nonlinear least-squares kinetic treatment of the experimental absorption traces. The results are thus based on the knowledge of exact absorption cross sections of the peroxy radicals.

A new terminating reaction route for the reaction between CH_3COO_2 and CH_3O_2 radicals has been proposed:

$$CH_3COO_2 + CH_3O_2 \rightarrow CH_3COOH + HCHO + O_2 \qquad (3b)$$

The results show that the reactions between CH_3COO_2 and CH_3O_2 radicals produce organic acids. These reactions might be a source of organic acid formation (especially CH_3COOH) in the remote regions of the troposphere, where at lower NO concentrations (<10 ppt), reactions between peroxy radicals predominate.

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Registry No. CH_3COO_2, 36709-10-1; CH_3O_2, 2143-58-0.

Kinetics and Mechanism of the Photooxidation of Formaldehyde. 1. Flash Photolysis Study

Bernard Veyret,* Robert Lesclaux, Marie-Thérèse Rayez, Jean-Claude Rayez,

Laboratoire de Chimie Physique A (UA 348 and 503, CNRS), Université de Bordeaux 1, 33405 Talence Cedex, France

Richard A. Cox,*

Combustion Centre, Harwell Laboratory, Didcot, Oxfordshire, UK

and Geert K. Moortgat*

Air Chemistry Department, Max Planck Institut für Chemie, D 6500 Mainz, FRG *(Received: March 31, 1988; In Final Form: September 12, 1988)*

Transient species in the photooxidation of formaldehyde in air have been investigated by using the technique of flash photolysis kinetic spectroscopy. The absorption spectrum attributed to the $HOCH_2O_2$ radical was observed with a maximum near 230 nm. This radical is formed by the reaction $HO_2 + HCHO \Leftrightarrow HOCH_2O_2$ (1, −1). The rate constants were measured for the two reactions: $k_1 = 7.7 \times 10^{-15} \exp[(625 \pm 550)/T]$ cm^3 molecule^{-1} s^{-1} and $k_{-1} = 2.0 \times 10^{12} \exp[(-7000 \pm 2000)/T]$ s^{-1}. The equilibrium constant is $K_1^* = 3.85 \times 10^{-27} \exp(7625/T)$ cm^3 molecule^{-1}, which corresponds to a reaction enthalpy $\Delta H_1^\circ = -16.25 \pm 0.30$ kcal mol^{-1}, which is based on the K_p value and quantum calculations of ΔS_0° and therefore determined accurately. Kinetic measurements performed under various experimental conditions allowed determinations of the rate constants for the reactions $HO_2 + HOCH_2O_2 \rightarrow$ products (3) and $2HOCH_2O_2 \rightarrow O_2 + CH_2(OH)_2 + HCOOH$ (4b); $k_3 = 5.6 \times 10^{-15} \exp[(2300 \pm 1100)/T]$; $k_{4b} = 5.65 \times 10^{-14} \exp[(750 \pm 400)/T]$ cm^3 molecule^{-1} s^{-1}. The branching ratios for k_3 and k_4 were determined in separate experiments described in part 2 of this work.

Introduction

The mechanism of the photooxidation of formaldehyde has been investigated by a number of groups in recents years[1-6] in view of its importance for atmospheric chemistry. At low-parts-per-million concentrations, CO and H_2O_2 are the major products. At higher HCHO concentrations, formic acid is formed together with smaller amounts of a peroxide identified as $HOCH_2O_2H$.[1-3] The following mechanism based on an addition reaction of HO_2 with HCHO has been proposed to explain these products:

$$HO_2 + HCHO \Leftrightarrow [HO_2CH_2O] \Leftrightarrow HOCH_2O_2\ (=RO_2) \qquad (1)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (2)$$

$$HO_2 + RO_2 \rightarrow HOCH_2O_2H\ (=RO_2H) + O_2 \qquad (3a)$$

$$RO_2 + RO_2 \rightarrow 2RO + O_2 \qquad (4a)$$

$$\rightarrow HCOOH + ROH + O_2 \qquad (4b)$$

$$RO + O_2 \rightarrow HCOOH + HO_2 \qquad (5)$$

Further support for the formation of the RO_2 radical comes from the observation of the product, $HOCH_2O_2NO_2$ (hydroxymethyl peroxynitrate) when the $HO_2 + HCHO + NO_2$ system was investigated.[6]

In a recently reported study[7] the equilibrium constant K_1^* was determined by cryotrapping HO_2 and RO_2 radicals and measuring their concentration by ESR spectroscopy.

The proposed radical species have not been detected in the gas phase, and there are no direct determinations of the rate constants for any of the reactions 3–5. Such estimates that have been made are based on product yields[3] and time-resolved studies of product formation.[4,6] There is a need for further studies of the kinetics and equilibrium constant in this system by direct gas-phase measurements of HO_2 and RO_2 concentrations.

In this paper we report the results of the study of the HO_2 + HCHO system using flash photolysis with long path absorption spectroscopy in the ultraviolet spectral region to investigate transient spectra and kinetics.

The HO_2 radical was produced by flash photolysis of Cl_2 in the presence of HCHO and O_2 where the following fast reactions occur:

$$Cl_2 + h\nu \rightarrow 2Cl \qquad (6)$$

$$Cl + HCHO \rightarrow HCl + HCO \qquad (7)$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (8)$$

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The subsequent addition of HO_2 to HCHO was expected to form the peroxy radical $HOCH_2O_2$ via reaction 1. The existence of this radical was demonstrated in this work by the observation of its UV spectrum in the presence of large amounts of HCHO. The approach to equilibrium and the kinetics of the subsequent reactions were investigated by monitoring the time-resolved absorptions at various wavelengths. Other complementary experiments were carried out with the technique of modulation photolysis long path kinetic spectroscopy. These experiments allowed for a separate measurement of K_1^* and for the kinetic study and product analysis of the reactions of the RO_2 radical. These results are described in part 2 of this publication.[8]

Experimental Section

The kinetics of the reaction of HO_2 with HCHO was studied by time-resolved absorption spectroscopy using the flash photolysis technique. A complete description of the apparatus has already been given elsewhere.[9] The reactant gas mixture flows through a thermostated Pyrex cell (−44 to +130 °C). Two flash lamps are used, with up to 600 J of flash energy delivered in a 5-μs pulse. The analyzing beam from a deuterium lamp passes through the cell twice (139 cm total path length) and is dispersed in a monochromator (1- or 2-nm bandpass). The signal from the photomultiplier detector is fed to a transient recorder and accumulated in a microcomputer, which can then process and store the absorption signal.

