Rate Constants for the Reactions of Cl Atoms with HCOOH and with HOCO Radicals

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ABSTRACT: Rate constants have been measured at room temperature for the reactions of Cl atoms with formic acid and with the HOCO radical:

$$Cl + HCOOH \longrightarrow HCl + HOCO \qquad (R1)$$

$$Cl + HOCO \longrightarrow HCl + CO_2 \qquad (R2)$$

Cl atoms were generated by flash photolysis of Cl_2 and the progress of reaction was followed by time-resolved infrared absorption measurements using tunable diode lasers on the CO_2 that was formed either in the pair of reactions (R1) plus (R2), or in reaction (R1) followed by

$$O_2 + HOCO \longrightarrow HO_2 + CO_2 \qquad (R3)$$

In a separate series of experiments, conditions were chosen so that the kinetics of CO_2 formation were dominated either by the rate of reaction (R1) or by that of reactions (R1) and (R2) combined. The results of our analysis of these experiments yielded:

$$k_1 = (1.8_3 \pm 0.12) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (4.8 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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INTRODUCTION

The hydroxy formyl radical HOCO is of great interest as a transitory intermediate in the important reaction between OH radicals and CO, which is virtually the only mechanism in the earth's atmosphere for converting CO to CO_2, the final oxidation product of fuel-based carbon. In the atmosphere, the initial reaction between OH and CO occurs, at competitive rates [1,2], by two parallel channels, both involving the energized HOCO radical, $(HOCO)^\dagger$, as an intermediate:

$$OH + CO \longrightarrow (HOCO)^\dagger \longrightarrow H + CO_2 \qquad (R4a)$$

$$+ M \longrightarrow HOCO \qquad (R4b)$$

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In practice, in an oxygen-rich atmosphere, reactions (R4a) and (R4b) lead to the same result because the radical product of each is rapidly converted to HO_2 by one of the two reactions [1,2]:

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (R5)$$

or

$$HOCO + O_2 \longrightarrow HO_2 + CO_2 \qquad \Delta_r H^\circ = -156 \text{ kJ mol}^{-1} \qquad (R3)$$

The HOCO radical can also be formed in the atmosphere via the attack on formic acid of OH radicals and to a minor extent of Cl atoms:

$$OH + HCOOH \longrightarrow H_2O + HOCO \qquad (R6)$$

$$Cl + HCOOH \longrightarrow HCl + HOCO \qquad \Delta_r H^\circ = -58 \text{ kJ mol}^{-1} \qquad (R1)$$

Moreover, reaction (R1) has proved to be a useful source of relatively unexcited HOCO radicals in laboratory studies of their kinetics [3,4]. Despite this, there have been no direct measurements of the rate constant k_1 for this reaction. By using the continuous photolysis–Fourier transform infrared (FTIR) spectroscopy technique, Wallington et al. [5] measured k_1 relative to the rate constants for the reactions between Cl atoms and CH_3Cl and between Cl atoms and CH_4, obtaining an average value of 2.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, a value to which Atkinson et al. [1] assign an uncertainty of $\Delta\log_{10} k_1 = 0.2$.

The present article reports the first direct, time-resolved, measurement of k_1. In addition, we have determined the rate constant k_2 for the reaction between Cl atoms and HOCO radicals,

$$Cl + HOCO \longrightarrow HCl + CO_2 \qquad \Delta_r H^\circ = -384 \text{ kJ mol}^{-1} \qquad (R2)$$

