The Oxidation of Formyl Radicals

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Dedicated to Prof. Dr. W. Groth on his seventieth birthday

Steady state concentrations of formyl radicals were measured with a photoionization mass spectrometer. The reaction of ethylene with oxygen atoms in a system free of O_2 was used to form CHO and CH_3. Preliminary experiments showed that the reaction of methyl radicals did not interfere with the CHO measurements. By using low concentrations of O and short reaction times, it was possible to observe the initial growth of the CHO concentration. From the rate of approach of CHO to its steady state concentration, the absolute rate constant for the reaction O + CHO was determined to be $(2.1 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}. Addition of molecular oxygen to this system caused a decrease in the steady state CHO concentration, due to the reaction,

$$CHO + O_2 \rightarrow HO_2 + CO$$

as was suggested by Groth and coworkers in 1938. The rate constant for this reaction was calculated to be $(5.7 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. The importance of these rate constants for combustion and atmospheric reactions are discussed briefly.

Introduction

The formyl radical, CHO, is thought to be an important intermediate in most hydrocarbon combustion systems[1] and it also participates in reactions in the lower and upper atmosphere[2]. However, most of the information about the chemical behavior of this radical comes from inferences and product analysis. Almost no quantitative kinetic information is available.

The CHO molecule has been observed spectroscopically[3], both in absorption, and in emission as the "hydrocarbon flame bands". The H – CO bond is thought to be very weak, approximately 100 kJ/mole.

The recent development of mass spectrometers utilizing high intensity vacuum ultraviolet lamps as photoionization ion sources now permits the direct detection of free radicals at very low concentrations[4–6]. Kanofsky, Lucas and Gutman[6] have reported observing the CHO radical as a direct product of the reaction of oxygen atoms with ethylene, propylene, and the butenes. Jones and Bayes[5] reported observing the steady state concentration of CHO in several oxygen atom-hydrocarbon reactions. The following paper reports a study of the reactions of atomic and molecular oxygen with CHO, using the approach to steady state to determine the absolute rate constants.

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Experimental

A cylindrical fast-flow reactor was coupled to a photoionization mass spectrometer, as described previously[4, 7]. Briefly, a microwave discharge in He containing a trace of N_2 generated nitrogen atoms, and then nitric oxide was added downstream to convert the N atoms to O atoms. Normally an excess of NO ($\sim 100\%$) was used to assure the complete reaction of nitrogen atoms. The ethylene was added as a mixture (3.5% C_2H_4 in He) through a movable inlet that was concentric with the oxygen atom flow. The total pressure was normally about 4 torr, as measured by an MKS pressure gage, and the linear flow velocity was 18.4 m sec^{-1}. Most experiments involved low concentrations of reactants so that no significant depletion of C_2H_4 or O occurred during the observed reaction times ($\leqq 8$ msec). All reactions were done at room temperature, 297 K.

The reacting gases were sampled through a thin Pyrex pinhole (0.2 mm diameter) into the ionization region of a quadrupole mass spectrometer. A hydrogen Lyman α lamp having a MgF_2 window was used to photoionize the free radicals. This lamp was used, instead of the krypton resonance lamp, because of less interference at mass 29 from isotopic C_2H_4. Corrections were always made for the background signal observed at mass 29 with just oxygen atoms present, and for the isotopic C_2H_4. The sensitivity of the mass spectrometer was monitored both before and after each run with known partial pressures of NO. The oxygen atom concentrations were determined by measuring the increase in the mass 30 signal when the N_2/He discharge was ex-

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tinguished. Some experiments were done using a discharge in a 0.5% O_2 in He mixture as the source of oxygen atoms. Values for the rate constants using this source of oxygen atoms were the same as those determined with the N_2/He system, but they were considered less reliable because of the presence of both $O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$.

Preliminary Experiments

Initially the reaction of oxygen atoms with formaldehyde was used as a source of formyl radicals.

$$O + CH_2O \rightarrow CHO + OH\,.$$

In order to achieve significant CHO signals it was necessary to use formaldehyde pressures of at least 1 mtorr, while in order to see the approach to steady state, oxygen atom pressures on the order of 0.2 mtorr were needed. For these conditions, with $[CH_2O] > [O]$, the OH radicals formed in the above reaction will attack another CH_2O molecule providing a secondary source of CHO [8, 9]. When the radical being measured can be formed in both a primary and secondary step, the kinetic equations become very complex and, in general, the time necessary to achieve a steady state becomes longer. For this reason, the $O + CH_2O$ reaction was not used for kinetic measurements.

