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Reactivity of the Ozone−Ethane System

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The reaction of ozone with ethane was studied in the range 24−150 °C. Added oxygen at 24 °C was found to cause a large induction period after which the reaction occurred rapidly accompanied by a flash of light. The light consisted of Meinel bands from vibrationally excited OH radicals as had been previously seen at higher temperatures in the methane−ozone system. Induction periods of more than 3 h were measured when an excess of oxygen was added. Total pressure measurements suggested a chain reaction, and several possible chain sequences are considered. A 42-step mechanism was used to simulate the system and found to account for the effect of added oxygen on the induction period and on the light emission.

Introduction

We wish to challenge two accepted beliefs: that ozone does not react with ethane at room temperature and that long induction periods in gas-phase oxidations are necessarily due to slow rises in temperature. In the process we give evidence for what may be the longest substantiated period of induction in a homogeneous reacting system.

In the liquid phase, oxidations of hydrocarbons by oxygen are initiated by free radical reactions such as

$$RH + O_2 \rightarrow R + HOO$$

and the systems are often characterized by induction periods before appreciable reaction occurs.[1] Induction periods also occur in the gas phase, and it has been known for many years[2] that some oxidations involve nonisothermal systems where explosions can occur as a result of a temperature rise from within the reaction vessel. In addition, chemiluminescence is sometimes seen after the induction period at the onset of the rapid reaction.[3] In fact, induction periods are common in gas-phase oxidations but the times are usually of the order of seconds.[4]

In previous work on the ozone−methane system we measured the reaction rate in the range 75−175 °C and found a period of induction of less than a minute.[5] Using a complex free radical mechanism, we were able to give a satisfactory computer simulation of the induction period. Since the C−H bond in ethane is about 15 kJ/mol weaker than in methane, one would expect more reactivity in the ozone−ethane system, and we report here on this reactivity.

An investigation by Morrissey and Schubert[6] of the ozone−ethane system was carried out at 0−60 °C, and rates and products were measured. The major products were carbon dioxide, water, formic acid, and methanol; carbon monoxide was found as a minor product as was unused ozone (even though ethane was in large excess). The oxygen mole balance was 65−80%, so there were clearly additional, undetected products. Morrissey and Schubert's kinetics were disputed by Atkinson and Carter[7] who pointed out that extremely small amounts of impurities in alkane−ozone systems could lead to chain-propagating reactions, yielding erroneously high observed reaction rates. They concluded that there was no evidence for a molecular reaction between ozone and ethane. We agree with Atkinson and Carter's conclusion but give experimental and computer-generated evidence for the initiation of chains from the very small oxygen atom concentrations present in ozone at room temperature.

Experimental Section

The apparatus has been previously described.[5] It was clear from the work of Morrissey and Schubert[6] that attempting to measure all of the many products of this reaction would be a lengthy undertaking that would not greatly add to our knowledge of the kinetics involved. We therefore followed the progress of the reaction by measuring three parameters: ozone concentration, total pressure, and light emission. We were able to measure any two of these quantities simultaneously as a function of time. Ozone concentration was measured by UV absorption at 254 nm. Since ozone was monitored with a 254 nm beam, there was the possibility that the beam itself initiated the reaction. Several runs were therefore done where the beam was shuttered except for very brief periods after the reaction had started when the ozone concentration was measured. No change in reaction rate was found. Total light emission was measured using a cooled Hamamatsu R636 photomuliplier placed at right angles to the axis of the cylindrical reaction cell. Some experiments were done in a flow system[5] and spectra taken with a 0.25 m Jarrell-Ash monochromator.

Commercial ethane (Matheson Co., Rutherford, NJ), oxygen, and carbon dioxide were distilled several times, liberally rejecting head and tail fractions. In the case of ethane, although no impurities were detected by GC, there was the possibility of trace impurities initiating chain reactions and two additional precautions were made. In one case ozone was left in contact with samples of excess ethane, which was later distilled off. In another, samples of ethane were left in contact with liquid bromine overnight to remove traces of alkenes and the ethane was subsequently redistilled. In all cases these samples of ethane reacted as the others did.

