Rate Coefficients for the Reactions of OH Radicals with Methylglyoxal and Acetaldehyde

GEOFFREY S. TYNDALL, THOMAS A. STAFFELBACH*,
JOHN J. ORLANDO, and JACK G. CALVERT
Atmospheric Chemistry Division, National Center for Atmospheric Research, P.O. Box 3000, Boulder Colorado 80307-3000

Abstract

Rate coefficients have been measured for the reaction of OH radicals with methylglyoxal from 260 to 333 K using the discharge flow technique and laser-induced fluorescence detection of OH. The rate coefficient was found to be $(1.32 \pm 0.30) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature, with a distinct negative temperature dependence (E/R of -830 ± 300 K). These are the first measurements of the temperature dependence of this reaction. The reaction of OH with acetaldehyde was also investigated, and a rate coefficient of $(1.45 \pm 0.25) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was found at room temperature, in accord with recent studies. Experiments in which O_2 was added to the flow showed regeneration of OH following the reaction of CH_3CO radicals with O_2. However, chamber experiments at atmospheric pressure using FTIR detection showed no evidence for OH production. FTIR experiments have also been used to investigate the chemistry of the CH_3COCO radical formed by hydrogen abstraction from methylglyoxal.

Introduction

Methylglyoxal is a key intermediate in the oxidation of isoprene, the most widely emitted hydrocarbon of biogenic origin [1]. A recent evaluation of the tropospheric oxidation mechanism of isoprene [2] suggests that around 30% of isoprene oxidized leads to the formation of methylglyoxal, making it an important albeit short-lived atmospheric component. Methylglyoxal has a fairly strong absorption spectrum in the UV-visible [3–5], and this leads to a photolysis lifetime in the atmosphere of around 2.5 h for overhead sun [3,5]. Reaction with OH is also anticipated to be a major loss process [3,6], and since photolysis and OH reaction may lead to different products it is important to quantify both these processes [5]. There have been two previous measurements of the rate coefficient for the reaction of methylglyoxal with the hydroxyl radical [3,6], both carried out at room temperature, and these two measurements differed by over a factor of two. As part of a study of the atmospheric chemistry of methylglyoxal we have measured the rate coefficient for the reaction of methylglyoxal with OH (1) between 260 and 333 K, bracketing the range of temperatures likely to be encountered in the lower troposphere.

$$OH + CH_3COCHO \longrightarrow H_2O + CH_3COCO \tag{1}$$

---

*Current address: Eidgenössische Forschungsanstalt für Agrikulturchemie und Umwelthygiene, CH-3097, Liebefeld-Bern, Switzerland.

International Journal of Chemical Kinetics, Vol. 27, 1009–1020 (1995)
CCC 0538-8066/95/101009-12

We also reinvestigated the reaction of acetaldehyde with OH (2) to validate the experimental system, and particularly to investigate the stability of aldehydes in the flow manifold.

$$\text{(2)} \qquad OH + CH_3CHO \longrightarrow H_2O + CH_3CO$$

While investigating the secondary chemistry occurring in the flow tube, evidence was found for a decomposition reaction of vibrationally excited acetylperoxy radicals to produce OH, as reported by Michael et al. [7]. Experiments were carried out both in the flow tube and in an atmospheric pressure environmental chamber to investigate the mechanism of this OH production. Some chamber experiments were also carried out at atmospheric pressure using FTIR detection to investigate the chemistry of the CH_3COCO radical formed from the reaction of methylglyoxal with OH.

Experimental

The discharge flow tube used was essentially the same as that described in a previous publication [8] with slight modifications. The flow tube itself (internal diameter 2.06 cm) had a reaction length of 1.2 meter which could be heated or cooled, and a 0.9-cm diameter sliding injector for addition of methylglyoxal. The major change made was that a length of teflon foil was inserted into the flow tube to provide an unreactive surface for the OH radicals. The presence of this teflon sleeve reduced the effective diameter of the flow tube to 1.72 (±0.03) cm. The outer surface of the sliding injector was coated regularly with halocarbon wax (Fisher Scientific Fluorolube GR-209).

