Temperature Dependence of the Rate Constant for the Reaction $HCO + O_2 \rightarrow HO_2 + CO$ at $T = 200-398$ K

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The absolute rate constant for the reaction $HCO + O_2$ has been measured over the temperature range $T = 200-398$ K in a discharge flow system at a pressure of 1 Torr (He). This study represents the first measurement of this rate constant at temperatures below $T = 298$ K. The decay of the HCO radical in the presence of excess O_2 was followed by collision-free sampling photoionization mass spectrometry. The results were as follows: $k_1(200\text{ K}) = 5.3 \pm 0.8$, $k_1(222\text{ K}) = 4.8 \pm 0.7$, $k_1(250\text{ K}) = 4.4 \pm 0.6$, $k_1(298\text{ K}) = 4.0 \pm 0.6$, $k_1(398\text{ K}) = 4.5 \pm 0.7$ in units 10^{-12} cm^3 molecule^{-1} s^{-1}. Over the range $T = 200-298$ K, the data suggest a slight negative temperature dependence and may be represented by the Arrhenius expression $k_1 = (2.2 \pm 0.2) \times 10^{-12} \exp[(170 \pm 22)/T]$ cm^3 molecule^{-1} s^{-1}. For the related reaction HCO + NO at $T = 298$ K we measure $k_2 = (1.3 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The results are compared with previous direct measurements of k_1 and k_2 and with recent theoretical calculations. For the $HCO + O_2$ reaction there are larger than expected differences between the measured values for what appears to be a relatively simple and well studied reaction. A recent theoretical expression for k_1, recommended for the region $T = 300-3000$ K, can be made to be in reasonable agreement with most of the results from direct, temperature-dependent studies between $T = 200-713$ K by an extrapolation to $T = 200$ K and by multiplying the theoretical expression by a minor uniform scaling factor of 0.80. Our result for HCO + NO at $T = 298$ K is in excellent agreement with all except one of the previous measurements of this rate constant.

Introduction

The reaction of the formyl radical with molecular oxygen

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (1)$$

is important in hydrocarbon oxidation in both low-temperature atmospheric chemistry and high-temperature combustion chemistry. There have been seven direct studies of this reaction at $T = 298$ K only,[1−7] two direct temperature-dependent studies at $T = 298$ K and above,[8,9] but no measurements below $T = 298$ K. We deem it advisable to have at least one study of this reaction at temperatures appropriate for stratospheric chemistry since reaction with O_2 is the only significant loss process for HCO in the atmosphere of Earth.

The majority of the previous studies of the $HCO + O_2$ reaction involved an absolute measurement of k_1 in which the primary reaction was essentially isolated but there were two studies in which modeling was required,[2,8] one which involved both absolute (high $[O_2]$) and modeled (low $[O_2]$) determinations[3] and one which was a relative measurement.[1] A variety of techniques have been employed in these studies. Thus HCO has been generated by flash photolysis (FP)[2,4,5,8] or laser photolysis (LP)[3,7,9] of H_2CO,[3,4,7,8] CH_3HCO,[2,4,5,8,9] or $(HCO)_2$[7] and by reaction of F with H_2CO [6] or $O(^3P)$ with C_2H_4[1] in discharge flow systems. The HCO radical was detected and its decay monitored via absorption spectroscopy (AS),[2] laser resonance absorption (LRA),[7,8] laser magnetic resonance (LMR),[6] intracavity dye laser spectroscopy (IDLS),[3−5] or photoionization mass spectrometry (PIMS).[1,9] The range of observed values for k_1 at $T = 298$ K is larger than expected for this reaction with values between $(3.8-6.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate constant appears to be pressure independent within the precision of the measurements. The observed discrepancies could be due to differences in the experimental technique employed. However, it should be noted that several of the groups[2−4,7,8] who studied the $HCO + O_2$ reaction also studied the related reaction

$$HCO + NO \rightarrow HNO + CO \qquad (2)$$

at $T = 298$ K and, with a single exception,[2] the agreement among them is excellent, $k_2 = (1.2-1.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Concerning the temperature dependence of k_1, Veyret and Lesclaux[8] observed a slight negative temperature dependence ($E/R = -153$) for $T = 298-503$ K but Timonen et al.[9] reported a small positive dependence ($E/R = 204$) for $T = 295-713$ K. While below $T = 500$ K, the measured values of k_1 from both studies do overlap within their quoted uncertainties, the differing temperature dependencies result in a 50% disagreement when extrapolated to lower temperatures (e.g., $T = 200$ K for atmospheric models) and a factor of 3 disagreement when extrapolated to higher temperatures (e.g., $T = 1500$ K for combustion models). In addition, the sign of the temperature