Computer simulations were carried out with ACUCHEM/ACUPLOT software.[8]

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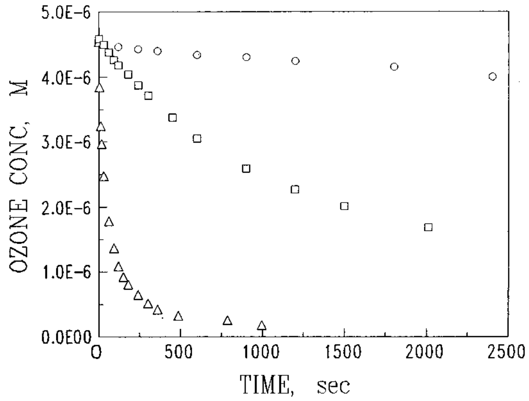

Figure 1. Ozone decay at 54 (○), 103 (□) and 150 (△) °C. Average initial concentrations (M) are the following: $[O_3]$, 4 × 10^{-6}; $[C_2H_6]$, 1 × 10^{-4}; $[O_2]$, 1 × 10^{-5}.

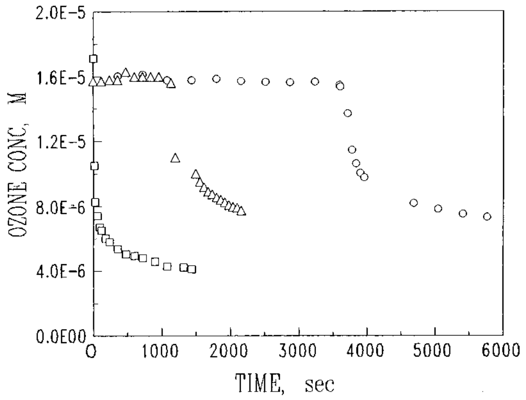

Figure 2. Ozone decay at 24 °C at $[C_2H_6]_0 = 1.0 \times 10^{-5}$ M with added O_2 pressure (Torr) of 0 (□), 0.40 (△), and 0.52 (○).

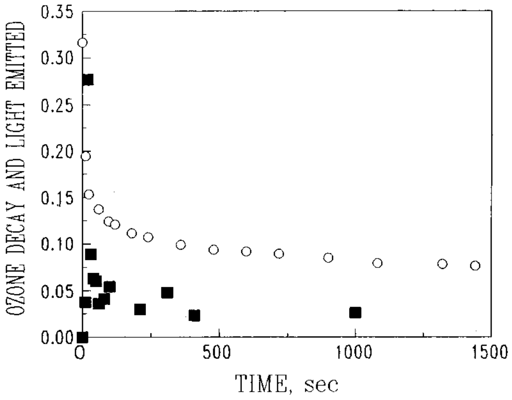

Figure 3. Ozone and light emission decay at 24 °C with no added O_2: (○) ozone in Torr; (■) light emission in nA, time in s. Initial pressures are the following: O_3, 0.295 Torr; C_2H_6, 0.189 Torr.

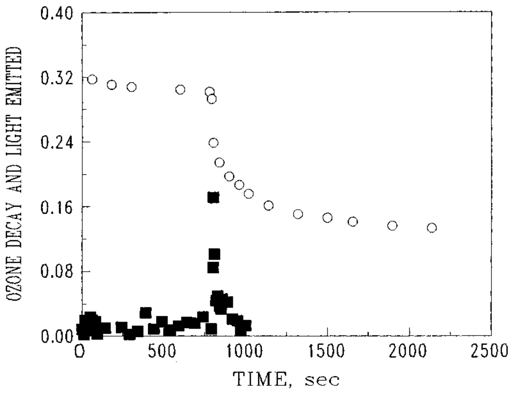

Figure 4. Ozone and light emission decay at 24 °C with added O_2: (○) ozone (Torr): (■) light emission (nA), time in s. Initial pressures are the following: O_3, 0.291; C_2H_6, 0.194; O_2, 0.319.

Results

Possible surface effects were checked by changing the quartz reaction vessel and by flaming it under vacuum between runs; this did not affect the data obtained. In the absence of ethane, there was no detectable loss of ozone in an O_3-O_2 mixture left at room temperature for several hours.

