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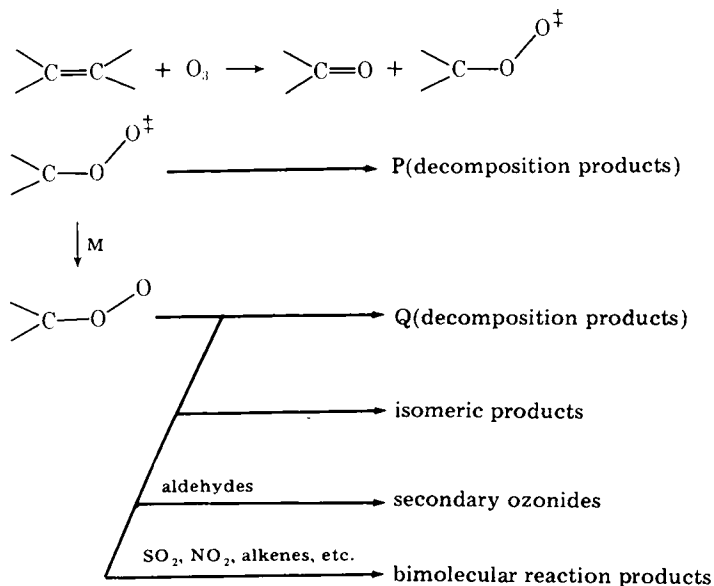
# Kinetics and Energetics of the Criegee Intermediate in the Gas Phase. I. The Criegee Intermediate in Ozone-Alkene Reactions

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## Abstract

The chemistry and energetics of the Criegee intermediate, a primary product of the ozonolysis of alkenes, are discussed in terms of recent *ab-initio* calculations and laboratory studies. The experimental observations in O<sub>3</sub>-alkene systems can be rationalized on the basis of a general mechanism:

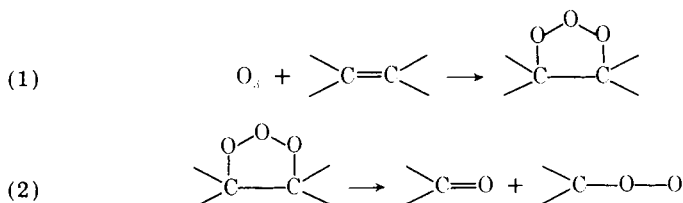


\* To whom correspondence should be addressed.

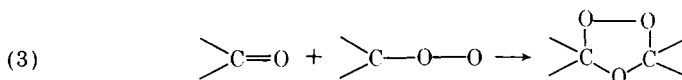
where the ‡ represents the range of internal excitation energies available to the planar dioxymethylenes (i.e., the Criegee intermediates) initially formed via exothermic  $O_3$ -alkene reactions. Estimates are given for the rate constants of these reactions, and a critique is provided of the possible role of the Criegee intermediate and its isomers in the formation of alkanolic acid anhydrides in  $O_3$ -alkene systems and in the formation of  $H_2SO_4$  aerosols in  $O_3$ -alkene- $SO_2$  systems.

### Introduction

There is now abundant evidence [1-5] that the primary reaction in the gas-phase ozonolysis of alkenes is that proposed by Criegee [6,7] for solution-phase ozonolysis:



where the 1,2,3-trioxolane (primary ozonide) initially formed in reaction (1) decomposes rapidly to the oxoalkane and Criegee intermediate of reaction (2). The Criegee intermediate formed in reaction (2) can react further, leading to final products which are critically dependent on the environment in which the Criegee intermediate is formed. In solution, reaction (2) may be followed by reaction (3):



yielding the 1,2,4-trioxolane, the expected secondary ozonide product. Secondary ozonides are known to be products also of the gas-phase reactions of ozone with hexenes and heptenes [5]. More recently it has been shown that addition of excess aldehyde leads to the formation of ozonides even for smaller alkenes both at high (atmospheric) [4] and low (4 torr<sup>1</sup>) pressures [8]. However, studies on the low-pressure (4-8 torr) ozonolysis of alkenes [1,2,9] lead to the conclusion that in the gas phase the dioxymethylene<sup>2</sup> intermediate (i.e., the Criegee intermediate) decomposes, or isomerizes and decomposes, to molecular and free-radical products. These studies suggest that the large number of products observed in gas-phase studies can probably be attributed to the complex chemistry of the Criegee intermediate and to the secondary radical-induced chemistry.

<sup>1</sup> 1 torr = 133.3 Pa.

<sup>2</sup> The systematic nomenclature for the various isomers of the Criegee intermediate is indicated in Table I. This nomenclature was kindly provided in a private communication by Dr. K. L. Loening, Director of Nomenclature of the Chemical Abstracts Service, Columbus, Ohio.





In this paper and in the paper which immediately follows [10] we discuss the gas-phase kinetics and energetics of the Criegee intermediate within the conceptual framework provided by the *ab-initio* calculations of Goddard and co-workers [11,12]. This paper addresses the role of the Criegee intermediate in  $O_3$ -alkene reactions, while the following paper [10] discusses its postulated role in reaction systems other than  $O_3 + \text{alkene}$ ; e.g., reactions of carbenes with molecular oxygen [13-16], alkylidioxo disproportionation reactions [17,18], etc.

### Thermochemistry of the Criegee Intermediate and its Isomers

*Ab-initio* calculations [11,12,19,20] indicate that the ground state of the Criegee intermediate formed in the ozone-ethene reaction is planar dioxymethylene. In addition, these calculations show that there are two other more stable configurations, dioxirane and methylenebis(oxy). Table I lists the configurations of interest using the notation of Wadt and Goddard [11]. Although the agreement among different workers on the absolute energy values or the *ab-initio* energy differences between states is not particularly good, they all lead to the same general ordering of relative energies.

The absolute values in Table I are based on calculated *ab-initio* energy differences [11,12,20], and on independently derived or estimated absolute values for one of the states. We have chosen here to use a derived heat of formation for perpendicular methylenebis(oxy) as a basis for putting these

TABLE I. Calculated  $\Delta H_{298}^\circ$  for dioxymethylene, dioxirane, and methylenebis(oxy) [kcal/mol].

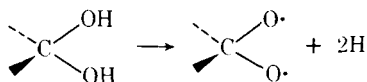
Species	Wadt and Goddard [11]		Harding and Goddard [12]		Karlstrom, et al. [20]	
	Reported	Recalculated	Reported	Recalculated	Reported <sup>a</sup>	Recalculated
 [perpendicular dioxymethylene]	65.0	48.6	56.1	51.6	---	---
 [planar dioxymethylene]	78.5	12.1	29.1	24.6	---	31.8
 [methylenebis(oxy)]	21.4	5.0 <sup>c</sup>	9.5 <sup>b</sup>	5.0 <sup>c</sup>	---	5.0 <sup>c</sup>
 [dioxirane]	7.5 <sup>b</sup>	-8.9	-5.7	-10.2	---	-1.2

<sup>a</sup> Reported as relative energies only.

<sup>b</sup> Reference state and value from original source.

<sup>c</sup> Reference state and value used here.

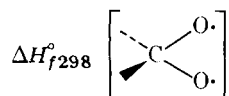
quantities on an absolute basis. For the process



for which we equate the enthalpy of reaction with  $2D[\text{CH}_3\text{O—H}]$ , we calculate

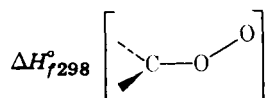
$$\begin{aligned} \Delta H_{f298}^\circ \left[ \begin{array}{c} \text{O} \cdot \\ \diagup \\ \text{---C} \\ \diagdown \\ \text{O} \cdot \end{array} \right] \\ = \Delta H_{f298}^\circ[\text{CH}_2(\text{OH})_2] + 2D[\text{CH}_3\text{O—H}] - 2\Delta H_{f298}^\circ[\text{H}] \\ = -98 + 2[103.6] - 2[52.1] = 5.0 \text{ kcal/mol} \end{aligned}$$

Thermochemical data are from [21–23].<sup>3</sup> Harding and Goddard [12] used  $\Delta H_{f298}^\circ[\text{CH}_2(\text{OH})_2] = -93.5 \text{ kcal/mol}$  in a similar calculation to arrive at the somewhat different value for

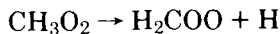


given in Table I.

