Fourier Transform Infrared Study of the Kinetics and Mechanisms for the CI-Atom- and HO-Radical-Initiated Oxidation of Glycolaldehyde

H. Niki,* P. D. Maker, C. M. Savage, and M. D. Hurley

Research Staff, Ford Motor Company, Dearborn, Michigan 48121 (Received: September 23, 1986)

The Cl-atom- and HO-radical-initiated oxidation of CH₂(OH)CHO was studied by the FTIR spectroscopic method in the steady-state photolyses ($\lambda \ge 300$ nm) of mixtures containing ppm concentrations of CH₂(OH)CHO and Cl₂, and CH₂(OH)CHO and C₂H₅ONO, respectively, in 700 Torr of N₂-O₂. HCHO and CHO-CHO were observed as major initial products in both the Cl and HO reactions. In the presence of added NO₂, the former product was partially replaced by a transient species identified as CH₂(OH)C(=O)OONO₂, while the CHO-CHO yield remained unchanged. The results are consistent with the occurrence of reactions 1a and 1b followed by the subsequent oxidation of the ensuing radicals CH₂(OH)C(=O) and CH(OH)CHO, i.e., CH₂(OH)CHO + Cl (or HO) \rightarrow CH₂(OH)C(=O) + HCl [or H₂O] (1a), CH₂(OH)CHO + Cl (or HO) \rightarrow CH(OH)CHO + HCl [or H₂O] (1b). Values for $k_{1b}/[k_{1a} + k_{1b}]$ were determined to be 0.35 and 0.22 for the Cl and HO reactions, respectively. Relative rate constants of k[Cl+CH₃CHO]/k[Cl+CH₂(OH)CHO] = 0.9 and k[HO+CH₃CHO]/k[HO+CH₂(OH)CHO] = 1.6 were also obtained.

Introduction

The possible formation of glycolaldehyde, CH₂(OH)CHO, as a reaction intermediate in the HO-radical-initiated oxidation of ethylene was first pointed out by Golden on the basis of thermochemical kinetics¹ and has subsequently been verified experimentally in this laboratory by the long-path-FTIR detection method.² Thus, $CH_2(OH)CHO$ is now recognized to be of potential importance to atmospheric chemistry.^{3,4} Reported in the present paper are the FTIR-based results on the relevant atmospheric reactions of this molecule. Notably, CH₂(OH)CHO is the lowest hydroxyaldehyde and therefore the simplest "sugar".5 Gaseous monomeric CH₂(OH)CHO is not very stable at the temperatures and sample pressures commonly used for kinetic and spectroscopic studies, e.g. >1 Torr at room temperature. As a result, prior to the above-mentioned FTIR study the only available IR spectrum of this compound in the gas phase was that recorded at 95 °C.⁵ There appears to be no previous kinetic studies of gas-phase reactions involving $CH_2(OH)CHO$ as a reactant.

By analogy with the Cl-atom- and HO-radical-initiated oxidation of $CH_3CHO,^6 CH_2(OH)CHO$ is expected to predominantly undergo H-atom abstraction of the aldehydic hydrogen followed by oxidation of the ensuing radical $CH_2(OH)CO$, as illustrated by channel A in the reaction scheme shown in Table I. However, a preliminary study revealed the formation of glyoxal, CHO-C-HO, as a conspicuous product in both the Cl and HO reactions. This suggested the occurrence of another reaction sequence, depicted by channel B in the reaction scheme of Table I. Thus, the present study was aimed at obtaining quantitative data on the kinetics and mechanism for the relevant elementary reactions.

