

Temperature dependence and deuterium kinetic isotope effects in the HCO (DCO) + O₂ reaction between 296 and 673 K

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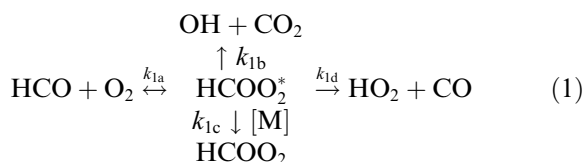
Received 11 July 2001

Abstract

The reactions HCO (DCO) + O₂ have been measured by the laser photolysis/CW laser-induced fluorescence (LIF) method from 296 to 673 K, probing the ($\tilde{B}^2A' \leftarrow \tilde{X}^2A'$) HCO (DCO) system. The HCO (DCO) + O₂ rate coefficients are 5.63 ± 0.31 and $5.61 \pm 0.23 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, respectively, at 296 K; both are nearly independent of temperature between 296 and 673 K. The observed deuterium kinetic isotope effect is within the error estimate of previous measurements but is significantly smaller than recent theoretical predictions. © 2001 Published by Elsevier Science B.V.

1. Introduction

The reaction of the formyl radical (HCO) with molecular oxygen (O₂) is of interest to the fields of both atmospheric chemistry and high temperature combustion. There have been many direct studies of the room temperature rate coefficient for HCO + O₂ [1–12]. However, there is only one published observation, by Langford and Moore [7] of the DCO + O₂ rate coefficient. The reaction is thought to proceed through an activated complex (HCOO₂) [13].



Tso et al. [14] have previously detected both the HCOO₂ and the DCOO₂ adducts by Fourier transform infrared spectroscopy in a low temperature matrix. The stabilized adduct and the OH production channels do not appear to be major product channels at room temperature and atmospheric pressures. Instead the reaction is thought to produce primarily the HO₂ + CO channel under these conditions. The three studies that observed the rate coefficient over the largest dynamic pressure range Shibuya et al. [2] (20–530 Torr), Veyret and Lesclaux [6] (45–500 Torr) and Langford and Moore [7] (5–1000 Torr) agree that there is no pressure effect on the rate coefficient. Temps and Wagner [8] report an upper limit on (k_{1b}/k_{1d}) of $<4 \times 10^{-3}$. Yamasaki et al. [12] have recently verified the results of Temps and Wagner placing an upper limit on the OH channel of $k_{1b}/k_{1d} < 3 \times 10^{-3}$.

Previous studies have used a wide variety of techniques to observe the absolute HCO + O₂ reaction rate coefficient including absorption [2,6,7],

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intracavity laser spectroscopy [3–5], laser magnetic resonance [8], photoionization mass spectrometry [1,9], cavity ring-down spectroscopy [11], and laser induced fluorescence [12]. The reported rate coefficients range from 3.8 to $6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, but cluster around two values: $\sim 5.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $\sim 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The values do not appear to depend on experimental technique, as similar experimental techniques produce results in either range. However, Veyret and Lesclaux have performed experiments that suggest that experiments done in static systems [3–5] may have underestimated the rate coefficient.

There are three independent measurements of the temperature dependence of the $\text{HCO} + \text{O}_2$ rate coefficient. Nesbitt et al. [10] investigated the rate coefficient as a function of temperature from 200 to 400 K and observed a decrease in the rate coefficient with increasing temperatures (fit to $2.2 \pm 0.2 \times 10^{-12} \text{ e}^{(170 \pm 22)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) between 200 and 296 K. Veyret and Lesclaux [6] observed the temperature dependence of the rate coefficient from 296 to 500 K and also observed that the rate coefficient decreased with increasing temperature (fit to $5.5 \pm 0.6 \times 10^{-11} T^{-(0.4 \pm 0.3)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). However, Timonen et al. [9] observed an opposite trend from 295 to 713 K with the rate coefficient increasing with an increase in temperature (fit to $1.3 \pm 0.6 \times 10^{-11} \text{ e}^{(-204 \pm 180)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). All the studies agree that the reaction rate coefficient has very little temperature dependence in the region from 296 to 550 K.