In order to obtain a good signal to noise ratio, the absorption time profiles were accumulated 10–40 times for each experiment. The gases were continuously flowed through the cell to avoid photolysis of the products. Chlorine (2% in nitrogen) was mixed with synthetic air (99.95% L'Air Liquide) and flowed directly into the cell. Cl_2 concentration was measured by its absorption at 330 nm. Formaldehyde was produced by heating paraformaldehyde at 375 K and was carried into the cell in a stream of oxygen through a trap at 196 K to remove water. The total pressure in the cell was set between 85 and 170 Torr. Typical concentrations of reactants, in molecule cm^{-3}, were as follows:

$$[Cl] = 3 \times 10^{16};\quad [O_2] = (3\text{–}6) \times 10^{17};$$
$$[HCHO] = (1\text{–}9) \times 10^{16}$$

Initial concentrations of HO_2 of up to 1×10^{14} molecule cm^{-3} were produced in the flash. Formaldehyde concentrations in the reaction vessel were measured in situ by UV absorption spectroscopy at 303.8 nm. The effective cross section was determined experimentally by using known pressures of pure HCHO. The value $\sigma = 6.0 \times 10^{-20}$ cm^2 $molecule^{-1}$ is in good agreement with the literature value[10] when the difference in spectral resolution is taken into account. Transient absorption curves were recorded in the wavelength range 200–270 nm. Most kinetic experiments were repeated at two wavelengths for the same conditions of concentrations and photolysis intensity. The wavelengths used were 210 nm at the maximum of the HO_2 radical spectrum and 250 nm where HO_2 absorbs weakly and RO_2 was found to absorb strongly.

The time decays for a given pair of runs were analyzed by computer simulation, using various sets of values for k_1–k_4. Both the shape of the absorption–time curves and the absolute optical density were fitted, thereby increasing the overall accuracy. The sensitivity of the fit to the values chosen for k_{1-4} depended on the initial concentration of radicals and hence on the absorption cross sections that were used (see below), the formaldehyde concentration, and the temperature (varied from 275 to 333 K). By successive trial and error at a given temperature, a consistent set of values for the rate constants was determined and a margin of error was obtained for each rate constant at each temperature.

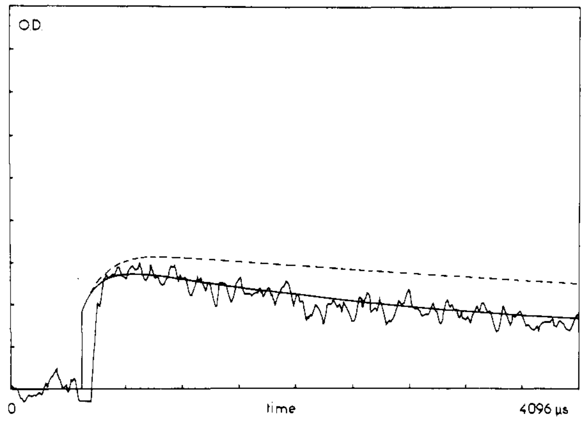

Figure 1. Cross section determination of $HOCH_2O_2$ at 240 nm. Initial $[HO_2] = 8.3 \times 10^{16}$ molecule cm^3. The simulations correspond to $\sigma = (3.6 \pm 0.3) \times 10^{-18}$ cm^2 $molecule^{-1}$ (solid line, $k_3 = 1.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; dashed line, $k_3 = 0$).

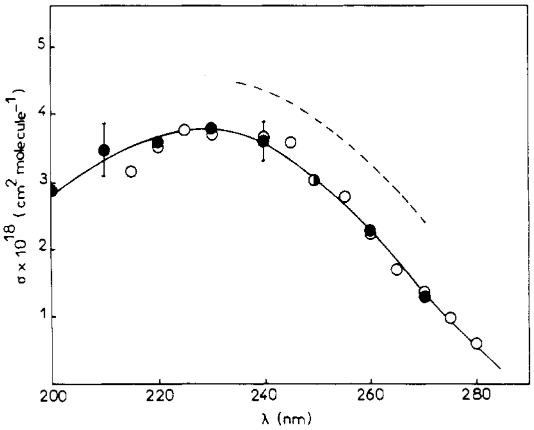

Figure 2. UV spectra for the $HOCH_2O_2$ radical normalized at 250 nm (line through the circles). Experimental method: open circles, molecular modulation spectroscopy;[8] closed circles, flash photolysis). The liquid-phase spectrum by Rabani et al.[16] is also shown (dashed line).

A quantum-mechanical study was undertaken in order to support the experimental results by allowing the estimation of some of the *A* factors for the postulated elementary steps involved in equilibrium 1. The UHF MINDO/3 method[11,12] was used to calculate the energies, the geometries, and the vibrational frequencies of the stable species and transition states (saddle points of the lowest potential energy surfaces). These quantities were then used in the calculation of the partition functions of the relevant species. Systematic studies[13–15] of the capability of the MINDO/3 method to provide reliable vibrational frequencies have shown a satisfactory overall agreement, within 10%, between the uncorrected calculated values and the experimental ones.