Runs were carried out in the range 24−150 °C, and the ozone decay followed no simple order. Experiments at the higher temperatures made it clear that the rapid reaction was slowed considerably by the presence of O_2. Typical results of ozone decay in the presence of added O_2 are shown in Figure 1. No appreciable induction periods were found, where "induction period" is loosely defined as a sudden drop in initial reactant concentration of more than 10%. At room temperature, however, the ozone decay curves in the presence of O_2 were dramatically different, as shown in Figure 2, where the addition of 0, 0.40, and 0.52 Torr of O_2 to 0.30 Torr of O_3 and 0.19 Torr of C_2H_6 at 24 °C caused induction periods of 0, 1560, and 3650 s, respectively.

In the flow system, a comparison of the chemiluminescence accompanying the reactions of ozone with methane, ethane, propane, and ethylene was made. No emission was seen in the O_3-CH_4 system at room temperature as had previously been found,[5] but above 100 °C Meinel bands from vibrationally excited OH ($X^2\Pi$, $v < 10$) were emitted. At room temperature Meinel bands were easily detected from the reactions of O_3 with C_2H_6, C_3H_8, and C_2H_4. Since there was the possibility that some C_2H_4 impurity in the C_2H_6 was responsible for the emission, some samples of C_2H_6 were treated with bromine and redistilled. The Meinel band intensities were found to be unchanged. Increasing the temperature increased the Meinel band intensities from the O_3-CH_4, $O_3-C_2H_6$, and $O_3-C_3H_8$ systems.

In the static system at room temperature, there was an immediate pulse of light emitted when the reactants were mixed in the absence of O_2, as seen in Figure 3, which shows total light emitted and O_3 decay as a function of time. In the presence of 0.19 Torr of added O_2, however, an 800 s period of induction for O_3 decay coincided with light emission, shown in Figure 4. The times for the light peaks were always within a few seconds of the end of the induction period. Although the times for the light peaks were easily measurable, the light peaks were short-lived and we were unable to measure their magnitude accurately. We did, however, observe an inverse effect of added O_2 on peak height.

The total pressure remained approximately constant during induction periods and then rose as the pressure of O_3 fell. The large effect of the presence of O_2 on pressure measurements at 24 °C is seen in Figure 5.

The effect of O_2 on the induction periods, shown in Figure 2, was studied at 24 °C over a range of added O_2 from 0 to 0.87 Torr. This gave observed induction periods varying from 0 to more than 3 h, shown as the squares in Figure 6. There is no indication that an upper value was reached, and the limit of the induction period may depend on the patience of the experimenters!

Discussion

Stoichiometry from Pressure Measurements. A reaction occurs at room temperature between O_3 and C_2H_6 where the

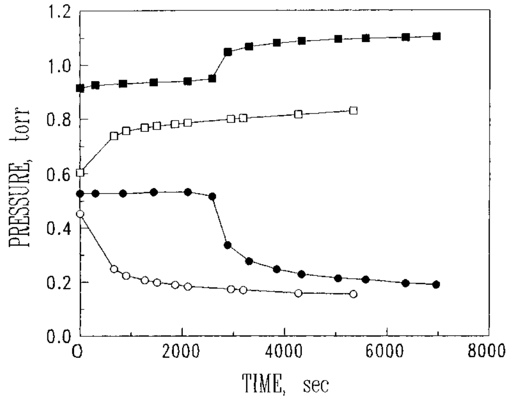

Figure 5. Ozone decay and total pressure increase at 24 °C without and with added O_2. For no added O_2: (○) O_3; (□) total pressure. For added O_2: (●) O_3; (■) total pressure. For no added O_2, initial pressures (Torr): O_3, 0.45; C_2H_6, 0.11. For added O_2, initial pressures (Torr): O_3, 0.57; C_2H_6, 0.11; O_2, 0.25.