Harding and Goddard [12] also calculated



from the process



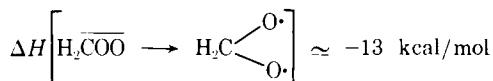
by equating the enthalpy of this reaction with  $D[\text{CH}_2\text{O}_2\text{—H}]$ , from which

$$\begin{aligned} \Delta H_{f298}^\circ \left[ \begin{array}{c} \text{O} \\ \diagup \\ \text{---C} \text{---O} \text{---O} \\ \diagdown \end{array} \right] \\ = D[\text{CH}_2\text{O}_2\text{—H}] - \Delta H_{f298}^\circ[\text{H}] + \Delta H_{f298}^\circ[\text{CH}_3\text{O}_2] \\ = 98 - 52.1 + 6.7 = 52.6 \text{ kcal/mol} \end{aligned}$$

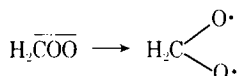
<sup>3</sup> 1 kcal/mol = 4.184 kJ/mol.

in excellent agreement with the recalculated value of 51.6 kcal/mol given in Table I.<sup>4</sup>

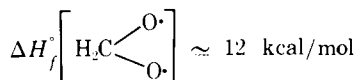
Nangia and Benson [17] estimated that (i)  $\Delta H_f^\circ[\text{H}_2\dot{\text{C}}\text{OO}\cdot] = 46.1$  kcal/mol for an "ideal" biradical  $\text{H}_2\dot{\text{C}}\text{OO}\cdot$ ; (ii) the stabilization energy in the zwitterion  $\text{H}_2\overline{\text{C}}\text{OO}\cdot$ , which they call  $\Delta$ , is  $\Delta_{\text{H}_2\text{CO}_2} = \Delta H[\text{H}_2\overline{\text{C}}\text{OO} \rightarrow \text{H}_2\dot{\text{C}}\text{OO}\cdot] = 21$  kcal/mol<sup>5</sup>; (iii)



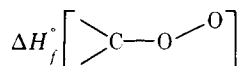
and (iv) the activation energy for



is probably on the order of 30 kcal/mol, where they identified the zwitterion  $\text{H}_2\overline{\text{C}}\text{OO}$  as the *ground state* of the Criegee intermediate. Notwithstanding the inconsistencies in nomenclature,<sup>6</sup> one can estimate from the values of Nangia and Benson [17] cited above that

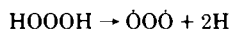


and that the formation enthalpy of the *ground state* of the Criegee intermediate ( $\Delta H_f^\circ[\text{H}_2\overline{\text{C}}\text{OO}]$ ) in their nomenclature;



<sup>4</sup> Note that this is an average value for the two lowest lying electronic states of perpendicular dioxymethylene, <sup>1,3</sup>(3 $\pi$ ), and that Harding and Goddard [12] used a value for  $D[\text{CH}_2\text{O}_2\text{—H}]$  comparable to  $D[\text{C}_2\text{H}_5\text{—H}]$  rather than to  $D[\text{CH}_2\text{OH—H}]$ , since they argued that the lower C—H bond strength in methanol is due to a three-electron bonding interaction in the  $\text{CH}_2\text{OH}$  biradical, an effect not present in perpendicular dioxymethylene.

<sup>5</sup> In their analysis, Nangia and Benson [17] estimated that the stabilization energy in the zwitterion  $\overline{\text{OOO}}$  is  $\Delta_{\text{O}_3} = \Delta H[\overline{\text{OOO}} \rightarrow \dot{\text{O}}\text{OO}] = 19.2$  kcal/mol on the basis of the process



by equating the enthalpy of reaction with  $2D[\text{O—H}] = 175.2$  kcal/mol and the experimental value of  $\Delta H_f^\circ[\text{O}_3] = 34.1$  kcal/mol with their  $\Delta H_f^\circ[\overline{\text{OOO}}]$ , and by using a group additivity estimate for  $\Delta H_f^\circ[\text{HOOOH}] = -17.7$  kcal/mol. By analogy with their  $\Delta_{\text{O}_3}$  they argued in favor of their  $\Delta_{\text{H}_2\text{CO}_2} = 21$  kcal/mol cited above.

<sup>6</sup> *Ab-initio* calculations have consistently identified the ground states of both  $\text{H}_2\text{CO}_2$  and  $\text{O}_3$  as planar biradicals [11,12,19,20] and the corresponding zwitterions as excited states (for  $\text{O}_3$ , the zwitterion lies about 100 kcal/mol above the biradical ground state [12]). Consequently in this paper we use a nomenclature consistent with the *ab-initio* calculations, as discussed above and indicated in Table I.

in the *ab-initio* nomenclature of Table I) is 25.1 kcal/mol, which is in good agreement with the corresponding recalculated values in Table I.

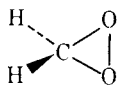
As Harding and Goddard [12] point out, the effect of substituents on the Criegee intermediate will be to shift the energy differences between biradical and zwitterionic states from about 23 kcal/mol for  $\text{CH}_2\text{O}_2$ , to 12 kcal/mol for  $\text{CH}_3\text{CHO}_2$ , to 0 kcal/mol for  $(\text{CH}_3)_2\text{CO}_2$ . Solvation may lead to comparable effects. In the gas phase we expect the particular configuration to have little or no effect on the chemistry, unless interactions involving strongly polar reactants play a role.

Karlström et al. [20] have expanded on the work of Goddard and co-workers [11,12] using multiconfiguration-configuration interaction (MC-CI) calculations and have obtained the same ordering of energies for the ethene-ozone system. The absolute separations, however, are somewhat different, as shown in Table I.

We have arbitrarily selected from Table I the recalculated values of Harding and Goddard [12] to construct in Figure 1 an energy level diagram for the various isomeric forms of  $\text{CH}_2\text{O}_2$ , and for the various source reactions, and transformation and decomposition paths. However, because of the significant differences between sets of calculations it is important to note that Table I and Figure 1 are provided for comparative purposes only, and no special significance should be ascribed to our choice of the values recalculated from the data of Harding and Goddard [12]. The derivation of the activation energies used in this figure is discussed below.

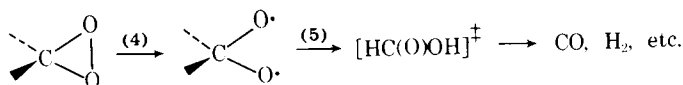
### Stability of Dioxirane

Of the four potentially reactive species listed in Table I, only one has been positively identified. Dioxirane,



has been positively identified and the structure assigned by means of microwave spectroscopy [24]. It has also been identified by mass spectrometry [25] at low temperatures, and its disappearance was monitored upon warming. At temperatures above about  $-90^\circ\text{C}$ , dioxirane decomposes, accompanied by the formation of  $\text{H}_2$  and  $\text{CO}$ . These are expected products of the unimolecular decomposition of dioxirane from earlier conclusions based on a study of the ozone-ethene reaction [1].