The reaction of oxygen atoms with ethylene is known to form CHO, CH_3 and smaller amounts of CH_2CO [6]. Pruss, Slagle and Gutman [10] have shown that 96% of the reaction goes according to the channel,

$$O + C_2H_4 \rightarrow CHO + CH_3\,. \qquad (1)$$

This reaction would be a good source of CHO if the subsequent reactions of the methyl radical do not complicate the kinetics.

Recent work has shown that the reaction of oxygen atoms with methyl radicals is very fast [11, 12] and so the CH_3 formed in reaction (1) will react primarily with another oxygen atom. Niki, Daby, and Weinstock [13] have shown that reaction (2 a) dominates over reaction (2 b):

$$O + CH_3 \begin{array}{l} \nearrow CH_2O + H \qquad (2\,a) \\ \searrow CHO + H_2\,. \qquad (2\,b) \end{array}$$

However, when working with the methane-oxygen atom system, Jones and Bayes [5] observed significant concentrations of both CH_3 and CHO. Since the first step in the $O + CH_4$ reaction almost certainly involves the formation of methyl radicals, it was concluded that reaction (2 b), as the only probable source of CHO, could not be neglected. Subsequently it was learned that the methane used in the above experiment contained traces of ethylene and that this ethylene was responsible for the observed CH_3 and CHO. Repeating the experiment with purer methane (Matheson, 99.999%) at 337 °K (to increase the $O + CH_4$ rate constant) resulted in a net accumulation of 3131 (±282) counts in 300 seconds at mass 15 with a net signal of -213 (±225) counts in 300 seconds at mass 29. The negative signal at mass 29 means that the background count with oxygen atoms alone was slightly larger than the count with both oxygen atoms and methane present. Within the expected statistical error, the CHO signal was zero. It is concluded that the $O + CH_3$ reaction forms only formaldehyde (<5% CHO), and since the rate constant for $O + CH_2O$ is considerably slower than for ethylene [8, 9], the $O + C_2H_4$ reaction can be used as an uncomplicated source of formyl radicals.

Results

If CHO radicals are formed in reaction (1) only and are subsequently destroyed in reactions (3),

$$CHO + O \begin{array}{l} \nearrow CO_2 + H \qquad (3\,a) \\ \searrow CO + OH \qquad (3\,b) \end{array}$$

then the concentration of CHO will be governed by a differential equation of the form,

$$\frac{d[CHO]}{dt} = k_1[C_2H_4][O] - k_3\,[CHO][O]\,. \qquad (1)$$

The solution to this differential equation is,

$$[CHO] = \frac{k_1[C_2H_4]}{k_3}\,(1 - e^{-k_3[O]t}) \qquad (2)$$

where it is assumed that the reactants are mixed instantaneously at time $t = 0$, and that both [O] and $[C_2H_4]$ are not significantly depleted during the observation time. The form of Eq. (2) shows that as time increases [CHO] will approach a constant steady state value given by,

$$[CHO]_{ss} = k_1[C_2H_4]/k_3\,. \qquad (3)$$

The observed CHO signals support the kinetic equations derived above. Figure 1 shows that the observed $[CHO]_{ss}$ were proportional to the partial