Experimental Section

The IR absorption measurements were carried out using an FTIR system described previously.² In brief, it consists of an IDAC Model 1000 interferometer, a PDP 11/60 on-line computer, and in-house developed software. The interferometer is equipped with a liquid-helium-cooled (closed cycle, Air Products) Ge:Cu detector (Santa Barbara Research) and is capable of monitoring IR signals in the 450-4000-cm⁻¹ range with 0.03-cm⁻¹ resolution





at a scan time of less than 10 s. Spectra were derived from interferograms, ratioed against background and converted to absorbance. Typical data shown in this paper were recorded in 1.5 min (16 scans) at 0.06-cm⁻¹ resolution and transformed in 30 s. Two IR absorption cells were employed in the present study. For the generation of appropriate reference spectra, a 1-m path length Pyrex cell (50 cm long, 5 cm diameter with KBr windows and external mirrors) was used. A 180-m path length cell (3 m long, 15 cm diameter, KBr windows, internal mirrors) equipped with UV fluorescent lamps (GE F40BLB) was used for the photochemical experiments.

Reactions were carried out with ppm concentrations of reactants in 700 Torr of air. Cl atoms were generated photochemically from Cl₂ and HO radicals from RONO (R = CH₃ or C₂H₅), i.e. RONO + $h\nu$ (>300 nm) \rightarrow RO[•] + NO; RO[•] + O₂ \rightarrow HOO[•] + carbonyl product; and HOO[•] + NO \rightarrow HO[•] + NO₂.² Typical photodissociative rates of Cl₂ and RONO were determined to be

⁽¹⁾ Golden, D. M. Chemical Kinetic Data Needs for Modeling the Lower Troposphere; National Bureau of Standards: Washington, DC, 1978; NBS Spec. Publ. No. 513.

⁽²⁾ Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. Chem. Phys. Lett. 1981, 80, 499.

 ⁽³⁾ Finlayson-Pitts, B.; Pitts, Jr., J. N. Atmospheric Chemistry: Fundamentals and Experimental Techniques; Wiley-Interscience: New York, 1986.
 (4) Atkinson, R. Chem. Rev. 1986, 86, 69.

⁽⁵⁾ Michelson, H.; Klaboe, P. J. Mol. Struct. 1969, 4, 293.

⁽⁶⁾ Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. J. Phys. Chem. 1985, 89, 588.



Figure 1. Spectral data in the frequency region of 2600–3000 cm⁻¹ from the photolysis of a mixture containing Cl₂ (20 ppm) and CH₂(OH)CHO (10 ppm) in 700 Torr of air: (A) before irradiation; (B) recorded after 1 min in irradiation; (C) residual spectrum from (B) after spectral subtraction of HCHO (1.6 ppm); (D) reference spectrum of CHO–CHO (1.7 ppm).

0.5 and 0.1 min⁻¹, respectively. No detectable decay (<2%) was observed for CH₂(OH)CHO, CHO–CHO, and HCHO when irradiated individually for ca. 15 min in the presence of 700 Torr of air. Quantitative IR absorbance spectra for all the reactants and identified products were already available from numerous previous studies carried out in this laboratory.^{2.6}

Results and Discussion

Cl-Atom-Initiated Oxidation. Illustrated in Figures 1, 2, and 3 are representative spectral data obtained in the Cl-atom-initiated oxidation of CH₂(OH)CHO. Namely, Figure 1 shows the formation of HCHO and CHO-CHO in the photolysis of a mixture initially containing Cl₂ (50 ppm) and CH₂(OH)CHO (10 ppm) in 700 Torr of air. The absorbance spectra displayed in Figure 1, A and B, in the frequency range of 2600-3000 cm⁻¹ (i.e. C-H stretching region) were recorded before and after 1 min of irradiation. In Figure 1B, the evenly spaced progression of doublets belongs to H³⁵Cl and H³⁷Cl, and the fine rotational structure is largely attributable to HCHO. The residual spectrum in Figure 1C was derived from Figure 1B by subtracting the spectral contribution of HCHO (1.6 ppm). The presence of CHO-CHO (1.7 ppm) in this spectrum can be readily noted from a comparison with its reference spectrum, Figure 1D.