Results

Absorption Spectrum and Cross Section of the Hydroxymethylperoxy Radical. On the basis of analogy with other organic peroxy radicals it was anticipated that the RO_2 radical formed following the addition of HO_2 to HCHO in reaction 1 would exhibit an absorption spectrum in the 200–300 nm region. The UV spectrum was investigated by using a high concentration of formaldehyde, thereby ensuring that the HO_2 contribution to the transient absorption spectrum was minimized and that the equilibrium would be attained rapidly due to the fast forward rate of reaction 1. The assumption that the equilibrium was sufficiently

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displaced in these conditions was verified in independent measurements of the equilibrium constant (see below).

Mixtures of HCHO (8.3×10^{16} molecule cm^{-3}), air, and Cl_2 (6.0×10^{16} molecule cm^{-3}) were photolyzed and the initial optical density was measured at different wavelengths. A typical absorption–time profile at 240 nm is shown in Figure 1. Strong absorption was observed throughout the 200–270-nm region with a maximum at about 230 nm. In view of this observation of a UV absorption spectrum similar to that of other peroxy radicals and of the lifetime for the buildup of the absorption, the transient species was assumed to be the hydroxymethylperoxy radical. A slow decay in absorption was observed, which was attributed to the self-reaction of this radical, and the initial absorption could be obtained from a short back-extrapolation of the curve to $t = 0$. The absorption spectrum obtained is shown in Figure 2.

The absolute absorption cross section for the RO_2 radical was determined relative to that of the HO_2 radical at 210 nm. The value $\sigma_{HO_2} = 4.9 \times 10^{-18}$ cm^2 molecule^{-1}[16] was used as a reference, but there is still some disagreement on this value ($\sigma = 5.3 \times 10^{-18}$ and 4.3×10^{-18} cm^2 molecule^{-1} from our own measurements[9] and from the latest NASA compilation[17]) and the cross section values of RO_2 are thus uncertain as well. Depending on the actual value of σ_{HO_2}, the values of the rate constants for reactions 3 and 4 will be modified accordingly, but the first-order rate constants 1 and −1 will not be affected. The initial concentration of HO_2 was determined from back-extrapolation of the 210-nm absorption to $t = 0$ when mixtures with reduced formaldehyde concentration ([HCHO] = 1.6×10^{16} molecule cm^{-3}) were photolyzed with the same flash energy and Cl_2 concentration as those having high HCHO concentration. Under these conditions, conversion of HO_2 to RO_2 is slow and absorption at short delay times is mainly due to HO_2. Alternatively CH_3OH was used instead of HCHO to scavenge Cl atoms and produce HO_2 via the reactions

$$Cl + CH_3OH \rightarrow HCl + CH_2OH$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$

Measurements of optical density at 240 nm at $t = 0$ were then made at a higher formaldehyde concentration favoring RO_2 production and the absolute absorption coefficient determined, assuming that HO_2 was converted quantitatively to RO_2. Subsequent determination of the rate coefficients for the HO_2 and RO_2 reactions dictated a small correction to the cross section due to the loss of radicals via the fast cross reaction between HO_2 and RO_2 that occurred on the time scale of the conversion of HO_2 to RO_2. An example of the simulation of a decay curve used to determine the cross section of RO_2 at 240 nm is shown in Figure 1. It will be seen that the cross section is quite well determined with a value of $\sigma = (3.6 \pm 0.3) \times 10^{-18}$ cm^2 molecule^{-1} at 240 nm and a maximum of 3.75×10^{-18} cm^2 molecule^{-1} at around 230 nm. The correction was applied at all wavelengths to give the cross sections plotted in Figure 2.

Equilibrium Constant K_1^*. The equilibrium constant K_1^* was determined from measurements at 210 and 240 nm of the forward and reverse rate constants from the time-resolved absorption in the flash photolysis of Cl_2–HCHO–O_2 mixtures for different concentrations of formaldehyde. HO_2 is formed following the flash, and equilibrium is reached with a time constant τ, given by

$$\tau = 1/(k_1[HCHO] + k_{-1})$$

At low temperature (275 K) and HCHO concentrations of $(1.3–2.1) \times 10^{16}$ molecule cm^{-3}, the reverse rate was apparently quite slow and the forward rate (1000–1700 s^{-1}) could be measured from observation of the time dependence and magnitude of absorption at 240 nm during the first 4 ms following the flash. The kinetics were complicated by the fact that significant loss of radicals occurred on the same time scale via the rapid reaction

$$HO_2 + RO_2 \rightarrow \text{products} \qquad (3)$$

In order to describe the observed absorptions at 210 and 240 nm, it was necessary to specify the value of k_3 (see below) and the initial HO_2 concentration. A model of the chemistry involving reactions 1–5 was then used to simulate the experiments, and k_1 and k_{-1} were varied to give the best fit. Figure 3a shows the buildup of $HOCH_2O_2$ at 250 nm for an experiment with initial [HO_2] = 4.7×10^{13} molecule cm^{-3}. The average best fit value for k_1 from three experiments was $(8.0 \pm 2.0) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 275 K. At this temperature the value of k_{-1} was undetermined ($k_{-1} < 100$ s^{-1}).

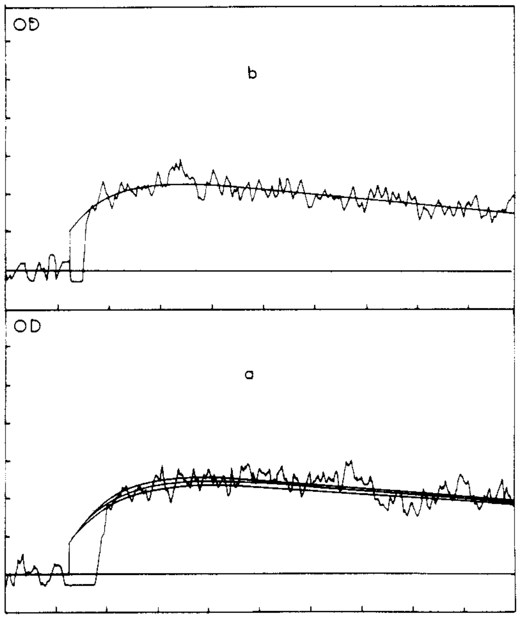

Figure 3. Kinetic simulations performed at 275 and 333 K (a and b, respectively). The wavelength is 250 nm and the rate constant values are as follows: plot a, $k_1 = (7.6 \pm 0.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, $k_3 = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and [HCHO] = 1.36×10^{16} molecule cm^{-3}; plot b, $k_1 = 5.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, $k_{-1} = 1300$ s^{-1}, $k_3 = 6.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and [HCHO] = 1.76×10^{16} molecule cm^{-3}.