Hsu et al. [13] have calculated the rate coefficient by an ab initio and statistical theory approach from 300 to 3500 K. They found that the rate for direct abstraction of the hydrogen from HCO by O_2 is insignificant below 2000 K, and that the reaction is dominated at temperatures below 2000 K by dissociation of a collisional complex (HCOO_2). The production of HO_2 is predicted to proceed via elimination from a four centered transition state. The rate coefficient k_{1c} is calculated to be much smaller than k_{1d} for pressures lower than 2000 Torr. Thus, the presence of a collision complex is consistent with the observed pressure independence, as earlier proposed by Langford and Moore [7]. Also reproduced in the

calculation is the insignificance of the OH channel with k_{1b}/k_{1d} calculated to be 4.0×10^{-7} . The calculated rate coefficient (fit by $k_1 = 2.0 \times 10^{-14} T^{-807} \exp(366.0/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) decreases with increased temperature for temperatures below ~ 400 K and increases with increased temperature above ~ 400 K remaining relatively independent of temperature in the region between 296 and 700 K. The calculated overall rate coefficient at room temperature, $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is on the high side of the range of observed values.

Less is known about the kinetic isotope effect in this reaction. Langford and Moore [7] previously observed that deuterium substitution increases the rate coefficient by $\sim 10\%$, and performed a Rice–Ramsperger–Kassel–Marcus (RRKM) calculation to rationalize their observation. Their calculation utilized a transition state with a three membered ring where one of the oxygen atoms from the O_2 bridges the H–C bond of HCO. Langford and Moore explained the greater reactivity of DCO in terms of the greater number of open product channels for the smaller zero point energy of the deuterium transition state. This interpretation implies a significant dissociation of the initially formed complex back to reactants. Hsu et al. [13] calculate little returning flux and predict the opposite effect for deuteration of the HCO than observed by Langford and Moore. Their calculation predicts the $\text{HCO} + \text{O}_2$ rate coefficient to be 15–20% larger than for $\text{DCO} + \text{O}_2$ from 300 to 2000 K. Unpublished results from Imamura and Washida using pulsed-laser photolysis/photoionization mass spectrometry also suggest a normal ($k_H > k_D$) kinetic isotope effect [15,16].

This study investigates both the $\text{HCO} + \text{O}_2$ and $\text{DCO} + \text{O}_2$ reaction rate coefficient as a function of temperature (296–673 K). The time behavior of HCO (DCO) radical is directly observed by using a laser photolysis/CW laser-induced fluorescence (cwLIF) method. The ($\tilde{\text{B}}^2\text{A}' \leftarrow \tilde{\text{X}}^2\text{A}'$) system of both isotopomers has been previously characterized [17–22] and can be used to observe the progress of the reaction for either isotopomer independently. Both reactions are nearly temperature independent between 296 and 673 K, and the kinetic isotope effect is unity within experimental

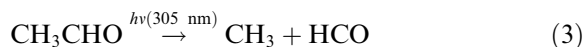
uncertainty. While this observation is within the precision of the previous experiments of Langford and Moore, it cannot corroborate their interpretation of a reversible association based on an inverse kinetic isotope effect. The observed kinetic isotope effect is also significantly smaller than predicted by the *ab initio* and statistical calculations of Hsu et al. [13].

2. Experiment

The reaction of $\text{HCO(DCO)} + \text{O}_2$ is investigated by using the laser photolysis/CW laser-induced fluorescence (LP/cwLIF) method, similar to that employed in previous experiments [23,24]. The experiments are performed in a flow reactor, where the gas flow is slow compared to the reaction time scale, but fast enough to prevent the build up of products. The reaction is initiated by Cl abstraction from formaldehyde (H_2CO). The Cl is generated by photolysis at 193 nm of either CCl_4 or CCl_3F , and the HCO (DCO) is generated by subsequent Cl abstraction from H_2CO (D_2CO). The HCO (DCO) radical then reacts with O_2 .



In some experiments the reaction is initiated by photolysis of acetaldehyde (CH_3CHO) at 305 nm, or of formaldehyde at 284 nm.