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dependence may be significant with respect to the reaction mechanism. A negative temperature dependence suggests that the reaction may occur via a collision complex and a positive temperature dependence suggests a direct abstraction mechanism. Veyret and Lesclaux[8] also examined the temperature dependence of the HCO + NO reaction and, as for the case of reaction 1, they observed a slight negative temperature dependence ($E/R = -152$) for $T = 298-503$ K.

Given the above considerations, we undertook a discharge flow photoionization mass spectrometric (DF-PIMS) study of the $HCO + O_2$ reaction over the interval $T = 200-398$ K. We also made some measurements at $T = 298$ K of the rate of the HCO + NO reaction which, as noted above, has been studied by several of the same groups[2-4,7,8] reporting reaction 1.

Experimental Section

Experiments were conducted in a discharge-flow system with mass spectrometric detection of transient radical species. The apparatus has been described in detail previously.[10] The discharge flow tube consisted of a Pyrex tube ~60 cm long and 2.8 cm in diameter. The flow tube was heated or cooled by circulating fluids from a reservoir through a jacket surrounding the flow tube. The flow tube was coupled via a two-stage stainless steel collision-free sampling system to a quadrupole mass spectrometer (Extrel, Inc.). The mass spectrometer was modified so that ion production was accomplished by photoionization at 10.2 eV with an H-atom Lyman-alpha VUV lamp ($\lambda = 121.6$ nm). The microwave discharge lamp was operated at approximately 2 Torr total pressure with He and H_2 flows in the ratio of 13:1. Experiments were performed at $T = 200-398$ K at a pressure of 1 Torr He. The linear flow velocity ranged from 1500 to 3000 cm s^{-1}. Flows of He, H_2CO/He, Cl_2/He, and O_2/He were measured and controlled by separate electronic flow meters (ASM International N. V.).

The formyl radical was produced at the upstream end of the flow tube via the reaction of atomic chlorine with formaldehyde.

$$Cl + H_2CO \rightarrow HCO + HCl \tag{3}$$

$$k_3(200-500\ K) = 7.5 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}\ (ref\ 11)$$

With $[H_2CO] = (0.7-1.5) \times 10^{13}$ molecule cm^{-3}, formaldehyde was in large excess over atomic chlorine, and HCO formation was complete in a few milliseconds. Atomic chlorine was formed by passing a 1.31-1.52% Cl_2/He mixture, further diluted in He, through a microwave discharge (<70 W, 2450 MHz) located on a sidearm at the upstream end of the flow tube. HCO (IE = 8.6 eV; ref 12) was monitored at $m/z = 29$ by photoionization at 10.2 eV. Contribution from dissociative ionization of H_2CO to the observed HCO^+ signal does not occur since the process $H_2CO \rightarrow HCO^+ + H$ has a threshold at 12.4 eV (ref 12). The O_2 reactant was added through the movable glass injector (which was covered with a Teflon sleeve) at reaction times from 2 to 20 ms. Although HCO can also be lost via reaction with residual Cl_2 ($HCO + Cl_2 \rightarrow HCOCl + Cl$; $k(295-582\ K) = 7.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; ref 9), this effect is negligible for two reasons. First, the residual $[Cl_2]$ was only 5×10^{11} molecule cm^{-3} while $[O_2]$ was $(0.5-9.9) \times 10^{13}$ cm^{-3}. Second, the $HCO + Cl_2$ reaction is immediately followed by the rapid reformation of HCO via reaction 3 since H_2CO is in large excess.

