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Rate Constant of the Reaction of F atoms with Methane over the Temperature Range 220–960 K

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ABSTRACT

Reaction F + CH_4 $\rightarrow$ HF + CH_3 (1) has been studied using a discharge flow reactor combined with mass spectrometry in the temperature range 220 – 960 K. The rate constant of the reaction was determined using both absolute and relative rate measurements: k_1 = (1.28 ± 0.04) × 10^{-10} exp(-(219 ± 9)/T) $cm^3 molecule^{-1} s^{-1}$ (the uncertainties represent precision at the 2σ level, the estimated total uncertainty on k_1 being 15% at all temperatures). The kinetic data from the present work are discussed in comparison with previous measurements and theoretical calculations.

Keywords: Fluorine atom, Methane, Kinetics, Rate constant, Activation energy.

1. Introduction

This study reports an experimental investigation of the kinetics of the reaction of fluorine atoms with CH_4:

$$F + CH_4 \rightarrow HF + CH_3 \quad (1)$$

The role of this reaction in atmospheric chemistry consists in converting F atoms to stable species HF, which is removed from the stratosphere via deposition/rain-out. This is one of the main reasons why catalytic ozone destroying cycles involving F atoms are not efficient [1,2]. In the laboratory studies, reaction (1) is frequently used as a source of CH_3 radical, which is an important intermediate in atmospheric and combustion chemistry. Consequently, the information on the kinetics of the reaction (1) in an extended temperature range covering atmospheric temperatures and those under combustion conditions is required. In addition, reaction of F atoms with CH_4 is very often used as a reference one in relative rate kinetic measurements. According to the NIST Chemical Kinetics Database [3], the rate constants of the F-atom reactions with about 50 different molecules were measured relative to the rate constant of reaction (1). Obviously, accurate data on the rate constant of the reference reaction is essential to place the relative measurements on an absolute basis.

Reaction of F atoms with CH_4, being a prototypical example of a polyatomic reaction, was a subject of numerous theoretical and dynamic studies ([4,5] and refs therein). Surprisingly, despite the considerable practical and theoretical interest in this reaction, the reaction rate constant is not well established, particularly in terms of its temperature dependence. Only three measurements of the temperature dependence of the reaction rate constant are available in the literature [6-8]. Two of them reported significantly different activation energies (1.15±0.35 at T = 253-352 K [6] and 0.43±0.12 kcal mol^{-1} at T = 184-406 K [8], updated in [9]), while in the third one (T = 139-294 K), a negative temperature dependence of k_1 was observed [7]. There are no experimental data for the reaction rate constant at temperatures above 406 K.

The purpose of the present work was to determine the rate constant of the title reaction in a wide temperature range, T = 220-960 K, in order to reduce the existing uncertainties on k_1 and provide a new extended and reliable data set for practical use and an experimental basis for validation and refining theoretical calculations.

2. Experimental

The title reaction was studied in a discharge-flow system, using modulated molecular beam mass spectrometry with electron impact ionization (25–30 eV energy) to monitor the species involved (Figs. S1a-S1c, Supplementary Material). The apparatus and experimental approach were similar to those used in previous studies of the elementary reactions of fluorine atoms in this group [10-13]. Two flow reactors were used in this study. The first one, used at low temperatures (220 – 326 K), was Halocarbon wax-coated Pyrex tube (45 cm length and 2.4 cm i.d.) surrounded by a jacket for circulation of the thermostated fluid (water or ethanol). The reactor used at high temperatures (T = 299 – 960 K) was an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) [14].

Fluorine atoms were produced in the microwave discharge of trace amounts of F_2 in He in an alumina tube (more than 90% of F_2, monitored by mass spectrometry, was found to be dissociated). F-atoms were detected indirectly at m/z = 98/100 (FBr^+) by using their chemical conversion in a rapid reaction with an excess of Br_2 (added 6 cm upstream of the sampling cone of the mass spectrometer, Figs. S1a-S1c):

$$F + Br_2 \rightarrow Br + FBr \qquad (2)$$

$k_2 = (1.28 \pm 0.20) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (T = 299 – 940 K) [12]

This reaction was also used for the determination of the absolute concentrations of F-atoms considering their stoichiometric conversion to FBr in excess of Br_2: [F] = [FBr] = Δ[Br_2]. The absolute concentrations of all stable species (CH_4, Br_2, F_2, D_2) in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in reservoirs of known volume.

