted with He were stored in darkened flasks.

**Computational Methods.** In previous work,<sup>13</sup> we have used many-body perturbation theory (MBPT), coupled-cluster (CC) theory, and density functional theory to find a reliable but economic method that provides a fairly accurate description of carbonyl oxides. This method turned out to be DFT with Becke's three-parameter hybrid functional B3LYP and a 6-31G-(d,p) basis set. Accordingly, we have used in the present work second-order Møller–Plesset perturbation theory (MP2)<sup>23</sup> with the 6-31G(d,p) basis<sup>25</sup> to achieve reasonable starting geometries and reference energies, which then were utilized for energy, geometry, and frequency calculations at the B3LYP/6-31G(d,p) level of theory.<sup>24</sup>

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Zero-point energy (ZPE) and temperature corrections for  $T = 298$  K were calculated by scaling harmonic MP2/6-31G(d,p) frequencies by a factor of 0.930 and the corresponding B3LYP/6-31G(d,p) values by 0.963. Calculations have been performed with COLOGNE94<sup>40</sup> and GAUSSIAN 92.<sup>41</sup> The calculated energies and geometries of all molecules considered in this work are given in the Supporting Information.

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(NFR). All calculations were done on the CRAY YMP/J932 of the Rechenzentrum Kiel and on the CRAY YMP/464 of the Nationellt Superdatorcentrum (NSC), Linköping, Sweden. E.C. and D.C. thank the NSC for a generous allotment of computer time.

**Supporting Information Available:** The calculated energies and geometries of all molecules considered in this work (12 pages). See any current masthead page for ordering and Internet access instructions.

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