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Kinetics and mechanism of the reaction of fluorine atoms with trifluoroacetic acid

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ABSTRACT

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Article history: Received 28 June 2011 In final form 6 July 2011 Available online 13 July 2011 The kinetics of the reaction between fluorine atoms and trifluoroacetic acid has been studied experimentally at T = 258-343 K. The overall reaction rate constant decreases with temperature: $k_1(T) = 1.09 \times 10^{-12}$ exp((+1034 K)/T) cm³ molecule⁻¹ s⁻¹. The potential energy surface of the reaction has been studied using quantum chemistry. The results were used in transition state theory calculations of the temperature dependences of the rate constants of the two channels of the reaction. The abstraction channel ultimately producing HF is dominant at the experimental temperatures; the addition–elimination channel producing CF₃ and CF(O)OH becomes important above 1000 K.

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1. Introduction

Trifluoroacetic acid (CF₃C(O)OH, TFA) is a molecule of significant environmental interest and concern (e.g., [1,2]). It has been found in substantial amounts in aqueous environments and in the Earth's atmosphere, with a fraction of its abundance attributed to anthropogenic origins [3,4]. Very little is known about the reactivity of TFA in the gas phase, with only a few reactions studied experimentally [5–8]. In the current study, we report the results of our experimental and computational study of the kinetics and mechanism of the reaction of TFA with fluorine atoms:

$$\begin{split} F+CF_3C(0)OH &\rightarrow HF+CF_3C(0)O^{*} \eqno(1a) \\ &\rightarrow CF_3CF(0^{*})OH \rightarrow CF_{3^{*}}+CF(0)OH \eqno(1b) \end{split}$$

Reaction (1) has been studied before at room temperature by Wallington and Hurley [5]. These authors used the relative rates technique with methane and deuterated methane as the reference compounds to determine the overall rate constant of reaction (1) at the temperature of 295 K: $k_1(295 \text{ K}) = (5.6 \pm 1.8) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹, where error limits include experimental and relative-rate uncertainties. The current study focused on the temperature dependence of the rate constant of reaction (1) in the 258–343 K temperature range. The relative rates technique based on mass spectrometric detection of the reactants was used. The potential energy surface of reaction (1) was studied using quantum chemical methods and the competition between the two possible channels (1a and 1b) was analyzed. Transition state theory modeling was used to extrapolate the rate constants of

the reaction channel 1a to temperatures outside the experimental range and to predict the rate constants of channel 1b as a function of temperature.

2. Experimental study and results

The experimental setup and methodology of relative rates kinetic experiments have been described in detail before [9]; thus, only a brief description is given here. The experiments were performed in a discharge flow reactor, 5 cm long and 2.3 cm i.d., coupled to a molecular beam electron impact quadrupole mass spectrometer. Fluorine atoms were produced in a microwave discharge in a F₂/He mixture in a side arm of the reactor located 40 cm upstream from the mass spectrometer sampling inlet. The discharge zone contained an alumina insert to minimize production of oxygen atoms (due to the reaction of fluorine with the wall) in the discharge. The central inlet of the reactor (1.7 cm i.d., 20 cm upstream from the mass spectrometer sampling inlet) was used to supply flows of the reactants, $CF_3C(0)OH$ and the reference compound, diluted in the carrier gas, helium, in varying concentrations. A typical flow velocity inside the reactor was 1.6 m s⁻¹ and the reactor pressure was 0.80 Torr.

The concentrations of the reactants and products in the reactor detection zone were monitored using a molecular beam mass spectrometer. The molecular beam was formed by the nozzle and a skimmer; a modulating chopper was located between the skimmer and the electron impact ion source. Electron impact energy of 70 eV was used. The following gases were used: helium (99.996%), trifluoroacetic acid (99.5%, Fluka), chloroform (99.9%, Sigma–Aldrich), 1,1,1-trichloroethane (99%, Sigma–Aldrich), fluorine (99.9%, 5% mixture in helium, Merck AG).