thereby adding to the limited kinetic database [3,4,6] for reactions of these radicals. Our method relied on the generation of Cl atoms by flash photolysis of molecular chlorine in the near ultraviolet and the observation of CO_2 production by time-resolved infrared absorption using tunable diode lasers and transitions within the $(00^01,00^00)$ fundamental band of CO_2 [7,8]. To find k_1, experiments were performed on gas mixtures that contained small concentrations of Cl_2 relative to HCOOH, so that $[Cl] \ll [HCOOH]$ at all times, and concentrations of O_2 large enough to ensure that the transformation of HOCO to CO_2 was essentially instantaneous. Under these conditions, the kinetics of CO_2 formation are first-order and determined by k_1[HCOOH] so that the value of k_1 can be found by observing how the pseudo-first-order rate constant associated with production of CO_2 varies with [HCOOH]. To find k_2, experiments were performed in the absence of O_2 and with larger ratios of [Cl] to [HCOOH]. The traces recording how the absorbance of CO_2 varied with time were then modeled to yield k_2. The modeling calculations were also used to confirm our interpretation of the experimental results.

EXPERIMENTAL

The apparatus and method used in the present experiments are similar to those described in detail by us in two recent articles [7,8] and are described only briefly here, highlighting the modifications made for the present experiments.

Cl atoms were produced by photolysis of Cl_2 using an annular Xe-filled flashlamp around a cylindrical reaction cell. The cell was constructed from a Pyrex tube that restricted the light entering the reaction vessel to wavelengths $>$ ca. 300 nm with the result that only Cl_2 and not HCOOH could be photolyzed. In the present experiments, the main disadvantage of using a flashlamp instead of a pulsed laser to effect photodissociation was the poorer time resolution that could be achieved because the flash from the lamp lasted approximately 10 μs.

Infrared radiation of a selected narrowband frequency was provided by a liquid N_2 cooled diode laser system (Mutek GmbH, MDS 1150). The methods employed for determining and tuning the frequency of the diode output have been described previously [7]. Collimating optics were employed to generate a suitable probe beam that then made a single pass along the length of the reaction cell. After this beam emerged from the reaction vessel, it was focused onto the entrance slit of a monochromator (Hilger D330) that selected a single mode from the laser and directed this radiation onto a liquid N_2 cooled InSb photovoltaic detector (Infrared Associates) placed at the exit slit of the monochromator. The presence of CO_2 in the atmosphere made it essential to enclose and purge the complete path of the probe laser with N_2. An AC-coupled amplifier was used in conjunction with the detector and its output was passed to a digital storage oscilloscope. The time response of the detector–amplifier combination was approximately 10 μs in the experiments that are reported in the present article.

Generally, 20 traces were averaged before subsequent processing.

The reaction cell and flashlamp were connected to a standard gas-handling line constructed from Pyrex and fitted with greaseless stopcocks. Gas mixtures were passed through the reaction cell at a rate that ensured it was refilled with a fresh mixture for every pulse from the flashlamp, the flows of the individual components being set and monitored using mass flow controllers (MKS and Bronkhurst Hi-Tec). O_2 (BOC, 99.6%) and He (Air Products, GC grade) were delivered straight from cylinders without further purification. Cl_2 (Matheson, UHP) was diluted in He to give a 2% mixture and this mixture was introduced from a 10-liter storage bulb. Formic acid (Fisher, 98–100%) was delivered, diluted in He, using a "bubbler" followed by a cold trap. The trap was maintained at (10 ± 0.5)°C. By varying the pressure in this flow line, the partial pressure of formic acid in the reaction vessel could be varied between 60 and 310 mTorr.

In calculating the concentration of formic acid in the reaction cell, it was necessary to allow for its dimerization. The equilibrium constant for this dimerization has been measured [9], so it was straightforward to estimate the concentration of monomer in the reaction cell. At the highest partial pressure of formic acid (310 mTorr), 9.8% of the species present were dimers. All concentrations quoted in the following text are those of the formic acid monomer, assuming that the dimer is less reactive.

