of ca. 10^4 s⁻¹. We propose that this corresponds to the rate of dissociation of a (partially) vibrationally relaxed primary product, either HCO or FCO. Excitation of HFCO at 193 nm results in rapid, detector-limited formation of CO(v=0-2) but slow formation of CO(v=3,4). This observation is attributed to the fact that the energy supplied by a 193-nm photon is sufficient to form CO(v=0-2), but CO(v>2) can be formed only from that fraction of the HCO (or FCO) population with energy in excess of the threshold for secondary decomposition, i.e., only from the highenergy "tail" of the triatomic's energy distribution function. We conclude that the chemistry of HFCO following UV photoexcitation qualitatively differs from the "thermal" chemistry of this species: Bond fission is the dominant process in the former case while molecular elimination, yielding HF and CO, is observed in the latter.

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Stopped-Flow Studies of the Mechanisms of Ozone-Alkene Reactions in the Gas Phase: trans-2-Butene

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The reaction of ozone with trans-2-butene has been studied in the gas phase at 294 K and 530 Pa (4 Torr) by using a stopped-flow reactor coupled to a photoionization mass spectrometer. The concentrations of reactants and products were determined as a function of reaction time. A mechanism is proposed to account for the observed products: CH₃CHO, H₂CO, CO₂, CH₄, CH₃C(O)C(H)(OH)CH₃, H₂C=C=O, H₂O, 2-butanone, 2,3-epoxybutane, CH₃C(O)C(O)CH₃, and HC(O)C(O)H. This work again indicates that the simple "hot" ester hypothesis needs to be critically reconsidered for gas-phase ozonolysis.

Introduction

The mechanisms of the reactions of ozone with alkenes in the gas phase continue to present very serious interpretive problems.¹⁻³ In earlier work from this laboratory, we developed a detailed mechanism for the ozone-ethene reaction⁴ that had as its starting point the Criegee mechanism^{5,6} for solution-phase ozonolysis:

> $O_3 + C_2H_4 \rightarrow POZ$ $POZ \rightarrow H_2CO + H_2\dot{C}OO \cdot$ $H_2CO + H_2\dot{C}OO \rightarrow SOZ$

where POZ is the primary and SOZ the secondary ozonide. In the gas phase at low pressure we found that the reaction leading to SOZ was inoperative and that the fate of the dioxymethylene biradical (the Criegee intermediate $R_b C(R_a)OO$) was determined by unimolecular loss processes:⁴

In this paper an asterisk is used to designate a highly excited, chemically activated state that can undergo further unimolecular reactions (isomerizations, decompositions, etc.). See p 417 of ref 6b for a review of the rearrangement of dioxymethylenes to excited acids and/or esters via dioxiranes (I) and methylenebis(oxy)s (II).



Rearrangements of biradicals, such as the one above

that involve migration of an alkyl group or H atom from carbon to carbon or from carbon to oxygen appear to be commonplace in photochemically initiated and chemically activated systems (see the Appendix). See also p 419 of ref 6b and p 231 of ref 1 for a synopsis of the product channels accessed by excited acids and esters.

Extension of this work to propene and isobutene⁷ was not as successful in that the particular dioxymethylene decomposition channels were more difficult to identify unambiguously. We had tentatively proposed a general mechanism involving isomerization of the dioxymethylene to a "hot" acid or ester which then decomposed:



Our inability to fit the propene and isobutene data in a satisfactory manner indicated that knowledge of the secondary chemistry was incomplete or incorrect or that other isomerization/decomposition

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channels were available to dioxymethylenes.

Since that earlier work, an extensive mass spectrometric analysis of the products of a broad range of ozone-alkene reactions² revealed that the mechanism is more complex.

The possible role of an oxygen atom product channel

$$\begin{array}{ccc} & & & & \\ R_{a} & & & \\ R_{b} & - & C \end{array} \xrightarrow{R_{a}} & R_{b} & - & C = 0 \end{array}$$

0

0

was discussed^{1,2} and later was confirmed. Thus, an FTIR study of the atmospheric pressure ozonation of trans-C₂H₂Cl₂⁸ provided evidence for the reaction