The progress of the $\text{HCO (DCO)} + \text{O}_2$ reaction is monitored by LIF in the ($\tilde{\text{B}}^2\text{A}' \leftarrow \tilde{\text{X}}^2\text{A}'$) system using the doubled output of a CW ring laser operating near 258 nm [25]. The ring laser output is doubled in an external buildup cavity with a BBO crystal as the second harmonic generation medium. The probe beam ($\sim 50\text{ mW cm}^{-2}$) at 38692.6 cm^{-1} (38631.6 cm^{-1} for DCO) enters the flow reactor through a CaF_2 window. The unfocused

photolysis beam first passes through an aperture and then enters the reactor ($<3\text{ mJ/pulse}$ in $\sim 0.15\text{ cm}^2$) at a right angle to the probe beam. The fluorescence is detected perpendicular to both laser beams with a photomultiplier tube operating in a single photon counting mode. A UV filter is placed between the photomultiplier tube and the reactor to remove stray 193 nm light and scattered room light. The photomultiplier output is transferred to a multichannel scaler, where typically 2048 channels with a width of $1.28\text{ }\mu\text{s}$ are accumulated. To achieve a good signal to noise ratio the signal is typically added over 2000–6000 excimer laser shots.

The stainless steel flow reactor is resistively heated. The temperature of the cell is monitored by a retractable thermocouple placed inside the cell directly above the reaction zone. The gas flows are set by calibrated mass flow controllers, and the pressure in the reactor is monitored with a capacitance manometer. The formaldehyde is prepared by cracking paraformaldehyde, purified by vacuum distillation, and stored in 12 l glass bulbs. Typical gas concentrations are $[\text{O}_2] = 0.5\text{--}3 \times 10^{15}\text{ cm}^{-3}$, $[\text{CCl}_3\text{F}]$ or $[\text{CCl}_4] = 6 \times 10^{15}\text{ cm}^{-3}$, and $[\text{H}_2\text{CO}] = 3 \times 10^{15}\text{ cm}^{-3}$. Helium is added to the desired total pressure. Initial HCO concentrations are estimated to be $\sim 1\text{--}3 \times 10^{13}\text{ cm}^{-3}$ based on the time constant of the second-order decay in the absence of O_2 and the evaluated self-reaction rate coefficient of $5 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ [26]. A similar estimate is obtained using the 193 nm photolysis flux, the photolyte concentration and its absorption cross-section [27]. The reactions were monitored under pseudo-first order conditions, where the $[\text{O}_2] \gg [\text{HCO}]$. The HCO time profile is fitted by a single exponential, and the second-order rate coefficient obtained from the slope of a plot of the pseudo-first order rate coefficient versus O_2 concentration.

3. Results

The HCO signal without added O_2 decays by a second-order process, shown in Fig. 1. The inset of Fig. 1 shows that the inverse of the HCO signal is linear. The loss of HCO (DCO) in the temperature

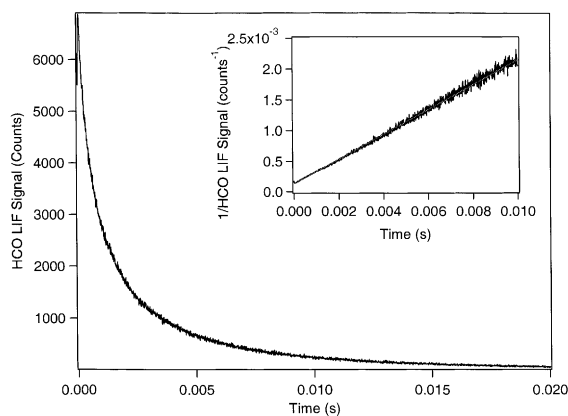


Fig. 1. The time profile of the cwLIF signal for HCO taken at 296 K and 30.0 Torr. The imbedded trace is the inverse if the HCO time profile. The linearity of the inverse signal demonstrates that HCO decays by a second-order process in the absence of O_2 .

range of this study is most likely due to HCO self-reaction. Removal by self-reaction ($\tau_{1/2} \sim 1$ ms) is considerably slower than the $HCO + O_2$ reaction at the O_2 concentrations used in this study, and the pseudo-first order decay traces can be fit well by a single exponential. Fig. 2 shows an HCO time trace with $2.7 \times 10^{15} \text{ cm}^{-3}$ of O_2 at 296 K and 30 Torr total pressure. The residuals show that the