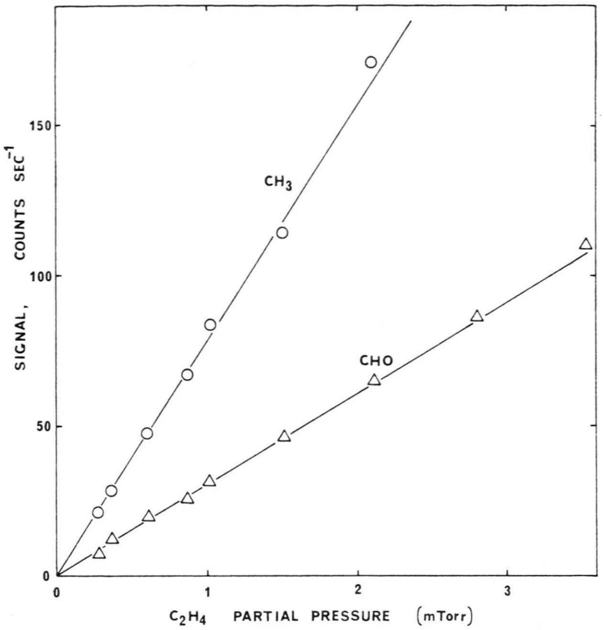

Fig. 1. The signals observed at mass 15 (CH_3) and mass 29 (CHO) vs. ethylene partial pressure. The initial oxygen atom concentration was 1.2 mtorr, the total pressure was 4.1 torr, and the reaction time was 2.8 msec.

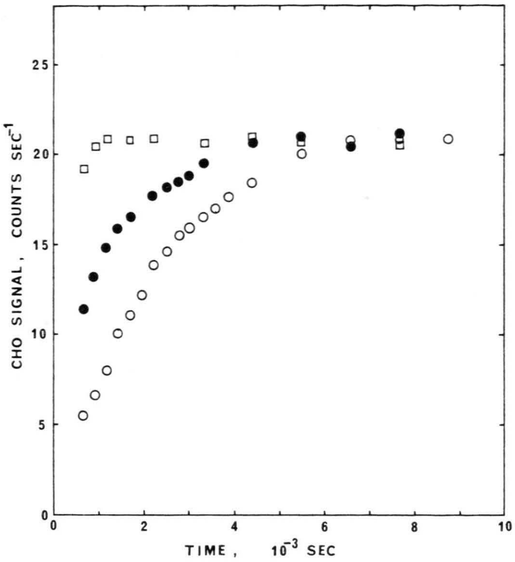

Fig. 2. The observed formyl radical signals vs. reaction time for three different oxygen atom concentrations: ○ 0.0715 mtorr; ● 0.149 mtorr; □ 0.530 mtorr. For all runs, the partial pressure of C_2H_4 was 0.54 mtorr and the total pressure was 3.83 torr.

pressure of ethylene as required by Equation (3). The time dependence of the CHO signal is shown in Fig. 2 for three different oxygen atom concentrations. At long reaction times [CHO] approaches the same final value for different oxygen atom concentrations, again in agreement with Equation (3). The fact that [CHO] does not depend on [O] is the

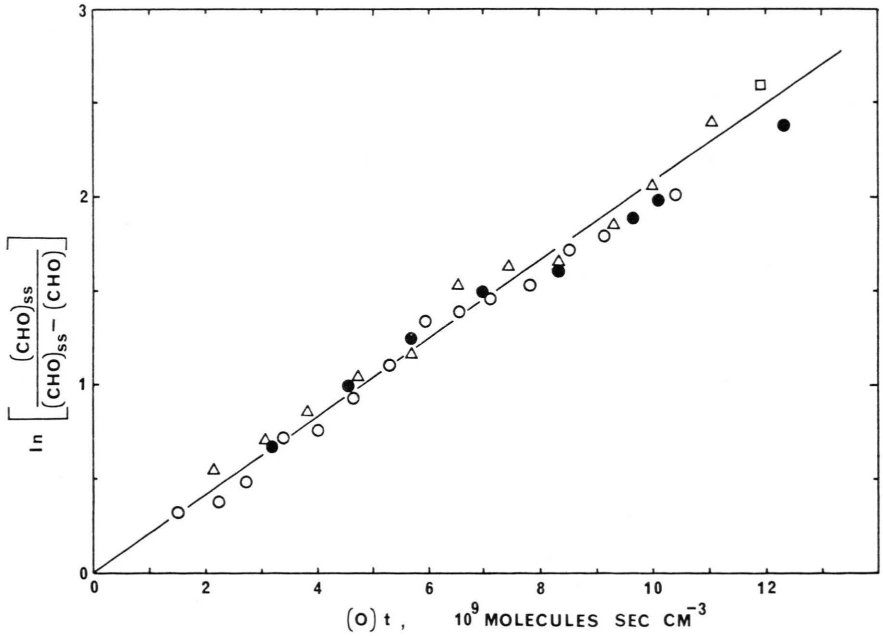

Fig. 3. The left hand side of Eq. (4) plotted against the product of oxygen atom concentration and reaction time for different oxygen concentrations: ○ 0.0715 mtorr; △ 0.101 mtorr; ● 0.149 mtorr; □ 0.530 mtorr. For all runs, the C_2H_4 partial pressure was 0.54 mtorr and the total pressure was 3.83 torr.

result of the formyl radical being formed and destroyed by reactions involving oxygen atoms.