TABLE I: Kinetics Measurements of k_1 and k_{-1} as a Function of Temperature

T, K	$10^{14}k_1$, cm^3 molecule^{-1} s^{-1}	k_{-1}, s^{-1}
275	8.0 ± 2.0	≈30
295	6.0 ± 0.7	100 ± 50
308	6.2 ± 0.8	200 ± 100
323	5.7 ± 0.8	800 ± 100
333	5.1 ± 0.6	1350 ± 300

Similar experiments were performed at 295, 308, 323, and 333 K. The signal to noise ratio was rather low due to the short acquisition times dictated by the difficulty in maintaining constant [HCHO] over long periods. The accuracy of the kinetic determinations was provided by the consistency between the results obtained in numerous experiments performed under various experimental conditions. As the temperature increased, the accuracy of the determination of k_{-1} increased and kinetic complication due to reaction 3 became less troublesome because of the decline in k_3 with temperature. Figure 3b shows simulations of an experiment at 333 K with initial [HO_2] = 6.9×10^{13} molecule cm^{-3}. A good fit was obtained with $k_1 = 5.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, i.e. lower than at 275 K, and k_{-1} was well defined at 1300 ± 200 s^{-1}.

The results of these determinations of k_{-1} and k_1 at the five temperatures investigated are summarized in Table I and in Figure 4, which shows an Arrhenius plot of these rate coefficients. The

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(16) De More, W. B.; Margitan, J. J.; Molina, M. J.; Watson, R. T.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling*; Evaluation No. 7; J.P.L. Publication, 1985, 85-37.

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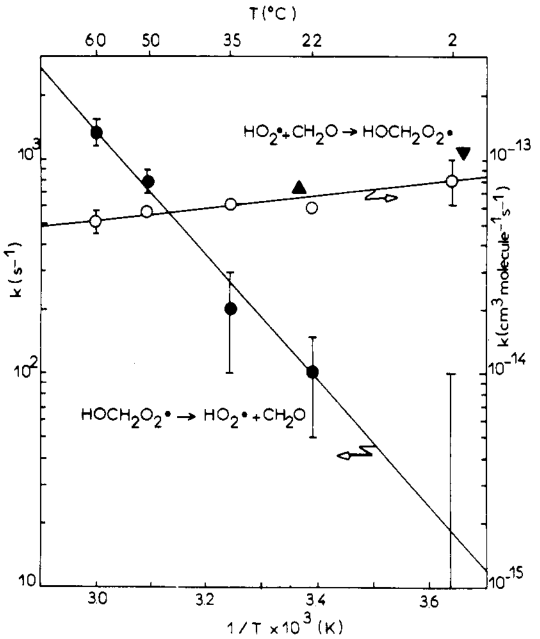

Figure 4. Arrhenius plot for k_1 and k_{-1}. The errors bars correspond to the acceptable limits in fitting the experiments. Key: ▲, data from ref 4; ▼, data from ref 6.

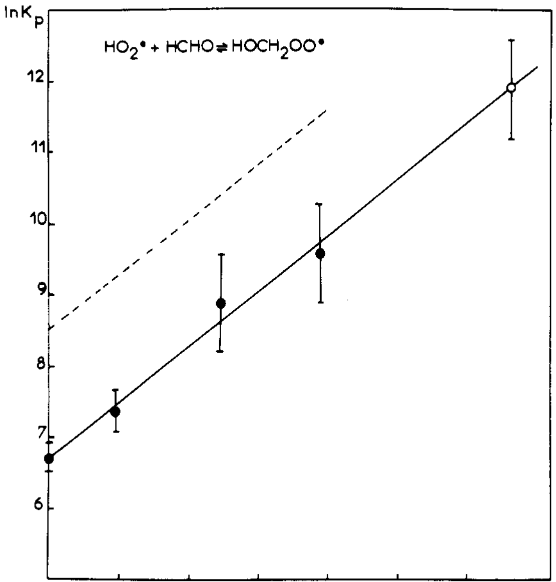

Figure 5. Temperature dependence of the equilibrium constant (open circle from ref 6, dashed line from ref 7). The linear least-squares treatment includes the data of ref 6.

error bars show estimated experimental errors in the determination of the rate constant values and do not include any contribution from possible systematic errors. The temperature dependences are given by the following expressions for the rate constants:

$$k_1 = 7.7 \times 10^{-15} \exp[(625 \pm 550)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_{-1} = 2.0 \times 10^{12} \exp[(-7000 \pm 1800)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

(where the errors margins include the possible systematic errors), and for the equilibrium constant:

$$K_1{}^* = k_1/k_{-1} = 3.85 \times 10^{-27} \exp(7625/T)\ \text{cm}^3\ \text{molecule}^{-1}$$

In order to evaluate the standard enthalpy and entropy change in the reaction, a plot of $K_p = K_1{}^*(RT)^{-1}$ atm^{-1} vs $1/T$ was constructed, and $\Delta H_1{}^\circ$ and $\Delta S_1{}^\circ$ at 298 K were determined from the slope and intercept. The data are shown in Figure 5 together with a K_p value at 273 K obtained from a previous measurement of $K_1{}^*$ by Barnes et al.[6] from studies of the thermal reaction between HO_2NO_2 and HCHO. This result is seen to agree well with the extrapolation from the present results. In the same Figure 5 is plotted the Arrhenius curve for $K_1{}^*$ obtained by Zabel et al.,[7] which has a slope that is the same within experimental error as that obtained in this study.