In Figure 2, spectral data from the same run as in Figure 1 are displayed over the entire frequency range of $700-3700 \text{ cm}^{-1}$. It can be seen from a comparison of Figure 2A and Figure 2B that 1 min of irradiation caused the decay of the initial CH₂(O-H)CHO (10 ppm) by 68% and the concomitant formation of CO (3.3), CO₂ (3.3), and HCl (6.1) in ppm units. In addition to the HCHO (1.6) and CHO-CHO (1.7) mentioned already, H₂O₂ (ca. 2), HC(O)OH (0.23), and O_3 (0.15) were the remaining products identified in this reaction. Altogether, based on the carbon balance, as much as 93% of the CH₂(OH)CHO molecules reacted could be accounted for by these products. Formation of other minor product(s) is seen in the residual spectrum, Figure 2C, which was derived from Figure 2B by subtracting spectral contributions from all the identified species. Group frequencies corresponding to C=O (1765 cm⁻¹), C-O (1094 cm⁻¹), and H-O (3605 cm⁻¹) are evident in this spectrum. Also, the band centered at 3341 cm⁻¹ is characteristic of the internally H-bonded O-H group (cf. 3300

(A) $t = 0 \min \left[H_2 C(OH) - CHO(IOppm) \right]$



Figure 2. Spectral data in the frequency region of $700-3700 \text{ cm}^{-1}$ from the same photolysis run as in Figure 1. The residual spectrum in (C) was derived from (B) by subtracting spectral contributions of all the identified products (see text).





Figure 3. Spectral data in the frequency region of 900-1400 cm⁻¹ from the photolysis of Cl_2 (20 ppm)- CH_2 (OH)CHO (23 ppm) mixture: (A) before irradiation; (B) product spectrum after 3 min of irradiation; (C) spectral subtraction of HC(O)OH from (B).

cm⁻¹ for CH₃C(O)OOH).⁶ There are other weaker but distinct bands which are not readily discernible in the residual spectrum Figure 2C. Some of these bands appearing in the frequency region of 1000–1400 cm⁻¹ are illustrated in Figure 3. Namely, the spectral data shown in Figure 3, A and B, were recorded before and after 3 min of irradiation of a mixture containing CH₂(O-H)CHO (23 ppm) and Cl₂ (20 ppm). Removal of HC(O)OH from Figure 3B revealed unidentified bands at 1094.2, 1149.5, and 1341 cm⁻¹, cf. Figure 3C. The band at 1094.2 cm⁻¹ was already mentioned and was tentatively assigned to a C–O



Figure 4. Observed concentration/time profiles for the products CO, CO₂, HCHO, and CHO-CHO in the photolysis of a mixture initially containing Cl₂ (20 ppm) and CH₂(OH)CHO (23 ppm) in 700 Torr of air.

stretching mode. The two other bands at 1149.5 and 1341 cm⁻¹ may be attributable to C-OH stretching and bending modes, respectively.7

The reaction products observed above point to the occurrence of both channel A and channel B, Table I. Among the elementary reactions listed in this table, the two series of reactions 5a-7a and 3b-5b have been studied previously.⁸⁻¹¹ Reactions 2a-4a are analogous to those involving CH₃CO[•] radicals.⁶ In particular, it should be noted that the HOO' + $CH_3C(O)OO'$ reaction has been shown to yield $CH_3C(O)OOH + O_2 (\simeq 75\%)$ and CH_3C -(O)OH + O₃ ($\simeq 25\%$).⁶ Thus, the formation of O₃ in the present system may be taken as evidence for the occurrence of the reaction HOO' + $CH_2(OH)C(O)OO' \rightarrow O_3 + CH_2(OH)C(O)OH$ and also $O_2 + CH_2(OH)C(O)OOH$, and the residual spectra in Figures 2 and 3 may be attributable to these acidic products. Furthermore, the observed O_3 yield of 2-3% and the missing carbon balance of ca. 8% of the CH₂(OH)CHO consumed are consistent with a branching ratio for these two channels comparable to that for the HOO[•] + $CH_3C(O)OO^{•}$ reaction.