The concentration of OH radicals was measured using laser-induced fluorescence near 282 nm [9]. The fluorescence chamber was machined from a stainless steel cube (length of sides 7.5 cm). It had an anodized cylindrical insert to reduce the dead volume and was fitted with baffles to reduce scattered light [8]. Radiation at 282 nm was produced by taking the output from an excimer laser pumped dye laser (Questek 2440 excimer with PDL dye laser) and doubling it using a KDP crystal. The dye laser energy varied between 2 and 5 mJ per pulse, depending on the age of the dye solution, leading to a doubled output at 282 nm of 100–200 μJ per pulse. The pulse repetition rate was 11 Hz. Laser-induced fluorescence was detected using a photomultiplier tube (Hamamatsu R374) equipped with a band pass filter transmitting at 310 ± 5 nm (Corion, Inc.). This led to the detection of radiation predominantly from $v' = 1$ of the upper electronic state, since vibrational quenching is slow at the pressures used in the flow tube. Fluorescence decays from OH were recorded using a digital oscilloscope (LeCroy 9450, 350 MHz) and averaged for 1000 laser pulses. The fluorescence decays were integrated digitally starting about 100 ns after the laser pulse to allow for RF disturbance to subside. The integrated fluorescence values (at least two per injector position) were then transferred to a spread sheet for kinetics analysis. At the beginning and end of each kinetics decay a background was taken with the laser blocked, and the integral obtained from this experiment was subtracted from each measured point to account for residual RF pick-up. The injector loss (for fixed radical source) or wall loss (for the movable source) of OH was measured regularly by monitoring the decay of OH in the absence of reactant, and this value was added to (fixed source) or subtracted from each data point, so that data from different days could be compared directly. The estimated detection limit for OH was 5×10^8 molecule cm^{-3} for 1000 pulses. The decays were corrected for axial and radial diffusion using the coefficients given by Keyser [10]. The magnitude of this correction was less than 5%.

Hydroxyl radicals were produced either by the reaction of F atoms with H_2O or by reaction of H atoms with NO_2 in the main flow tube; the atoms were produced by the action of a microwave discharge on dilute mixtures of F_2, CF_4, or H_2 in an alumina sidearm.

$$F + H_2O \longrightarrow HF + OH \tag{3}$$

$$H + NO_2 \longrightarrow NO + OH \tag{4}$$

The discharge side-arm could be attached either to the main flow tube, providing a fixed radical source, or to the movable injector for measurements with a movable radical source. Helium was bubbled through distilled water to generate the H_2O flow. The total pressure in the bubbler was monitored and the resulting flow of water vapor estimated using the saturation vapor pressure at room temperature. Fluorine was taken from a 5% mixture in helium (Spectra Gases, Inc); otherwise dilute mixtures were made up in 5-liter storage bulbs using pure gases and helium diluent. Gas flows were measured using calibrated mass flow controllers, and pressures using capacitance manometers. Total pressures in the flow tube were usually between 2.0 and 3.0 torr, using a carrier gas flow rate of typically 500 sccm, giving flow velocities of ca. 1500 cm s^{-1}. The concentration of OH was less than 4×10^{11} molecule cm^{-3} (estimated by titration with CH_3CHO), while the aldehyde was in the range $(1.3-13.2) \times 10^{12}$ molecule cm^{-3}. Sufficient time was allowed for the OH source reaction to take place before addition of the aldehyde. A large excess of the aldehyde was maintained in all cases in order that pseudo-first-order conditions prevailed. Experiments carried out using low acetaldehyde indicated that a very fast secondary reaction of OH with acetyl radicals was occurring, and that a high ratio of [aldehyde]/[OH] should be used.

The use of a teflon wall provided an inert surface for OH, and led to increased signal and better reproducibility compared to experiments in which the teflon was absent. Injector losses of OH in the absence of methylglyoxal or acetaldehyde were measured regularly and were typically 5 s^{-1}. If the injector loss increased to above 20 s^{-1}, or if the OH signal level decreased significantly due to losses on the flow tube wall, the apparatus was taken apart and washed out with HF and distilled water. The signal recovered to its original level following this procedure. For the experiments at lower temperature the moving radical source with the H + NO_2 reaction was used, since the wall loss increased as the temperature decreased. The wall loss, measured by following the decay of OH in the absence of aldehyde, was less than 20 s^{-1} even at 260 K.

Methylglyoxal was prepared, as described in a previous publication [5], by dehydrating a 40% aqueous solution (Sigma Chemicals) with P_2O_5 and distilling off the methylglyoxal. Dilute mixtures of methylglyoxal in helium were prepared in a glass bulb and their concentrations were checked regularly using UV-visible spectrometry [5]. The mixing ratio of methylglyoxal in the bulb was found to decay slowly (at a rate of typically 1% per day), with no detectable decomposition products in the UV. Traces of HCHO, CH_3CHO, HCOOH, and CH_3COOH (at the percent level) were found by infrared analysis of the aged mixtures. Acetaldehyde (Aldrich Chemicals, 99%) was degassed thoroughly by several freeze–pump–thaw cycles, then dilute mixtures were made up in helium. Ultraviolet analysis of the acetaldehyde bulbs showed no evidence for decomposition.

One concern for both methylglyoxal and acetaldehyde was that they would partially decompose on passing through a mass flow controller. In order to test this, the dilute mixture was passed through a mass flow controller and into the 90-cm UV absorption cell. The mixing ratio thus determined was identical (within 2%) to that found when the mixture was simply expanded into the absorption cell, indicating that neither methylglyoxal nor acetaldehyde was lost to a measurable extent in the mass flow controller.