Oxygen atom production has also been validated for⁹

$$\begin{array}{c} H \\ Ph - C: + O_2 \end{array} + Ph - C \\ \hline H \\ C \end{array} + O_2 + Ph - C \\ \hline H \\ - Ph - C = 0 + O \\ \hline H \\ - C = 0 +$$

for^{1,10,11}

$$C: + O_2 \longrightarrow H_2C \bullet \longrightarrow H_2CO +$$

and for12,13

 H_2

More recently, two studies reported work on the gas-phase reaction of O₃ with 2,3-dimethyl-2-butene.^{12,14} These studies showed that there is a significant change in the mechanistic path followed by a dioxymethylene, $R_b C(R_a)OO$, depending on the nature of R_a and R_b . For $R_a = R_b = H$, it follows the ester channel. For $R_a = R_b = CH_3$, the ester channel apparently cannot compete with the O-atom channel¹² and the hydroperoxide channel.^{12,14} {Refer to Figure 3 of ref 12 for the thermochemistry of the chemically activated transformations discussed below for the hydroperoxide channel of Scheme I.

Thus the secondary chemistry for dialkyl-substituted dioxymethylene $R_1C(R_2)OO$ is substantially different from that for $H_2\dot{C}OO$. Note that $R' = CH_3$ and R'' = H for the dioxyThe Journal of Physical Chemistry, Vol. 92, No. 16, 1988 4645





methylene Me₂COO from the $O_3 + 2,3$ -dimethyl-2-butene reaction. Also, R' = R'' = H for the dioxymethylene CH₃C(H)OOfrom the O_3 + 2-butene reaction.

The rearrangement of a dioxymethylene $R''CH_2\dot{C}(R')OO$ to a hydroxyalkanone R'C(O)-CH(OH)R"* via a hydroperoxide $R''CH=C(R')-OOH^*$ was first reported to occur in 1967¹⁵ (see p 87 of ref 6a for a review of these rearrangements; see the Appendix for the mechanistic details of the 1,4-migration of H from carbon to oxygen). For the $O_3 + 2,3$ -dimethyl-2-butene reaction, these rearrangements have since been validated in the gas phase also.^{12,14} However, the hydroperoxide is not observed;¹⁴ hence it is not stabilized even at atmospheric pressure¹⁴ (see thermochemistry in Figure 3 of ref 12). The partial decomposition $(\leq 10\%)$ of the hydroxyalkanone to the alkanedione R'C(O)-C-(O)R" was also reported in ref 12 for the $O_3 + 2,3$ -dimethyl-2butene reaction (see thermochemistry in Figure 3 of ref 12). The real-time temporal profiles (Figure 2 of ref 12) indicated that the alkanedione was produced directly and not via secondary freeradical reactions.12

It was not clear, however, which channels would be operative with only one alkyl substituent $[RC(H)OO \cdot]$.

If the hydroperoxide channel were operative for the dioxymethylene CH₃C(H)OO· from O₃ + trans-2-butene (and O₃ + propene), where R' = R'' = H, one might expect production of $HC(O)-CH_2OH$ (glycolaldehyde) and HC(O)-C(O)H (glyoxal). These are analogous to the products observed in the $O_3 + 2,3$ dimethyl-2-butene reaction: $CH_3C(O)$ - CH_2OH (hydroxyacetone) and $CH_3C(O)-C(O)H$ (methylglyoxal).¹²

If the ester channel shown in Scheme II were also operative, one would expect to find methane in this chemically activated reaction system. Methane is a unique product of the decomposition of excited ethanoic acid, CH₃C(O)OH*, and methyl methanoate, HC(O)OCH₃* [see p 417 of ref 6b (ref 11 also) for a review of the rearrangement of dioxymethylenes to excited acids and/or esters via dioxiranes (I); see also p 419 of ref 6b and p 231 of ref 1 for a synopsis of the product channels accessed by excited acids and esters}.

Niki¹⁶ has identified glycolaldehyde, glyoxal, methane, and ketene as products of the $O_3 + trans-2$ -butene reaction at atmospheric pressure in the gas phase (the hydroperoxide was not observed). With our instrument we cannot distinguish glycolaldehyde from acetic acid or the dioxymethylene (all three are 60 amu; a mass spectral peak at m/e 60 was reported in our earlier mass spectrometric study of the $O_3 + trans-2$ -butene reaction²).

Here we report a more detailed study of the $O_3 + trans-2$ -butene reaction using stopped-flow mass spectrometry. The focus of the work in this paper is the same as that of our earlier work on the $O_3 + 2,3$ -dimethyl-2-butene reaction;¹² viz., a definition of which reaction channels (ester channel and/or O-atom channel and/or hydroperoxide channel) are accessed by the dioxymethylene that is formed by the initial O_3 + alkene interaction. The work in this paper again indicates that the simple "hot" ester hypothesis needs to be critically reconsidered.