Standard relative rate procedures were employed. Mixtures of TFA and reference compounds in varying concentrations diluted



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in the excess of helium carrier gas were supplied through the central injector. The extent of depletion of TFA relative to that of the reference compound (REF) was monitored and rate constant ratios, k_1/k_{REF} , were determined using the following equation:

$$\frac{k_1}{k_{\text{REF}}} = \frac{\ln([\text{TFA}]_0/[\text{TFA}])}{\ln([\text{REF}]_0/[\text{REF}])} \tag{I}$$

The mass spectrum of TFA has the base peak at m/z = 45 (attributed to the $C(O)OH^+$ ion). The molecular ion peak is very weak, only 2.7% relative to the base peak. The spectrum is in qualitative, if not quantitative agreement with the two database spectra obtained from the NIST Mass Spectral database [10] and from [11]. A comparison between these mass spectra is provided in the Supplementary material, where mass spectra of other compounds used are also given. Because of the weakness of the molecular ion peak, it was not possible to use it for monitoring the concentration of TFA. Instead, the m/z = 45 base peak was used for this purpose. The products of the reaction channel 1a $(HF + CF_3C(0)O)$ cannot provide any contribution to this mass. The products of the other possible channel of reaction (1), channel 1b, potentially, can contribute to the m/z = 45 peak. However, as is shown below, the branching fraction of channel 1b is negligible under the conditions of the experiments performed in the current study. Therefore, the observed mass peak at m/z = 45 can be fully attributed to TFA only.

The choice of the reference compounds to be used in kinetics measurements is guided by three considerations. First, both the reference compound and the products of its reaction with atomic fluorine should have mass spectra that do not interfere with the mass peak used for the detection of TFA. Second, rate constant of the reaction between F atoms and the reference compound should be reasonably close in value to that of the reaction under study, reaction (1). If the second requirement is not satisfied, then the accuracy of the relative rate measurement suffers. Ideally, the most favorable signal-to-noise ratio is obtained under the conditions where both the [TFA]₀/[TFA] and the [REF]₀/[REF] ratios significantly differ from unity but are not too large, roughly in the 1.2-10 range. If the rate constants of the reference reaction and that of the reaction under study differ by an order of magnitude or more, it becomes difficult to find the optimal experimental conditions and even more difficult to vary the extent of reaction ratios while still staying in the good signal-to-noise ratio range. And finally, the third requirement is that the rate constant of the reference reaction has to be known at the temperature of interest.

The first reference compound used in the experiments was chloroform, $CHCl_3$. The kinetics of the reaction between fluorine atoms and chloroform

$$F + CHCl_3 \rightarrow HF + CCl_3$$
 (2)

has been studied by several groups, using both direct [12-14] and relative rate [15-17] methods. The mass spectra of chloroform and CCl₃ do not have any peaks at m/z = 45 and thus do not interfere with the signal of TFA. Due to the weakness of the molecular ion peak, the base peak at m/z = 83 (CHCl₂⁺) was used to monitor the concentration of CHCl₃.

During the experiments, the ratio of the flows of TFA and the reference compound was varied and the resulting changes in the [TFA]₀/[TFA] and [REF]₀/[REF] ratios were recorded. The results obtained at the room temperature (295 K) are presented in Figure 1a. The slope of the fitted straight line yields the k_1/k_2 ratio of 14.6 ± 2.0 (2 σ). This relatively large ratio results in significant differences between the measured extents of reactions, as can be seen from the plot in Figure 1a, thus putting many of the measurements outside the optimal range of conditions (see above). The room-temperature rate constant of the reference reaction has been reported by five groups, with the values ranging from 1.69×10^{-12}



Figure 1. Dependences of the extents of depletion of TFA relative on those of the reference compounds (REF) obtained in room-temperature experiments. The ratios of the rate constants k_1/k_{REF} were obtained from the slopes of the fitted straight lines (reaction (1)).

to 6.19×10^{-12} cm³ molecule⁻¹ s⁻¹. Using the latest direct determination of Louis and Sawerysyn [14], $k_2 = (2.67 \pm 0.20) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, one obtains the value of $k_1 = (3.90 \pm 0.83) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. On the other hand, combining the above k_1/k_2 value with that of $k_2 = (5.4 \pm 1.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ determined by Catoire et al. [17] in relative rate measurements results in $k_1 = (7.9 \pm 3.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. These two values of k_1 bracket the room-temperature determination of Hurley and Wallington ((5.6 ± 1.8) $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹), and uncertainties overlap (see inset in Figure 2).