RESULTS

To determine the rate constant for reaction (R1) between Cl atoms and formic acid, traces of time-resolved infrared absorbance were recorded on the P(4) line in the $(00^01,00^00)$ fundamental band of CO_2; the reaction having been initiated by flash photolysis of mixtures containing 0.05 mTorr of Cl_2 and 0.8 Torr of O_2 at a total pressure of 10 Torr, with the diluent being He. The partial pressure of formic acid was varied between 60 and 245 mTorr. An example of such a trace is given in Figure 1. Experiments on mixtures from which Cl_2 was omitted revealed no significant CO_2 absorption confirming that HCOOH was not photolyzed under the conditions of our experiments.

If it is assumed (i) that under these conditions CO_2 is formed in reaction (R3) of HOCO radicals with O_2, following the reaction between Cl atoms with HCOOH, and (ii) that the photochemical production of Cl atoms is effectively instantaneous then the concentration of CO_2 at time delay t is given by:

$$[CO_2]_t = [Cl]_0\left\{1 - \frac{k_b}{(k_b - k_a)}\exp(-k_a t) - \frac{k_a}{(k_a - k_b)}\exp(-k_b t)\right\} \quad (1)$$

where $k_a = k_1$ [HCOOH] and $k_b = k_3$ [O_2] are pseudo-first-order rate constants for reactions (R1) and (R3), respectively. The value of k_3 is established [1–4,6] to be 1.9×10^{-12} cm^3 molecule^{-1} s^{-1} so at the partial pressure of O_2 present in these experiments, $k_b = 4.7 \times 10^4$ s^{-1} and is much greater than k_a. Consequently, the equation for $[CO_2]t$ can be simplified to

$$[CO_2]_t = [Cl]_0\left\{1 - \frac{k_b}{(k_b - k_a)}\exp(-k_a t)\right\} \quad (2)$$

and this expression was used to fit the traces of infrared absorbance vs. time. The quality of the fits can be assessed from Figure 1.

In these experiments, the initial concentration of Cl atoms, that is, $[Cl]_0$ in Eqs. (1) and (2), should be equal to the final yield of CO_2, that is, the concentration of CO_2 at long times. In any series of experiments with the concentration of Cl_2 included in the gas mixture kept constant but [HCOOH] varied, the yield of CO_2 should therefore be constant, and this was confirmed experimentally. Values of k_a were extracted from the analysis of experiments of this kind and plotted against [HCOOH] as shown in Figure 2. The slopes of such plots reveal k_1, the rate constant for reaction of Cl atoms with HCOOH, to be $(1.8_3 \pm 0.12) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at room temperature, where the cited error corresponds to two standard deviations.

To determine k_2 (i.e., the rate constant for the radical–radical reaction between Cl atoms and HOCO) very different experimental conditions were selected from those used when finding k_1. O_2 was excluded and higher initial concentrations of Cl atoms were created by including higher concentrations of Cl_2 in the reaction mixture. Now CO_2 was formed in the sequence of reactions (R1) and (R2) and both the yield of CO_2 and its kinetics of formation reflect the value of k_2, as well as that of k_1. The yields of CO_2 could be calculated from the absorbance measured at long delay times. In all these experiments, the total pressure was kept at 10 Torr and the partial pressure of formic acid at 310 mTorr. This high formic acid concentration ensured efficient relaxation of any vibrationally excited CO_2. The partial pressure of the Cl_2 included in the mixture was varied between 0.55 and 2.50 mTorr.