The purities of the gases used were as follows: He >99.9995% (Alphagaz), passed through liquid nitrogen trap; CH_4 ≥ 99.995% (Alphagaz); F_2, 5% in helium (Alphagaz); Br_2 >99.99% (Aldrich); D_2 >99.7% (Alphagaz).

3. Results and Discussion

3.1. Rate constant of reaction (1).

Rate constant of the title reaction was determined using two different methods: absolute one, where k_1 was measured from F-atom decays monitored in an excess of CH_4, and a relative rate method employing reactions of F atoms with Br_2 and D_2 as a reference.

Absolute measurements of k_1. Both reactants were introduced into the reactor through a movable injector: F-atoms through Halocarbon wax-coated central tube and CH_4 through external output of the injector as shown in Fig. S1a. For all experiments, pseudo-first-order conditions were maintained with CH_4 in excess over fluorine atoms. Initial concentration of fluorine atoms in these experiments was in the range $(1 – 4)\times10^{11}$ molecule cm^{-3}; the flow velocity in the reactor was in the range (2145-2965) cm s^{-1}. The F-atom decays followed equation $[F] = [F]_0\times\exp(-k_1'\times t)$, where [F] and $[F]_0$ are F-atom concentrations at time *t* and zero and $k_1' = k_1\times[CH_4]+k_w$ is the pseudo-first-order rate constant with k_w representing the heterogeneous loss of F atoms. Some typical temporal profiles of F-atoms measured at T = 440 K with different concentrations of CH_4 are shown in Fig. S2 (Supplementary Material). Values of k_1' obtained from these plots were corrected for axial and radial diffusion of F-atom in the carrier gas (corrections generally less than 10%) [15]. In Figs. 1 and S3 (Supplementary Material), the pseudo-first order rate constants observed at different temperatures in the reactor are plotted against concentration of CH_4.

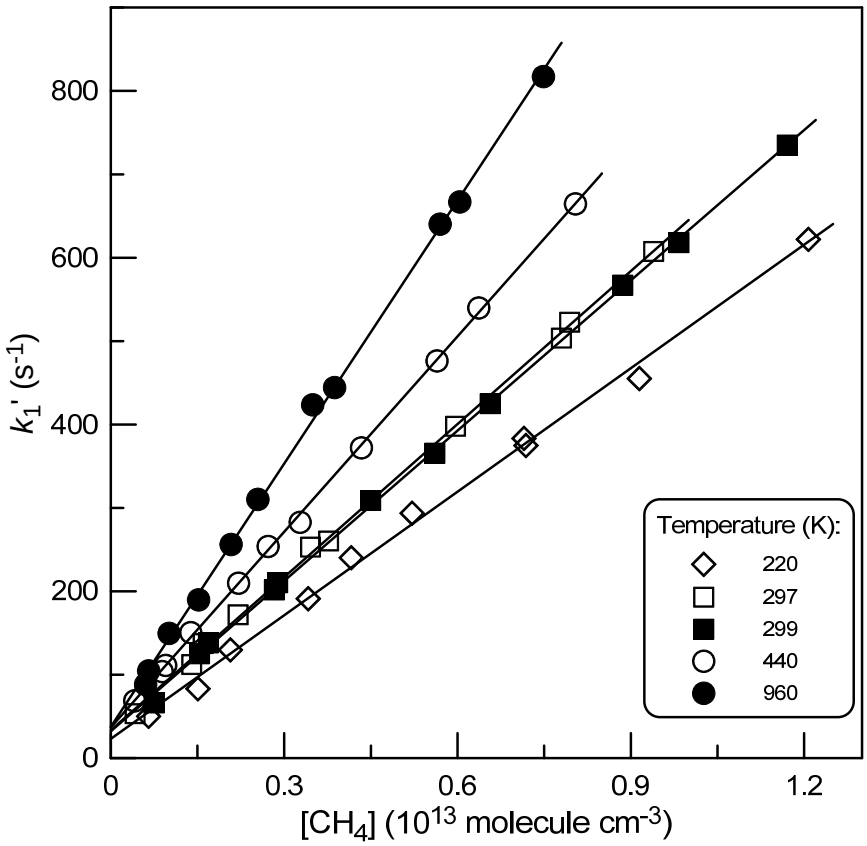

Fig. 1. Pseudo-first order rate constant, $k_1' = k_1[CH_4]+k_w$, as a function of the CH_4 concentration at different temperatures.