If the reaction is a simple bond scission,



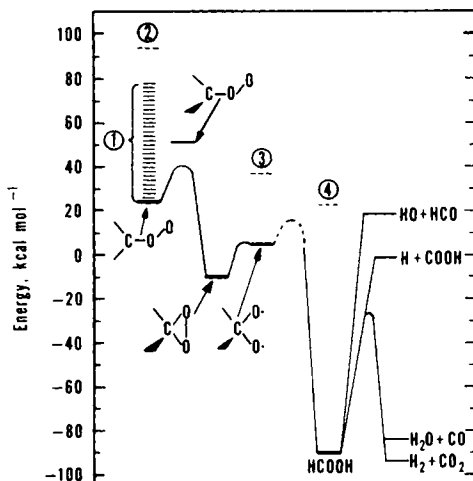


Figure 1. Thermochemistry of the various isomeric forms of  $\text{CH}_2\text{O}_2$  and of their various source reactions and transformation and decomposition paths: ①—the bracket represents the range of internal energies available to planar dioxymethylene when formed in the  $\text{O}_3 + \text{C}_2\text{H}_4$  reaction [based on the measured activation energy (5 kcal/mol) and the calculated exothermicity for  $\text{O}_3 + \text{C}_2\text{H}_4$ ; the energy level spacings are for illustration only and have no significance]; ②—internal excitation of  $\text{H}_2\text{COO}$  when formed in the  $\text{CH}_2 + \text{O}_2$  reaction (assumes zero activation energy for  $\text{CH}_2 + \text{O}_2$ ); ③—internal excitation of a  $\text{CH}_2\text{O}_2$  species when formed in the  $\text{O} + \text{H}_2\text{CO}$  addition reaction (includes the 3.1-kcal/mol activation energy experimentally determined for  $\text{O} + \text{H}_2\text{CO}$ ) (refer to the discussion in [10], with reference to the possible identity of this postulated  $\text{O} + \text{H}_2\text{CO}$  adduct); ④—internal excitation of  $\text{HC(O)OH}$  when excited by the  $\text{Hg}^*$ -photosensitization technique. Refer to the pertinent sections of the text for a discussion of the various activation barriers represented in this figure.

then, since dioxirane is a three-membered ring compound with a peroxidic O—O bond, one can estimate a preexponential factor of  $A_4 \sim 10^{15}\text{--}10^{16} \text{ s}^{-1}$  by analogy with the preexponential factors [23] (i) for homolytic cleavage of the peroxidic O—O bond of normal peroxides ( $A \sim 10^{15.6} \text{ s}^{-1}$ ) and (ii) for ring opening of cyclopropane to a biradical ( $A \sim 10^{15.8} \text{ s}^{-1}$ ). In Table II we have calculated the specific rates and half-lives for dioxirane for  $A_4 = 10^{15}$ ,  $10^{15.5}$ , and  $10^{16} \text{ s}^{-1}$  with different assumed values of the activation energy  $E_4$ . Hence from Table II it becomes apparent that if  $A_4$  is restricted to values of  $10^{15}\text{--}10^{16} \text{ s}^{-1}$ , only combinations of  $A_4 = 10^{15}\text{--}10^{16} \text{ s}^{-1}$  and  $E_4 = 15\text{--}16 \text{ kcal/mol}$  give  $t_{1/2}$  values in the observed range,  $t_{1/2} \sim 130\text{--}1000 \text{ s}$ .<sup>7</sup> Thus we propose an estimated  $k_4 \simeq 10^{(15.5 \pm 0.5)} e^{-(7800 \pm 250)/T} \text{ s}^{-1}$ , and at 300 K,  $k_4 \simeq 1.6 \times 10^4 \text{ s}^{-1}$  and  $t_{1/2} \simeq 4.3 \times 10^{-5} \text{ s}$ . Based on the preceding arguments, we used for Figure 1 the value of  $E_4 = 15.5 \text{ kcal/mol}$ .<sup>8</sup>



TABLE II. Stability of dioxirane: unimolecular rate constants and half-lives calculated from the expression  $k = Ae^{-E/RT}$ <sup>a</sup>

T, K	$\log_{10}[A(s^{-1})]$	E = 12 kcal mol <sup>-1</sup>		E = 14 kcal mol <sup>-1</sup>		E = 15 kcal mol <sup>-1</sup>		E = 16 kcal mol <sup>-1</sup>	
		k, s <sup>-1</sup>	t <sub>1/2</sub> , s	k, s <sup>-1</sup>	t <sub>1/2</sub> , s	k, s <sup>-1</sup>	t <sub>1/2</sub> , s	k, s <sup>-1</sup>	t <sub>1/2</sub> , s
150	15	3.3(-3)	2.1(2)	4.0(-6)	1.7(5)	1.4(-7)	5.0(6)	4.9(-9)	1.4(8)
	15.5	1.0(-2)	6.7(1)	1.3(-5)	5.5(4)	4.4(-7)	1.6(6)	1.5(-8)	4.5(7)
	16	3.3(-2)	2.1(1)	4.0(-5)	1.7(4)	1.4(-6)	5.0(5)	4.9(-8)	1.4(7)
180	15	2.7	2.6(-1)	1.0(-2)	6.9(1)	6.1(-4)	1.1(3)	3.7(-5)	1.8(4)
	15.5	8.5	8.1(-2)	3.2(-2)	2.2(1)	1.9(-3)	3.6(2)	1.2(-4)	5.8(3)
	16	2.7(1)	2.6(-2)	1.0(-1)	6.9	6.1(-3)	1.1(2)	3.7(-4)	1.8(3)
300	15	1.8(6)	3.8(-7)	6.3(4)	1.1(-5)	1.2(4)	5.9(-5)	2.2(3)	3.1(-4)
	15.5	5.7(6)	1.2(-7)	2.0(5)	3.5(-6)	3.7(4)	1.8(-5)	7.0(3)	9.9(-5)
	16	1.8(7)	3.8(-8)	6.3(5)	1.1(-6)	1.2(5)	5.9(-6)	2.2(4)	3.1(-5)

<sup>a</sup> Numbers in parentheses represent exponents to the base 10; e.g., 3.3(-3)  $\equiv$   $3.3 \times 10^{-3}$ .

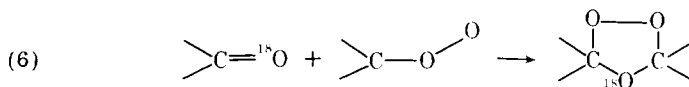
## The Role of the Criegee Intermediate and its Isomers in the Formation and Decomposition of Secondary Ozonides

### Secondary Ozonide Formation from Criegee Intermediates

As noted above, secondary ozonides are formed in solution by the reaction of the Criegee intermediate with an aldehyde. The use of <sup>18</sup>O-labeled aldehydes has shown convincingly that the aldehydic oxygen is incorporated almost exclusively into the ether position of the secondary ozonide [26]:

<sup>7</sup> The experimental procedure used to acquire the data for the cryogenic experiments reported in [25] necessitates that to be detected at 180 K (-93°C) the dioxirane must be present for at least 130 s, despite its relatively fast pumpout ( $k_{\text{pumpout}} \sim 0.02 \text{ s}^{-1}$ ) into the mass spectrometer through the orifice of the cryogenic reactor [25]. These observations suggest that, exclusive of pumpout, dioxirane probably has a reactive half-life of approximately 130–1000 s, and possibly longer.

<sup>8</sup> This value of  $E_4$  is very close to the *ab-initio* estimate of  $E_4 = 15.2 \text{ kcal/mol}$  provided by Karlström et al. [20], and to the  $\Delta H_4 = 15.2 \text{ kcal/mol}$  one estimates from the recalculated values of Harding and Goddard [12] of Table I. This small difference between  $E_4$  and  $\Delta H_4$  suggests the possibility of a very small activation barrier for the reverse process [methylenebis(oxy)  $\rightarrow$  dioxirane], and, depending on the height of the activation barrier  $E_5$  for reaction (5), may suggest an equilibrium {dioxirane  $\rightleftharpoons$  methylenebis(oxy)} which strongly favors dioxirane, but which can be shifted by processes which remove methylenebis(oxy); e.g., processes such as collisional activation of reaction (5), or the postulated reaction (25) of methylenebis(oxy) with H<sub>2</sub>CO which is discussed later in this paper. As is discussed in [10], it has been estimated (cf. ref. 15 of [10]) that  $E_5 \lesssim 10.5 \text{ kcal/mol}$ , so that the implications just discussed for the kinetics of methylenebis(oxy) become especially significant and warrant further study. In Figure 1 we have included this latter estimate of  $E_5$ . However, this estimate of  $E_5$  is certainly too large if we assume that our estimate of  $E_4$  is correct.

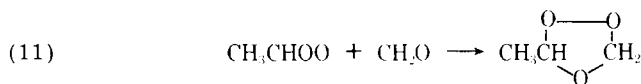
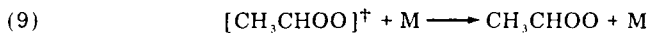
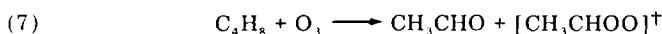


This seems to rule out methylenebis(oxy) as a secondary ozonide precursor. However, although it is likely that the solution-phase results are applicable to the gas-phase studies, we cannot totally rule out secondary ozonide formation from methylenebis(oxy) until the labeling experiments are repeated for the gas-phase reactions.