The uncertainty in the value of the reference reaction (2) rate constant and the large, far from optimum value of k_1/k_2 motivated a search for more suitable reference reactions. The second reference reaction used was that of fluorine atom with 1,1,1-trichloroethane:

$$F + CH_3CCl_3 \rightarrow HF + CH_2CCl_3 \tag{3}$$

The rate constant of this reaction at 295 K has been determined by Platz et al. [18] as $k_3 = (6.79 \pm 1.49) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ in relative rates experiments. The mass spectrum of 1,1,1-trichloroethane has the base peak at m/z = 97 (CH₃CCl₂⁺) and the intensity of the molecular ion peak is less that 0.1% of that of the base peak. No peaks at m/z = 45 (used to detect TFA) are present in the mass



Figure 2. Main plot: the experimental (circles, rate constants obtained using reaction (4) as the reference reaction) and the calculated (lines) $k_1(T)$ dependences. Dashed line – Model 1 (fitted energy barrier); dotted line – Model 2 (fitted energy barrier and four lowest vibrational frequencies of transition state TS1). Inset: room temperature values of k_1 obtained from the results of [5] (open symbols) and those of the current study (filled symbols) using different reference reactions. Axes of the plot have the same meanings as in the main plot. Open square, k_1 from [5], as reported; open circle, k_1 recalculated using tata from [5] and k_6 from [38]; filled squares, two values of k_1 obtained nrond, reaction (2) as reference, with different k_2 values (see text); filled diamond, reaction (3) used as reference; filled circle, reaction (4) used as reference. The data points corresponding to T = 295 K are shifted relative to each other along the 1000 K/T axis to avoid overlap.

spectra of either CH_3CCl_3 or CH_2CCl_3 . However, a small peak (2.8% of the base m/z = 45 peak) at m/z = 97 is present in the mass spectrum of TFA. Thus, the results of measurements of the concentrations of CH_3CCl_3 had to be corrected for this minor interference from TFA.

The results of the relative rate measurements using reaction (3) as the reference reaction are presented in Figure 1b. The value of k_1/k_3 obtained is $8.40 \pm 0.60 (2\sigma)$. Combining this value with the rate constant of the reference reaction, one obtains $k_1 = (5.70 \pm 1.66) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in agreement with the value of [5]. The value of k_1/k_{REF} is still not optimal for the best signal-to-noise ration, and the temperature dependence of k_3 is unknown. Therefore, a third reference reaction had to be selected for the study of the kinetics of reaction (1) at temperatures other than ambient.

The third reference reaction used in the current work is that of fluorine atoms with gaseous nitric acid:

$$F + HNO_3 \rightarrow Products$$
 (4)

The room temperature kinetics of this reaction has been studied experimentally by four groups [19–22], with reasonable agreement on the value of the rate constant $(2.1–2.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The temperature dependence of the k_4 has been determined by Wine et al. [21] in the temperature range of 260– 373 K. The values of the rate constant decrease with increasing temperature in the 260–320 K range but stay independent of temperature above 330 K. The authors of [21] attributed this complex temperature dependence to changing relative importance of two channels of reaction (4), with abstraction of an H atom dominating at low temperatures and substitution channel(s) being more important at higher temperatures. The expected products of all possible channels of reaction (4) include HF, NO₃, OH, FNO₂, FNO, and HO₂. None of these compounds interfere with mass spectrometric monitoring of the concentration of TFA at m/z = 45. In the experiments performed in the current work, the concentration of HNO_3 was monitored using the molecular ion at m/z = 63, where neither TFA nor products of reaction (1) provide any contribution.

The results of the room-temperature relative rates experiment performed using reaction (4) as reference are presented in Figure 1c. The obtained value of $k_1/k_4 = 1.57 \pm 0.30$, combined with the value of $k_4(295 \text{ K}) = (2.33 \pm 0.35) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained from the Arrhenius expression and quoted 15% absolute uncertainty of [21], results in the room temperature rate constant of reaction (1) $k_1(295 \text{ K}) = (3.66 \pm 0.91) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Reaction (4) was used as the reference reaction in experiments performed at temperatures below and above ambient, T = 258– 343 K. The results are presented in Figure 2 and in Table 1. Two sets of error bars are given for the data points on the Arrhenius plot. The smaller, wider-cap error bars represent the uncertainties of the current experimental relative-rates study (2σ). The larger, narrow-cap error bars show the overall uncertainties of k_1 determinations, which include the 15% uncertainties for the rate constants of the reference reaction (4) reported by Wine et al. [21]. As can be seen from the plot, k_1 shows noticeable negative temperature dependence, which can be expressed with the following equation:

$$\begin{aligned} k_1(T) &= (1.09 \pm 0.38) \times 10^{-12} \exp(+(1034 \\ &\pm 101 \text{ K})/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \end{aligned} \tag{II}$$

Table 1

Conditions and results of the experiments to determine k_1 .