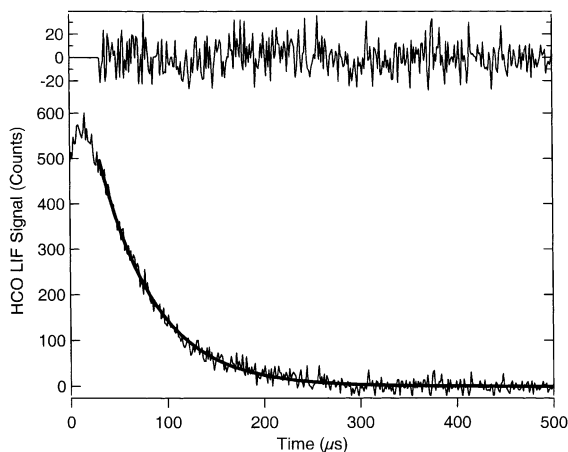


Fig. 2. The time profile of the cwLIF signal for HCO taken at 296 K and 30.0 Torr with $2.7 \times 10^{15} \text{ cm}^{-3}$ of O_2 . With oxygen present the decay of the HCO signal is fit well by a single exponential with the residuals as shown. The decay corresponds to a pseudo-first order rate coefficient of 17800 s^{-1} .

decay of the HCO is described well by a single exponential. A plot of the pseudo-first order rate coefficient against $[O_2]$ is shown in Fig. 3 for $HCO + O_2$ at 296 K and 30 Torr total pressure. The linear fit in Fig. 3 yields a second-order rate coefficient of $5.63 \pm 0.31(2\sigma) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The error estimate is the statistical error as measured by two standard deviations of the fit to the slope.

The second-order rate coefficients (k_1) for both $HCO + O_2$ and $DCO + O_2$ obtained at different temperatures are listed in Table 1. The $HCO + O_2$ rate coefficient at 298 K is independent of pressure between 8 and 30 Torr. The temperature dependence is investigated at constant total gas density corresponding to the total density at 296 K and 30 Torr ($= 9.8 \times 10^{17} \text{ cm}^{-3}$). An Arrhenius plot of the second-order rate coefficient is shown in Fig. 4 for temperatures between 296 and 673 K. The plot shows at most a slight increase in the rate coefficient with increasing temperature. A weighted least squares fit yields the Arrhenius expression $k_1 = 6.1 \pm 1.0 \times 10^{-12} e^{(-26 \pm 72)/T}$, where the error limits are 2σ of the uncertainty in the fitting parameters. The $DCO + O_2$ rate coefficient is also temperature insensitive between 296 and 673 K. As seen in Fig. 4, the rate coefficients of $DCO + O_2$ (k_D) and $HCO + O_2$ (k_H) are nearly identical at both 673 and 296 K. The kinetic iso-

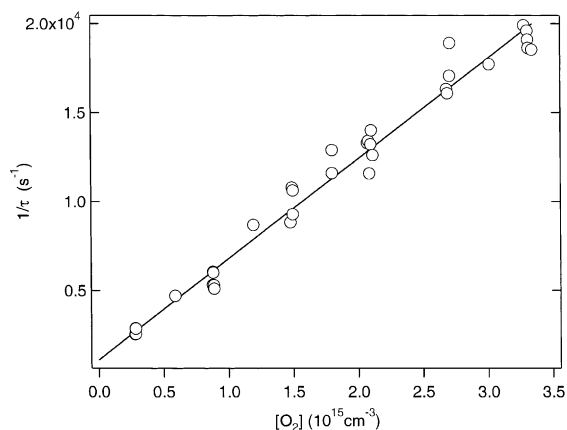


Fig. 3. Pseudo-first order rate coefficient ($k_1[O_2]$) as a function of O_2 concentration at 296 K and 30 Torr. The linear fit yields a second-order rate coefficient (k_1) of $5.63 \pm 0.31 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The uncertainty is listed as 2σ of the fit.

Table 1

Measured rate coefficients for $\text{HCO}(\text{DCO}) + \text{O}_2^{\text{a}}$

Reaction	Pressure (Torr)	Temperature (K)	Second-order rate coefficient ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{HCO} + \text{O}_2$	8	296	5.57 ± 0.35
$\text{HCO} + \text{O}_2$	30	296	5.63 ± 0.31
$\text{HCO} + \text{O}_2$	38	373	5.68 ± 0.30
$\text{HCO} + \text{O}_2$	48	473	5.80 ± 0.47
$\text{HCO} + \text{O}_2$	58	573	6.16 ± 0.37
$\text{HCO} + \text{O}_2$	68	673	5.71 ± 0.33
$\text{DCO} + \text{O}_2$	30	296	5.61 ± 0.23
$\text{DCO} + \text{O}_2$	68	673	5.73 ± 0.34
$\text{HCO} + \text{O}_2$	30	296	$5.65 \pm 0.54^{\text{b}}$
$\text{HCO} + \text{O}_2$	10	296	$6.76 \pm 0.36^{\text{c}}$
$\text{DCO} + \text{O}_2$	10	296	$6.98 \pm 0.40^{\text{c}}$