half-life of ozone at comparable pressures with inert diluents would be expected to be several months. Under typical conditions at room temperature we found the half-life of ozone in the presence of ethane to be of the order of minutes once the induction period had elapsed. This relatively fast rate at room temperature suggests the possibility of one or more chains. A sequence of reactions producing five possible chains is

$$O_3 + M \rightarrow O_2 + O + M \qquad k_1$$

$$O + C_2H_6 \rightarrow C_2H_5 + OH \qquad k_2$$

$$OH + C_2H_6 \rightarrow H_2O + C_2H_5 \qquad k_3$$

$$C_2H_5 + O_3 \rightarrow 2CH_2O + OH \qquad k_{4a}$$

$$C_2H_5 + O_3 \rightarrow C_2H_4 + HO + O_2 \qquad k_{4b}$$

$$C_2H_5 + O_3 \rightarrow C_2H_5O + O_2 \qquad k_{4c}$$

$$O_3 + OH \rightarrow O_2 + HO_2 \qquad k_5$$

$$O_3 + HO_2 \rightarrow OH + 2O_2 \qquad k_6$$

$$C_2H_5O + C_2H_6 \rightarrow C_2H_5OH + C_2H_5 \qquad k_5$$

$$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2 \qquad k_8$$

Five resulting chain sequences are designated as shown in Table 1.

The chains may be distinguished by the pressure changes they give:

$$\text{chains I, III:} \quad P_{TOT} = P_{E0} + 2P_{OZ0} - P_{OZ} + P_{ADD} \qquad (1)$$

$$\text{chains II, IV:} \quad P_{TOT} = P_{E0} + 1.5P_{OZ0} - 0.5P_{OZ} + P_{ADD} \qquad (2)$$

$$\text{chains V:} \quad P_{TOT} = P_{E0} + P_{OZ0} + P_{ADD} \qquad (3)$$

where P_{TOT} represents the total pressure, P_{E0} and P_{OZ0} are the initial pressures of ethane and ozone, P_{OZ} is the instantaneous ozone pressure, and P_{ADD} is the pressure of an excess added gas; in the present case oxygen was added in some experiments.

We can rule out chain V because eq 3 predicts that the total pressure should be constant as P_{OZ} decreases and this was never found. Plots of P_{TOT} vs P_{OZ} should therefore be linear with negative slopes and with intercepts that are governed by the chain (or chains) operating. Typical results are shown in Figure 7 and show good linearity with constant slopes, regardless of whether an induction period occurred or not. The slopes and intercepts of plots of total pressure vs P_{OZ} were measured, and these slopes have a mean value of −0.486 (σ = 0.045), independent of the effect of added oxygen, in agreement with eq 2. The intercepts (INT) according to eq 2 equal P_{E0} + $1.5P_{OZ0}$ + P_{ADD}, and a plot of INT − P_{E0} − P_{ADD} vs P_{OZ0} is shown in Figure 8. The slope is 1.49 (σ = 0.027) and confirms eq 2 as the governing stoichiometry and indicates chains II and/or IV are operative. It should be emphasized that added O_2 has a large effect on the induction period (as seen in Figure 2) but does not affect the stoichiometry (Figure 8).

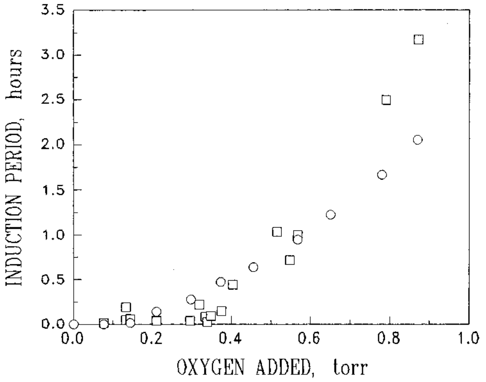

Figure 6. Induction period as a function of added O_2 at 24 °C: (□) experimental values; (○) simulated values.