Some experiments were carried out to investigate the mechanism of the oxidation of methylglyoxal using FTIR detection in a 48-liter stainless steel cell described previously [5,11]. The oxidation was initiated using Cl atoms formed in the photolysis of Cl_2 using a filtered Xe-arc lamp.

Results and Discussion

OH + Acetaldehyde

The rate coefficient for the reaction of OH with acetaldehyde was measured at room temperature in order to validate the OH detection system, and to test whether it was possible to flow aldehydes reproducibly through the manifold. The rate coefficient for this reaction is relatively well-known [7,12–19]. At other temperatures the reaction was used as a check on the reproducibility of the OH signal, but not enough systematic data were taken to be able to report reliable rate coefficients.

The initial measurements were made using the F + H_2O source, and it was found that when large amounts of CH_3CHO were added the OH concentration did not decay to zero, but rather reached a steady value estimated at about 3×10^9 molecule cm^{-3}. It is known that discharges containing fluorine atoms produce O atoms, which can react slowly with CH_3CHO to generate OH [20].

$$(5) \qquad O + CH_3CHO \longrightarrow OH + CH_3CO$$

Measurements made at low and intermediate acetaldehyde concentrations (where the OH did not have time to decay completely away) were not influenced too much by this regeneration, and these points could be corrected by adding a large excess of the aldehyde in order to determine the appropriate background to use. If a small flow of NO_2 was added to the main flow, the OH concentration decayed to zero, indicating that the O atoms had been removed via reaction (6) before the addition of acetaldehyde.

$$(6) \qquad O + NO_2 \longrightarrow O_2 + NO$$

Furthermore, the initial OH concentration increased, indicating that some H atoms were probably also being formed in the discharge. The amount of NO_2 added (or NO formed) was not sufficient to react with OH at flow tube pressures. Rate coefficients were also measured using the H + NO_2 source. This was deployed either as a fixed source, or by flowing H atoms down the injector and adding NO_2 and CH_3CHO into the main flow. Results obtained using these various source configurations agreed with one another and showed no systematic discrepancies.

Data from room temperature are shown in Figure 1 using acetaldehyde concentrations in the range $(1.4–12.0) \times 10^{12}$ molecule cm^{-3}. Unweighted linear least-squares fitting of the data gives a rate coefficient $k_2 = (1.44 \pm 0.10) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, uncertainty 2σ precision only. Including systematic uncertainties from the cross sectional area of the flow tube (4%) and flow controller and pressure calibrations (typically ±5% total) we obtain $k_2 = (1.44 \pm 0.25) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

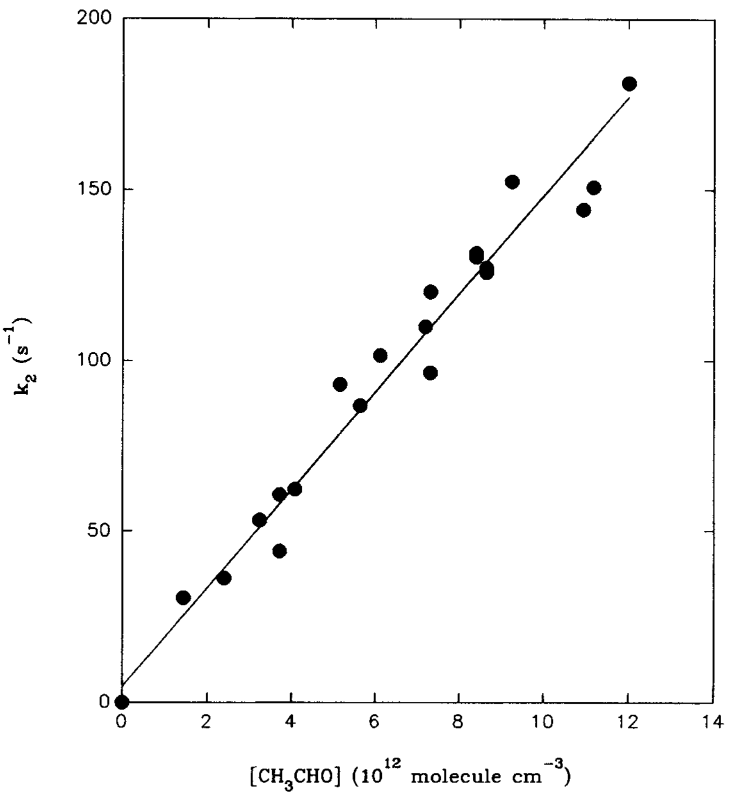

Figure 1. Second-order plot for OH + CH_3CHO at 298 K. The line is an unweighted linear least-squares fit to the data. The slope is $(1.44 \pm 0.10) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, with an intercept of 5 ± 14 s^{-1}.