Experimental Section

The reaction was studied at 294 K and 530 Pa (4 Torr) by using a stopped-flow reactor coupled to a photoionization mass spectrometer as described in detail elsewhere.^{2,4} The reactor was a

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Figure 1. Temporal profiles of the concentrations of reactants and products for the reaction of *trans*-2-butene with excess O₃ at 294 K and 4 Torr: $[O_2]_0 \simeq 2.2 \times 10^{-7}$, $[O_3]_0 \simeq 5.8 \times 10^{-9}$, [trans-2-butene]₀ $\simeq 5.7 \times 10^{-10}$ mol cm⁻³. Reaction time t = 0 corresponds to $t_{expl} \simeq -0.48$ s.



Figure 2. Temporal profiles of the concentrations of reactants and products for the reaction of O₃ with excess *trans*-2-butene at 294 K and 4 Torr: $[O_2]_0 \simeq 2.2 \times 10^{-7}$, [trans-2-butene]₀ $\simeq 4.2 \times 10^{-9}$, $[O_3]_0 \simeq 7.8 \times 10^{-10}$ mol cm⁻³. The temporal profile for CH₄ production is not shown for the sake of clarity because it coincides with that for acetoin. Reaction time t = 0 corresponds to $t_{exptl} \simeq -0.48$ s.

300-cm³ sphere. Reactants were premixed prior to their entry into the reactor and flowed through the reactor. Gas within the reactor could be isolated by closing simultaneously solenoid valves at the inlet and outlet. The gas within the reactor was sampled continuously through a 200- μ m orifice into a photoionization mass spectrometer.

In a typical experiment, a stream of O_2 containing O_3 was flowed through the reactor. A mixture consisting of *trans*-2-butene in O_2 was then injected into the O_3/O_2 gas flow at a point ca. 90 cm upstream from the sampling orifice of the mass spectrometer. The reactants are well mixed before they enter the reactor. The partial pressures of O_3 (ca 0.3–2.9% mol of O_3 at 4 Torr) and *trans*-2-butene (ca. 0.006–1.9% mol of *trans*-2-butene at 4 Torr) were adjusted as required for each experiment. The mass spectrometer was then focused on a particular reactant or product peak in the mass spectrum.

For Figures 1 and 2, the inlet/outlet valves were closed simultaneously, and the temporal profile of each species was obtained in the isolated *static* reactor. This process was repeated anywhere from 2 to 50 times to build up sufficient signal for each reactant and product. In this way, we developed temporal profiles for the reactants O_3 and *trans*-2-butene and each of the products



Figure 3. Yield of selected reaction products versus [*trans*-2-butene]₀ at 294 K and 4 Torr. Measured with reaction time fixed at $t \simeq 1.1$ s; excess O₃ and O₂ fixed at $[O_2]_0 \simeq 2.2 \times 10^{-7}$ and $[O_3]_0 \simeq 6.3 \times 10^{-9}$ mol cm⁻³.

shown in Figures 1 and 2. Limiting values were obtained for CO.

For Figure 3, the inlet/outlet valves were left open (the reactor used as a *stirred-flow* reactor). The reaction time was set by throttling the reactor's pump-out line.

Converting mass spectrometric signals to partial pressure and then concentrations required the use of calibration mixtures. For the stable gases, we used procedures described in ref 4 and 7 and for formaldehyde that described in ref. 17.

Experimental Results

Figures 1 and 2 show the temporal profiles for the reactants and products. The temporal profile for CH₄ production is not shown in Figure 2 for the sake of clarity because it coincides with that for acetoin. The upper limit for the yield of CO was estimated to be <0.2 mol per mol of *trans*-2-butene consumed. No other products were found in significant yield.

The t = 0 of Figures 1 and 2 is the *true* (absolute) reaction time zero from the point of admixture of the dilute O_3/O_2 and *trans*-2-butene/ O_2 mixtures. The dashed portions of the products' temporal profiles correspond to the time it takes (ca. 0.48 s) for the reacting mixture to flow from the point of admixture to the sampling orifice of the mass spectrometer. The time at which the inlet/outlet valves are closed is defined as $t_{exptl} = 0$ and corresponds to $t \simeq 0.48$ s. This is consistent with the flow times previously estimated.¹² The solid portions of the products' temporal profiles correspond to the signals measured in the isolated *static* reactor (inlet/outlet valves closed).