*The Initially Formed "Hot" Criegee Intermediate and its Role in Secondary Ozonide Formation*

Referring to Figure 1 it can be seen that the initially formed Criegee intermediate may have sufficient internal energy to decompose to various molecular and free-radical products, as is in fact observed at low pressures [1,2,9]. This "hot" Criegee intermediate can be collisionally stabilized to varying degrees, however, depending on pressure. In solution, this "hot" Criegee intermediate is probably totally quenched. If we accept the hypothesis that secondary ozonides are formed in the gas phase from Criegee intermediates, then the yields of secondary ozonides can be used to characterize the degree of stabilization and the thermal stability of the Criegee intermediate.

Niki et al. [4] have studied the formation of propene ozonide in the reaction of 10 ppm *cis*-2-butene with 5 ppm ozone in the presence of 10 ppm added formaldehyde, at a total pressure of 700 torr of air and a reaction time of 120 s. The reactions leading to ozonide formation are:



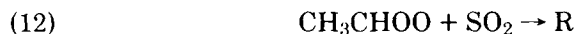
The yield of propene ozonide with respect to butene consumed was found to be 18% [4], which can be interpreted as meaning that 18% of the "hot"

Criegee intermediates formed in the primary step are quenched and then these "stabilized" Criegee intermediates react with the added aldehyde. It is possible that not enough formaldehyde was added to react with all of the "stabilized" Criegee intermediate. However, it was further observed that when 5 ppm  $\text{SO}_2$  was added to this system, the secondary ozonide disappeared, and the amount of  $\text{SO}_2$  consumed was about equal to the amount of secondary ozonide originally formed. These observations strongly support the hypothesis that *all* of the "stabilized" Criegee intermediate was trapped. On that basis one can estimate the ratio of the rates of reaction of formaldehyde with the "stabilized" Criegee intermediate and its rate of unimolecular isomerization and/or scission.

### *Estimation of Specific Rates for Reactions of the "Stabilized" Criegee Intermediate*

If we assume that at least 90% of the "stabilized" Criegee intermediate reacts to form secondary ozonide (SOZ) and the remainder is lost in a unimolecular reaction to yield products Q, then  $d[\text{SOZ}]/d[\text{Q}] = k_{11}[\text{H}_2\text{CO}]/k_{10} \geq 9$ , from which  $k_{10}/k_{11} \leq 4 \times 10^{-11} \text{ mol/cm}^3$  for  $[\text{H}_2\text{CO}] = 10 \text{ ppm}$  [4].

The data of Niki et al. [4] also allow us to set a limit for the value of  $k_{11}$ . Thus addition of 5 ppm  $\text{SO}_2$  leads to competition between  $\text{SO}_2$  and  $\text{H}_2\text{CO}$  for the Criegee intermediate

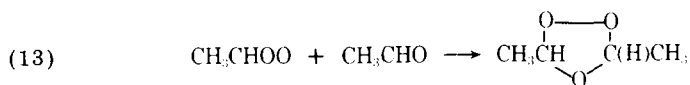


and, assuming that  $\text{SO}_2$  removes at least 90% of the "stabilized" Criegee intermediate, then  $d[\text{SOZ}]/d[\text{R}] = k_{11}[\text{H}_2\text{CO}]/k_{12}[\text{SO}_2] \leq 1/9$ , and  $k_{11}/k_{12} \leq 0.05$ , since  $[\text{SO}_2]/[\text{H}_2\text{CO}] = 0.5$ .

If  $k_{12} \leq 10^{13} \text{ cm}^3/\text{mol}\cdot\text{s}$ , which is a reasonable upper limit for this rate constant, then  $k_{11} \leq 5 \times 10^{11} \text{ cm}^3/\text{mol}\cdot\text{s}$ . Nangia and Benson [17] estimate that  $k_{11} \simeq 3.2 \times 10^9 \exp(-2000/RT) \text{ cm}^3/\text{mol}\cdot\text{s}$ , where the estimated 2 kcal/mol activation energy is probably an upper limit. This expression yields  $k_{11} \simeq 1 \times 10^8 \text{ cm}^3/\text{mol}\cdot\text{s}$  at 300 K, which is compatible with the upper limit derived here on the basis of the data of Niki et al. [4]. If one accepts the value of  $k_{11}$  from Nangia and Benson [17], one can estimate, from the value derived above for  $k_{11}/k_{12} \leq 0.05$ , that  $k_{12} \geq 2 \times 10^9 \text{ cm}^3/\text{mol}\cdot\text{s}$ . Using the  $k_{11}$  value of Nangia and Benson [17], we also calculate  $k_{10} \leq 4 \times 10^{-3} \text{ s}^{-1}$  based on the upper limit of  $k_{10}/k_{11}$  estimated above. Thus if one were to assume an upper limit of  $A_{10} \lesssim 10^{13} \text{ s}^{-1}$ , which is reasonable in view of the constrained requirements for a plausible transition state (see below), then  $E_{10} \gtrsim 21 \text{ kcal/mol}$ , and the "stabilized" Criegee intermediate would have a half-life at room temperature in excess of 2 min with respect to unimolecular decomposition. On the other hand, if one were to use the upper limit derived above of  $k_{11} \lesssim 5 \times 10^{11} \text{ cm}^3/\text{mol}\cdot\text{s}$ , then one would ob-

tain  $k_{10} \lesssim 20 \text{ s}^{-1}$ ,  $E_{10} \gtrsim 16 \text{ kcal/mol}$ , and hence a lower limit of  $t_{1/2} > 3.5 \times 10^{-2} \text{ s}$ , which is still a significantly long half-life. In Figure 1 we have assumed that the activation barrier for conversion of planar dioxymethylene to dioxirane corresponds to  $E_{10} \sim 16 \text{ kcal/mol}$ .<sup>9</sup>

On the basis of the above discussion of reactions (7)–(12), one would expect that the yield of secondary ozonide would decrease with decreasing pressure. Niki [27] has recently found this to be the case for propene ozonide produced by the ozonolysis of *cis*-2-butene in the presence of added formaldehyde. In our separate experiments [8], the yield of butene ozonide from the reaction of *trans*-2-butene with ozone at a total pressure of 4 torr has been measured as a function of added acetaldehyde. The ozonide was formed in a reaction analogous to reaction (11):



Although the absolute yield of the secondary ozonide was not determined, it is possible to estimate  $k_{10}/k_{13}$  from the secondary ozonide yield curve shown in Figure 2. It can be readily shown that if the limiting (plateau) value of the yield of secondary ozonide is equated to the total amount of "stabilized" Criegee intermediate produced, then

$$R_{\text{SOZ}} = \frac{[\text{SOZ}]_A}{[\text{SOZ}]_\alpha - [\text{SOZ}]_A} = \frac{k_{13}}{k_{10}} [\text{CH}_3\text{CHO}]$$

where  $[\text{SOZ}]_A$  is the yield of ozonide when the amount of added acetalde-

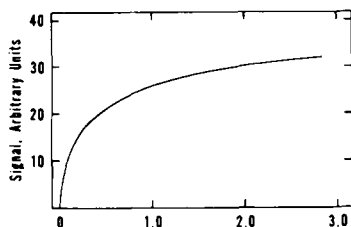


Figure 2. Secondary ozonide formation in the  $\text{O}_3$ -*trans*-2- $\text{C}_4\text{H}_8$  reaction system measured at  $m/e$  104 as a function of added  $\text{CH}_3\text{CHO}$ .  $[\text{O}_3]_0 \approx 1.1 \times 10^{-8}$ ,  $[\text{trans-2-C}_4\text{H}_8]_0 \approx 6.1 \times 10^{-10}$ , and  $[\text{O}_2]_0 \approx 2.1 \times 10^{-7} \text{ mol/cm}^3$ ; total pressure  $\approx 4$  torr; reaction time  $\approx 5$  s; 294 K. See [8] for experimental details.