Consumption of the excess reactant, CH_4, although insignificant, was taken into account through use of the average concentration of CH_4 in the reaction zone, which was calculated as $[CH_4]=[CH_4]_0-\Delta[F]\times(k_1'-k_w)/k_1'$. The corrections on the methane concentration were quite small (within a few percent) in the most kinetic runs, however reached up to 15% in a few experiments with the lowest concentrations of CH_4. The slopes of the straight lines in Figs. 1 and S3 provide the values of k_1 at respective temperatures. All the results of the absolute measurements of k_1 at different temperatures are shown in Table 1. The combined uncertainty on the measurements of the rate constants was estimated to be ≤ 15 %, including (in quadrature) statistical error (within a few percent, Table 1) and those on the measurements of the flows (5%), pressure (3%), temperature (1%) and absolute concentration of CH_4 (< 10%).

Table 1
Experimental Conditions and Results of the Absolute Measurements of the Rate Constant of Reaction (1).

T (K)[a]	$[CH_4]$ (10^{12} molecule cm^{-3})	k_1 (± 2σ) (10^{-11} cm^3 molecule^{-1} s^{-1})	Reactor surface[b]
220	0.69-12.3	4.94±0.10	HW
230	0.59-10.6	5.08±0.07	HW
242	1.06-13.2	5.25±0.08	HW
256	0.67-9.43	5.38±0.07	HW
265	1.01-11.2	5.71±0.10	HW
280	0.51-10.0	5.84±0.05	HW
297	0.49-9.77	6.12±0.07	HW
299	0.85-12.2	6.01±0.05	Q
326	0.91-10.5	6.37±0.05	HW
365	0.62-7.53	6.94±0.09	Q
440	0.52-8.36	7.81±0.06	Q
535	0.71-8.24	8.43±0.09	Q
650	0.68-7.91	9.06±0.11	Q
790	0.53-7.00	9.99±0.10	Q
960	0.72-7.78	10.5±0.12	Q

[a] 10-13 kinetic runs at each temperature.
[b] HW: halocarbon wax; Q: quartz.

One can note (Fig. 1 and Table 1) that similar, within experimental uncertainty, data were obtained at room temperature (297-299 K) in two reactors with different surfaces (Quartz and Halocarbon wax coating). In general, in this work, we did not observe any signs of heterogeneous complications that often accompany kinetic measurements in flow reactors. The potential impact on the measurements of k_1 of the secondary reaction,

$$F + CH_3 \rightarrow \text{products} \quad (3),$$

is expected to be insignificant, considering the relatively low initial concentrations of fluorine atoms used in the experiments. This seems to be supported by the experimental evidence of the invariance of k_1' with respect to $[F]_0$, observed at T = 280 K (Fig. S3, Supplementary Material).

Relative measurements of k_1 with reaction F+Br$_2$ as a reference. These measurements were carried out in an uncoated quartz reactor (Fig. S1b) at three temperatures: T = 310, 400 and 660 K and consisted in a monitoring of FBr formed upon fast titration of F atoms by a mixture of CH_4 and Br_2:

$$F + CH_4 \rightarrow HF + CH_3 \quad (1)$$

$$F + Br_2 \rightarrow FBr + Br \quad (2)$$

The fraction of the initial concentration of F atoms, $[F]_0$, transformed to FBr in reaction 2, is:

$$[\mathrm{FBr}] = \frac{k_2[\mathrm{Br_2}]}{k_2[\mathrm{Br_2}]+k_1[\mathrm{CH_4}]+k_w} \times [\mathrm{F}]_0$$

Rearrangement of this expression provides:

$$\frac{[\mathrm{F}]_0}{[\mathrm{FBr}]} - 1 = \frac{k_1[\mathrm{CH_4}]}{k_2[\mathrm{Br_2}]} + \frac{k_w}{k_2[\mathrm{Br_2}]} \quad (\mathrm{I})$$