Previous determinations of this rate coefficient fall in the range $(1.2-1.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} with a mean of 1.52×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Our measurement is thus in good accord with recent evaluations for this reaction [21,22], and within the combined experimental uncertainty of the most recent determinations [7,16–19]. All prior measurements of this rate coefficient are summarized in Table I of ref. [19], and are not reproduced here. Four of the earlier studies [7,14,16,17] measured the rate coefficient over a wide temperature range, and found negative activation temperatures of the order (250 ± 100) K. Over the temperature range studied here, that would correspond to only a ±10% change in rate coefficient, and not enough data were taken to be able to report a reliable determination of k_2 at these temperatures.

When an insufficient excess of CH_3CHO was used the apparent rate coefficients for OH loss increased, consistent with a reaction between OH and acetyl radicals. Since we did not have a reliable absolute calibration for OH, a measurement of this rate coefficient was not possible. There are no data available in the literature concerning such a reaction. However, some indirect evidence is contained in the work of Michael at al. [7], who reported high intercepts and ostensibly lower slopes in their second-order plots when high initial OH concentrations were used. This effect would be consistent with secondary consumption of OH at low CH_3CHO. Computer simulations of their reported pseudo-first-order loss rates for OH are consistent with a rate coefficient of $(8-10) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for OH + CH_3CO.

TABLE I. Measurements of the rate coefficient for OH with methylglyoxal.

Temperature (K)	k (10^{-11} cm^3 molecule^{-1} s^{-1})	Ref.
333	1.01 ± 0.15	this work
298	1.32 ± 0.15	this work
273	1.84 ± 0.25	this work
260	1.96 ± 0.25	this work
298	1.73 ± 0.13	[3]
298	0.71 ± 0.2	[6]

OH + Methylglyoxal

Rate coefficients were measured for the reaction of OH with methylglyoxal between 260 and 333 K. Methylglyoxal concentrations were in the range (1.3–13.2) × 10^{12} molecule cm^{-3}. Data from 33 experiments carried out at room temperature are shown in Figure 2, where all three OH sources were used. The slope of the second-order plot gives $k_1 = (1.32 \pm 0.12) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, uncertainty 2σ precision only. As mentioned in the experimental section, methylglyoxal was fairly stable in a glass bulb, decaying at a rate typically 1% per day. The actual concentration in the bulb was measured every few days using UV spectrometry, and interpolated between

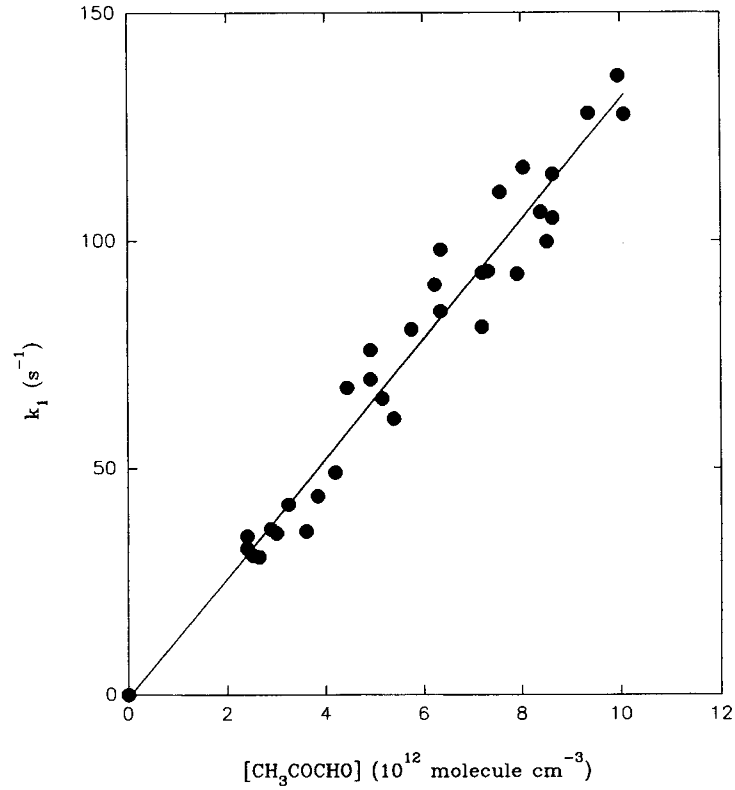

Figure 2. Second-order plot for OH + CH3COCHO at 298 K. The line is an unweighted linear least-squares fit to the data. The slope is $(1.32 \pm 0.12) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, with an intercept of -1 ± 8 s^{-1}.

these values. Infrared analysis of the contents of the bulb showed minor traces of HCOOH and CH_3COOH, neither of which reacts particularly rapidly with OH, and very low levels (approximately 1%) of HCHO and CH_3CHO, too low to interfere with the kinetics measurements. Nevertheless, in view of potential unidentified systematic uncertainties associated with the handling of methylglyoxal, we have increased the error bars larger than those in the acetaldehyde experiment. Thus at 298 K we recommend $k_1 = (1.32 \pm 0.30) \times 10^{-11}$ cm^3 molecule $^{-1}$ s^{-1}.