TABLE II: Calculated Entropy and Enthalpy Changes in Reaction 1 (in eu and kcal mol^{-1}, Respectively)

	S°_{298}			
method	HO_2	HCHO	RO_2	ΔS°_{298}
MINDO/3[a]	54.42	52.20	71.27	−35.35
Benson[17]	54.4	52.3	73.0	−33.6
	$\Delta H_f{}^\circ$			
method	HO_2	HCHO	RO_2	ΔH°_{298}
MINDO/3[a]	−3.4	−25.6	−45.9	−16.9
Benson	5.2	−26.0	−39.8[b]	−19.0
exptl	3.5[c]	−26.0		−16.25

[a] UHF calculations for the radicals. [b] Reference 18. [c] Reference 20.

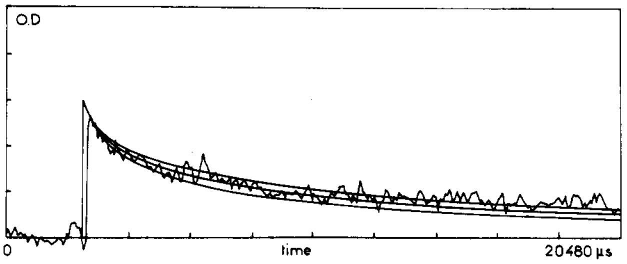

Figure 6. Kinetic simulations performed at 333 K and 210 nm; k_3 = (4, 6, and 9) × 10^{-12}; [HCHO] = 6.8 × 10^{16} molecule cm^{-3}.

The experimental entropy change of $\Delta S_1{}^\circ = -35 \pm 5$ eu was calculated by incorporating the value of Barnes[6] with our values and performing a least-squares treatment of the data. A MINDO/3 calculation was performed for each species of reaction 1, and the value of $\Delta S_1{}^\circ = -35.35 \pm 1.0$ eu was derived (see Table II). The estimation of the same quantity by the method of Benson[18] gives a similar value but with less accuracy. The experimental value is therefore consistent with the calculated values, of which the MINDO/3 determination is most accurate. The calculated value of $\Delta S_1{}^\circ/R$ (= ln K_p at $1/T = 0$) was included in the least-squares analysis to provide a more accurate determination of $\Delta H_1{}^\circ$ based on the third law method.[19] A value of −16.25 ± 0.3 kcal mol^{-1} was obtained. The estimated value based on the method of Benson[18] (see Table II) is in good agreement with our experimental value. These experiments allow the first determintion of the heat of formation of $HOCH_2O_2$: $\Delta H_f{}^\circ$ = −38.75 ± 0.5 kcal mol^{-1} when $\Delta H_f{}^\circ(HO_2)$ = 3.5 kcal mol^{-1}.[20] Table II shows that there is a very good agreement between the results of the experiment and the value of $\Delta H_{298}{}^\circ$ for reaction 1 calculated by using the MINDO/3 approach.

Reactions of the $HOCH_2O_2$ Radical. The kinetics of reactions 3 and 4 of the RO_2 radical were studied under conditions such that the sensitivity of the fits to the required rate constant was optimal: equal amounts of HO_2 and RO_2 in the measurement of k_3 and a large excess of RO_2 in the determination of k_4.

(a) *Reaction between RO_2 and HO_2.* Figure 6 shows an absorption time profile at 210 nm and 333 K with initial [HO_2] = 6.7 × 10^{13} molecule cm^{-3} and [HCHO] = 8.6 × 10^{16} molecule cm^{-3}. Under these conditions the equilibrium is established with a time constant of ca. 1 ms. The rate of decay under these conditions was found to be quite sensitive to the value of the rate constant k_3 as shown by the three curves in Figure 6, which were obtained with values of k_3 = 4.0, 6.0, and 9.0 × 10^{-12} cm^3 molecule^{-1} s^{-1}. At low temperature (275 K), the magnitude of the absorption both at 210 and 250 nm was sensitive to k_3 due to the

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TABLE III: Kinetic Measurements of k_3 as a Function of Temperature

T/K	$10^{11}k_3$/ (cm^3 $molecule^{-1}$ s^{-1})
275	2.5 ± 0.5
295	1.2 ± 0.4
308	1.2 ± 0.6
323	0.6 ± 0.4
333	0.6 ± 0.2

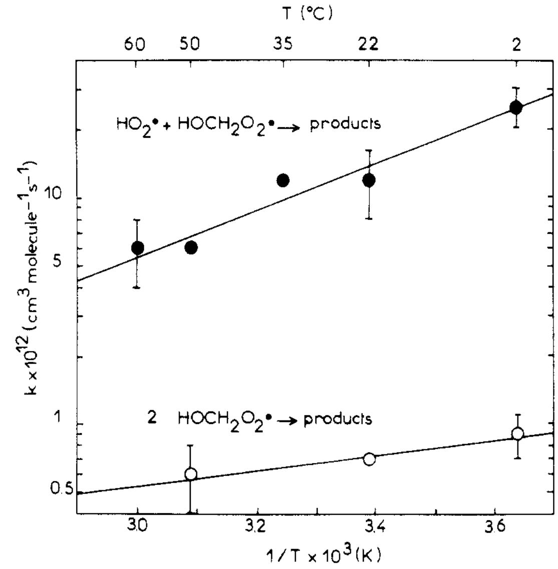

Figure 7. Arrhenius plots for k_3 and k_{4b}.

rapid rate of reaction 3 consuming RO_2. The best fit value given in Table III was obtained from six experiments with [HCHO] ranging from 1.32 to 8.0 × 10^{16} molecule cm^{-3}. The values of k_3 at the five temperatures studied are given in Table III. The Arrhenius curve is shown in Figure 7, and the corresponding expression for the temperature dependence of the rate constant is

$$k_3 = 5.6 \times 10^{-15} \exp[(2300 \pm 1100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