Figure 4 illustrates the concentration/time profiles for the products CO, CO₂, HCHO, and CHO-CHO in a photochemical run made with a reactant mixture identical with that in Figure 3 but recorded at shorter irradiation time intervals. In this figure CO₂, HCHO, and CHO-CHO but not CO are seen to be formed in the initial stages of the photolysis. Formation of CO_2 and HCHO in comparable amounts provides further evidence for the occurrence of reactions 1a, 2a, 3a, and 5a of channel A. The initial yield of CHO-CHO in this run was determined to be 38% of the $CH_2(OH)CHO$ consumed with an estimated error limit of $\pm 5\%$. An average value of $35 \pm 5\%$ obtained from several other runs can be taken to correspond to $k_{1b}/[k_{1a} + k_{1b}]$. Also, the subsequent Cl-atom reactions of both HCHO and CHO-CHO have been shown to yield CO as the major carbon-containing product under





Figure 5. Photolysis of a mixture containing Cl₂ (20 ppm), CH₂(OH)-CHO (7.9 ppm), and NO₂ (3.4 ppm) in 700 Torr of air: (A) before irradiation; (B) after 25 s of irradiation; and (C) difference spectrum (B) - (A).

(A) Difference Spectrum (x4)



(B) Residual Spectrum CH₂(OH)C(O)OONO₂



Figure 6. Spectral desynthesis of Figure 5C: Detection of CH₂(OH)C-(O)OONO₂ in the Cl-atom-initiated oxidation of CH₂(OH)CHO in the presence of NO₂: (A) scale expansion of Figure 4C by \times 4; (B) residual spectrum from (A) corresponding to the spectrum of CH₂(OH)C(O)O-ÓNO₂.

these conditions, i.e., reactions 6a-7a and 3b-5b.9-11 Literature values for k_{6a} and k_{3b} at 289 K are 7.3×10^{-11} and 3.8×10^{-11} cm³ molecule⁻¹ s⁻¹, respectively.^{8,11} Quantitative analysis of the temporal behavior of all the products shown in Figure 4 requires knowledge of $[k_{1a} + k_{1b}]$, k_{3a} , and k_{4a} , as will be discussed later.

To further verify the reaction scheme shown in Table I, the product distribution was examined in the presence of added NO₂. Of particular interest is the detection of a labile peroxynitrate to be expected from the reaction $CH_2(OH)C(O)OO^{\bullet} + NO_2 (+M)$ \Rightarrow CH₂(OH)C(O)OONO₂ (+M) which is analogous to the NO₂ reaction of $CH_3C(O)OO^{\bullet}$ or other peroxy radicals.^{9,12} Typical

⁽⁷⁾ Avram, M.; Mateescu, GH. D. Infrared Spectroscopy: Application in Organic Chemistry; Wiley-Interscience: New York, 1972.
(8) Evaluation No. 7, NASA Chemical Kinetic and Photochemical Data for Use in Stratospheric Modeling; U.S. GPO: Washington, DC, 1985.
(9) Su, F.; Calvert, J. G.; Shaw, J. H.; Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. Chem. Phys. Lett. 1979, 65, 221.
(10) Su, F.; Calvert, J. G.; Shaw, J. H.; Phys. Chem. 1979, 83, 2185.

 ⁽¹⁰⁾ Su, F.; Calvert, J. G.; Shaw, J. H. J. Phys. Chem. 1979, 83, 3185.
 (11) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. Int. J.