Traces of absorbance vs. time on the P(4) line of

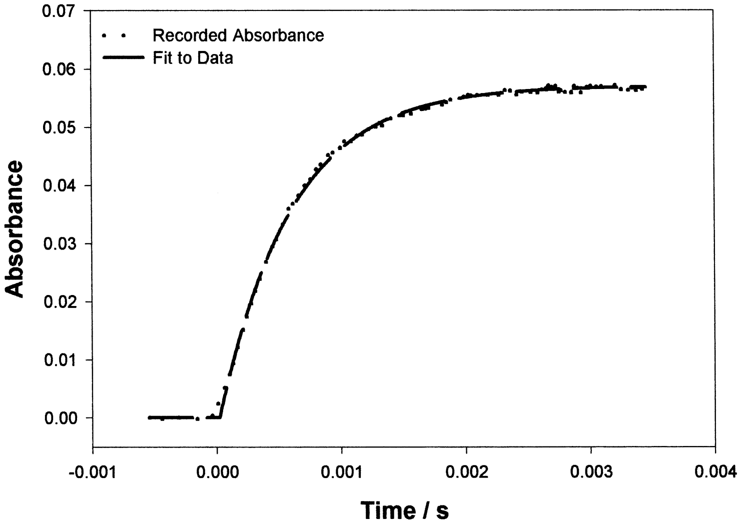

Figure 1 Typical trace of infrared absorbance measured on the P(4) line of the ($00^01,00^00$) band of CO_2 following flash photolysis of a mixture containing 0.05 mTorr Cl_2, 244 mTorr HCOOH, and 800 mTorr O_2 diluted in He to a total pressure of 10 Torr. The dashed line shows the results of a fit to the form given in Eq. (2).

the CO_2 ($00^01,00^00$) fundamental band were recorded. Because the bandwidth of the diode laser was much less than that of the absorption line, the measured absorbances were converted to absolute concentrations of CO_2 using an estimate of the absorption cross section at the center of this line. At a total pressure of 10 Torr of helium, the line shape is determined by a mixture of pressure and Doppler broadening. Therefore, in calculating the absorption cross section, the line was assumed to have a Voight profile [10]. The integrated intensity of the ($00^01,00^00$) fundamental band was taken from the review of Smith et al. [11], and the pressure-broadened line width was based on the measurements of Brownsword et al. [12].

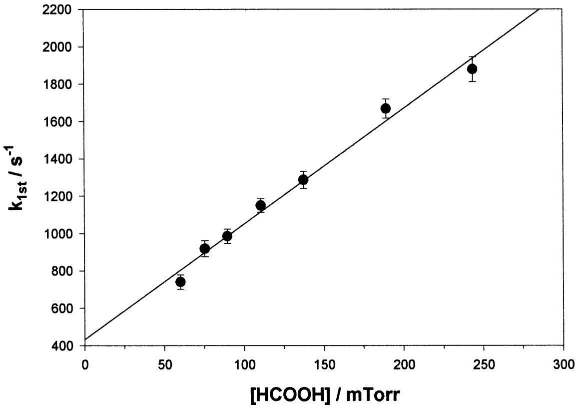

Figure 2 Plot of the pseudo-first-order rate constants obtained from fits of the kind shown in Figure 1 vs. the concentration of HCOOH included in the reaction mixture. The error bars shown on individual points correspond to $\pm 2\sigma$ and are generated from fits to the experimental traces as shown in Figure 1.

A typical trace of $[CO_2]$ vs. time is displayed in Figure 3. To model these traces, it was also necessary to know $[Cl]_0$, the concentration of Cl atoms initially produced by the flash photolysis of Cl_2. This was estimated in a separate series of experiments in which a large excess of O_2 was included in the reaction mixture so that essentially all the HOCO reacted with O_2 instead of Cl atoms. Then there is a unit stoichiometric yield of CO_2 from each Cl atom generated photolytically, and the measurement of $[CO_2]$ at long delay times provides a measure of $[Cl]_0$.

There was then sufficient information to model the observed variation of $[CO_2]$ with time. For this purpose, we employed the FACSIMILE modeling program [13] with k_1 set to the value that we had already obtained and k_2 allowed to float to give the best match to the variation of the absolute concentrations of CO_2 with time that were derived from the experimentally recorded traces. The high quality of the resultant fit is demonstrated in Figure 3. A number of experiments were performed with different concentrations of Cl_2 included in the gas mixture. Each experiment yielded a value of k_2 and these values are plotted against $[Cl]_0$ in Figure 4. Although the results show a fair degree of scatter, there is no evidence of any trend with changes in $[Cl]_0$. Therefore, we have calculated a simple average of the individual values as our best estimate of the rate constant for reaction between Cl atoms and HOCO radicals: $k_2 = (4.8 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, where the cited error corresponds to