The approach of [CHO] to its final steady state value, as shown in Fig. 2, can be used to determine the rate constant k_3. Equation (2) can be rearranged to the form,

$$\ln\left[\frac{[\mathrm{CHO}]_{ss}}{[\mathrm{CHO}]_{ss}-[\mathrm{CHO}]}\right]=k_3[\mathrm{O}]t\,. \qquad (4)$$

In Fig. 3 the left hand side of Eq. (4) is plotted against the variable $[\mathrm{O}]t$ for the data of Figure 2. The slope of the line gives a value for k_3 of $(2.1 \pm 0.4)\times 10^{-10}$ cm^3 molecules^{-1} sec^{-1}. The error limits for k_3 were derived from the estimated accuracy of absolute oxygen atom concentrations (15%), the time scale (5%), and the slope of the line in Figure 3. There are no previous determinations of k_3 with which this value can be compared.

The rate constant determined above would be in error if the formyl radicals were reacting with some component of the gas mixture other than oxygen atoms. The reaction of CHO with ethylene cannot be significant for these conditions since the points in Fig. 1 show no departure from linearity, as would be expected if ethylene participated in the destruction of CHO as well as in its formation. Except for the reactants C_2H_4 and O and the carrier gas He, the only other gases added to the flow system were N_2 and NO. Nitric oxide was added in slight excess to assure the complete conversion of nitrogen atoms to oxygen atoms. Since NO is also a free radical, it could react with CHO rapidly. This possibility was tested by adding even more NO while observing $[\mathrm{CHO}]_{ss}$ as shown in Figure 4. Even when the NO was added in large excess, there was no significant effect on the $[\mathrm{CHO}]_{ss}$. It is concluded that the rate constant for the reaction of CHO with NO is at least forty times smaller than k_3 and so the presence of NO in concentrations comparable to the oxygen atom concentration does not affect the CHO concentration.

Molecular oxygen was added to the system in order to measure the rate constant for reaction (4).

$$\mathrm{CHO} + \mathrm{O}_2 \rightarrow \text{Products}\,. \qquad (4)$$

When O_2 competes with O for CHO, the steady state formyl radical concentration should decrease. This competition would result in a Stern-Volmer type of equation,

$$\frac{[\mathrm{CHO}]^0_{ss}}{[\mathrm{CHO}]_{ss}}=1+\frac{k_4[\mathrm{O}_2]}{k_3[\mathrm{O}]} \qquad (5)$$

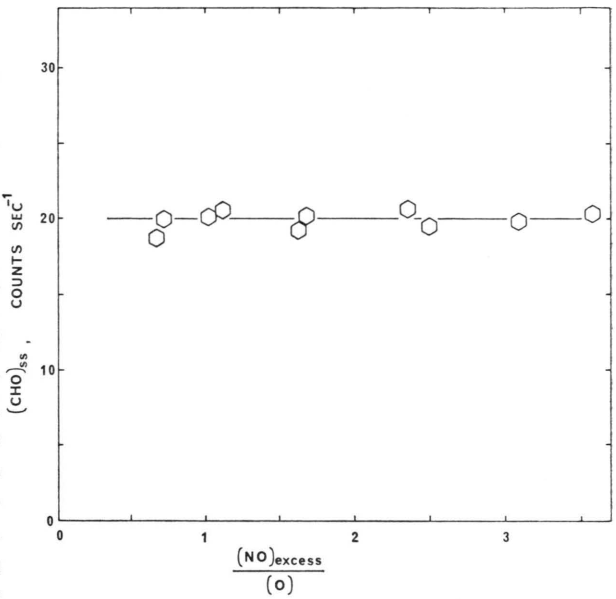

Fig. 4. The observed steady state formyl radical signal vs. the ratio of the excess NO to oxygen atom concentration. Oxygen atom partial pressure, C_2H_4 partial pressure and total pressure was 0.98 mtorr, 0.62 mtorr and 4.1 torr, respectively, and the reaction time was 1.7 msec.