It should be noted that the reaction between HO_2 and $HOCH_2O_2$ can occur by two molecular channels:

$$HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2O_2H \quad (3a)$$

$$\rightarrow O_2 + HCOOH + H_2O \quad (3b)$$

In the flash photolysis experiments no distinction could be made between the two routes, but information on the branching ratio k_{3a}/k_{3b} was obtained from the HCOOH formation yields, described in the following paper.[8]

(b) *Self-Reaction of RO_2.* Under the conditions of high formaldehyde concentration, only the radical RO_2 is present in the system shortly after the flash. The decay in absorption at 250 nm was relatively slow, as will be seen from Figure 8, which shows data for $[HO_2]_0$ = 7.0 × 10^{13} molecule cm^{-3} and [HCHO] = 8.3 × 10^{16} molecule cm^{-3} at 295 K. Under these conditions RO_2 is the dominant radical and decay is predominantly due to the self-reaction of RO_2.

There are two main channels for the reaction between $HOCH_2O_2$ radicals:

$$2HOCH_2O_2 \rightarrow O_2 + 2HOCH_2O \quad (4a)$$

$$\rightarrow O_2 + HOCH_2OH + HCOOH \quad (4b)$$

The latter reaction leads to a termination while the former carries a chain via the formation of HO_2 radicals:

$$HOCH_2O + O_2 \rightarrow HCOOH + HO_2 \quad (9)$$

Since the equilibrium between HO_2 and RO_2 is established rapidly, this process does not lead to overall loss of radicals and the decay in RO_2 absorption reflects only the termination reaction (4b). A plot of 1/OD vs time was linear, showing that the overall decay of the radical was second order. However, because of the possibility of a small contribution from the reaction of RO_2 with HO_2 to the overall decay, the rate constant k_{4b} was determined by simulation of the decay curve using a mechanism involving reactions 1–4 and 9. The simulated curve in Figure 8 was obtained with the following values of the rate constants at 295 K: k_1 = 6.0 × 10^{-14}, k_2 = 2.0 × 10^{-12}, k_3 = 1.2 × 10^{-11}, k_{4a} = 5.2 × 10^{-12}, and k_{4b} = 7.0 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} and k_{-1} = 100 s^{-1}. The value of k_{4a} is based on the quantum yields for HCOOH formation as discussed in the following paper,[8] and the value of k_{4b} was varied to give the best fit. The experiment was repeated at different temperatures to determine values of k_{4b}, which are given in Table IV. The corresponding Arrhenius plot is shown in Figure 7. The temperature dependence, which is weakly negative, is given by the expression

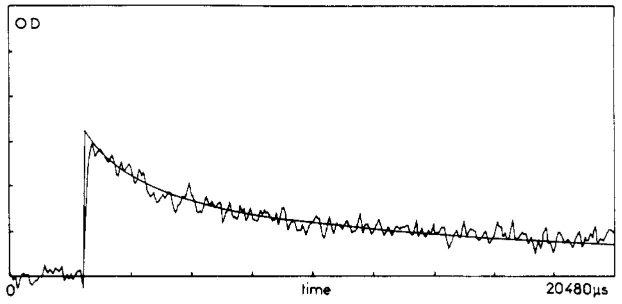

Figure 8. Decay of the absorption of the RO_2 radical at 250 nm and 295 K: k_{4a} = 5.2 × 10^{-12} and k_{4b} = 8 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

TABLE IV: Kinetic Measurements of k_{4b} as a Function of Temperature

T/K	$10^{13}k_{4b}$/ (cm^3 $molecule^{-1}$ s^{-1})
275	9.0 ± 2.0
295	7.0 ± 2.1
323	6.0 ± 2.0

$$k_{4b} = 5.65 \times 10^{-14} \exp[(745 \pm 400)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The value of k_{4b} is remarkably well-determined because k_{4a} only makes a small contribution to the decay.

Discussion

UV Spectrum of the Hydroxymethylperoxy Radical. The spectral and kinetic results that are reported in this paper show clear evidence for the formation of a species via the addition of HO_2 to formaldehyde. This species has a UV spectrum similar to that of other peroxy radicals, and it is postulated that it corresponds to the $HOCH_2O_2$ radical as proposed initially by the groups of Niki and Calvert.[1-3] The only other published spectrum of the $HOCH_2O_2$ radical was obtained in the liquid phase by Rabani et al.,[21] using pulse radiolysis of methanol solutions containing O_2. The liquid-phase spectrum is shown in Figure 1. The maximum cross section is 4.3 × 10^{-18} cm^2 $molecule^{-1}$, i.e. ≈13% higher than in the gas phase. In the liquid phase the radical was formed by the addition of O_2 to the CH_2OH radical:

$$CH_2OH + O_2 \rightarrow HOCH_2O_2$$

This reaction does not occur in the gas phase because of the fast decomposition of the energy-rich peroxy radical into HCHO and HO_2.[22]

The spectrum obtained by the technique of modulated photolysis–long path kinetic spectroscopy as reported in part 2 of this work is shown in Figure 1, where it is plotted normalized at 250 nm with the flash photolysis spectrum. The shapes of the two spectra are very similar.

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[21] Rabani, J.; Klug-Roth, D.; Henglein, A. *J. Phys. Chem.* **1974**, *78*, 2089.

[22] Dobé, S.; Temps, F.; Böhland, T.; Wagner, H. Gg. *Z. Naturforsch.* **1985**, *40a*, 1289.

TABLE V: Previous Determinations of k_1, k_{-1}, and K_1*

$10^{14}k_1$/ (cm^3 molecule^{-1} s^{-1})	k_{-1}/s^{-1}	$10^{16}K_1$*/ (cm^3 molecule^{-1})	temp/K	ref
1.0	1.5	67	298	1
14–32	–	–	298	23
7.5	≈30	≈25	298	9
≤2	–	–	298	5
11.0	20	55	273	6
–	–	34	298	7
6.6	126	5.2	298	*a*
–	–	4.0	298	*b*

[a] This paper. [b] Part 2 of this work (ref 8).