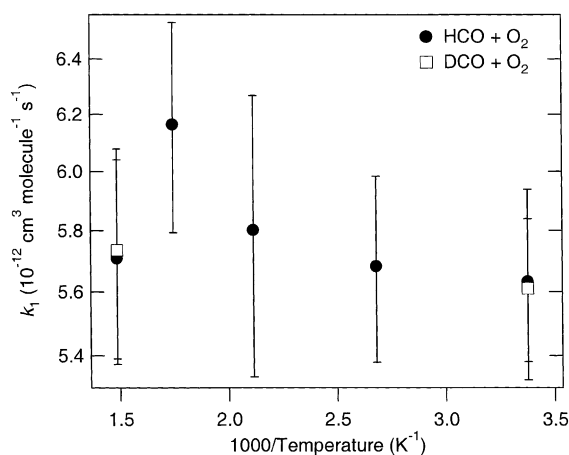
^a The uncertainty is listed as 2σ of the fit.^b Formaldehyde photolysis.^c Acetaldehyde photolysis.

Fig. 4. The temperature dependence of the second-order rate coefficient (k_1) for $\text{HCO} + \text{O}_2$ (●) and $\text{DCO} + \text{O}_2$ (□) measured at a constant density of $9.72 \times 10^{17} \text{ cm}^{-3}$. Error bars represent 2σ .

tope effect is $k_{\text{H}}/k_{\text{D}} = 1.00 \pm 0.07$ at 296 K and $k_{\text{H}}/k_{\text{D}} = 1.00 \pm 0.08$ at 673 K.

4. Discussion

The room temperature rate coefficient obtained in this experiment is listed in Table 2 along with previous measurements for comparison. As noted above, the rate coefficient measurements for

$\text{HCO} + \text{O}_2$ fall into two groups. The present room temperature rate coefficient measurement agrees very well with the higher grouping around $\sim 5.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The most recent evaluations from JPL [27] and the IUPAC subcommittee [28] recommend values of $5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively for the room temperature $\text{HCO} + \text{O}_2$ rate coefficient. There are four reports between 3.8 and $4.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and one at $4.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Three of the lower values [3–5] for the rate coefficient were obtained by using a static system and thus were subject to successive photolysis pulses. Veyret and Lesclaux [6] point out that depletion of the O_2 in these experiments may have resulted in a systematic underestimation of the rate coefficient. If the static experiments are disregarded, only the discharge flow/mass spectrometric experiments of Nesbitt et al., with $k_1 = 4.0 \pm 0.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, produce a value in the lower range. The results of Langford and Moore [7] fall slightly below the higher range of values and those of Temps and Wagner [8] are consistent with either range. Considering the agreement of the present measurements with the pulsed LIF results of Yamasaki et al. [12] under similar conditions (see below) there are at least eight absolute measurements supporting a value for k_1 in the higher range.

Table 2

Comparison of observed rate coefficients for $\text{HCO} + \text{O}_2$ at room temperature

k_1^a	Method	Reference
3.8 ± 1.0	Flash photolysis/Intracavity laser spectroscopy	[4]
4.2 ± 0.7	Flash photolysis/Intracavity laser spectroscopy	[5]
4.0 ± 0.8	Laser photolysis/Intracavity laser spectroscopy	[3]
4.0 ± 0.6	Discharge flow/Photoionization mass spectrometry	[10]
4.6 ± 0.6	Laser photolysis/Laser absorption	[7]
5.1 ± 1.0	Discharge flow/Laser magnetic resonance	[8]
6.2 ± 1.2	Laser photolysis/Photoionization mass spectrometry	[9]
6.6 ± 0.3	Laser photolysis/Pulsed laser-induced fluorescence	[12]
5.6 ± 0.6	Laser photolysis/Laser absorption	[6]
5.6 ± 0.9	Flash photolysis/Visible absorption	[2]
5.7 ± 1.2	Discharge flow/Photoionization mass spectrometry	[1]
5.9 ± 0.5	Laser photolysis/Cavity ring-down spectroscopy	[11]
5.6 ± 0.3	Laser photolysis/CW Laser-induced fluorescence	This work