At a constant concentration of Br_2, k_1/k_2 can be determined as a slope of the linear dependence of ($[F]_0/[FBr]$ - 1) on the $[CH_4]/[Br_2]$ ratio. The measurements of the absolute concentrations of F atoms were not necessary in these experiments, since FBr was monitored in the presence of Br_2 in both CH_4 - free system, corresponding to $[F]_0$, and in the presence of CH_4 in the reactor, corresponding to the fraction of $[F]_0$ reacted with Br_2. Reaction time was around 0.02 s, $[Br_2]$ = (0.9-1.1)×10^{13} molecule cm^{-3}, the ranges of concentrations of CH_4 are given in Table 2.

Table 2

Experimental conditions and results of the relative measurements of k_1 with reaction F+Br$_2$ as a reference.

T (K)	$[CH_4]$ [(a)]	$[CH_4]/[Br_2]$	k_1/k_2 (± 2σ)	k_1 [(b)]

310	0.19-5.61	0.19-5.19	0.496±0.007	6.34
400	0.18-4.41	0.19-4.75	0.561±0.006	7.18
660	0.20-3.64	0.22-4.17	0.741±0.005	9.49

[a] Units of 10^{13} molecule cm^{-3}.
[b] Units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, estimated total uncertainty on k_1 is nearly 20% and includes that on the reference reaction.

The experimental data are shown in Fig. 2. In accordance with Equation I, the slopes of the straight lines in Fig. 2 provide the values of k_1/k_2 at respective temperatures. Final values of k_1 (Table 2) were calculated with k_2 = (1.28 ± 0.20) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (T = 299 – 940 K), determined in a recent study from this group [12].

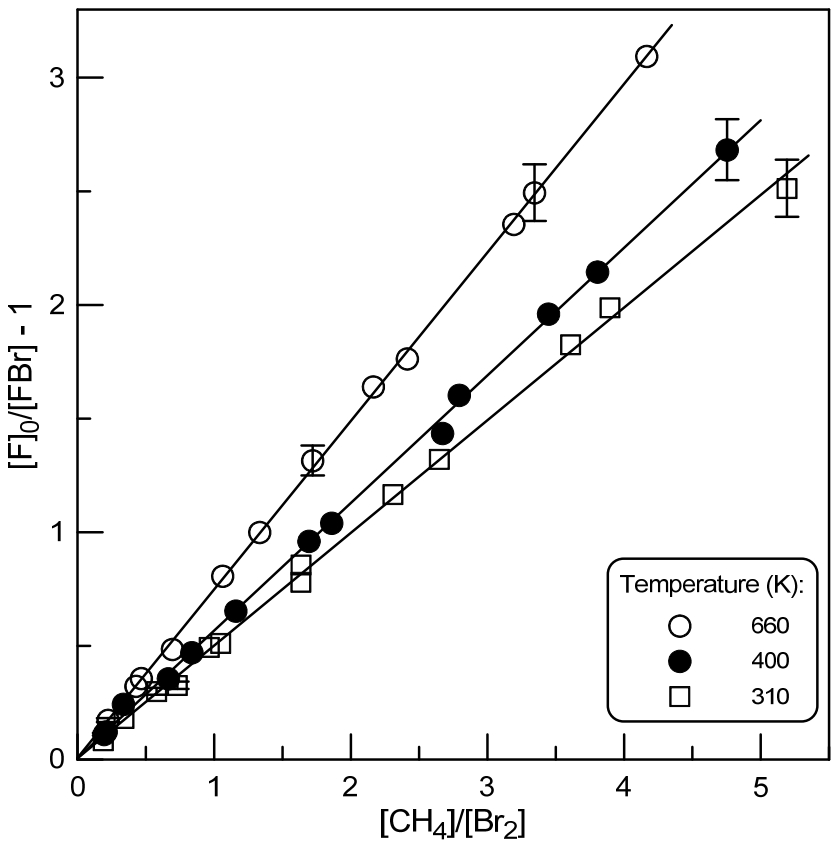

Fig. 2. Yield of FBr from titration of F atoms by Br_2 + CH_4 mixtures at different temperatures. Partially shown error bars represent typical uncertainties of the measurements (~ 5%).