The Equilibrium $HO_2 + HCHO \Leftrightarrow HOCH_2O_2$. The kinetic measurements in this study showed that the equilibrium between HO_2 and the hydroxymethylperoxy radical was established within a few milliseconds under the experimental conditions, allowing the equilibrium constant to be determined directly from the rate constants for the forward and reverse reactions. The values of k_1, k_{-1}, and K_1* are compared with previously reported values in Table V.

Su et al.[1] performed end product analysis by FTIR in the photooxidation of formaldehyde. The kinetic determinations were rather indirect, and estimated values of the rate constants of the RO_2 radical reactions were much lower than the values measured in this study. Furthermore, the production of HCOOH via reaction between HO_2 and the RO_2 radical was not considered.

In the product analysis by Morrison and Heicklen,[23] NO_2 was photolyzed at 366 nm in the presence of HCHO and NO and the yield of formic acid was monitored. Since the actual sequence of reactions leading to formic acid was not known, the rate constant determination based on the observation of only one of the products was inaccurate.

In the flash photolysis study of Veyret et al.,[4] the formation rate and yield of NO_2 product were measured in the flash photolysis of $HCHO/O_2/NO$ mixtures. Kinetic simulations were performed for various experimental conditions, and the values of the rate constants for reaction 1 and the reaction beteen $HOCH_2O$ and O_2 were determined. This involved modeling of a rather complicated chemical scheme in spite of the simplification brought by the introduction of NO. In these simulations, the value of $k_{-1} = 30$ s^{-1} at 298 K was evaluated by fitting the experimental data of Su et al.,[1,3] using an improved chemical scheme. When the same data were modeled again with the kinetic parameters of our study incorporated, the fits were very sensitive to the value of k_{-1}, which had to be greater than 60 s^{-1}, corresponding to $K_1^* \leq 1.15 \times 10^{-15}$ cm^3 molecule^{-1}.

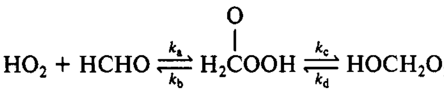
Flash photolysis coupled with IR diode laser absorption was used by Thrush and Tyndall[5] in the photolysis of $Cl_2/HCHO/O_2$. The time profiles of the HO_2 absorption were monitored as well as the yield of HCOOH. An upper limit of 2×10^{-14} was determined for k_1, but small deviations from second-order behavior would have been hard to observe, particularly if k_3 is so fast.

The kinetic study of Barnes et al.[6] provided some rather direct determinations of both k_1 and k_{-1} values. In these experiments, the decay of HO_2NO_2 was monitored in the presence of formaldehyde. The decay rates of HCHO and formation rates of HCOOH and $HOCH_2O_2NO_2$ were determined as a function of time at 273 K. The final value of $k_1 = (1.1 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} is in good agreement with our value at 275 K: $k_1 = (8.0 \pm 2.0) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The k_{-1} value of Barnes et al.[6] at 273 K, $k_{-1} = 20$ (+20, −10) s^{-1}, is also in good agreement with our extrapolated value at the same temperature: $k_{-1} \approx 16$ s^{-1}.

A recent publication by Zabel et al.[7] describes a determination of K_1* in the photolysis of $HCHO/O_2$ mixtures over a temperature range 303–373 K using ESR spectroscopy to measure the ratio of the concentrations of HO_2 and $HOCH_2O_2$ radicals. The authors derived an Arrhenius expression for $K_1^* = 2.4 \times 10^{-26} \exp(7650/T)$ cm^3 molecule^{-1} where the exponential term is similar to ours ($7625/T$) but the preexponential factor is about 6 times larger. The exact cause of this large discrepancy is not obvious. The method used by Zabel et al.[7] was not calibrated on a known equilibrium system, and there is a possibility of error associated with sampling of the gases and with the absolute calibration of the RO_2 radical concentration, which was based on a calculated ESR spectrum.

In the present work, the determination of the equilibrium constant was done by two methods that are almost independent (see ref 8). There is a very good agreement between the two results and also with the value of Barnes et al.[6] at 273 K and some indication of an agreement with the previous determination by Su et al.[1] when the present scheme is used in the modeling.

Mechanism of Reaction 1. The mechanism of reaction 1 as originally suggested by Su et al.[1] involves isomerization of the initial adduct of the HO_2 + HCHO reaction by H-atom transfer:



$$HO_2 + HCHO \underset{k_b}{\overset{k_a}{\rightleftharpoons}} H_2\overset{\overset{O}{|}}{C}OOH \underset{k_d}{\overset{k_c}{\rightleftharpoons}} HOCH_2O_2 \quad (1, -1)$$

Thermochemical bond additivity calculations[4] show that the first step of reaction 1 giving an alkoxy radical is nearly themoneutral, while the second step involving an isomerization is ca. 16 kcal mol^{-1} exothermic. The measurement of the Arrhenius parameter for reaction 1 showed that the preexponential factor is very low for such an addition reaction and that the apparent activation energy is negative (ca. 1.2 kcal mol^{-1}). Knoll et al.[24] had measured the Arrhenius parameters for the addition of the C_3H_7 to HCHO and found a preexponential factor value of ca. 1.3×10^{-13} cm^3 molecule^{-1} s^{-1} and an activation energy of 6.7 kcal mol^{-1}. The results of work by Baldwin et al.[25] on the addition of HO_2 to alkenes showed even greater activation energies and preexponential factors; e.g. $E = 14.9$ kcal mol^{-1} and $A = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in the case of propene.

Clearly these data indicate that reaction 1 proceeds via a mechanism that is peculiar. One possibility is that the intermediate HO_2CH_2O is in equilibrium with the reactants via a low barrier and that it can isomerize to RO_2 via an energy barrier that is slightly below the energy of the reactants.