T/K	[TFA] ^a	[REF] ^b	$k_1/k_{\rm REF}^{\rm c}$	k_{REF}^{d}	k ₁ ^e				
Reaction (2) used as reference ^f									
295	35-80	12.4-	14.6 ± 2.0	0.267 ± 0.020^{g}	3.90 ± 0.53				
		19.9			(±0.83)				
295	35-80	12.4-	14.6 ± 2.0	0.540 ± 0.150^{h}	7.88 ± 1.08				
		19.9			(±3.27)				
Reaction (3) used as reference ^f									
295	4.0-18	6.2-9.7	8.40 ± 0.60	0.679 ± 0.149 ⁱ	5.70 ± 0.41				
					(±1.66)				
Reaction (4) used as reference ^{j}									
258	0.11-	3.5-5.2	2.19 ± 0.97	2.83 ± 0.42^{k}	6.19 ± 2.73				
	0.9				(±3.66)				
268	0.22-	3.4-4.7	1.97 ± 0.25	2.67 ± 0.40	5.26 ± 0.67				
	1.0				(±1.46)				
273	0.56-	4.9-14.6	1.75 ± 0.56	2.59 ± 0.39	4.54 ± 1.45				
	3.0				(±2.13)				
296	0.56-	19.6–48	1.57 ± 0.16	2.33 ± 0.35	3.66 ± 0.36				
212	1.7	41 5 0	1 20 + 0 17	2 15 1 0 22	(±0.91)				
313	0.67-	4.1-5.8	1.29 ± 0.17	2.15 ± 0.32	2.77 ± 0.37				
222	3.8	10.0	1 25 + 0 25	2.00 ± 0.20	(± 0.79)				
222	1.6	10.9-	1.25 ± 0.55	2.00 ± 0.50	2.49 ± 0.09				
3/3	0.78_	12_16.3	114 + 037	2.00 ± 0.30	(± 1.07)				
545	44	12-10.5	1.14 ± 0.57	2.00 ± 0.00	(+1.08)				
					(1.00)				

^a Concentrations of CF₃C(O)OH in units of 10¹² molecule cm⁻³.

^b Concentrations of reference compounds in units of 10¹² molecule cm⁻³.

^c The error limits are given as twice the standard error of the fit.

^d In units of 10^{-11} cm³ molecule⁻¹ s⁻¹.

^e In units of 10^{-11} cm³ molecule⁻¹ s⁻¹. Error limits given without parentheses are derived from the uncertainties in k_1k_{REF} . Error limits given in parentheses include the uncertainties in the rate constant of the reference reaction as a systematic contribution [40].

^f Concentrations of fluorine atoms were in the $(4-6) \times 10^{13}$ atom cm⁻³ range, as determined from the measured molecular fluorine flows and the percentage of dissociation of F₂ in the microwave discharge.

ⁱ [18].

^j Concentrations of fluorine atoms were in the $(2-11) \times 10^{12}$ atom cm⁻³ range.

^k [21].

^g [14]. ^h [17].

Here, the quoted uncertainties of the preexponential factor and the activation energy are given as twice the standard error if the fit and bear no physical meaning. The inset in Figure 2 shows the room-temperature determinations of the rate constant, including the two values resulting from the study of Wallington and Hurley [5] (see below, in the Section 4). The data points corresponding to T = 295 K are shifted relative to each other along the 1000 K/T axis to avoid overlap.

3. Potential energy surface and transition state theory model of reaction (1)

The potential energy surface (PES) of reaction (1) was studied using quantum chemical methods. Optimization of molecular structures and calculation of vibrational frequencies were performed using the density functional BH&HLYP [23.24] method and single-point CCSD(T) [25,26] energies were calculated for PES stationary points. The aug-cc-pVDZ [27] basis set was used in all calculations. The GAUSSIAN 03 program [28] was used in all potential energy surface (PES) calculations. The version of the BH&HLYP functional implemented in GAUSSIAN 03 was used which, as described in the GAUSSIAN manual, is different from that of [23]. Energy values quoted in the text henceforth are given as X/Y, where the first value is obtained in CCSD(T) and the second - in BH&HLYP calculations and include vibrational zero point energies unless stated otherwise. The results of the PES study are summarized in Table 2 and Figure 3 and the detailed information is given in the Supplementary material.