Figure 3 shows the yield of selected reaction products as a function of [trans-2-butene]₀ at a fixed reaction time. The extent of reaction of the *trans*-2-butene, $\Delta[C_4H_8]$, is shown relative to its initial concentration. For these experiments, $\Delta[C_4H_8]/[C_4H_8]_0 \approx 0.4-0.5$. So for any product whose yield is ca. 1.0 (e.g., CH₃CHO), its concentration is approximately equal to that of the unreacted *trans*-2-butene.

In Figure 3 the assignment of the mass spectral peak at m/e 58 to glyoxal was based on its kinetic behavior in this work and on the FTIR atmospheric pressure study of the reaction by Niki et al.¹⁶ The absolute concentrations assigned to the 72-amu signal was based on the relative sensitivities and known composition of 2-butanone and 2,3-epoxybutane, both of which originate from the same reaction.²

Discussion

The matching of computer-modeled temporal profiles to the experimentally observed ones could provide some insights about the relative importance of key primary reactions. But even then it could not define unambiguously the primary chemistry of any system as complex as the O_3 + alkene reactions. Nonetheless, the modeling of the O_3 + 2,3-dimethyl-2-butene reaction system¹² indicated that the key features of the O_3 + alkene reaction mechanism are controlled primarily by the branching ratios for isomerization, decomposition, etc., of the initially formed dioxy-

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SCHEME III



methylene. The key mechanistic features ("prompt" production of methylglyoxal and hydroxyacetone, etc.)¹² could not be explained by the secondary radical chemistry which occurs subsequent to the unimolecular reactions (isomerization, decomposition, etc.) of the initially formed dioxymethylene. Modeling is not feasible for the $O_3 + trans$ -2-butene reaction, however, because the specific rates of the key secondary radical-molecule or radical-radical reactions have not been characterized.

The origin of the major products shown in Figures 1–3 have been discussed in detail elsewhere.^{1,2,18,19} For example, acetoin (CH₃C(O)C(H)(OH)CH₃) is formed by a sequence of secondary reactions initiated by the addition of OH to the 2-butene in the presence of O_2 .^{2,18} The H₂CO is formed by several commonplace reactions of species such as CH₃, CH₃O, CH₂OH, CH₃C(O), etc., with species such as O, O_2 , O_3 , etc.; such commonplace reactions were enumerated in Table II of ref 12. Hence, the discussion of the secondary free-radical chemistry^{1,2,18,19} will not be repeated here.

Consistent with the focus of this paper (see Introduction), therefore, the Discussion will be limited to a succinct assessment of which reaction channels (ester channel and/or O-atom channel and/or hydroperoxide channel) are accessed by the dioxymethylene $CH_3C(H)OO$. To do so, we focus on those products that are unique indicators for each channel (the selection of each unique indicator is based on the detailed discussions in ref 1, 2, 11-13, 18, and 19). The discussion is developed in the context of the mechanism of Scheme III. This mechanism is proposed for the key reactions of the dioxymethylene produced in the primary O₃ + trans-2-butene reaction. It is consistent with all the observations reported to date from product analysis² and radical-scavenging experiments^{2,18} in the $O_3 + trans-2$ -butene reaction system and from a study of the O + trans-2-butene reaction, ¹⁹ etc.^{1,12,13} The italicized products of Scheme III are the unique indicators for each respective channel (discussed below).

The product data suggest that all three channels are operative. But the branching ratios for each channel cannot be determined from the product yields alone because some products have more than one primary source (e.g., H_2CO and H_2O originate from both the ester and hydroperoxide channels). However, the yields of the unique indicators $(CH_4, O, HC(O)-C(O)H)$ can provide a lower limit for the relative importance of each channel.

As discussed in the Introduction, CH_4 is a unique indicator for the ester channel. Figures 1 and 2 clearly indicate that CH_4 is produced in significant yield (ca. 6–11%). So the ester channel is operative in the $O_3 + trans-2$ -butene reaction, while it is not in the $O_3 + 2,3$ -dimethyl-2-butene reaction.¹² On the basis of the yield of CH_4 , the ester channel contributes at least 10% of the total $CH_3\dot{C}(H)OO$ decomposition.

Diacetyl is a unique indicator for the O-atom channel. Radical-scavenging experiments^{2,18} with CH₃CHO or NO₂ added to the O₃ + *trans*-2-butene reaction system, indicated that CH₃C-(O)C(H)(CH₃)OO is the precursor of diacetyl. But the source of this RO₂ radical precursor was unknown. Scavenging experiments with added CH₃CHO suggested that it might have been formed via some complex reaction sequence initiated by the OH + *trans*-2-butene reaction in the presence of excess O₂.^{2,18} Later work showed that diacetyl and its RO₂ radical precursor are produced by the O + *trans*-2-butene reaction in the presence of excess O₂.¹⁹ In retrospect, CH₃CHO is a good scavenger for both O and OH, but the O-atom channel was not known then.^{2,18} On the basis of the yield of diacetyl in Figure 3, the O-atom channel contributes on the order of $\leq 5\%$ of the total CH₃C(H)OO decomposition.