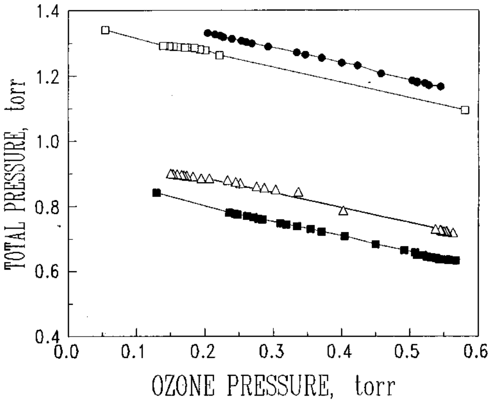

Figure 7. Typical plots of total pressure vs ozone pressure in Torr. Filled points are from experiments with added O_2.

TABLE 1: Chain Sequences

reactions	chain	overall stoichiometry
3, 4a	I	$C_2H_6 + O_3 \rightarrow H_2O + 2CH_2O$
5, 6	II	$2O_3 \rightarrow 3O_2$
3, 4b	III	$C_2H_6 + O_3 \rightarrow C_2H_4 + H_2O + O_2$
3, 4c, 6, 8	IV	$C_2H_6 + 2O_3 \rightarrow CH_3CHO + H_2O + 2O_2$
4c, 7	V	$C_2H_6 + O_3 \rightarrow C_2H_5OH + O_2$

Chain II would not account for the products found by Morrissey and Schubert[6] but chain IV would, if the resulting acetaldehyde were oxidized by ozone to form a variety of products in subsequent reactions. We therefore tentatively postulate chain IV as occurring with chain carriers sensitive to the concentration of O_2. We cannot, however, be certain of the identity of the chain carriers and will return to this aspect of the mechanism in the discussion of the computer simulation of the system.

Simulation of Induction Period. The possibility that the induction periods arose as a result of increases in temperature

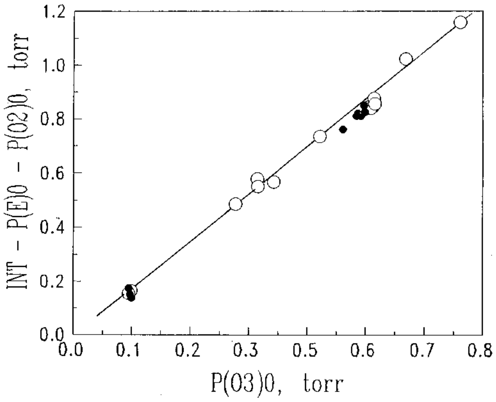

Figure 8. Test of eq 2; see text. Filled points are from runs with added O_2.

will now be considered. There are three pieces of evidence against this possibility. First, we take Benson's expression[9] for the mean time τ for the conductive dissipation of heat in a spherical reactor:

$$\tau = \frac{r_o^2 P C_V}{\pi^2 R T_w \kappa}$$

where r_o is the vessel radius, P the gas pressure, C_V the molar heat, T_w the temperature of the vessel walls, and κ the thermal conductivity of the gas. This gives $\tau < 1$ s under our conditions, which is negligible compared with induction times measured in hours so that a large temperature rise in the center of the reaction vessel would be almost immediately transmitted to the wall. Second, although most of the work on induction periods was done at room temperature, we also found a short (~1 min) induction period at 54 °C in the presence of 0.14 Torr of O_2. At both 27 and 54 °C in the absence of oxygen, the reaction was immediate and rapid, even in the presence of up to 11 Torr of CO_2 with 0.5 Torr each of ozone and ethane. That the induction period was not increased by a large excess of CO_2 is strong evidence against the reaction occurring as a result of a temperature increase. Finally, we were able to simulate the induction periods of both reaction and light emission at varying amounts of added O_2 using room-temperature rate constants only.

By use of the mechanism given in Table 2, the reaction was simulated using the ACUCHEM/ACUPLOT program[8] with varying amounts of added O_2. Most of the data were taken from the NIST compilation[10] with rate constants at 298 K. We were able to simulate the oxygen-sensitive induction period only by introducing a step involving the catalytic decomposition of ozone. Best results were obtained if the catalyst was the CH_3O radical, although it is possible that another species is involved. We found experimentally that some ozone remains at the end of the run even with ethane in excess as noted by Morrissey and Schubert[6] and as our simulation predicted. Figure 9 shows a typical ozone decay plot in the presence of added O_2 where squares represent the experimental points and circles the simulation. In Figure 6 the circles represent the simulation. The simulation plots of the concentrations of intermediates vs time showed that during the induction period the free radical concentrations initially increased slowly, then more rapidly, peaked at the induction period, and then rapidly fell. One exception to this was the C_2H_5O radical, which kept slowly increasing in concentration even after the induction period before slowly falling.