Absolute concentrations of atomic chlorine were obtained from the rapid titration reaction

$$Cl + n\text{-}C_6H_{14} \rightarrow n\text{-}C_6H_{13} + HCl \tag{4}$$

$$k_4(298\ K) = 3.2 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}\ (ref\ 13)$$

by measuring the decrease in the $C_6H_{14}^+$ ion peak at mass 86 when the discharge was initiated. The Cl concentration is given by $[Cl] = [C_6H_{14}]_{disk.off} - [C_6H_{14}]_{disk.on}$. The dilute n-C_6H_{14}/He mixture was admitted through the movable injector. The position of the injector was chosen to ensure that reaction 4 went to completion. The choice of n-C_6H_{14} (IE = 10.1 eV; ref 12) in these photoionization experiments is dictated by the fixed 10.2 eV energy of the Lyman-alpha lamp. In electron impact ionization experiments involving atomic chlorine, a typical choice of titrant would be Br_2 (IE = 10.5 eV; ref 12). With rapid and complete conversion of Cl to HCO via reaction 3, the initial HCO concentration is equal to the chlorine atom concentration. HCO concentrations in the reaction region between the movable injector and the sampling pinhole were about 1×10^{11} molecule cm^{-3}. The minimum detectable level of HCO was 5×10^9 molecule cm^{-3} at a signal-to-noise ratio of 1 and a 10 s integration time.

Helium (99.9995%, Air Products) was drawn through a molecular sieve trap held at $T = 77$ K. Formaldehyde was prepared from paraformaldehyde by heating at $T = 373$ K using the method of Spence and Wild.[14] The monomer was trapped and stored at $T = 77$ K. Cl_2 (99.9%, Matheson) and n-C_6H_{14} (Aldrich Chemicals, 98.5 mol %) were degassed at $T = 77$ K. Molecular oxygen (99.999%, Scientific Gas Products UHP) and H_2 (99.999%, Matheson UHP) were used without further purification.

Results

The rate coefficient for the reaction

$$HCO + X \rightarrow products \tag{5}$$

where $X = O_2$ or NO, was measured under pseudo-first-order conditions by monitoring the decay of HCO as a function of contact time in the presence of excess X. With $[X] \gg [HCO]$, the decay of HCO is given by the expression

$$\ln[HCO] = -k_{obs}(d/v) + \ln[HCO]_0 \tag{6}$$

where k_{obs} is the pseudo-first-order decay constant, d is the contact distance from the tip of the sliding injector to the sampling pinhole, and v is the linear flow velocity. Plots of ln(HCO signal) vs reaction time (d/v) were analyzed with a linear least-squares method. Figure 1 shows such plots for the decay of HCO at $T = 298$ K in the presence of three different concentrations of excess O_2. The slopes of these plots provided the observed experimental first-order decay constant, k_{obs}. The experimental first-order decay constants were corrected for axial diffusion of the radical in helium gas with the relationship

$$k_{corr} = k_{obs}\,(1 + k_{obs}D/v^2) \tag{7}$$

where v is the linear flow velocity and D is the diffusion coefficient of the HCO radical in helium. The latter was estimated according to the method of Lewis et al.[15] to be $D = 571$ cm^2 s^{-1} at $T = 298$ K and $P = 1$ Torr. A $T^{3/2}$ dependence of D on T was assumed in estimating D at other temperatures. The diffusion correction was small, ranging from a minimum of 0.5% to a maximum of 3%. A small stoichiometric correction

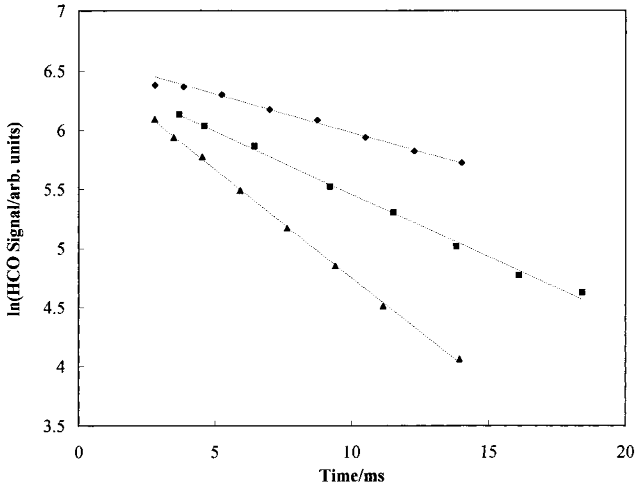

Figure 1. ln(HCO signal) vs reaction time at $T = 298$ K. $[O_2]$ in units molecule cm^{-3} are: (◆) 1.54×10^{13}; (■) 2.50×10^{13}; (▲) 4.39×10^{13}.