Chem. Kinet. 1985, 17, 547.

results thus obtained are illustrated in Figures 5 and 6. Namely, Figures 5, A and B, corresponds to the spectra in the frequency region of 700-3700 cm⁻¹ recorded before and after 25 s of irradiation of a mixture containing Cl₂ (20), CH₂(OH)CHO (7.9), and NO_2 (3.4) in ppm units in 700 Torr of air. The short irradiation time and the low reactant conversion, cf. Figure 5C, were chosen to optimize the detection of the suspected peroxynitrate. Figure 6A is a scale-expanded display of the difference spectrum, Figure 5C, and shows more clearly the decay of the reactants $CH_2(OH)CHO$ (-0.95) and NO_2 (-1.0) and the resulting composite product spectra. Among the products identified were CO (0.08), CO₂ (0.27), HCHO (0.26), CHO-CHO (0.49), HONO₂ (0.23), HOONO₂ (0.35), ClNO₂ (0.03), and N₂O₅ (0.01) in ppm units. Thus, altogether these products amount to ca. 75% of both the $CH_2(OH)CHO$ and NO_2 consumed, and ca. 0.35 ppm each of these reactants reacted still remain unaccounted for. Figure 6B shows the residual spectrum derived from Figure 6A by removing all the above species. This spectrum exhibits bands characteristic of -OONO₂ (791, 1300, and 1747 cm⁻¹), -C=O (1831 cm⁻¹), and -OH (3600 cm⁻¹). Note, for comparison, that $CH_3C(O)OONO_2$, PAN, has bands for the $-OONO_2$ group at 794, 1302, and 1741 cm⁻¹ and for the -C=O group at 1841 cm⁻¹.^{13,14} Furthermore, this residual spectrum was shown to belong to a transient product, since, upon aging in the dark for 15 min, it disappeared completely with the concomitant formation of CO_2 and HCHO. These spectroscopic and kinetic data are consistent with the formation of the $CH_2(OH)C(O)OONO_2$ and its subsequent decay via reactions 3a and 5a. The observed decay time of this peroxynitrate in the presence of NO2 was significantly shorter than that of PAN, i.e. $\tau \simeq 50$ min at 25 °C, in the absence of NO₂.¹⁴ However, the possible decay of this polar compound via heterogeneous process on the reactor walls could not be ruled out in the present study. It should also be noted that, consistent with the reaction scheme in Table I, the CHO-CHO yield was not affected by the presence of added NO2. Namely, by analogy with the fast O_2 reaction of $CH_2(OH)$, reaction 5a,⁹ the precursor radical CH(OH)CHO is expected to be too short-lived in air to react competitively with NO₂.

The major remaining uncertainties in the reaction scheme given in Table I are the values of $[k_{1a} + k_{1b}]$, k_{3a} , and k_{4b} . Of these, $[k_{1a} + k_{1b}]$ could be determined experimentally by using the relative rate method with reference to k[Cl+CH₃CHO]. Namely, in the photolysis of a mixture containing 10 ppm each of CH₂-(OH)CHO, CH₃CHO, and Cl₂ in 700 Torr of air, k[Cl+- $CH_3CHO]/k[Cl+CH_2(OH)CHO] = 1.1$ was derived from an observed relative rate ln {[CH₃CHO]₁/[CH₃CHO]₀}/ln {[CH₂- $(OH)CHO]_{t}/[CH_{2}(OH)CHO]_{0}$. A maximum uncertainty estimated for this value was $\pm 17\%$. A value of $k[Cl+CH_2(OH)-$ CHO] = 7.0×10^{-11} cm³ molecule⁻¹ s⁻¹ can be derived from this relative rate constant combined with $k[Cl+CH_3CHO] = 7.6 \times$ 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ determined previously in this laboratory.⁶ Plausible values for k_{1a} , k_{1b} , k_{3a} , and k_{4a} were then examined by numerical simulation of the temporal data on reaction products, in particular, HCHO and CHO-CHO. One additional reaction step included in the computation was the self-reaction 2HOO[•] \rightarrow H₂O₂ + O₂,⁸ which is competitive with reaction 3a and 4a. Cl-atom concentrations were derived from the observed decay profiles of the reactant CH₂(OH)CHO together with the above-mentioned value for $[k_{1a} + k_{1b}]$. Unfortunately, the product data did not encompass a sufficiently wide range of experimental conditions to permit the unique, independent solution for k_{3a} and k_{4a} . However, it was possible to fit the data from two independent runs to the empirical relationship given by $k_{1b}/[k_{1a} + k_{1b}] = 36 \pm 4\%$ and $k_{4a} = (7.5 \pm 5.0) \times 10^{-7} (k_{3a})^{1/2}$. Previously, Addison et al. studied the Cl-atom-initiated oxidation of CH₃CHO in the Cl₂-CH₃CHO-O₂ system using the molecular modulation technique.15 Based on numerical simulation for the observed