The data taken at 333 K were also well-behaved, with reproducible OH wall losses and very low intercepts in the second-order plots. Measurements below room temperature showed some evidence for increased losses of OH at the walls in the presence of methylglyoxal. These measurements were mostly carried out using the movable radical source, and a wall loss of 15 ± 5 s^{-1} could be measured in the absence of CH_3COCHO. At 260 K, an intercept of about 20 s^{-1} was obtained in the second-order plot, even after the appropriate wall loss for OH (measured in the absence of methylglyoxal) had been subtracted. If the methylglyoxal flow was turned off at the end of a decay, the OH signal was found to recover slowly to its initial value. Thus, the effect is probably due to reversible adsorption of methylglyoxal on the cooled surfaces of the flow tube. At 273 K the data seemed reproducible, but a small intercept can not be ruled out. Thus, these data are reported with a larger uncertainty. The rate coefficient could not be measured reliably at 248 K because of the large intercept caused by the OH wall loss. Similar complications were encountered in our recent study of the temperature dependence of the ultraviolet absorption cross sections of methylglyoxal [5]. All the data obtained on k_1 are summarized in Figure 3 and Table I.

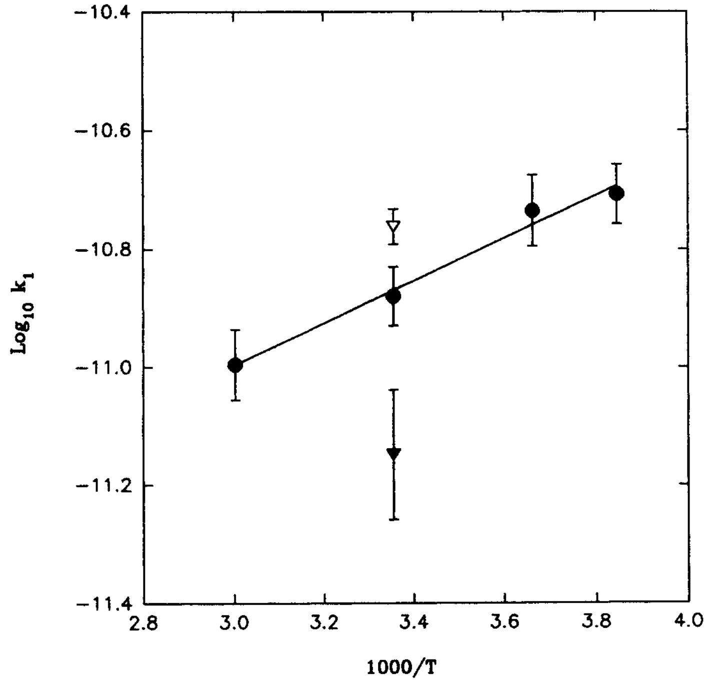

Figure 3. Arrhenius plot for OH + CH_3COCHO. Symbols: (●) this work; (▽) Plum et al. [3]; and (▼) Kleindienst et al. [6].

The Arrhenius expression best describing the data is:

$$k_1 = (8.4 \pm 1.2) \times 10^{-13} \exp((830 \pm 50)/T$$

The room temperature rate coefficient for the reaction of OH with methylglyoxal is about 20% lower than the value of 1.73×10^{-11} cm^3 $molecule^{-1}$ s^{-1} determined using the relative rate method by Plum et al. [3], and roughly twice the value obtained (7.1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) in the absolute study of Kleindienst et al. [6]. This is consistent with the hypothesis of Plum et al., that the sample of Kleindienst et al. contained some unreactive impurity. In the relative rate study of Plum et al. the OH was produced by the photolysis of CH_3ONO—NO—air mixtures. It appears that very low levels of NO were used in this study, which would presumably have been depleted during the irradiation, allowing HO_2 to build up. We have recently derived an effective rate coefficient of 1.4×10^{-15} cm^3 $molecule^{-1}$ s^{-1} for the reaction between HO_2 and methylglyoxal [5]. Reaction of HO_2 in the Plum et al. study may account for part of the discrepancy between their results and ours. Nevertheless, we consider the two measurements to be in very good agreement. No studies of the temperature dependence of this reaction have been reported previously.