TABLE 1: Temperature Dependence of the Rate Constant for the Reaction HCO + O_2[a]

T/K	$[O_2]_{mean}/10^{13}$ molecule cm^{-3}	$[O_2]/[HCO]_0$	$k_1/10^{-12}$ cm^3 molecule^{-1} s^{-1}
200	0.5−7.6	50−760	5.27 ± 0.80
222	0.5−8.2	50−820	4.83 ± 0.72
250	0.6−7.7	60−770	4.35 ± 0.65
298	0.5−8.8	50−880	4.00 ± 0.60
398	0.8−9.9	80−990	4.46 ± 0.67

[a] Errors are based on a propagation of errors analysis. $[HCO]_0 = 1 \times 10^{11}$ molecule cm^{-3}.

to $[O_2]$ was made to allow for the depletion of O_2 during the reaction.

$$[O_2]_{mean} = [O_2]_0 - 1/2[HCO]_0 \tag{8}$$

A stoichiometric correction to [NO] was made in a similar manner. In both cases, the stoichiometric correction was very small, i.e., 1% or less.

The bimolecular rate constant k_1 is related to the corrected pseudo-first-order rate constant k_{corr} through the expression

$$k_{corr} = k_1[O_2]_{mean} + k_w \tag{9}$$

where $[O_2]_{mean}$ is calculated from eq 8 and k_w is the first-order rate constant for the loss of HCO on the wall. Figure 2 shows plots of k_{corr} vs $[O_2]_{mean}$ at the lowest temperature ($T = 200$ K), room temperature ($T = 298$ K), and the highest temperature ($T = 398$ K), respectively. The plots exhibit good linearity as required by eq 9 and the very small intercepts show that loss of HCO on the walls of the flow tube is quite small ($k_w < 10$ s^{-1}) over this temperature range. At $T = 298$ K we determine $k_1 = 4.00 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} with a 1σ error of $\pm$ 0.07. The overall error estimate (statistical plus systematic) of $\pm$0.60 was obtained by a propagation of errors analysis. Table 1 summarizes the rate data for reaction 1 obtained from the slopes of such plots over the temperature range $T = 200{-}398$ K. The initial $[O_2]$ was varied by a factor of about 20; the ratio $[O_2]/[HCO]$ ranged from 50 to 990.

TABLE 2: Comparison of Values of the Rate Constant for the Reaction HCO + NO → HNO + CO at $T = 298$ K from Direct Experiments

$k_2/10^{-11}$ cm^3 molecule^{-1} s^{-1}	$[NO]^a/[HCO]_0$	technique[b,c]	ref
0.85 ± 0.10	40	FP/AS	2
1.4 ± 0.2	60	LP/IDLS	3
1.2 ± 0.4		FP/IDLS	4
1.3 ± 0.2	3000	LP/LRA	7a
1.2 ± 0.2	12	FP/LRA	8
1.3 ± 0.2	200	DF/PIMS	this work

[a] Ratio of mean value of [NO] to $[HCO]_0$. [b] DF = discharge flow; FP = flash photolysis; LP = laser photolysis. [c] PIMS = photoionization mass spectrometry; AS = absorption spectroscopy; IDLS = intracavity dye laser spectroscopy; LMR = laser magnetic resonance; LRA = laser resonance absorption.

Kinetic modeling using the computer program ACUCHEM[16] was performed to probe for secondary chemistry that might occur in the system. The model included the following reactions: Cl + H_2CO → HCO + HCl, $k(298\text{ K}) = 7.5 \times 10^{-11}$ (ref 11); HCO + O_2 → HO_2 + CO, $k(298\text{ K}) = 4.0 \times 10^{-12}$ (Table 1); HCO + HCO → products, $k(298\text{ K}) = 4.5 \times 10^{-11}$ (ref 6); HCO + Cl_2 → HCOCl + Cl, $k(298\text{ K}) = 7.2 \times 10^{-12}$ (ref 9), where the units for the rate constants are cm^3 molecule^{-1} s^{-1}. The modeled and experimental HCO decays agreed to within 10%, demonstrating that secondary chemistry was unimportant and that the pseudo-first-order analysis was accurate.