<sup>9</sup> Note that if  $E_{10}$  were  $\geq 21 \text{ kcal/mol}$ , then in the absence of scavengers such as aldehydes,  $\text{SO}_2$ , etc., it should be possible to isolate the "stabilized" Criegee intermediate if at very high pressures it were possible to quench the dioxymethylene formed via the  $\text{CH}_2 + \text{O}_2$  reaction (see discussion in [10]). Karlström and Roos [*Chem. Phys. Lett.*, **79**, 416 (1981)] very recently reported an *ab-initio* estimate of about 21.5 kcal/mol for the energy barrier of conversion of dioxymethylene to dioxirane.

hyde is  $[\text{CH}_3\text{CHO}] = A$ , and  $[\text{SOZ}]_\alpha$  is the limiting yield of ozonide. A plot of  $R_{\text{SOZ}}$  versus  $[\text{CH}_3\text{CHO}]$  using an estimated value of  $[\text{SOZ}]_\alpha = 40$  (arbitrary units of Figure 2) yields  $k_{10}/k_{13} \simeq 6 \times 10^{-9} \text{ mol/cm}^3$ . This ratio is 100 times higher than the upper limit for the ratio of  $k_{10}/k_{11}$  calculated above from the data of Niki et al. [4]. There are two plausible explanations for this difference, both of which may be applicable. First we note that in the low-pressure experiments the partial pressure of added acetaldehyde approaches 15% of the total pressure. Thus if acetaldehyde is significantly more efficient as a quenching gas than the carrier gas ( $\text{O}_2$ ), then the effective rate of reaction (9) would be enhanced. A second possibility is that acetaldehyde is reacting with the "hot" Criegee intermediate  $(\text{CH}_3\text{CHOO})^\dagger$ , leading to an apparent enhancement of  $k_{13}$ .<sup>10</sup> We consider it very unlikely that the difference between  $k_{10}/k_{11}$  and  $k_{10}/k_{13}$  could be due to a large difference between  $k_{11}$  and  $k_{13}$ .<sup>11</sup>

Although we cannot separate the various effects, i.e., quenching of the Criegee intermediate or reactions with "hot" or "stabilized" Criegee intermediates, we believe that at low pressure the Criegee intermediate is almost entirely lost as a result of reaction (8). This means that the only practical way to study the chemistry of the Criegee intermediate is through experiments carried out at high pressure (atmospheric and above).

### *Mechanisms Postulated for the Thermally and Chemically Activated Decompositions of Secondary Ozonides*

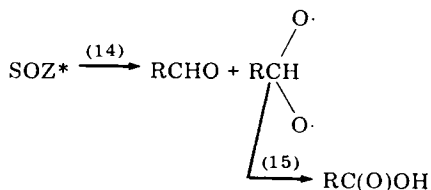
It has been assumed in the calculations of the preceding subsection that the secondary ozonides formed in reactions (11) and (13) are quenched before they can themselves undergo further unimolecular decomposition via the concerted mechanism established by Hull et al. [28]. In the discussion that follows we examine some of the apparent inconsistencies in the mechanisms proposed by Nangia and Benson [17] with reference to alkyldioxy disproportionation reactions, and by Su et al. [29] with reference to alkanolic acid anhydride formation in  $\text{O}_3$ -alkene systems. Each of these postulated mechanisms necessitates that one invoke a different activated state of the secondary ozonide than the one accessed thermally by Hull et al. [28] and/or that some other unique chemistry specific to the  $\text{H}_2\text{COO}$  Criegee intermediate be involved.

<sup>10</sup> A complementary view of these two possibilities is that the same acetaldehyde molecule quenches the initially formed "hot" Criegee intermediate and then immediately scavenges the resulting "stabilized" Criegee intermediate. In subsequent sections such a process, in which the quenching molecule immediately becomes the scavenger of the quenched species, is termed a "quasi-concerted" process.

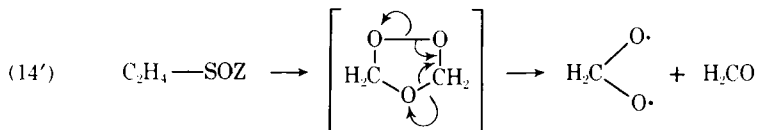
<sup>11</sup> If we accept the estimated rate constant for  $k_{11} \simeq 1 \times 10^8 \text{ cm}^3/\text{mol}\cdot\text{s}$  and  $k_{13} \simeq k_{11}$ , then it can be shown that the "stabilized" Criegee intermediate would be 90% converted to secondary ozonide in the low-pressure experiments with about  $5 \times 10^{-9} \text{ mol/cm}^3$  of added acetaldehyde. (Note that the reaction time in the low-pressure experiments was about 5 s, compared with 120 s in the case of the high-pressure experiments.)

To facilitate the discussion that follows, it should be noted that the "Energy" ordinate of Figure 1 may also be viewed as [Total Energy -  $\Delta H_f(\text{H}_2\text{CO})$ ] if, with reference to the  $\text{O}_3\text{—C}_2\text{H}_4$  reaction system, the Total Energy refers to [ $\Delta H_f(\text{CH}_2\text{O}_2) + \Delta H_f(\text{H}_2\text{CO})$ ], [ $\Delta H_f(\text{C}_2\text{H}_4) + \Delta H_f(\text{O}_3)$ ],  $\Delta H_f(\text{C}_2\text{H}_4\text{—SOZ})$ , etc., where  $\text{C}_2\text{H}_4\text{—SOZ}$  is the secondary ozonide of ethylene,  $\text{CH}_2\text{—O—CH}_2\text{OO}$ . Therefore, one may represent the  $\text{C}_2\text{H}_4\text{—SOZ}$  on the "Energy" ordinate of Figure 1 at an energy which corresponds to [ $\Delta H_f(\text{C}_2\text{H}_4\text{—SOZ}) - \Delta H_f(\text{H}_2\text{CO})$ ] ( $\approx -50 - (-26) \approx -24$  kcal/mol) [12], and hence it becomes evident with reference to Figure 1 that  $\Delta H(\text{C}_2\text{H}_4\text{—SOZ} \rightarrow \text{H}_2\dot{\text{C}}\text{OO}\cdot + \text{H}_2\text{CO}) \equiv \Delta H(\text{C}_2\text{H}_4\text{—SOZ—H}_2\text{CO} \rightarrow \text{H}_2\dot{\text{C}}\text{OO}\cdot) \approx +24.6 - (-24) = +48.6$  kcal/mol.

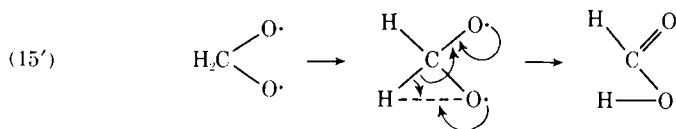
*Postulated role of methylenebis(oxy).* Nangia and Benson [17] postulated that the secondary ozonides formed in reactions such as reactions (11) and (13) decompose to an appreciable degree via a biradical intermediate to yield an aldehyde and a substituted methylenebis(oxy), and that the latter isomerizes to the acid:



[It is noteworthy that if  $\text{C}_2\text{H}_4\text{—SOZ}$  were to decompose via (14) to methylenebis(oxy),



then the conversion of the latter to  $\text{HC(O)OH}$  via (15) probably would favor an *anti*-conformation for the  $\text{HC(O)OH}\{\text{O—H anti to C=O}\}$ .



If reaction (14) were to lead to substituted methylenebis(oxy), however, then one would expect, on the basis of the energetics illustrated in Figure

1, that this species would isomerize to a "hot" acid and decompose to molecular and free-radical products, rather than isomerize via reaction (15) to a stabilized acid as postulated by Nangia and Benson [17]. Moreover it is known from the work of Hull et al. [28] that even though the thermally activated decomposition of neat secondary ozonides does lead to acids and aldehydes, the measured activation energies strongly suggest a concerted rather than a biradical mechanism. Therefore one would have to invoke a different activated state for the  $\text{SOZ}^*$  of reaction (14) than the one accessed thermally by Hull et al. [28].