The rate coefficient for OH with methylglyoxal exhibits a distinct negative temperature dependence, slightly larger than those for aliphatic aldehydes with two or more carbon atoms [16]. The explanation for the origin of this temperature dependence in what appears to be a simple hydrogen abstraction is not apparent. Semmes et al. [16] suggested that a long-lived complex may be formed. Recent theoretical articles have addressed the temperature dependences of the OH reactions with aldehydes. Soto and Page [23] predicted a barrier of 7 kcal mol^{-1} for addition of OH to the carbon atom of HCHO, and a barrier of 3.6 kcal mol^{-1} for direct abstraction. This contrasts with the measured activation energy of essentially zero. Rayez et al. considered the formation of a loose complex participating in an addition-elimination reaction in the case of acetaldehyde and its halogenated analogs [24]. They concluded that the potential wells should be shallow (2-3 kcal mol^{-1}) and that a direct abstraction would be more likely to occur. Calculated activation energies for a direct abstraction reaction are close to zero [24–26]. On substitution of hydrogen by halogen atoms the calculated activation energies increased, in accord with measurements. This was interpreted in terms of polar effects in the transition state, related to the electron-withdrawing ability of the substituent. In the case of methylglyoxal, replacement of a hydrogen atom by a conjugated acetyl group might be expected to stabilize the transition state, and lead to the negative activation energy observed here.

Acetyl + O_2

During the course of their study of OH + CH_3CHO Michael et al. [7] reported that the reaction of O_2 with acetyl radicals resulted in essentially complete regeneration of OH. We carried out several experiments to verify this observation and to investigate the mechanism further. When O_2 was added to the reactions of OH with both CH_3CHO and methylglyoxal essentially complete regeneration of OH was observed. The reaction of Cl atoms with CH_3CHO was then used to generate acetyl, and addition of around 10^{14} cm^{-3} O_2 led to rapid production of OH. Attempts to follow the time resolved production of OH were difficult due to the rapid reaction, but titration experiments using a fixed injector position and variable O_2 flows suggested a rate coefficient of at least 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The only direct study of the rate coefficient for $CH_3CO + O_2$ obtained 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [27], assuming an addition reaction to be the only mechanism occurring. The current recommendation [21] for the rate coefficient for $CH_3CO + O_2$ is 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at flow tube pressures, and 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at high pressures, by analogy with $C_2H_5 + O_2$. The reaction measured here corresponds closely with this low pressure evaluation, although the $CH_3CO.O_2$ intermediate is clearly not being stabilized at 2 torr. At the initial OH concentrations used, $< 10^{12}$ molecule cm^{-3}, it is unlikely that radical–radical chemistry involving acetylperoxy could be leading to formation of OH on the timescale observed.

In the mass spectrometric study of the $CH_3CO + O$ reaction of Miyoshi et al. [28] it was noted that addition of O_2 decreased the yields of CH_3 and CH_2CO.

$$CH_3CO + O \longrightarrow CH_3 + CO_2 \tag{7}$$

$$CH_3CO + O \longrightarrow CH_2CO + OH \tag{8}$$

This was interpreted as being due to formation of acetylperoxy, and different product ratios for its reaction with O atoms.

$$CH_3CO + O_2 + M \longrightarrow CH_3CO.O_2 + M \tag{9}$$

$$CH_3CO.O_2 + O \longrightarrow CH_3 + CO_2 + O_2 \tag{10}$$

$$CH_3CO.O_2 + O \longrightarrow CH_2CO + OH + O_2 \tag{11}$$

However, a bimolecular reaction of CH_3CO with O_2 to form entirely different products is much more likely, since if acetylperoxy is formed and reacts with O atoms, reaction (10) seems much more plausible than reaction (11).

Two mechanistic implications are possible; a pressure-independent channel which occurs in addition to the production of acetylperoxy, or a concerted mechanism in which the acetylperoxy is increasingly stabilized at higher pressure at the expense of the low pressure channel. The second type of behavior is seen in the reaction of C_2H_5 with O_2 [29,30]. The exact mechanism for the generation of OH is not determined, but an intermediate can be envisaged in which internal hydrogen abstraction occurs in the newly formed acetylperoxy radical followed by fragmentation to give OH. The remaining fragment, with the empirical formula $C_2H_2O_2$ could be a cyclic α-lactone [7], $CH_2C(O)O$, which may be expected to decompose readily to $HCHO + CO$ [31].

Experiments using methylglyoxal also showed regeneration of OH when O_2 was added to the flow tube, implying that the CH_3COCO decomposes at least partially to acetyl radicals at flow tube pressures. The behavior of CH_3COCO will be discussed in more detail in the next section.

FTIR Studies

Experiments were carried out in a large reaction chamber using FTIR detection [5,11] to see if there was any evidence that the production of OH occurs in the reaction of CH_3CO with O_2 at atmospheric pressure. These took the form of relative rate experiments, in which the rate coefficients for Cl atoms with CH_3CHO and CH_3OH were measured relative to one another. Since the reaction of OH with CH_3CHO is fifteen times faster than the reaction of OH with CH_3OH, production of OH would result in an enhanced loss of CH_3CHO when O_2 was present. No enhancement was observed, however. These kinetics measurements will be discussed in a forthcoming article on Cl atom kinetics [32]; with regard to this discussion it is only necessary to point out that at atmospheric pressure the reaction of acetyl radicals with O_2 probably proceeds exclusively by addition.