A plot of $\ln k_1$ vs $1/T$ is shown in Figure 3. For the temperature range $T = 200{-}298$ K, the Arrhenius plot shows a negative temperature dependence; the results at $T = 398$ K suggest a slight positive temperature dependence between $T = 298$ and 398 K. A linear least-squares fit of the data for the temperature range $T = 200{-}298$ K yields the Arrhenius expression

$$k_1 = (2.2 \pm 0.2) \times 10^{-12} \exp[(170 \pm 22)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{10}$$

where the error limits are $\pm 2\sigma$. This corresponds to a small negative activation energy of -0.3 kcal mol^{-1}.

Experiments were also performed in a similar fashion for the reaction HCO + NO at $T = 298$ K and 1 Torr total pressure (He). The concentration of NO ranged from 5.1×10^{12} to 3.4×10^{13} molecule cm^{-3} and therefore the ratio [NO]/[HCO] varied from 50 to 340. Figure 4 shows a plot of k_{corr} vs $[NO]_{mean}$ at $T = 298$ K. As was the case for the HCO + O_2 reaction, the plot exhibits good linearity and the intercept yields a low value ($k_w = 7$ s^{-1}) for the wall loss of HCO. From the slope of the line in Figure 4 we obtain $k_2 = (1.3 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} where the error limits are determined by a propagation of errors analysis.

Discussion

We begin with a consideration of the HCO + NO reaction since there is a consensus that its rate constant is reasonably well established. Our results for this reaction thus serve as a check on the reliability of the present experimental approach used to study the HCO + O_2 reaction.

A summary of the experimental values of the rate constant for the reaction HCO + NO at $T = 298$ K is shown in Table 2. All previous measurements[2−4,7,8] employed some combination of photolysis (FP or LP) and absorption spectroscopy (AS, IDLS, or LRA). Our DF-PIMS result, $k_2 = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, is in excellent agreement with all but one[2] of the five previous measurements. Veyret and Lesclaux[8] have suggested that the virtual absence of NO consumption in the static systems used to study this reaction accounts for the good agreement as compared to the poorer agreement evidenced in