Figure 7. Experimental vs. computed concentration/time profiles for HCHO. $k_7 = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used for the simulation (see text).

 $CH_3C(O)OO^{\bullet}$ decay, these authors derived a value of (2.5 ± 1.0) $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for the rate constant of the self-reaction $2CH_3C(O)OO^{\bullet} \rightarrow 2CH_3^{\bullet} + 2CO_2 + O_2$, which is analogous to reaction 3a. Figure 7 shows an example of the fit of a data set and also the sensitivity of k_{4a} to an arbitrarily chosen value of k_{3a} = 1×10^{-12} cm³ molecule⁻¹ s⁻¹. It appears reasonable to assume that both k_{3a} and k_{4a} are less than 1×10^{-11} cm³ molecule⁻¹ s⁻¹. According to the above relationship between k_{3a} and k_{4a} , k_{4a} is at most 4×10^{-12} for $k_{3a} = 1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. On the other hand, k_{3a} is in excess of 2×10^{-11} with a value of k_{4a} chosen to be identical with that for the HOO[•] + $CH_3OO^{•}$ reaction, i.e. $6.5 \times 10^{-12.16}$

HO-Radical-Initiated Oxidation. Glyoxal, CHO-CHO, was also observed among the products in the photolysis of mixtures containing $CH_2(OH)CHO$, NO, and RONO (R = CH_3 or C_2H_3) in ppm concentrations in 700 Torr of air, and, thus, a mechanism analogous to the Cl-atom-initiated oxidation should be operative in this system. As a prerequisite to the determination of the primary CHO-CHO yield, the rate constant for the HO reaction of $CH_2(OH)CHO$, $k[HO+CH_2(OH)CHO]$, was measured by using the relative rate with reference to $k[HO+CH_3CHO]$. Namely, in the photolysis of mixtures containing CH₂(OH)CHO, CH₃CHO, CH₃ONO, and NO in air, values for k[HO+- $CH_3CHO]/k[HO+CH_2(OH)CHO]$ were derived from the relative decay rates ln {[CH₃CHO]₁/[CH₃CHO]₀}/ln {[CH₂(OH)- $CHO]_t/[CH_2(OH)CHO]_0]$. The results are summarized in Table II. An average value of $k[HO+CH_3CHO]/k[HO+CH_2-$ (OH)CHO] = $1.6 \pm 0.15 (\sigma)$ thus obtained can be combined with a recommended value⁴ of k[HO+CH₃CHO] = (1.60 ± 0.16) × 10^{-11} cm³ molecule⁻¹ s⁻¹ to yield k[HO+CH₂(OH)CHO] = (1.0 \pm 0.2) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Notably, this value coincides with $k[HO+HCHO] = 1.0 \times 10^{-11}$ and k[HO+CHO-CHO] = $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.4}$

In the photolysis of mixtures typically containing 10 ppm each of CH₂(OH)CHO, C₂H₅ONO, and NO in air, CHO-CHO, CO₂, and HCHO were observed among the major products. The latter two products were expected from the reactions of the CH₂- $(OH)C(O)OO^{\bullet}$ radicals, i.e. $CH_2(OH)C(O)OO^{\bullet} + NO \rightarrow$ $\dot{C}H_2(OH) + CO_2 + NO_2$, and $\dot{C}H_2(OH) + O_2 \rightarrow HCHO +$

⁽¹²⁾ See, for example, Atkinson, R.; Lloyd, A. C. J. Phys. Chem. Ref. Data 1984, 13, 315

⁽¹³⁾ Stephens, E. R. Adv. Environ. Sci. 1969, 1, 119. (14) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. Int. J. Chem. Kinet. 1985, 17, 525.