where the superscript zero refers to the steady state formyl radical concentration in the absence of molecular oxygen. The observed $[\mathrm{CHO}]_{ss}$ at two different oxygen atom concentrations can be fit to this type of equation (see Fig. 5) and the slope of the line gives a value for k_4/k_3 of $(2.74 \pm 0.21)\times 10^{-2}$. Using the absolute value of k_3 determined above,

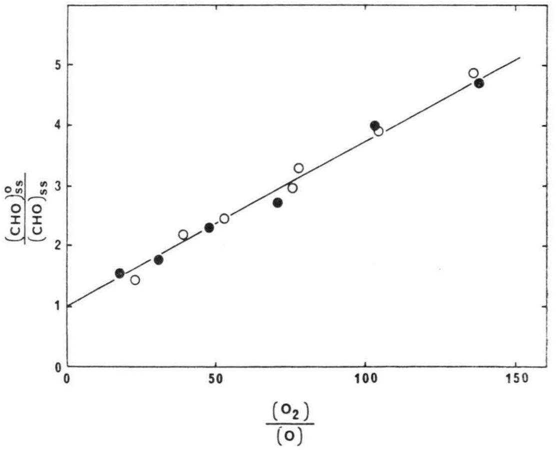

Fig. 5. The effect of molecular oxygen on the steady state formyl radical signal for two different oxygen atom concentrations: ○ 0.67 mtorr; ● 0.905 mtorr. The partial pressure of C_2H_4 was 0.67 mtorr, the total pressure was 3.85 torr, and the reaction time 1.7 msec.

the value of k_4 is calculated to be $(5.7 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. The larger fractional error in k_4 reflects the uncertainty in k_3 and the additional estimated errors in Figure 5. Similar experiments showed no variation in k_4/k_3 over the pressure range 1.5 to 5 torr and so this value for k_4 represents the two body rate constant. A previous value for k_4, derived by indirect means, does not appear reasonable[14].

Discussion

The reaction of the formyl radical with an oxygen atom is very fast, approaching the collision frequency. For comparison, the reaction of $O + NO$, which is isoelectronic with $O + CHO$, is approximately one hundred times slower, judging by its isotopic scrambling rate[15]. The large value of k_3 is probably related to the very weak $C-H$ bond in CHO.

The reaction of CHO with molecular oxygen is also quite fast. The corresponding two-body reaction of methyl radicals with O_2 is more than ten times slower[11]. This large value of k_4 suggests that even at atmospheric pressure the two-body reaction of CHO with O_2 will compete with the three-body recombination forming peroxyformyl radicals, HCO_3. At lower pressures, such as in the upper atmosphere, the two-body reaction will certainly dominate.

The products of reaction (4) are of interest. The early experiments of Faltings, Groth, and Harteck[15] showed that HO_2 is a major product, reaction (4 a).

$$CHO + O_2 \begin{cases} \nearrow HO_2 + CO & (4\,a) \\ \searrow OH + CO_2\,. & (4\,b) \end{cases}$$

However, reaction (4 b) was also suggested by Marcotte and Noyes[16] as a possible exothermic step. Work on the photooxidation of formaldehyde strongly favored reaction (4 a) over (4 b) since very little CO_2 was formed, at least at low temperatures[17]. Thus the present evidence suggests that the value of k_4 measured above refers primarily to reaction (4 a).

Using the recent values for the heat of formation of CHO, the exothermicity of reaction (4 b) is just sufficient to form OH in its first excited electronic state[18, 19]. Even though such a reaction path was very minor compared to reaction (4 a), it might explain the "cold" OH emission that is observed from the $O + O_2 + C_2H_4$ flames of Becker, Kley, and Norstrom[20]. Although it was claimed that O_2 was not involved in the reaction responsible for the "cold" OH emission, this conclusion should be reexamined in view of the ratio of k_4/k_3 measured above. Additional experiments will be needed to test the possibility that reaction (4 b) can result in OH chemiluminescence.

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