In order to investigate the reaction mechanism, we have performed semiempirical MINDO/3 calculations in order to evaluate the entropy and enthalpy of the HO_2CH_2O radical and to explore the potential energy surface for the reaction. The details of these calculations and the results, including those from similar calculations for other carbonyl molecules, will be published elsewhere.

The calculations showed clearly the presence of a saddle point between the reactants HO_2 and HCHO and the HO_2CH_2O radical (=RO), and the calculated entropy of the transition state corresponding to the maximum in the barrier was $S_{298}°(RO_{a,b}^{\ddagger}) = 71.10$ cal mol^{-1} K^{-1}.

The calculated value of $S_{298}°(HO_2CH_2O)$ was 68.77 cal mol^{-1} K^{-1}, which together with the entropies of HO_2 and HCHO (Table IV) allows the evaluation of the A factors for both the reverse and the forward of the initial step:

$$A_a = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$A_b = 5.4 \times 10^{13} \text{ s}^{-1}$$

Note that the entropy of the transition state $RO_{a,b}^{\ddagger}$ gives an unusually low A factor for the forward reaction, in agreement with the experiments, reflecting a very narrow entry channel for HO_2 attaching perpendicular to the plane of the HCHO molecule. Similar calculations done on the addition reaction of HO_2 to acetaldehyde (for which $k \approx 1.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} [26]) have shown that the HO_2 radical cannot attack the CH_3CHO molecule in the same perpendicular manner and indeed, the

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(23) Morrison, B. M.; Heicklen, J. *J. Photochem.* **1981**, *15*, 131.

(24) Knoll, H.; Nacsa, A.; Forgeteg, S.; Berces, T. *React. Kinet. Catal. Lett.* **1980**, *15*, 481.

(25) Baldwin, R. R.; Hisham, M. W. M.; Walker, R. W. *Twentieth Symposium (International) on Combustion*; Combustion Institute: Pittsburgh, PA, 1985; p 743.

(26) Zabel, F., private communication.

calculated *A* factor is 10 times smaller than that of reaction 1 and the energy barrier is ≈6.4 kcal mol^{-1} greater than that of step 1a. These values of the calculated thermochemical parameters can easily explain the difference by a factor of 10^4 between the rate constants.

Further calculations revealed a second saddle point between the HO_2CH_2O intermediate and RO_2, the transition state being a five-membered ring with an elongated O–O bond. The calculated entropy $S_{298}°(RO_{c,d}^{\ddagger})$ was 67.45 cal mol^{-1} K^{-1}, with a corresponding value of the *A* factor: $A_c = 8.6 \times 10^{12}$ s^{-1}. It is notable that this value is a factor of ca. 20 higher than the *A* factor calculated by the Benson rules[18] for internal H-atom transfer via a five-membered ring containing C atoms. The enthalpies at the saddle points for the transition states in reactions a,b and c,d are 9.4 and 4.8 kcal mol^{-1} above the HO_2CH_2O intermediate. The calculations have also revealed saddle points for concerted reaction pathways involving both four- and five-centered cyclic transition states. These saddle points occur at much higher energies (36.8 and 26 kcal mol^{-1} above the reactants) and almost certainly do not occur in competition with the lower energy pathway despite the entropic restriction on the latter. The calculated values of the transition-state enthalpies cannot be compared directly with the reactant values but nevertheless provide useful information on the energy ordering of these states. The details and implications of these energy calculations will be given in a later publication.

In conclusion, we propose a mechanism that explains the observed kinetics of reaction 1, and involves addition of HO_2 to formaldehyde via a pathway with virtually no energy barrier but severe entropy restrictions, to form an unstable adduct. The adduct rapidly isomerizes via a cyclic transition state with a small energy barrier to form the hydroxymethylperoxy radical, RO_2. The decomposition of RO_2 occurs by the same reverse pathway.

Reactions of the RO_2 Radical. The negative temperature dependence for reactions 3 and 4a (see Figure 7) indicates that they proceed through a complex mechanism, in line with other reactions between peroxy radicals. The overall rate constant k_3 for the reaction of HO_2 with RO_2 is very large, and the negative temperature coefficient, $E/R = 2300 \pm 1100$ K, is the largest yet reported among the reactions between peroxy radicals. The reaction of HO_2 radicals with CH_3O_2 has a lower E/R ($= -1300/T$).[17] Since the latter reaction is less exothermic than reaction 3, this may indicate that the position of the top of the energy barrier from the intermediate adduct to the products varies with the reaction enthalpy for this set of peroxy radical reactions.

The rate constant measured for the termination channel in the $RO_2 + RO_2$ reaction

$$RO_2 + RO_2 \rightarrow HCOOH + ROH + O_2$$

$$k_{4b} = 7 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at room temperature}$$

is considerably smaller than k_3 but somewhat larger than the rate coefficient for the equivalent termination channel in the self-reaction of the methylperoxy radical:

$$CH_3O_2 + CH_3O_2 \rightarrow HCHO + CH_3OH + O_2$$

($k = 2.2 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}),[16] showing that the OH substitution of the CH_3 group enhances the reaction rate due to the weakening of the C–H bond.

Conclusion

This work has provided new quantitative information on the kinetics of the gas-phase oxidation of formaldehyde by HO_2 radicals. The UV cross section for the $HOCH_2O_2$ radical was measured, and this allowed the determination of the rate constant values for the formation and dissociation of this radical as well as rate parameters for the reactions of the radical with itself and HO_2. A plausible mechanism of reaction 1 has been put forward, but further experimental and theoretical work is needed for confirmation of the picture. The branching ratios could not be determined with the flash photolysis technique, but their determination by molecular modulation spectroscopy is reported in the following paper[8] where another independent measurement of the equilibrium constant is reported in good agreement with the value above. Atmospheric implications of our kinetics measurements are given in part 2 of this publication.

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Registry No. HCHO, 50-00-0; $HOCH_2O_2$, 27828-51-9; HO_2, 3170-83-0.