The mechanism of reaction (1) involves two different reaction paths, those of H atom abstraction (1a) and addition to the carbon atom of the carbonyl followed by a decomposition of the vibrationally excited CF₃CF(O)OH adduct into CF₃ and CF(O) OH (1b). The reaction path of channel 1a has a weakly bound CF₃C(O)OH…F complex on the reactants side $(-17.6/-21.5 \text{ kJ mol}^{-1}$, denoted vdW1 in Figure 3), followed by an energy barrier. Both the BH&HLYP and the CCSD(T) calculations give energies of the barrier that are below the energy of the reactants. However, the barrier is substantial at the BH&HLYP level (13.3 kJ mol⁻¹ relative to the complex and -4.3 kJ mol^{-1} relative to the reactants, TS1 in Figure 3) but practically disappears at

Table 2

Energies of reactants, products, and stationary points on the PES of reaction (1) obtained in quantum chemical calculations.^a

Species	Method					
	BH&HLYP ^b	CCSD(T) ^c	Modeling ^d			
Channel 1a						
CF ₃ C(O)OH…F complex (vdW1)	-17.6	-21.5	-			
$CF_3C(O)O\cdots H\cdots F(TS1)$	-4.3	-24.0	-11.6 (-18.8)			
CF ₃ C(O)O…HF complex (vdW2)	-82.6	-94.4	-			
$HF + CF_3C(O)O$	-66.5	-79.0	-			
$HF + CF_3 \cdots C(O)O$ (TS3)	-44.8	-75.5	-			
$HF + CF_3 + C(O)O$	-152.1	-169.4	-			
Channel 1b						
$CF_3C(\dots F)(O)OH$ (TS2)	21.8	8.7	-			
CF ₃ CF(O)OH	-87.0	-86.0	-			
$CF_3 \cdots CF(O)OH$ (TS4)	-34.9	-49.0	-			
$CF_3 + CF(0)OH$	-106.3	-102.7	-			

^a Energy values are given in kJ mol⁻¹ relative to F + CF₃C(O)OH and include zeropoint vibrational energy (ZPE).

^b Optimized in BH&HLYP/aug-cc-pvdz calculations.

^c CCSD(T)/aug-cc-pvdz single point energies using BH&HLYP/aug-cc-pvdz optimization.

 $^{\rm d}$ Results of fitting the experimental data with Models 1 and 2 (the latter in parenthesis).



Figure 3. Potential energy surface of reaction (1) obtained in quantum chemical calculations (see text and Table 2). Solid lines – CCSD(T)/aug-cc-pdz//BH&HLYP/ aug-cc-pdz energies, dashed lines – BH&HLYP/aug-cc-pdz energies. The dotted line indicates the recommended fitted value of the TS1 energy barrier obtained in modeling of the experimental data.

the CCSD(T) level (8.8 kJ mol⁻¹ relative to the complex without ZPE but -2.5 kJ mol⁻¹ when ZPE is included). The products of channel 1a, HF + CF₃C(O)O, also form a weakly bound complex, -15.4/-16.1 kJ mol⁻¹ relative to the separated products (vdW2 in Figure 3). Reaction channel 1a can be expected to be followed by a rapid decomposition of the CF₃C(O)O radical to CF₃ + CO₂; the energy barrier to this decomposition is only 3.5/21.7 kJ mol⁻¹:

$$CF_3C(0)0 \rightarrow CF_3 + CO_2 \tag{5}$$

Addition to the carbon atoms of the carbonyl bond channel has a barrier of 21.8/8.7 kJ mol⁻¹ (TS2 in Figure 3). Addition to the oxygen atom of the carbonyl bond does not occur: any attempt to optimize the structure of the expected adduct results in convergence to the CF₃C(O)OH···F complex. The CF₃CF(O)OH adduct formed in the initial step of channel 1b is highly vibrationally excited (95/ 109 kJ mol⁻¹) and is expected to decompose to CF₃ + CF(O)OH via a 36.1/52.1 kJ mol⁻¹ barrier (TS4 in Figure 3).