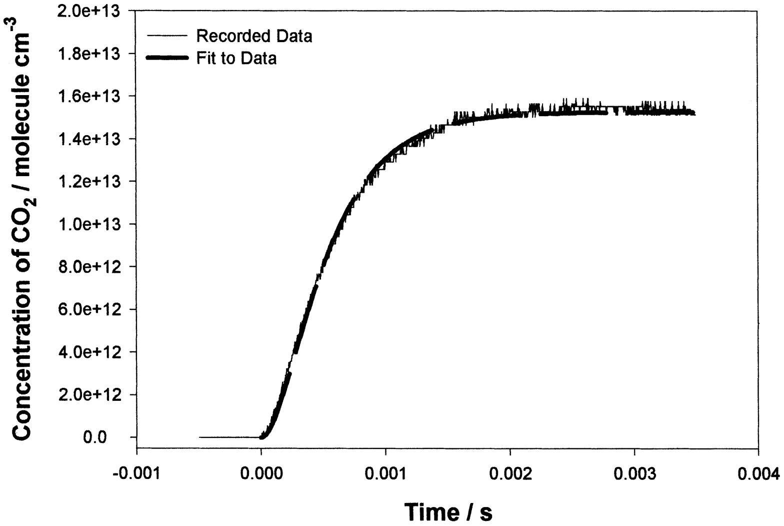

Figure 3 Variation of the CO_2 concentration with time, derived from measurements of infrared absorbance, in a mixture containing no O_2 but 1.36 mTorr Cl_2 and 310 mTorr HCOOH diluted in He to a total pressure of 10 Torr. The dashed line is the fit of the simulation described in the text that yields a value of k_2, the rate constant for reaction between Cl atoms and HOCO.

two standard deviations in the points shown in Figure 4. No allowance is made for possible systematic error.

Calculations using FACSIMILE were also used for two other purposes. First, we checked that the determination of the rate constant k_1 was not affected significantly by neglect of reaction (R2) between Cl atoms and HOCO. The calculations confirmed that the simple analysis used to extract k_1 that was presented earlier was satisfactory. Second, we considered whether reactions second-order in HOCO radicals, for example

$$\mathrm{HOCO} + \mathrm{HOCO} \longrightarrow \mathrm{HCOOH} + \mathrm{CO_2} \quad \text{(R7a)}$$

and

$$\mathrm{HOCO} + \mathrm{HOCO}\ (+\mathrm{M}) \longrightarrow (\mathrm{COOH})_2\ (+\mathrm{M}) \quad \text{(R7b)}$$

might influence our interpretation. For this purpose, calculations were performed with reactions (R1), (R2), and (R7) included in the model. The rate constants k_1 and k_2 were given the values already determined, and k_{7a} and k_{7b} were allowed to vary to see the effect on the variation of $[CO_2]$ with time. The effect of both reactions (R7a) and (R7b) on the traces of $[CO_2]$ vs. time should have been noticeable if the rate constants were greater than about 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. We conclude that mutual reactions of HOCO radicals are not important under the conditions of our experiments and that such reactions are not very fast.

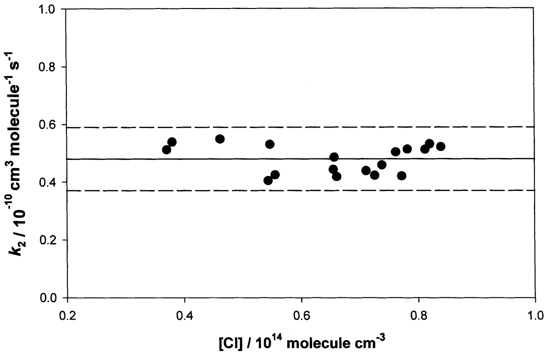

Figure 4 Plot of the values of k_2 derived from fits like those shown in Figure 3 against the initial concentration of Cl atoms derived by flash photolysis of Cl_2. All experiments were performed with the same partial pressure of HCOOH (310 mTorr) and on mixtures diluted in He to a total pressure of 10 Torr. The dashed lines show $\pm 2\sigma$ deviations from the mean value.