TABLE 2: Simulation Mechanism for Reaction of Ozone with Ethane at 298 K

no.	reaction	k(298 K)[a]	
1	$O_3 + M = OM + O_2$	5.00×10^{-26}	*b*
1A	$OM = O + M$	1.00×10^{10}	*c*
2	$O_2 + O\ (+M) = O_3\ (+M)$	2.11×10^{-17}	*b*
3	$O + O_3 = O_2 + O_2$	1.00×10^{-14}	*b*
4	$O + C_2H_6 = HO + C_2H_5$	3.46×10^{-15}	*b*
5	$C_2H_5 + O_3 = C_2H_5O + O_2$	2.53×10^{-11}	*b*
6	$C_2H_5O = CH_2O + CH_3$	1.44×10^{-1}	*b*
7	$C_2H_5 + O_2 = C_2H_5O_2$	9.21×10^{-12}	*b*
8	$C_2H_5O + O_2 = C_2H_4O + HO_2$	1.11×10^{-14}	*b*
9	$HO + C_2H_6 = H_2O + C_2H_5$	2.67×10^{-13}	*b*
10	$HO + O_3 = HO_2 + O_2$	6.64×10^{-14}	*b*
11	$HO_2 + O_3 = HO + O_4$	1.92×10^{-15}	*b*
11A	$O_4 = O_2 + O_2$	1.00×10^{15}	*c*
12	$C_2H_5O_2 + O_3 = C_2H_4O + HO_4$	5.00×10^{-18}	*d*
12A	$HO_4 = HO_2 + O_2$	1.00×10^{10}	*c*
13	$HO + C_2H_4O = H_2O + CH_3CO$	1.25×10^{-11}	*b*
14	$C_2H_5 + HO = C_2H_5OH$	1.28×10^{-10}	*b*
15	$O + C_2H_4O = HO + CH_3CO$	4.49×10^{-13}	*b*
16	$CH_3CO + O_2 = CH_3CO_3$	5.00×10^{-12}	*b*
17	$CH_3CO_3 + HO_2 = CH_3COOH + O_3$	1.41×10^{-11}	*b*
18	$CH_3CO_3 = CH_3 + CO_3$	7.50×10^{-1}	*d*
18A	$CO_3 = CO + O_2$	1.00×10^{10}	*c*
19	$C_2H_5O_2 + HO_2 = C_2H_5OOH + O_2$	1.11×10^{-11}	*b*
20	$HO_2 + HO_2 = H_2O_2 + O_2$	9.00×10^{-12}	*b*
21	$O + C_2H_5O_2 = O_2 + C_2H_5O$	6.00×10^{-10}	*d*
22	$HO + HO_2 = H_2O + O_2$	3.50×10^{-10}	*b*
23	$HO + CO = H + CO_2$	7.12×10^{-13}	*b*
24	$H + O_3 = HO^* + O_2$	4.45×10^{-11}	*b*
25	$C_2H_5O_2 + C_2H_5O_2 = (C_2H_5O)_2 + O_2$	4.40×10^{-14}	*b*
25A	$(C_2H_5O)_2 = C_2H_5O + C_2H_5O$	1.0×10^{5}	*c*
26	$C_2H_5OOH + O = C_2H_5OH + O_2$	3.32×10^{-13}	*b*
27	$HO^* = HO + h\nu$	4.00×10^{2}	*b*
27A	$h\nu =$	4.00×10^{1}	*d*
28	$CH_3CO + CH_3CO = (CH_3CO)_2$	3.52×10^{-11}	*b*
29	$CH_3CO = CO + CH_3$	2.42×10^{1}	*b*
30	$HO^* + C_2H_6 = H_2O + C_2H_5$	2.55×10^{-13}	*b*
31	$HO^* + O_3 = HO_2 + O_2$	6.64×10^{-14}	*b*
32	$CH_3 + O_3 = CH_3O + O_2$	5.10×10^{-12}	*b*
33	$CH_3O_2 = HCOOH + H$	1.17×10^{3}	*b*
34	$CH_3O + O = CH_3 + O_2$	1.59×10^{-11}	*b*
35	$CH_3O + O_2 = CH_2O + HO_2$	1.92×10^{-15}	*b*
36	$CH_3 + O_2 = CH_3O_2$	1.00×10^{-12}	*b*
37	$CH_3O + O_3 = CH_3O_2T + O_2$	3.00×10^{-14}	*d*
38	$CH_3O_2T = CH_3O + O$	1.00×10^{10}	*c*
39	$CH_3 + O = CH_2O + H$	1.40×10^{-10}	*b*
40	$C_2H_5O + O_3 = C_2H_5O_2T + O_2$	7.50×10^{-16}	*d*
41	$C_2H_5O_2T = C_2H_5O + O$	1.00×10^{10}	*c*
42	$C_2H_5O + O = C_2H_5 + O_2$	1.59×10^{-11}	*d*