Comparison of the yields of secondary ozonides to those of the acids formed in ozone-alkene systems also leads one to conclude that reactions (14) plus (15) are unimportant. For example, according to Hull et al. [28] the thermal unimolecular decomposition of propene ozonide is represented by reactions (20) and (21) of Figure 3, which account for 90% of the ozonide decomposed, and for which  $k_{20}/k_{21} = 6.5$ . [We will discuss other possible decomposition reactions such as reactions (19) and (22) later.] However, Niki et al [4] have measured the yields of both propene ozonide and formic acid in the  $\text{O}_3$ -*cis*-2- $\text{C}_4\text{H}_8$ - $\text{H}_2\text{CO}$  reaction system, where the ozonide presumably arises via reaction (11), and found  $R(\text{SOZ})/R(\text{HCOOH}) \approx 3.6$ . Then based on the latter ratio, if one assumes that the secondary ozonide

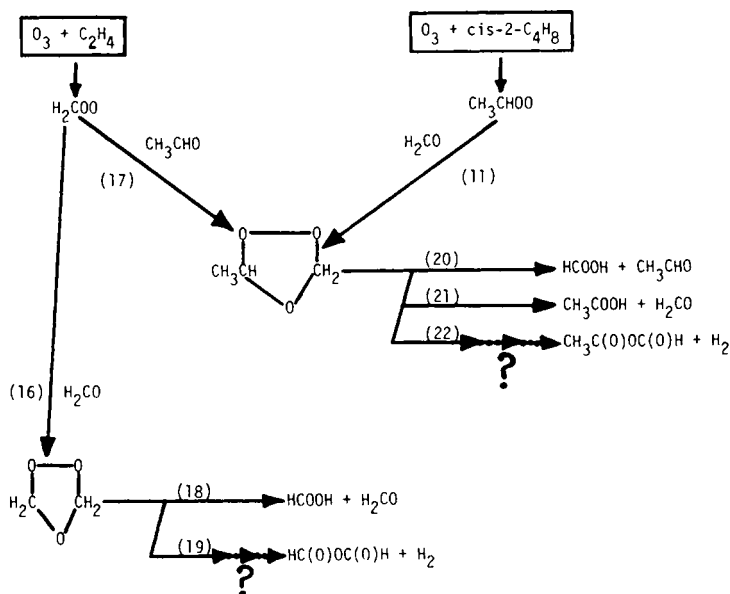
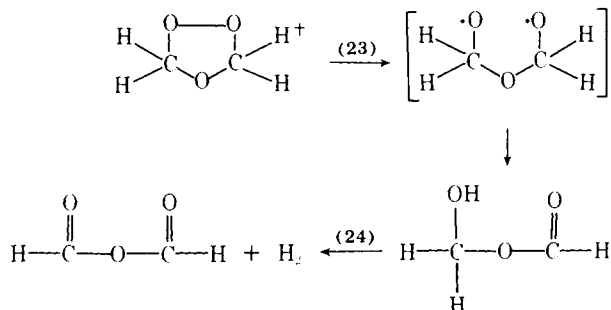


Figure 3. Secondary ozonide formation and decomposition paths.

formed in reaction (11) is not formed with such an excess of internal energy as to significantly change the relative rates of reactions (20) and (21), one can estimate that at most 25% of the initially formed ozonide might have decomposed via reactions (20) and (21). Considering that there are other sources of formic acid in this system, we expect reactions such as reactions (20) and (21) [and hence by inference also the proposed reactions (14) and (15)] to be unimportant in ozone-alkene reaction systems.

*Postulated decomposition to acid anhydrides.* There is, however, other evidence which has been interpreted to mean that secondary ozonides formed in gas-phase ozone-alkene reactions can decompose to products which differ from those observed in conventional pyrolysis studies. Thus, Su et al. [29] find at a total pressure of 700 torr that formic anhydride is a major product of the ozone-ethene reaction with yields varying from 18 to 35% (with respect to ethene consumed), depending on experimental conditions. To explain this observation, they postulated the following reaction sequence:



which is summarized in Figure 3 as reaction (19).

The production of both hydroxymethyl formate and formic anhydride in the  $\text{O}_3$ -ethene system at 700 torr total pressure was recently confirmed by Niki et al. [30]. However, they were not able to reproducibly establish the decay of the hydroxymethyl formate into formic anhydride via (24), presumably because of the heterogeneous nature of the process [30]. [Note added in proof: Kan et al. [*J. Phys. Chem.*, **85**, 2359 (1981)] recently confirmed Niki's observations concerning the heterogeneous nature of the conversion of hydroxymethyl formate into formic anhydride.] Moreover, they indicated that as the reactant concentrations are increased, the hydroxymethyl formate may in fact undergo gas-to-aerosol conversion in lieu of its postulated heterogeneous decomposition to formic anhydride.

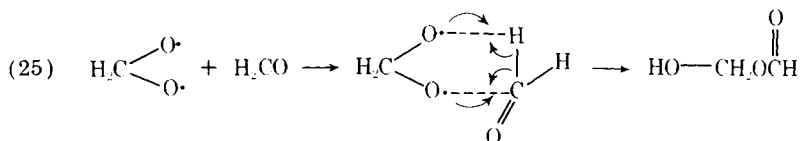
Su et al. [29] also found that reacting ozone with ethene in the presence of added acetaldehyde led to the formation of both propene ozonide and formic acetic anhydride. By analogy with the arguments given above to explain the formation of formic anhydride, they postulated the formation and decomposition of propene ozonide as illustrated in reactions (17) and



(22) of Figure 3. In support of that argument they note that under their conditions of added  $\text{CH}_3\text{CHO}$ , formic anhydride is produced only at the later stages of the reaction, when  $\text{H}_2\text{CO}$ , which is a primary product of the ozone-ethene reaction, builds up sufficiently in concentration to compete with  $\text{CH}_3\text{CHO}$  for the  $\text{CH}_2\text{OO}$ .

There are, however, some serious problems with this postulated mechanism. Hull et al. [28] did not report anhydrides to be products of the thermal decomposition of any normal ozonide, even though they were able to detect anhydrides; e.g., acetic anhydride was found to be a product of the thermal decomposition of 1,2-dimethylcyclopentene ozonide. Moreover, as noted above, their data suggest a concerted rather than a biradical mechanism. In addition, Niki et al. [4] found that anhydrides are not major products of the ozone-*cis*-2-butene reaction. More significantly, anhydrides are not major products of the  $\text{O}_3$ -*cis*-2-butene reaction in the presence of added formaldehyde. Thus with reference to Figure 3 it is especially important to note that propene ozonide is formed in the experiments of Su et al. [29] via reaction (17) and in the experiments of Niki et al. [4] via reaction (11), and yet formic acetic anhydride is reported to be a product only in the system used by Su et al. [29]. Hence in the context of the mechanism postulated by Su et al. [29], these observations would imply that different activated states of the initially formed ozonide are involved in the subsequent decomposition reactions, and/or that some other unique chemistry specific to the  $\text{CH}_2\text{OO}$  Criegee intermediate is involved.

*Possible alternative source of hydroxymethyl formate.* The observations of Niki et al. [30] suggest to us that the production of hydroxymethyl formate may occur *not* via the intermediacy of the secondary ozonide [reaction (23)], but rather via a direct reaction involving methylenebis(oxy), one of the isomers of the Criegee intermediate. Thus collisional stabilization of methylenebis(oxy) may become significant as the total pressure is increased so that it can undergo a "quasi-concerted" addition to  $\text{H}_2\text{CO}$ ,

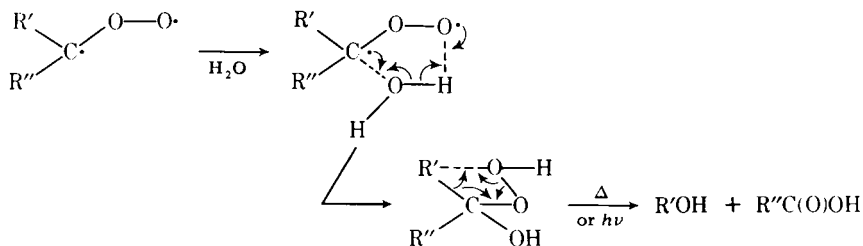


thus directly forming the hydroxymethyl formate observed by Su et al. [29] and Niki et al. [30].<sup>12</sup>

<sup>12</sup> In these experiments  $\text{H}_2\text{CO}$  is always in excess over the  $\text{CH}_2\text{O}_2$  species (as discussed in [29, p. 245]), and as the reactant concentrations are increased from the ppm range to the percent range,  $\text{H}_2\text{CO}$  would become an increasingly significant third body, acting simultaneously as a quencher and a scavenger for both the methylenebis(oxy) and its precursor, dioxymethylene. Niki et al. [30] used  $[\text{O}_3]_0$  and  $[\text{C}_2\text{H}_4]_0$  ranging from about 7 ppm to 0.7%.