DISCUSSION

The rate constant that we have directly determined for reaction (R1) between Cl atoms and formic acid [i.e., $(1.8_3 \pm 0.12) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}] is in good agreement with the value of 2.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1} inferred from the relative rate measurements of Wallington et al. [5]. Our measurement reduces appreciably the uncertainty in the room temperature value of this rate constant. The reaction of Cl atoms with HCOOH has two possible channels, the one represented by Eq. (R1) that produces HCl + HOCO radicals, and the other that produces HCl + HCOO. Based on the experimental [14] and theoretical [15–17] differences between the enthalpies of formation of HOCO ($\Delta_f H° = -233$ kJ mol^{-1}) and HCOO ($\Delta_f H° \approx -170$ kJ mol^{-1}), the second channel producing HCOO is approximately thermoneutral compared with the exothermic reaction (R1). Evidence that reaction (R1) is the dominant mechanism for reaction between Cl atoms and HCOOH comes from two sources.

Ruscic et al. [14], as part of the study that led to the enthalpies of formation of HOCO and HCOO and that employed photoionization mass spectrometry, reported that they could not detect HCOO from the reaction of F atoms with HCOOD or DCOO from F + DCOOH. Given that in this case both abstraction channels are exothermic, this observation strongly suggests that the H atom whose abstraction leads to the product HOCO is more labile than the other H atom whose loss gives HCOO. Rather similar observations, again using photoionization mass spectrometry, were made by Miyoshi et al. [4]. However, they employed reaction (R1) between Cl atoms and HCOOH to generate radicals. Again, results with monodeuterated formic acid indicated that abstraction was predominantly of the H atom leading to HOCO. Finally, we mention that the dominance of reaction (R1) is consistent with the results of Tyndall et al. [18]. In a continuous photolysis–FTIR study of the reaction between Cl atoms and HCOOH in 700 Torr of synthetic air, they showed CO_2 was produced in 100% yield, presumably as the result of reactions (R1) and (R3).

Before the present measurement of k_2, the only rate constants reported for reactions of HOCO radicals were those for HOCO + O_2 [3,4,6] and for HOCO + NO [6]. Petty et al. [6] also reported that the rate constants for the reactions of HOCO with CO, C_2H_4, and C_2H_2 at room temperature were all less than 10^{-14} cm^3 molecule^{-1} s^{-1}. The value of k_2 that we find is approximately 30 times the rate constant for HOCO + O_2 and 20 times that for HOCO + NO. However, this greater reactivity of Cl atoms is not surprising in view of the much greater exothermicity of the H atom abstraction reaction in this case.

The absolute magnitude of k_2 is similar to the rate constants found for many exothermic reactions between unstable free radicals. Our experiments demonstrate that CO_2 is a product of the Cl + HOCO reaction and the fact that the modeling fits both the yield and the kinetics of CO_2 formation show that it is, at least, the dominant channel of reaction. This reaction, represented by (R2), may proceed by direct H atom abstraction or by prior formation of an energized and transitory HOC(O)Cl complex; or it may be that an approaching Cl atom samples the potential well associated with the C—Cl bond but then immediately abstracts the H atom. In this regard, it is interesting to note that the reaction between Cl atoms and HO_2 radicals mainly forms HCl + O_2 with a minor (22%) channel yielding HO + OCl, presumably as the result of initial formation of an energized HOOCl species. Clearly dynamic measurements, such as the determination of product state distributions, might cast further light on these interesting questions.

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