Further FTIR experiments were carried out in which Cl_2—CH_3COCHO—O_2—NO_2—N_2 mixtures were photolyzed. In these experiments the NO_2 would scavenge acyl peroxy radicals to give the corresponding peroxyacyl nitrate, PAN ($CH_3CO.O_2NO_2$) from acetylperoxy or $CH_3COCO.O_2NO_2$ from the peruvylperoxy radical.

$$RCOO_2 + NO_2 \longrightarrow RCO.O_2NO_2$$

Total pressures up to 1500 torr were used, with O_2 partial pressures between 200 and 1500 torr. Relative to the amount of methylglyoxal lost, the yields of PAN and CO were each about 90%, implying that the CH_3COCO radical largely fragments, even at the highest pressures used.

(12) $$Cl_2 + h\nu \longrightarrow Cl + Cl$$

(13) $$Cl + CH_3COCHO \longrightarrow HCl + CH_3COCO$$

(14) $$CH_3COCO \longrightarrow CH_3CO + CO$$

(9) $$CH_3CO + O_2 \longrightarrow CH_3CO.O_2$$

(15) $$CH_3CO.O_2 + NO_2 + M \longrightarrow CH_3CO.O_2NO_2 + M$$

Close examination of the spectra failed to provide unequivocal evidence for a second PAN-type molecule due to the large number of bands in the carbonyl and nitrate regions. Green et al. also concluded that the CH_3COCO radical decomposes rapidly from experiments carried out in the absence of NO_2 [33]. The observation of OH regeneration following O_2 addition in the flow tube experiments is also indirect evidence for the decomposition of CH_3COCO to CH_3CO + CO.

Atmospheric Implications

In the atmosphere methylglyoxal will be lost both by photolysis and by reaction with OH. In a recent publication we determined methylglyoxal quantum yields for photolysis in the ultraviolet and showed that the photolytic lifetime will be of the order of 2.5 h at sea level [5]. The rate coefficients for OH attack can be used to derive a corresponding lifetime of about 4 h for an OH concentration of 5×10^6 molecule cm^{-3}. Such an OH concentration is not unreasonable for continental regions of high photochemical activity where methylglyoxal would be expected to be important. Thus, both photolysis and reaction with OH need to be considered in regional atmospheric models which include methylglyoxal.

The chamber experiments described here show that abstraction of the aldehydic hydrogen atom will be accompanied by loss of a CO molecule to form the acetyl radical, which will add O_2 at atmospheric pressure to give the acetylperoxy radical. Depending on the levels of NO and NO_2 present in the atmosphere, this will either form the reservoir PAN or lead directly to CO_2 formation.

(15) $$CH_3CO.O_2 + NO_2 + M \longrightarrow CH_3CO.O_2NO_2 + M$$

(16) $$CH_3CO.O_2 + NO \longrightarrow CH_3 + CO_2 + NO_2$$

Oxidation of the methyl radical is thought to lead to CO formation via formaldehyde. Zimmerman et al. [34] have pointed out that the oxidation of biogenic hydrocarbons can be a large source of CO in the troposphere, and this can affect the ambient OH concentration. Paulson and Seinfeld [2] and Miyoshi et al. [35] have modeled the ratio of CO to CO_2 formed in isoprene oxidation, using assumed photolysis rates and products for methylglyoxal. We have recently studied the photolysis of methylglyoxal at room temperature, and found the dominant process to be fission of the C—C bond between the two carbonyl groups [5].

(17) $$CH_3COCHO + h\nu \longrightarrow CH_3CO + HCO$$

(9) $$CH_3CO + O_2 \longrightarrow CH_3CO.O_2$$

(18) $$HCO + O_2 \longrightarrow HO_2 + CO$$

Thus, in terms of regional photochemical reactivity, the ratio of $CO{:}CO_2$ per methylglyoxal lost should be the same for both photolysis and OH reaction. The main difference is that the photolysis will result in the production of two free radicals, and hence increase ozone productivity, whereas the OH reaction leads to no net change in the number of free radicals. The overall mechanism and atmospheric implications are discussed in more detail in the paper by Staffelbach et al. [5].

Acknowledgment

The authors thank Chris Cantrell and Lee Mauldin for their careful reading of the manuscript. This work was supported in part by the Coordinating Research Council, project AQ-2-1. NCAR is sponsored by the National Science Foundation.