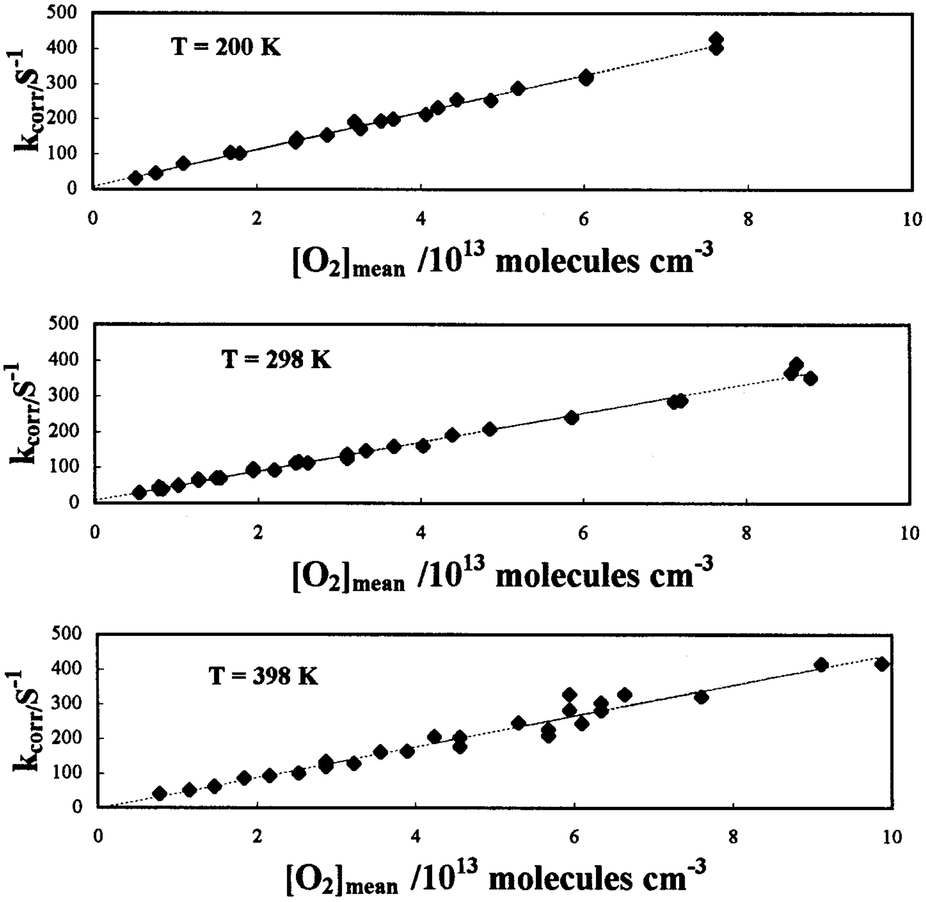

Figure 2. k_{corr} vs $[O_2]_{mean}$; errors are $\pm 1\sigma$. Top panel: $T = 200$ K. From the slope, $k_1 = (5.27 \pm 0.10) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and from the intercept, $k_w = 8 \pm 4$ s^{-1}. Middle panel: $T = 298$ K, $k_1 = (4.00 \pm 0.07) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and $k_w = 9 \pm 3$ s^{-1}. Bottom panel: $T = 398$ K, $k_1 = (4.46 \pm 0.18) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and $k_w = -2 \pm 9$ s^{-1}.

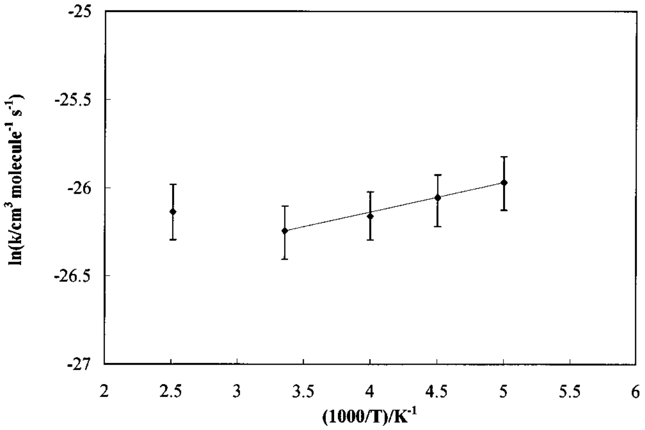

Figure 3. Arrhenius plot for k_1. The line is the least-squares fit of the data for the interval $T = 200-298$ K.

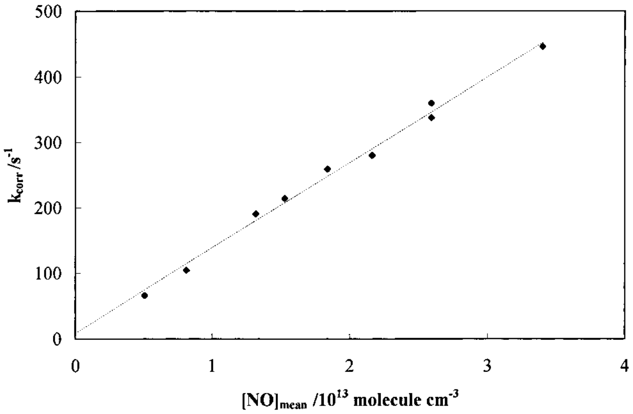

Figure 4. k_{corr} vs $[NO]_{mean}$ at $T = 298$ K. $k_2 = (1.30 \pm 0.05) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, and $k_w = 7 \pm 8$ s^{-1} where the errors are $\pm 1\sigma$.

the same static systems used to study the HCO + O_2 reaction. A very recent theoretical calculation[17] of the rate of formation of the initial CH(O)NO reaction complex yields $k_{2a} = 2.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at $T = 298$ K. This is in reasonable agreement with the experimental value of Langford and Moore[7b] of $k_{2a} = 3.4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} which is based on the rate of removal of vibrationally excited HCO by NO.

A review of this and all previous direct determinations of the rate constant for the HCO + O_2 reaction reveals, as mentioned in the Introduction, larger than expected discrepancies for what appears to be a relatively simple and well studied reaction. A summary of the reported values for k_1 at $T = 298$ K is given in Table 3. Our DF-PIMS result at $T = 298$ K, $k_1 = 4.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, is on the low end of the range of values and is most consistent with the studies[3-5] employing intracavity dye laser spectroscopy (IDLS). Some criticisms have been made of the IDLS experiments. One is that the relationship between HCO concentration and laser attenuation in an intracavity absorption experiment might not be linear. However, the good agreement among rate constant values k_2 for the HCO + NO reaction from both intracavity[3,4] and extracavity[7a,8] laser absorption techniques makes this suggestion unlikely. In addition, Reilly et al.[3] and Nadtochenko et al.[4] have demonstrated that measured HCO absorption optical densities in their IDLS experiments are proportional to the HCO concentrations. Another criticism, not so readily dismissed, is that there could