Relative measurements of k_1 with reaction F+D_2 as a reference. The procedure, applied in these experiments, was similar to that described above. F atoms were titrated by a mixture of CH_4 and D_2 (Fig. S1c) and the yield of DF (monitored at m/z = 21, DF^+)was measured as a function of the $[CH_4]/[D_2]$ ratio:

$$F + CH_4 \rightarrow HF + CH_3 \quad (1)$$

$$F + D_2 \rightarrow DF + D \quad (4)$$

The fraction of the initial concentration of F atoms, $[F]_0$, transformed to DF, is:

$$[DF] = \frac{k_4[D_2]}{k_4[D_2]+k_1[CH_4]+k_w} \times [F]_0,$$

or after rearrangement:

$$\frac{[F]_0}{[DF]} - 1 = \frac{k_1[CH_4]}{k_4[D_2]} + \frac{k_w}{k_4[D_2]} \quad (II)$$

The observed experimental data are shown in Fig. 3.

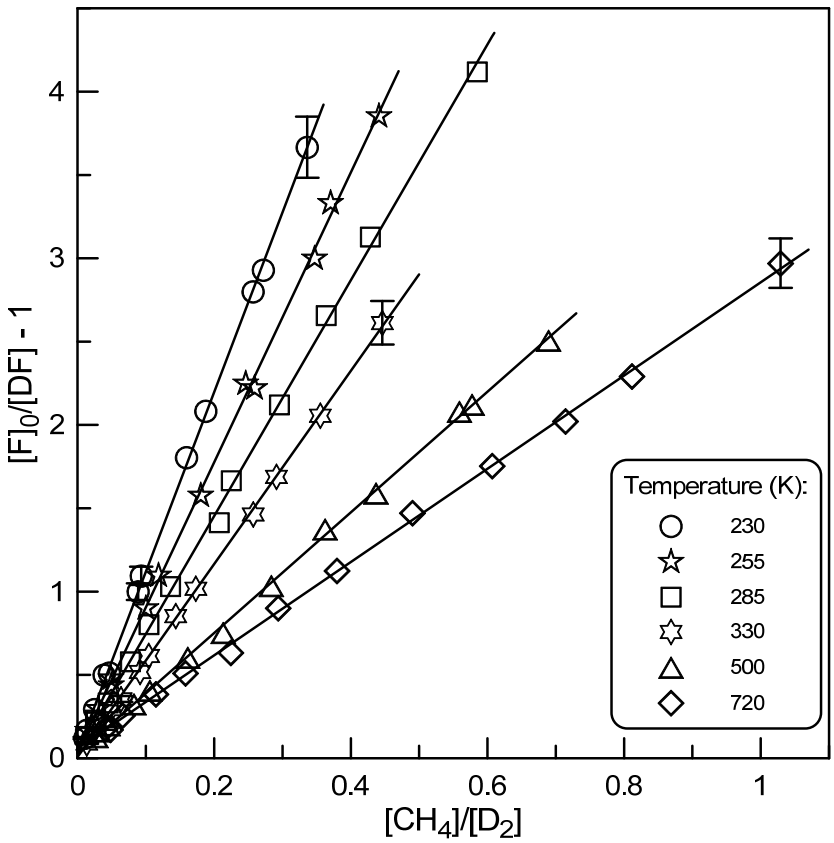

Fig. 3. Yield of DF from titration of F atoms by D_2 + CH_4 mixtures at different temperatures. Partially shown error bars represent typical uncertainties of the measurements (~ 5%).

The final values of k_1/k_4 at different temperatures, determined, in accordance with equation II, from the slopes of the linear dependencies in Fig. 3, are given in Table 3.

Table 3
Experimental conditions and results of the relative measurements of k_1 with reaction F+D_2 as a reference.

T (K)[(a)]	$[CH_4]$[(b)]	$[D_2]$[(b)]	k_1/k_4 (± 2σ)	k_1[(c)]

230	0.50-15.7	46.7	10.8±0.09	4.96
255	0.66-19.7	44.7	8.69±0.09	5.32
285	1.34-29.9	51.1	7.07±0.08	5.71
330	0.72-23.6	52.9	5.79±0.04	6.44
500	1.31-33.3	48.3	3.62±0.03	8.03
720	1.25-31.7	30.8	2,80±0.03	8.34

[a] 12-13 runs at each temperature.
[b] Units of 10^{12} molecule cm^{-3}.
[c] Units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, estimated total uncertainty on k_1 is nearly 20% and includes that on the reference reaction.