[a] Units of rate constants are s^{-1} (first order) and cm^3 $molecule^{-1}$ s^{-1} (second order). [b] Reference 10. [c] Program limitations. [d] Estimated by authors.

Some work was done on the simulation of the chemiluminescence, assumed proportional to the concentration of vibrationally excited hydroxyl radicals (HO* in the mechanism). Taking a typical 24 °C run with initial O_3, C_2H_6, and O_2 as 0.30, 0.20, and 0.56 Torr, respectively, the induction period was about 4000 s. During this time the value of [OH*] went from 1.5×10^{-15} M at 1000 s to a peak of 5.3×10^{-13} M near the induction period, accounting for the flash of light seen. The quenching effect of O_2 on chemiluminescence has also been seen in the O_3−ethylene system[11] presumably due to O_2 removing H atoms and reducing the Meinel emission.

The original definition of an induction period, as for example described in the classic analysis of Benson,[12] is the time it takes for the intermediate concentrations to reach a steady state. In the system described here, however, the intermediate concentrations do not reach steady states but peak near the induction period and then decline.

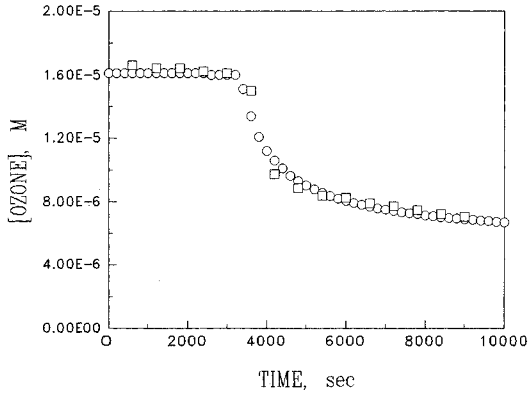

Figure 9. Ozone decay at 24 °C with added O_2: (□) experimental values; (○) simulation. Initial pressures (Torr) are the following: O_3, 0.300; C_2H_6, 0.195; O_2, 0.567.

Conclusions

Ethane and ozone react at room temperature. There is no evidence for a molecular reaction (as is the case for virtually all low-temperature alkane oxidations), but radical concentrations build up and a chain reaction then occurs. Added oxygen scavenges the radicals and slows the buildup, causing remarkable induction periods that can be several hours long. The highly oxygen-inhibited induction periods in the $O_3-C_2H_6$ system depend on a catalyst for ozone decomposition. Although we cannot be certain of the identity of the catalyst, we obtained good simulations assuming CH_3O is the key intermediate.

One final comment: chemical chaotic behavior arises because of the extreme sensitivity of a system to very small changes in the initial conditions.[3] At room temperature this system reacts as a result of the extremely small initial concentration of oxygen atoms. It may, therefore, be a good candidate for the study of chemical chaos.

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Supporting Information Available: Three tables of data for runs at 24, 54, 103, and 150 °C for the ozone−ethane system (15 pages). Ordering information is given on any current masthead page.

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