^a Units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Several different methods of HCO generation are compared in the present experiments. Most of the present experiments use hydrogen abstraction by Cl atom from formaldehyde to generate HCO radicals. The rate coefficient was also obtained by forming the HCO radical by direct photolysis of formaldehyde at 284 nm. The rate coefficient obtained by direct photolysis of formaldehyde ($5.65 \pm 0.54 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is the same as the rate coefficient obtained by Cl abstraction. However, to mimic the conditions of the one previous LIF measurement of this reaction [12], the $\text{HCO} + \text{O}_2$ rate coefficients were measured using our CW probe source and photolysis of acetaldehyde at 305 nm. A rate coefficient of $6.8 \pm 0.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained using acetaldehyde at 10 Torr of total pressure. This number is in good agreement with the Yamasaki et al. measurement but is $\sim 25\%$ larger than the number obtained by Cl abstraction from H_2CO , suggesting that LIF measurements of HCO from CH_3CHO photolysis may slightly overestimate k_1 .

The source of the discrepancy between the two methods is unclear. Nesbitt et al. suggest that uncharacterized secondary chemistry and reactions of side products of photolysis of H_2CO or CH_3CHO may help explain discrepant measurements of the $\text{HCO} + \text{O}_2$ rate coefficient. However, photolytic initiation has been employed in the bulk of the direct experiments, including rate coefficient

measurements across the entire experimentally reported range. The current measurement using $\text{Cl} + \text{H}_2\text{CO}$ initiation is in good agreement with results from other experimental methods using acetaldehyde photolysis as a source of HCO (such as the recent cavity ringdown experiment by Ninomiya et al. [11]). The laser absorption experiments of Veyret and Lesclaux [6] obtained the same rate coefficient when using either acetaldehyde or formaldehyde photolysis as the HCO source. It therefore appears unlikely that competing reaction with another photoproduct of acetaldehyde (e.g., CH_3) is the cause of the discrepancy. It is conceivable that interfering fluorescence signals are being generated from reactions of other acetaldehyde photoproducts such as CH_3CO . Formaldehyde photolysis produces either $\text{H} + \text{HCO}$ or $\text{H}_2 + \text{CO}$, and may be the cleaner precursor. The Cl abstraction system may be more reliable as it produces no reactive H atoms, but only the presumably less reactive CFCl_2 photoproduct. In any event the change in the counter radical from H (for the direct photolysis study) to CFCl_2 (for the Cl abstraction study) does not affect the measured rate coefficient. The present acetaldehyde experiments also show larger scatter and less day to day reproducibility. Since formaldehyde is a cleaner system and produces more consistent and repeatable results we have greater confidence in the rate coefficients obtained by LIF methods which use formaldehyde as the precursor

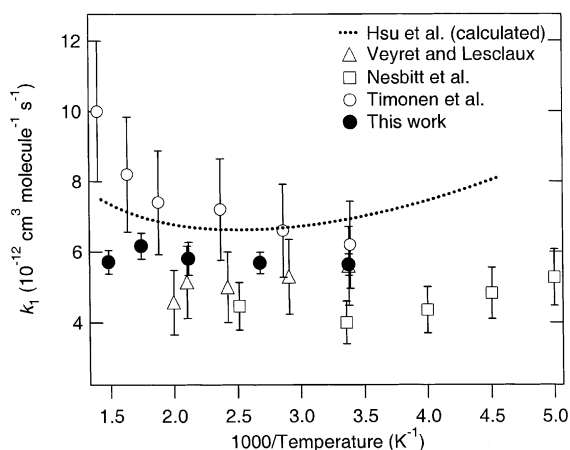


Fig. 5. Comparison of the temperature dependence of the second-order rate coefficient (k_1) for $\text{HCO} + \text{O}_2$. The direct measurements: Timonen et al. [9] (\circ), Veyret and Lesclaux [6] (Δ), Nesbitt et al. [10] (\square) and this work (\bullet). The rate coefficient calculated by Hsu et al. [13] is shown as the dotted line. Error bars represent (2σ).

to HCO than those obtained using the photolysis of acetaldehyde.