TABLE 3: Comparison of Values of the Rate Constant for the Reaction HCO + O_2 → HO_2 + CO at T = 298 K from Direct Experiments

$k_1/10^{-12}$ cm^3 molecule^{-1} s^{-1}	$[O_2]^a/[HCO]_0$	pressure/Torr	technique^b	ref
5.7 ± 1.2	100	1.5−5.0	DF/PIMS	1
5.6 ± 0.9	47	20; 530	FP/AS	2
4.0 ± 0.8	100	10	LP/IDLS	3
3.8 ± 1.0		13−100	FP/IDLS	4
4.2 ± 0.7	1000	5.0	FP/IDLS	5
5.1 ± 1.0	100	1.0−3.1	DF/LMR	6
4.6 ± 0.6	5000	3−5; 1000	LP/LRA	7a
5.6 ± 0.6	40	45; 500	FP/LRA	8
6.2 ± 1.2	600	0.5; 1.0	LP/PIMS	9
4.0 ± 0.6	400	1.0	DF/PIMS	this work

[a] Ratio of mean value of $[O_2]$ to $[HCO]_o$. [b] See footnotes b and c in Table 2.

have been significant depletion of the O_2 reactant in the static systems employed. Veyret and Lesclaux[8] summarize the considerable evidence for depletion of O_2 in a variety of systems, including their own, and suggest that unrecognized O_2 consumption would slow the decay of HCO as the delay between the photolyzing and analyzing pulses is increased and the concentration of O_2 decreases with subsequent photolyzing pulses. However, the good agreement between our DF-PIMS result for HCO + O_2 from a fast flow system and those obtained via pulsed photolysis-IDLS experiments in static systems suggests that O_2 depletion in the IDLS static systems may have been less serious than suggested.

There is no experimental evidence for a dependence of k_1 on total pressure. As summarized in Table 3, a discernible trend in the values for k_1 at T = 298 K is not evident for pressures in the range 0.5 to 1000 Torr. This is not inconsistent with the suggestion of complex formation in reaction 1. Langford and Moore[7a] have emphasized that "the pressure independence of rate constants implies only that most of the complexes which are formed dissociate to products or to the original reactants before being stabilized."

Concerning the primary products of reaction 1, Temps and Wagner[6] have shown that HO_2 + CO are the main and probably exclusive products (branching fraction $\Gamma = 1.00 \pm 0.07$) at T = 298 K and P = 1−3 Torr. Upper limits for the channels forming OH + CO_2 ($\Gamma \leq 0.004$) and the $HCOO_2$ adduct ($\Gamma \leq 0.07$) were also given. The lifetimes of the collision complexes formed in reaction 1 are evidently too short to be stabilized and yield measurable concentrations of the $HCOO_2$ adduct at pressures up to one atmosphere.[7a]

The variation in values for k_1 at T = 298 K may be due to varying and unrecognized secondary chemistry involving not only the HCO radical but also other accompanying products such as H from the photodissociation of H_2CO[3,4,7,8] and CH_3 from either the photodissociation of CH_3CHO[2,4,5,8,9] or as a product of the reaction $O(^3P) + C_2H_4 \rightarrow HCO + CH_3$ (ref 1). Langford and Moore[7a] have suggested that the chemistry of the rather complex formaldehyde photooxidation could be a complication in many of the HCO + O_2 studies. Secondary chemistry does not appear to be a problem in the corresponding HCO + NO studies.

This study represents the first determination of k_1 at temperatures below T = 298 K. A comparison of the Arrhenius parameters from all three direct temperature studies is given in Table 4, and the corresponding data are shown in Figure 5. Although all available laboratory data (a total of 22 values excluding only the T = 713 K value[9]) can be accommodated by a single temperature independent value of $k_1 = (5.3 \pm 2.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} ($\pm 2\sigma$) for $200 < T < 610$ K, this range of values seems unusually large and simple averaging may disguise genuine differences.