Glyoxal is a unique indicator for the hydroperoxide channel. For C_nH_{2n} alkenes, product analysis² and scavenging experiments^{2,18} had indicated that C_m dioxoalkanes [R'C(O)C(O)R''] and C_m ketenes [R'-C(R'')=C=O], where m < n, originate from the primary, excited dioxymethylene via its isomerization to the hydroperoxide. For example, ketene and glyoxal are C_m products of alkenes containing the CH₃C(H)= moiety, while methylketene and methylglyoxal are C_m products of alkenes containing, respectively, the CH₃CH₂C(H)= and (CH₃)₂C= moieties.² [For the O₃ + *trans*-2-butene reaction, the ester channel can provide a second source of H₂C=C=O.]

It was not clear,² however, if glyoxal was produced (a) by direct unimolecular reactions [intramolecular rearrangement of the hydroperoxide CH_2 =C(H)OOH* to HC(O)CH₂OH*, followed by intramolecular elimination of H₂ from HC(O)CH₂OH*] or (b) via secondary reactions (molecule-molecule reactions of the hydroperoxide² or radical-radical reactions subsequent to the decomposition of the hydroperoxide²).

More recent work¹² has shown that the temporal profiles observed for methylglyoxal and hydroxyacetone in the $O_3 + 2,3$ dimethyl-2-butene reaction are consistent with "prompt" products and not with secondary products formed in a complex radicalradical reaction sequence. So C_m dioxoalkanes such as glyoxal probably originate directly from the primary excited dioxymethylene via the complex sequence of isomerizations of the hydroperoxide channel. On the basis of yield of glyoxal in Figure 3, the hydroperoxide channel contributes *at least* 10% of the total $CH_3\dot{C}(H)OO$ decomposition.

 H_2O is produced primarily by secondary radical-radical reactions and not via the ester and hydroperoxide channels. Compare the yields of ketene shown in Figure 3 {<8% over a wide range of [*trans*-2-butene]₀} with the yield of H₂O shown in Figure 1 (ca. 30%) and 2 (ca. 8%). Figure 2 shows an induction period for H₂O production. This is consistent with scavenging of the radical precursors of H₂O by the excess *trans*-2-butene, which is consumed ca. 25% when O₃ has been consumed by ca. 90%.

Conclusions

The chemistry of dioxymethylenes is complicated by their facile interconversions and complex equilibria.^{2,13} The key to further advances lies in studies of the spectroscopic and chemical kinetic properties of the isolated species.¹³ There is currently no way to do this. A reinterpretation²⁰ of the recent work of Akimoto and co-workers^{21–23} on the matrix photolysis of alkene–O₂ mixtures

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indicates that it may be possible to isolate dioxymethylenes under carefully selected conditions.13,20

The gas-phase mechanism for alkyl-substituted alkenes needs to be modified to include the ester, hydroperoxide, and O-atom channels.

Appendix: Rearrangements of Biradicals

Rearrangements of biradicals with migration of an alkyl group or H atom from carbon to carbon or from carbon to oxygen appear to be commonplace in photochemically initiated and chemically activated systems.

There is substantial evidence for rearrangements of biradicals that involve 1,2-migration of an alkyl group and 1,2-, 1,4-, and 1,5-migrations of an H atom from carbon to carbon or from carbon to oxygen.²⁴⁻²⁶ The driving force for such migrations appears to be the conversion of a species with unpaired electrons (the biradicals) to one in which all the electrons are paired (the "stable" product).²⁴ For example²⁴



Two examples of biradical rearrangements apposite to O_3 + alkene reactions are provided below: (A) the rearrangement of a dioxymethylene to a hydroperoxide (this involves a 1,4-migration of H from C to O)^{6a,12,14,15} and (B) the O + alkene reactions (these involve 1,2-migration of alkyl and/or H from C to C).

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(A) Dioxymethylene to Hydroperoxide:^{6a,12,14,15}



The hydroperoxide subsequently isomerizes to a hydroxyalkanone.6a,12,14,15



In the gas phase, the hydroxyalkanone decomposes, in part, to an alkanedione:12





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