Fig. 5 shows the temperature dependence of the rate coefficient observed in this study and compares it to the three previous studies and the predicted temperature dependence by Hsu et al. Although Veyret and Lesclaux [6] observe a different temperature trend with their rate decreasing with increasing temperature, in general the present results are within the precision limits of their experiments. The results of Timonen et al. [9] are consistently slightly larger than the present results and show a stronger increase in the rate coefficient with temperature. They however also observe the rate coefficient to be essentially flat with temperature until ~ 550 K; below that temperature the present measurements are within the precision of their experiments. The discharge flow measurements of Nesbitt et al. [10] show a decreasing rate coefficient with increasing temperature below room temperature, followed by a slight increase as the temperature is raised to 398 K. The rate coefficient calculated by Hsu et al. [13] shows a negative temperature dependence below ~ 400 K with an upturn at higher temperature, and is in reasonable conformity with the experimental data.

While theory agrees with the observed pressure and temperature dependence of the $\text{HCO} + \text{O}_2$ reaction, a discrepancy remains between theory and experiment for the kinetic isotope effect for deuteration of the HCO radical. Langford and Moore [7] observed an increase in the reaction rate upon deuteration of the DCO at room temperature ($k_{\text{H}}/k_{\text{D}} = 0.91 \pm 0.17$). However, Hsu et al. [13] predict a decrease in the rate coefficient upon deuteration on the order of 15–20% ($k_{\text{H}}/k_{\text{D}} = 1.15\text{--}1.20$), outside the limits of the Langford and Moore experiment. The error estimates of Langford and Moore encompass the present measurement of the isotope effect at 296 K ($k_{\text{H}}/k_{\text{D}} = 1.00 \pm 0.07$). The kinetic isotope effect at 296 K measured by using the photolysis of CH_3CHO and CD_3CDO to generate HCO and DCO , respectively, ($k_{\text{H}}/k_{\text{D}} = 0.97 \pm 0.07$) is similar to that observed using Cl abstraction from formaldehyde to prepare HCO (DCO). Once again, this experiment and the experiment of Langford and Moore do not completely rule out a slightly smaller second-order rate coefficient for DCO , but neither is consistent with a decrease on the order of the 15–20% predicted by Hsu et al.

The kinetic isotope effect in a complex-mediated reaction can reflect a delicate balance among isotope effects for stabilization, redissociation to reactants, and formation of products. Langford and Moore proposed a model for the $\text{HCO} + \text{O}_2$ reaction which included a kinetically significant redissociation of the $\text{HC}(\text{O}_2)\text{O}$ complex to reactants in order to produce an inverse kinetic isotope effect. The present measurements suggest that the returning flux from complex to reactants need not be significant, which is in agreement with the ab initio calculations of Hsu et al. [13]. However, the measured kinetic isotope effect is smaller than that predicted by their statistical calculations. The present measurement is not significantly different from the collision frequency ratio, $Z_{\text{HCO}+\text{O}_2}/Z_{\text{DCO}+\text{O}_2} = 1.0089$. The rapid dissociation of the $\text{HC}(\text{O}_2)\text{O}$ complex to $\text{HO}_2 + \text{CO}$, with minor regeneration of $\text{HCO} + \text{O}_2$, implied by the ab initio calculations, may suggest that the reaction is largely governed by (the high pressure limit of) the association step. Variational transition state theory calculations of kinetic isotope effects for

barrierless association reactions are sensitive to the nature of the reaction coordinate. [29,30] It is possible that a refined treatment of the entrance channel would produce closer agreement between experiment and theory.

5. Conclusion

The $\text{HCO} + \text{O}_2$ and $\text{DCO} + \text{O}_2$ rate coefficients have been investigated as a function of pressure and temperature. The room temperature rate coefficient is $k_{\text{H}} = 5.63 \pm 0.31 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{D}} = 5.61 \pm 0.23 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Only a slight increase in the rate coefficients was observed when the temperature was increased from 296 to 673 K. No pressure dependence was observed. Both these observations are in agreement with several previous investigations and theoretical predictions. No significant isotope effect is observed ($k_{\text{H}}/k_{\text{D}} = 1.00 \pm 0.07$ at 296 K), while ab initio and statistical calculations predict a normal kinetic isotope effect of 15–20%. The exact nature of the discrepancy between theory and experiment is unknown, but may lie in the treatment of the association step.

Acknowledgements

The establishment of the CW LIF experiments on HCO depended on the persistent efforts of Dr. Eileen Clifford. This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the US Department of Energy.

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