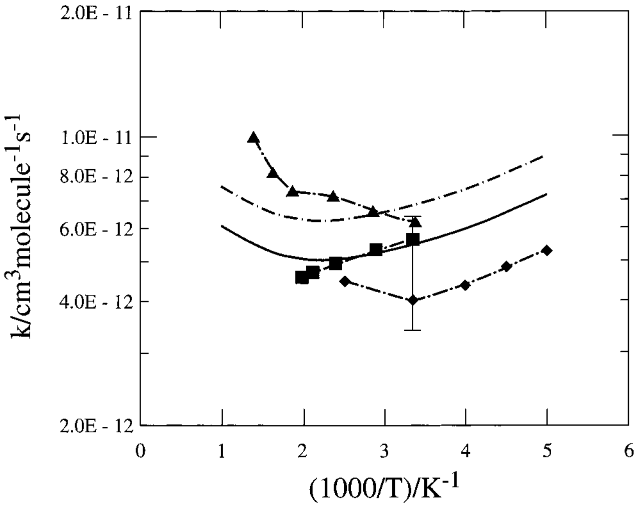

Figure 5. Comparison of the temperature dependence of k_1. Direct experiments: (▲) Timonen et al. (1988),[9] (■) Veyret and Lesclaux (1981),[8] (◆) this study [for these three studies, dashed lines connect the data points to show the trend in the data]; (I) range of values at T = 298 K for 10 studies listed in Table 3. Recent calculation of Hsu et al. (1996)[18]: (– - –) eq 11 in this paper; (—) eq 11 multiplied by 0.80.

TABLE 4: Comparison of the Arrhenius Parameters A and E/R for the Reaction HCO + O_2 → HO_2 + CO from Direct Experiments

A/cm^3 molecule^{-1} s^{-1}	E/R	temperature range (K)	ref
3.4×10^{-12}	−153	298−503	8
1.3×10^{-11}	+204	295−713	9
2.2×10^{-12}	−170	200−298	this work

A discussion of the consistency among the three direct experimental studies of the temperature dependence of k_1 will be facilitated by a consideration of the results of a recent theoretical calculation. Hsu et al.[18] reported variational transition state calculations for the direct hydrogen abstraction channel and RRKM calculations for the complex formation channel. Their derived expression for the total rate constant (both channels) for the temperature range T = 300−3000 K is

$$k_1 = 2.0 \times 10^{-14} T^{0.807} \exp(366/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (11)$$

This is in good agreement with most of the experimental results over this temperature range. This expression reproduces the positive temperature dependence of k_1 between T = 700 and 500 K observed by Timonen et al.[9] since the direct abstraction channel dominates at higher temperatures. Competition between the direct abstraction channel (positive T dependence) and the complex formation channel (negative T dependence) results in the relatively flat temperature dependence of k_1 between T = 500 and 300 K, as observed in all three direct temperature-dependent studies (refs 8 and 9 and the present work). If the calculated expression for the total rate constant (eq 11) is extended below T = 298 K, the eventual dominance of the complex formation channel at lower temperatures results in calculated k_1 values which follow a negative temperature dependence similar to that observed in our experiments from T = 298 K to 200 K but with the absolute rate constant values about 75% higher. Better agreement is obtained with a modified expression obtained by mutiplying eq 11 by a minor uniform scaling factor of 0.80. This expression bridges the gap between the higher and lower values of k_1 and also accommodates the Veyret and Lesclaux[8] observations somewhat better. The comparison between these calculations, both original[18] and modified, and direct experiments between $T = 200$ and 713 K is shown in Figure 5. Agreement of the direct experiments with the calculations of Langford and Moore[7a] and Bozzelli and Dean[19] is less satisfactory.

Since the temperature dependencies observed in the three direct laboratory studies are rather small and the disagreement between different studies somewhat large, a resolution of the experimental uncertainty concerning the sign and the magnitude of the temperature dependence requires a substantial extension of the temperature range over which direct measurements of k_1 are made. Previously, the range covered was $T = 295-713$ K, and the present study has extended this down to $T = 200$ K. Extension to significantly lower temperatures could possibly be achieved by studying the HCO + O_2 reaction down to about $T = 80$ K using cryogenic cooling[20] or even down to $T = 20$ K using the CRESU technique.[20-22] Extension to higher temperatures could employ the combined shock tube/flash photolysis technique[23-25] or the high-temperature photochemistry reactor technique[26] in the range $T = 700$ K to perhaps 1000 K; the upper temperature range will be limited by the thermal decomposition of the HCO radical.

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