In an attempt to provide means for an extrapolation of the experimental $k_1(T)$ dependence to temperatures outside the experimental range, and to estimate the contribution of the reaction channel 1b to the overall reaction, an RRKM / transition state theory model of reaction (1) was created in the current work. Molecular structure and vibrational frequencies of the saddle point obtained in the BH&HLYP/aug-cc-pvdz calculations were used. Energy and frequencies of the transition state for the reaction channel 1a were adjusted to reproduce the experimental $k_1(T)$ dependence in a procedure described below. For channel 1b, transition state theory [29] calculations using the CCSD(T)-level barrier energy were performed. Contribution of this channel to the overall reaction is negligible at the temperatures of the experiments but becomes important at higher temperatures.

Modeling of channel 1a was performed under the assumption that most of the trajectories sampling the coordinate space of the CF₃C(O)OH···F complex and having energies above that of the reactants proceed back to $F + CF_3C(O)OH$ and only a small fraction passes through the PES saddle point and leads to the HF + CF₃C(O)O products. Thus, the saddle point was assumed to represent the dynamic bottleneck of the reaction. This is a reasonable assumption given the fact that the decomposition of the CF₃C(O)OH···F complex back to the reactants is expected to have a transition state that is significantly 'looser' and thus has larger density of states than that of the CF₃C(O)OH···F \rightarrow HF + CF₃C(O)O route. Rate constant values were calculated using the equation:

$$k(T) = \frac{Q_{\text{trans}}^{\ddagger}(T)Q_{\text{inact}}^{\ddagger}(T)}{Q_{\text{F}}(T)Q_{\text{CF}_{3}\text{C}(0)\text{OH}}(T)} \int_{E_{0}}^{\infty} W^{\ddagger}(E-E_{1}) \exp\left(-\frac{E-E_{0}}{k_{\text{B}}T}\right) dE \qquad (\text{III})$$

where $Q_{trans}^{\dagger}(T)$ and $Q_{inact}^{\dagger}(T)$ are the partition functions of the translational and the overall 2-dimensional (inactive) rotational degrees of freedom of the transition state, $Q_{\rm F}(T)$ and $Q_{\rm CE_2C(0)OH}(T)$ are the partition functions of the F and CF₃C(O)OH reactants, $W^{\ddagger}(E - E_1)$ is the sum-of-states function of the active [30-32] degrees of freedom of the transition state, E_0 and E_1 are the energies of the reactants and the transition state, respectively $(E_0 > E_1)$, and k_B is the Boltzmann constant. Eq. (III) was obtained in [33] by simplification of a formula derived by Mozurkewich and Benson [34] (Eq. (12) of [34]) for reactions proceeding over shallow potential energy wells. The simplification resulted from the above mentioned assumption of predominant dissociation of the CF₃C(0)OH…F complexes to $F + CF_3C(O)OH$ and from an approximate treatment of the effects of angular momentum (J) conservation where the rate constant value obtained for I = 0 is multiplied by the ratio of the partition functions of the 2-dimensional rotational (inactive) degrees of freedom of the transition state and the active molecule. The latter ratio is close to unity (0.94), which justifies the use of the approximation. The effective width of the energy barrier [35,36] (0.931 amu^{1/2} Å) was obtained by fitting the potential energy profile resulting from intrinsic reaction coordinate calculations. However, tunneling has no influence on the calculated rate constants because k(E) dependences with and without tunneling differ very little above the energy barrier [36,37] and energies of the reactive trajectories passing from the CF₃C(0)OH…F complex to the products part of the PES are higher than that of the reactants and thus are always above the energy barrier.

As the divergence of the BH&HLYP and the CCSD(T) results demonstrates, the location of the barrier for channel 1a on the energy scale is uncertain; thus the optimum value was obtained in fitting the properties of the model to the experimental $k_1(T)$ dependence. This fitting exercise can be performed in two possible ways: by fixing the vibrational frequencies of the reactants and the transition state at the BH&HLYP values and optimizing the energy barrier only, or by optimizing both the energy barrier and the frequencies. The first approach results in the energy of the transition state equal to -11.6 kJ mol⁻¹ and the calculated temperature dependence shown by the dashed line in Figure 2 (denoted as Model 1). The resultant temperature dependence of the rate constant of reaction channel 1a can be represented with the following modified Arrhenius expression:

$$k_{1a} = 6.83 \times 10^{-10} T^{-0.83} \exp(508 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(200-1000 K) (IV)