### Degree of Stabilization of the Initially Formed "Hot" Criegee Intermediates

<sup>13</sup> An additional possibility, suggested by the observation of aerosol formation by Niki et al. [30] as the reactant concentrations were increased, is that the spectroscopic features they ascribed to an OH-containing compound in the condensed phase may instead be indicative of (HOO)CR'R''(OH) surrounded by water clusters [the (HOO)CR'R''(OH) is formed by the direct reaction of a Criegee intermediate with H<sub>2</sub>O].

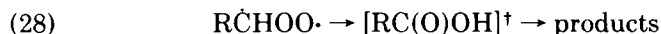
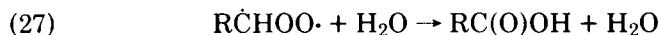


as discussed in [9]]. That is, the dioxymethylene may, by its reaction with  $\text{H}_2\text{O}$ , provide a highly hydrophilic nucleating center which initiates the agglomeration of  $\text{H}_2\text{O}$  clusters leading to the observed aerosol formation. And since the dioxymethylene is the precursor of methylenebis(oxy), and hence of the hydroxymethyl formate, it is not unexpected that one would naturally associate such aerosol formation with the formation of hydroxymethyl formate.

## Bimolecular Reactions of the "Stabilized" Criegee Intermediate

As discussed in the preceding sections, there is considerable evidence that the "stabilized" Criegee intermediate has a long lifetime at room temperature and can react with aldehydes and sulfur dioxide. In this section we consider evidence for bimolecular reactions of the Criegee intermediate with other molecular or free-radical species.

Cox and Penkett [31] in a study of the ozonation of alkenes in the presence of added SO<sub>2</sub>, in which the course of the reaction was followed by monitoring the rate of formation of sulfate aerosol, found that the rate was strongly dependent on relative humidity. Calvert et al. [32] reinterpreted the data of Cox and Penkett [31] on the basis of the following mechanism (where we have omitted reactions of the Criegee intermediate with alkenes, ozone, or oxygen):



Their [32] reanalysis of the data for the O<sub>3</sub>-*cis*-2-butene reaction led to  $k_{27}/k_{26} \simeq 6 \times 10^{-5}$ . In conjunction with the estimate made before for  $k_{26}$  (see Table III) one would estimate  $10^5 < k_{27} < 6 \times 10^8 \text{ cm}^3/\text{mol}\cdot\text{s}$ . However, the kinetic analysis of Calvert et al. [32] is *not* consistent with the very important conclusion of Cox and Penkett [31] that the formation of the H<sub>2</sub>SO<sub>4</sub> aerosol they monitored probably occurs in a concerted process, and *not* via hydration of SO<sub>3</sub>, since SO<sub>3</sub> does *not* react rapidly with water vapor to form an aerosol. A different mechanistic interpretation of the data of

TABLE III. Bimolecular reactions of the stabilized Criegee intermediate.

Reactant	Observation	Estimated $k$ (300K), $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Source
SO <sub>2</sub>	Suppression of secondary ozonide formation.	$2 \times 10^9 < k < 10^{13}$	this work (based on the data of references 4 and 17).
Aldehydes	Formation of secondary ozonides.	$10^8 < k < 5 \times 10^{11}$ $\sim 10^8$	this work (based on the data of references 4 and 17). 17
NO <sub>2</sub>	Reduction of secondary ozonide formation.	$7 \times 10^6 < k < 4 \times 10^{10}$	this work (based on the data of reference 8).
H <sub>2</sub> O	Effect of water vapor on sulfate aerosol formation in ozone-alkene-SO <sub>2</sub> mixtures.	$10^5 < k < 6 \times 10^8$	this work (based on the data of references 31 and 32).
O <sub>2</sub>	No observable effect on ozonide formation.	$< 5 \times 10^2$	this work (based on the data of reference 4).
Alkenes	Formation of epoxides in solution.	-----	14

Cox and Penkett [31] will be discussed in detail in [33].<sup>14</sup> Moreover, based on our analysis, it will also be shown in [33] that the data of Cox and Penkett [31] also suggest that at atmospheric pressure the initially formed "hot" Criegee intermediates are stabilized to the extent of about 40% for C<sub>3</sub> alkenes and to about 80% for C<sub>6</sub> alkenes.

In the case of nitrogen dioxide we reported previously [8] that nitrogen dioxide reduces the yield of secondary ozonide formed in the reaction of ozone with *trans*-2-butene. Thus addition of  $6 \times 10^{-9}$  mol/cm<sup>3</sup> of NO<sub>2</sub> to a mixture of  $4.4 \times 10^{-9}$  mol/cm<sup>3</sup> of O<sub>3</sub> and  $3.3 \times 10^{-9}$  mol/cm<sup>3</sup> of *trans*-2-butene reduced the yield of secondary ozonide from 100 to 77 (in arbitrary units corrected for the effect of NO<sub>2</sub> on ozone consumption). Under conditions of these experiments, the reaction proceeded almost to completion, the yield of CH<sub>3</sub>CHO approaching a maximum value of about  $3 \times 10^{-9}$  mol/cm<sup>3</sup>. The reactions of the "stabilized" Criegee intermediate can be represented by:



for which we can write  $d[\text{SOZ}]/d[\text{P}] = k_{29}[\text{CH}_3\text{CHOO}][\text{CH}_3\text{CHO}]/k_{30}[\text{CH}_3\text{CHOO}][\text{NO}_2]$ . The effective concentration of CH<sub>3</sub>CHO is less than  $3 \times 10^{-9}$  mol/cm<sup>3</sup>, and we use an average value of  $1.5 \times 10^{-9}$  mol/cm<sup>3</sup>, leading to  $k_{29}/k_{30} \simeq 14$ . Hence by using the limiting values shown in Table III for  $k_{29}$ , one obtains the limiting values of  $7 \times 10^6 < k_{30} < 4 \times 10^{10}$  cm<sup>3</sup>/mol-s.

The reaction

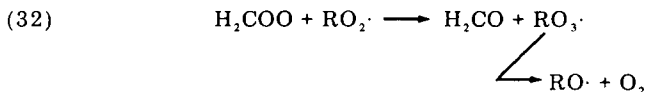


has often been suggested as a reaction of importance in the atmosphere. An attempt was made to study this reaction by measuring the yield of <sup>18,18,16</sup>O<sub>3</sub> produced in the reaction of ozone with propene in the presence of added <sup>18,18</sup>O<sub>2</sub> at about 4 torr total pressure [34]. It was found that a maximum of 1% of the original ozone could have been converted to the labeled form. In retrospect it seems apparent that at low pressure very little of the Criegee intermediate would be stabilized in any case, and this experiment should be repeated at high pressure. It is clear, however, from the observations of Niki et al. [4] that the reaction of the Criegee intermediate with O<sub>2</sub> must be exceedingly slow since secondary ozonide formation is readily effected with 10 ppm of added formaldehyde in the presence of 700 torr of air. Assuming that a maximum of 10% of the "stabilized"

<sup>14</sup> It should be noted that in [33] we argue that dioxymethylenes probably do not react with H<sub>2</sub>O via reaction (27), but instead probably proceed via the direct addition reaction discussed in footnote 13. [Note added in proof: Hatakeyama et al. [*J. Phys. Chem.*, 85, 2249 (1981)] recently reported evidence which provides further support for the direct addition of H<sub>2</sub>O to dioxymethylene, as discussed in footnote 13 above and in refs. [9] and [33].]

Criegee intermediate reacts with  $O_2$  in reaction (31), we estimate that  $k_{31}/k_{11} \leq 5 \times 10^{-6}$ , and hence  $k_{31} \leq 5 \times 10^2 \text{ cm}^3/\text{mol}\cdot\text{s}$ .