Bibliography

[1] B. Lamb, A. Guenther, D. Gay, and H. Westberg, *Atmos. Environ.*, **21,** 1695 (1987).
[2] S.E. Paulson and J.H. Seinfeld, *J. Geophys. Res.*, **97,** 20,703 (1992).
[3] C.N. Plum, E. Sanhueza, R. Atkinson, W.P.L. Carter, and J.N. Pitts, Jr., *Environ. Sci. Tech.*, **17,** 479 (1983).
[4] R. Meller, W. Raber, J.N. Crowley, M.E. Jenkin, and G.K. Moortgat, *J. Photochem. Photobiol. A: Chem.*, **62,** 163 (1991).
[5] T.A. Staffelbach, J.J. Orlando, G.S. Tyndall, and J.G. Calvert, *J. Geophys. Res.*, in press.
[6] T.E. Kleindienst, G.W. Harris, and J.N. Pitts, Jr., *Environ. Sci. Tech.*, **16,** 844 (1982).
[7] J.V. Michael, D.G. Keil, and R.B. Klemm, *J. Chem. Phys.*, **83,** 1631 (1985).
[8] G.S. Tyndall, J.J. Orlando, C.A. Cantrell, R.E. Shetter, and J.G. Calvert, *J. Phys. Chem.*, **95,** 4382 (1991).
[9] G.L. Vaghjiani and A.R. Ravishankara, *J. Phys. Chem.*, **93,** 1948 (1989).
[10] L.F. Keyser, *J. Phys. Chem.*, **88,** 4750 (1984).
[11] R.E. Shetter, J.A. Davidson, C.A. Cantrell, and J.G. Calvert, *Rev. Sci. Instrum.*, **58,** 1427 (1987).
[12] E.D. Morris, Jr., D.H. Stedman, and H. Niki, *J. Am. Chem. Soc.*, **93,** 3571 (1971).
[13] H. Niki, P.D. Maker, C.M. Savage, and L.P. Breitenbach, *J. Phys. Chem.*, **82,** 132 (1978).
[14] R. Atkinson and J.N. Pitts, Jr., *J. Chem. Phys.*, **68,** 3581 (1978).
[15] J.A. Kerr and D.W. Sheppard, *Environ. Sci. Tech.*, **15,** 960 (1981).
[16] D.H. Semmes, A.R. Ravishankara, C.A. Gump-Perkins, and P.H. Wine, *Int. J. Chem. Kinet.*, **17,** 303 (1985).
[17] S. Dóbé, L.A. Kachatryan, and T. Berces, *Ber. Bunsenges. Phys. Chem.*, **93,** 847 (1989).
[18] C. Balestra-Garcia, G. LeBras, and H. MacLeod, *J. Phys. Chem.*, **96,** 3312 (1992).
[19] D.J. Scollard, J.J. Treacy, H.W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. LeBras, H. MacLeod, and S. Téton, *J. Phys. Chem.*, **97,** 4683 (1993).
[20] M. Bartels, J. Edelbüttel-Einhaus, and K. Hoyermann, *Twenty-Third Symposium (International) on Combustion,* The Combustion Institute, 131, 1990.

[21] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, J.A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data,* **21,** 1125 (1992).

[22] W.B. DeMore, S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.R. Kolb, and M.J. Molina, NASA JPL Publication 92-20 (1992).

[23] M.R. Soto and M. Page, *J. Phys. Chem.,* **94,** 3242 (1990).

[24] M.T. Rayez, J.C. Rayez, T. Berces, and G. Lendvay, *J. Phys. Chem.,* **97,** 5570 (1993).

[25] M.T. Rayez, D.J. Scollard, J.J. Treacy, H.W. Sidebottom, C. Balestra-Garcia, S. Téton, and G. LeBras, *Chem. Phys. Lett.,* **223,** 452 (1994).

[26] J.S. Francisco, *J. Chem. Soc. Faraday Trans.,* **88,** 1943 (1992).

[27] C.E. McDade, T.M. Lenhardt, and K.D. Bayes, *J. Photochem.,* **20,** 1 (1982).

[28] A. Miyoshi, H. Matsui, and N. Washida, *J. Phys. Chem.,* **93,** 5813 (1989).

[29] A.F. Wagner, I.R. Slagle, D. Sarzynski, and D. Gutman, *J. Phys. Chem.,* **94,** 1853 (1990).

[30] E.W. Kaiser, T.J. Wallington, and J.M. Andino, *Chem. Phys. Lett.,* **168,** 309 (1990).

[31] O.L. Chapman, P.W. Wojtkowski, W. Adam, O. Rodriquez, and R. Rucktäschel, *J. Amer. Chem. Soc.,* **94,** 1365 (1972).

[32] G.S. Tyndall, J.J. Orlando, C.S. Kegley-Owen, T.J. Wallington, and M.D. Hurley, in preparation.

[33] M. Green, G. Yarwood, and H. Niki, *Int. J. Chem. Kinet.,* **22,** 689 (1990).

[34] P.R. Zimmerman, R.B. Chatfield, J. Fishman, P.J. Crutzen, and P.L. Hanst, *Geophys. Res. Lett.,* **5,** 679 (1978).

[35] A. Miyoshi, S. Hatakeyama, and N. Washida, *J. Geophys. Res.,* **99,** 18,779 (1994).

Received February 6, 1995
Accepted April 7, 1995