⁽¹⁵⁾ Addison, M. C.; Burrows, J. P.; Cox, R. A.; Patrick, R. Chem. Phys. Lett. 1980, 73, 283.

⁽¹⁶⁾ Cox, R. A.; Tyndall, G. S. Chem. Phys. Lett. 1979, 65, 635.

TABLE II: Relative Rate Constants for the HO Reactions of CH2(OH)CHO and CH3CHO

	initial concn ^a				conversion ^b	
[gly] ₀	[ace] ₀	[CH ₃ ONO] ₀	[NO] ₀	[gly] ₁ /[gly] ₀	[ace],/[ace]0	$(k_{\rm ace}/k_{\rm gly})^c$
4.7	3.7	5.4	5.2	0.89	0.83	1.6
7.5	9.2	4.9	4.9	0.92	0.88	1.5
8.7	8.2	5.5	6.2	0.93	0.90	1.5
7.0	8.1	5.8	10.1	0.90	0.82	1.9
7.6	9.7	6.5	14.5	0.86	0.78	1.6
						$1.6 \pm 0.15 (\sigma)$

^aGiven in ppm. Diluent air at 700 Torr; gly = CH₂(OH)CHO; ace = CH₃CHO. ^bIrradiation times ranged from 3 to 15 min. ^c k_{acc} and k_{gly} denote $k[HO+CH_3CHO]$ and $k[HO+CH_2(OH)CHO]$, respectively; $k_{acc}/k_{gly} = \ln \{[ace]_i/[ace]_0]/\ln \{[gly]_i/[gly]_0\}$.

HOO'. With the irradiation time up to 10 min, the reactant $CH_2(OH)CHO$ was consumed by <25%, and the extent of the secondary HO reactions of the products HCHO and CHO-CHO were <10%. Average values for the primary yields from five runs were CHO-CHO (21.1 \pm 2.4%), CO₂ (81.3 \pm 3.2%), and HCHO $(82.4 \pm 4.6\%)$ of the CH₂(OH)CHO reacted. These values correspond to the two H-abstraction channels $HO + CH_2(O-$ H)CHO \rightarrow ĊH(OH)CHO + H₂O (ca. 20%) and CH₂(OH)ĊO + H₂O (ca. 80%). Thus, the results indicate that HO radicals are slightly more selective than Cl atoms toward abstraction of the aldehydic hydrogen.

In summary, the present study has yielded quantitative data on the kinetics and mechanism for the Cl- and HO-initiated oxidation of glycolaldehyde $CH_2(OH)CHO$ at 298 ± 2 K, and the results have been discussed with reference to the corresponding reactions of CH₃CHO. The observation of CH₂(OH)C(O)OO- NO_2 as a major product in the presence of added NO_2 may be of particular relevance to atmospheric chemistry by analogy with the well-recognized role of PAN.³ Thus, further characterization of the thermal dissociation of this PAN-type compound as well as the $CH_2(OH)CHO$ yield in the HO-initiated oxidation of C_2H_4 is warranted.

Effects of Nonequimolar Reactant Flux on the Oscillatory Oxidation of Acetaldehyde

Spencer A. Pugh[†] and John Ross^{*}

Department of Chemistry, Stanford University, Stanford, California 94305 (Received: October 17, 1986)

Some measurements are reported on the dependence of the dynamics of the oscillatory combustion of acetaldehyde in a CSTR upon reactant input rates. We map a kinetic phase diagram for the different types of behavior, stationary states and oscillations, found with nonequimolar input fluxes of acetaldehyde and oxygen. Hysteresis is observed in the transition from steady dark oxidation to oscillatory cool flames as the oxygen input flux is varied. We measure the dependence of the period and amplitude of the oscillatory cool flame light emission on both input fluxes. Under our conditions, the period of the oscillation is found to be more strongly dependent upon the acetaldehyde input rate than the oxygen input rate. These results compare favorably with calculations made with a five-variable, twelve-step model.