There are many other probable gas-phase reactions of the Criegee intermediate for which at present there are no data. Reaction with NO appears probable as well as reaction with alkenes, which are known in solution to result in the formation of epoxides. Reactions of Criegee intermediates with alkylldioxy radicals could be of importance. Nangia and Benson [17] have suggested a mechanism:

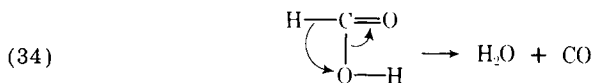
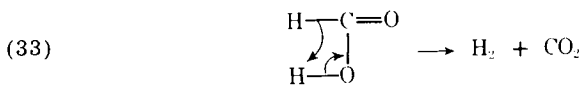


with an estimated  $k_{32} \approx 10^{12} \text{ cm}^3/\text{mol}\cdot\text{s}$ .

Table III represents an initial attempt to compile rate constants for reactions of a generalized Criegee intermediate with various reactive species.

### Origin of Decomposition Products of Criegee Intermediates Formed by Gas-Phase Ozonolysis of Alkenes

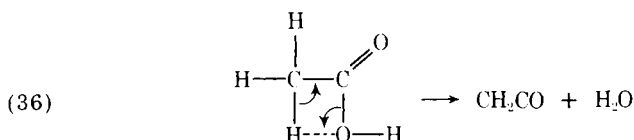
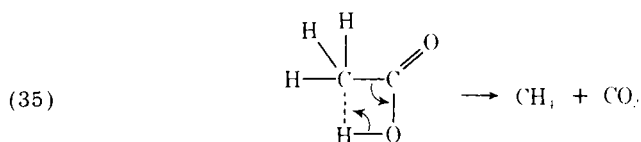
With reference to Figure 1 we have implicitly treated the fate of the initially formed "hot" Criegee intermediate in terms of quenching to a thermally "stable" ground state, or of isomerization to yield a "hot" acid or ester which decomposes to molecular or free-radical products. While this may be the case, we cannot exclude the direct unimolecular decomposition of the "hot" Criegee intermediate, or of "hot" dioxirane or methylenebis(oxy) as possible sources of the decomposition products. However, we are constrained to derive plausible transition states to account for the proposed products. In particular, we note that the transition states which give rise to the observed molecular products are necessarily based on acid or ester structures. In the case of formic acid, for example, we would have:



There are no reliable data available on the pyrolysis of formic acid. Mercury photosensitization studies [35] indicate that free-radical channels are at best minor processes, and that reaction (33) accounts for 30% and reaction (34) for 70% of the acid decomposed. As can be seen from Figure

1, however, the formic acid can be excited sufficiently by mercury photo-sensitization ( $\lambda = 253.7$  nm) to lead to both molecular and free-radical products. Modeling [1] of the data obtained in the low-pressure ozonolysis study of ethene in fact indicated that about 9% of the Criegee intermediate or its formic acid isomer decomposed via a free-radical mechanism.

Studies of acetic acid pyrolysis [36] indicate that the reaction is molecular, suggesting transition states such as the following:



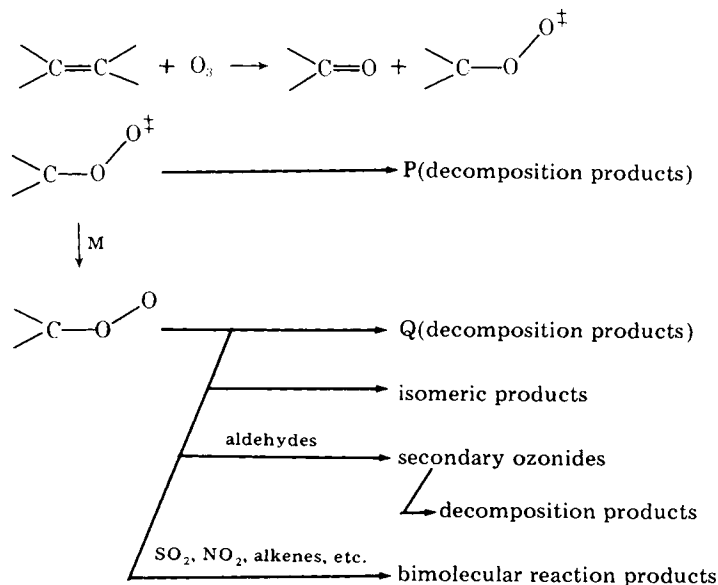
Mercury photosensitization studies [35] indicate that both molecular and free-radical processes are important, and the same conclusions were derived from studies of the ozonolysis of propene [2]. Of particular significance is the observation of Niki et al. [4] that at 700 torr total pressure, where 18% (or more) of the Criegee intermediate is stabilized, the yield of  $\text{CH}_4$  is 13%. This  $\text{CH}_4$  is presumably arising entirely from the decomposition of the "hot" Criegee intermediate or the isomeric "hot" acetic acid. In the absence of a Criegee intermediate scavenger (i.e., aldehyde), one might anticipate a different temporal behavior from products arising from the decomposition of "hot" Criegee intermediates and the stabilized species.

## Summary and Conclusions

In this paper we have attempted to outline the chemical kinetics of the Criegee intermediate and its isomers: the dioxiranes, derivatives of methylenebis(oxy), and carboxylic acids and/or esters. The identification of some of the reactions of the Criegee intermediate means that a characterization of its reaction kinetics is feasible. In particular the use of secondary ozonides [13] or epoxides [14] should be developed as measures of the concentrations of Criegee intermediates. However, the origin of the anhydrides which were presumed to be decomposition products of the secondary ozonides [29] remains to be resolved. Table III represents an initial attempt to compile rate constants for reactions of a generalized Criegee intermediate with various reactive species.

The role of Criegee intermediates in gas-phase  $\text{O}_3$ -alkene reactions is

suitably represented by the following very generalized scheme:



Thus, as has been discussed elsewhere [9], the extremely complex secondary chemistry found in  $\text{O}_3$ -alkene reactions is a consequence of the complex chemistry of the Criegee intermediate, and possibly also of its isomers. However, the relative rates of reactions participating in  $\text{O}_3$ -alkene systems are very significantly altered by reaction conditions, thereby influencing observed product distributions and assumed mechanisms. For example, as discussed in section above, high aldehyde concentrations will tend to "stabilize" the "hot" Criegee intermediate, thereby reducing the free-radical activity of the system, while encouraging secondary ozonide formation, and possibly also formation of hydroxymethyl formate via reaction (25). Increasing the total pressure will also affect the product distribution because of third-body effects. However, these will not only alter the secondary radical chemistry (e.g.,  $\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2$  followed by  $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$ ), but also affect to varying degrees the stabilization of the initially-formed "hot" Criegee intermediate, and consequently the free-radical activity of the  $\text{O}_3$ -alkene system. In a similar vein it is apparent that  $[\text{H}_2\text{O}]$  will also influence the observed product distributions because of reactions such as reaction (27) (see footnotes 13 and 14). Thus it is clear from the preceding discussion that the chemistry of the Criegee intermediate remains the single most important problem area in understanding the gas-phase mechanism of  $\text{O}_3$ -alkene reactions, and of  $\text{H}_2\text{SO}_4$  aerosol formation in  $\text{O}_3$ -alkene- $\text{SO}_2$  systems [31]. For a discussion of other reactions of the Criegee intermediate not discussed in this paper, the reader is referred to [9] and [10].

In terms of atmospheric chemistry it would appear that for many small alkenes (smaller than  $C_5$ ), decomposition to yield radical and molecular products will be a major loss process for the initially formed "hot" Criegee intermediate. The degree of quenching to form the thermally "stable" Criegee intermediate will depend on the size and structure of the alkene. The "stabilized" Criegee intermediates may react with aldehydes to form secondary ozonides. However, there are no reports of secondary ozonides being atmospheric constituents, and it is probable either that the secondary ozonide is lost in subsequent atmospheric reactions, or that the "stabilized" Criegee intermediate is lost in reactions other than those leading to secondary ozonides. Such loss processes would include photolysis, reaction with OH radicals,  $RO_2$  radicals,  $SO_2$ ,  $NO_x$ , and hydrolysis.

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