The calculated dependence lies askew relative to the experimental one but still well within the envelope of uncertainties of the individual rate constant determinations. The second approach was implemented by applying a variable multiplier to the original four lowest vibrational frequencies of the transition state. The resultant optimized value of the multiplier is 2.5 and the fitted energy of the transition state is -18.8 kJ mol⁻¹. The corresponding temperature dependence of the calculated rate constants is shown in Figure 2 by the dotted line. The resultant 200–1000 K temperature dependence can be represented with the following modified Arrhenius expression:

$$k_{1a} = 4.58 \times 10^{-3} T^{-3.32} \exp(-52 \text{ K/T}) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(200–1000 K) (V)

The transition state theory calculations of the rate constant of reaction channel 1b (addition–decomposition) result in the following modified Arrhenius expression:

$$k_{1b} = 4.54 \times 10^{-18} T^{1.74} \exp(-663 \text{ K/T}) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(200–2000 K) (VI)

The contribution of channel 1b becomes comparable to that of channel 1a only at temperatures above 1000 K.

4. Discussion

The current study represents the first determination of the temperature dependence of the rate constant of reaction (1). The negative temperature dependence is consistent with the barrierless potential energy surface of the initial approach of the fluorine atom to TFA and the reaction bottleneck located below the energy of the reactants on the energy scale, as inferred from the quantum chemical part of the study.

The only previous study of reaction (1) is that of Wallington and Hurley, who used the reaction between the fluorine atom and methane

$$F + CH_4 \rightarrow HF + CH_3 \tag{6}$$

as well as the reaction of fluorine atoms with deuterated methane (with the rate constant derived from that of reaction (6)) as reference reactions in their room-temperature study. The authors of [5] reported $k_1(295 \text{ K}) = (5.6 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with additional 20% uncertainty resulting from that of the values of the rate constants of the reference reactions. The rate constant of reaction (6) has been studied by many groups; reviews can be found in [38,39] and references cited therein. Using the data of [5] and the most recent recommendation of the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry for reaction (6), $k_6(295 \text{ K}) =$ $(6.3 \pm 2.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [38], \text{ one obtains a somewhat}$ lower value of $k_1 = (5.2 \pm 2.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where large uncertainties reflect those of the rate of reaction (6). Both values resulting from the relative rates study of Wallington and Hurley are shown on the inset in Figure 2 with open symbols. The results of the current study obtained at room temperature using three different reference reactions ((2)-(4)) are shown on the same plot with filled symbols. Two data points are entered for the results obtained using reaction (2) as reference, with different values resulting from using different values for k_2 , as described above. As one can see from the plot, the results of the current study obtained using different reference reactions are in general agreement with each other and with those of [5], with difference largely attributable to the uncertainties in the rates of the reference reactions used. We recommend the data obtained with reaction (6) used as the reference reaction as it seems to have the lowest uncertainty associated with its rate constant: the temperature dependence used here was obtained in direct experimental study of [21] and is in a very good agreement with two other room-temperature determinations ([19,20]).

The computational study of reaction (1) was performed in this work to assess possible reaction pathways and to provide means for the extrapolation of the $k_1(T)$ temperature dependence to outside the experimental temperature range. As described above, two methods of fitting the experimental data with the model result in the energy barrier values for the reaction channel 1a that differ by 7.2 kJ mol⁻¹. Although Model 1 results in the calculated $k_1(T)$ dependence that lies askew relative to the experimental data on the Arrhenius plot (Figure 2) and Model 2 was fitted to reproduce the experimental temperature dependence exactly, the uncertainties of the experimental individual data points do not allow to meaningfully distinguish the qualities of fit of the two models. Model 2 involved changing the four lowest vibrational frequencies of the transition state TS1 by a factor of 2.5; the resultant frequency values are probably less realistic than the original BH&HLYP based frequencies. Thus, we recommend using the temperature dependence of Eq. (IV) over that of Eq. (V) for extrapolation to higher temperatures.

In the absence of any experimental data on the rate of the addition-decomposition pathway of reaction (1) (channel 1b), we recommend using the temperature dependence of Eq. (VI) based on the quantum chemistry study performed in this work and transition state theory calculations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2011.07.023.

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