Introduction

The combustion of hydrocarbons, under cool flame conditions, proceeds with complex reaction mechanisms; many studies have been devoted to this subject.¹⁻⁶ Such reactions can be studied conveniently under far-from-equilibrium conditions in continuous-flow, stirred, tank reactors (CSTR); the experiments reported so far have shown the occurrence of a number of interesting nonlinear phenomena including multiple stationary states, hysteresis, and various types of oscillations in concentrations of chemical reactants, intermediates, and products; temperature; pressure; and light emission. $^{6-12}$ The oxidation of acetaldehyde has received much attention: acetaldehyde is often a significant intermediate in the combustion of many hydrocarbons;¹³⁻¹⁵ furthermore, the two-stage ignition process in this system is similar to the slow combustion phenomenon which causes knock in internal combustion engines.¹⁶

Experimental results on the variety of kinetic behavior in the autonomous combustion of acetaldehyde have been reported in a number of publications.⁷⁻¹⁰ Gray and co-workers^{8,9} have presented a kinetic phase diagram in which regions of different behavior are determined as a function of the constraints of external temperature and average pressure. Five major regions were reported: dark oxidation in which steady states are obtained; oscillatory ignitions; multistage ignitions, which are oscillatory cool

(1) Halstead, M. P.; Prothero, A.; Quinn, C. P. Combust. Flame 1973, 20, 211.

- Felton, P. G.; Gray, B. F.; Shank, N. Combust. Flame 1976, 27, 363.
 Gonda, I.; Gray, B. F. Proc. R. Soc. London, Ser. A 1983, 389, 133.
 Gibson, C.; Gray, P.; Griffiths, J. F.; Hasko, S. M. Symp. (Int.)
- Combust., [Proc.], 20th 1985, 101. (5) Wang, X.-J.; Mou, C. Y. J. Chem. Phys. 1985, 83, 4554.

(6) Pugh, S. A.; Kim, H.-R.; Ross, J. J. Chem. Phys., accepted for publication.

(7) Felton, P. G.; Gray, B. F.; Shank, N. Second European Symposium on Combustion; The Combustion Institute: Orleans, 1975. (8) Gray, P.; Griffiths, J. F.; Hasko, S. M.; Lignola, P. G. Proc. R. Soc.

London, Ser. A 1981, 374, 313

- (9) Gray, P.; Griffiths, J. F.; Hasko, S. M.; Lignola, P. G. Combust. Flame 1981, 43, 174
 - (10) Gray, B. F.; Jones, J. C. Combust. Flame 1984, 57, 3.
- (11) Caprio, V.; Insola, A.; Lignola, P.-G. Ber. Bunsen-Ges. Phys. Chem. 1980, 84, 369.
- (12) Caprio, V.; Insola, A.; Lignola, P.-G. Symp. (Int.) Combust., [Proc.], 16th 1977, 1155.
- (13) Norrish, R. G. W. Discuss. Faraday Soc. 1951, 10, 269.
- (14) Griffiths, J. F.; Firth, A.; Gray, P. Symp. (Int.) Combust., [Proc.], 15th 1975, 1493 (15) Anastasi, C.; Maw, P. R. J. Chem. Soc., Faraday Trans. 1 1982, 78,
- 2423
- (16) Smith, J. R.; Green, R. M.; Westbrook, C. K.; Pitz, W. J. Symp. (Int.) Combust., [Proc.], 20th 1985, 91.

[†]Current address: Research Laboratories, Eastman Kodak Co., Rochester, NY 14650.