3.2. Comparison with previous studies.

The results obtained in the present work for the temperature dependence of k_1 are shown in Fig. 4 in line with all the temperature dependent data for k_1 available in the literature. The most recent room temperature measurements of the rate constant [16-19] are in the range (5.7-6.6)×10^{-11} $cm^3$$molecule^{-1}$$s^{-1}$ (T = 298 K), i.e. in very good agreement with the present data (Table 1 and Fig. 4).

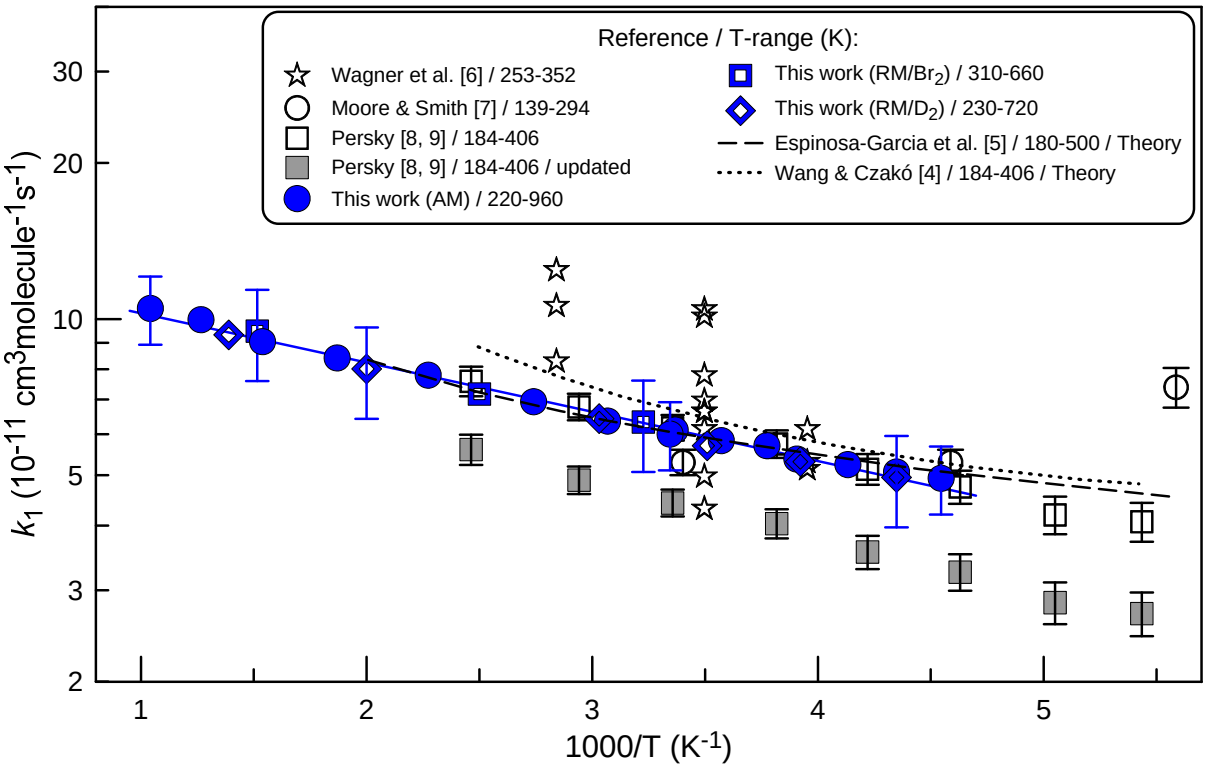

Fig. 4. Summary of the data on the temperature dependence of the rate constant of reaction (1): AM, absolute measurements; RM/Br_2 and RM/D_2, relative rate method with F+Br_2 and F+D_2

reference reactions, respectively. Partly shown uncertainties on the values of k_1 from the present study correspond to 15 and 20% for absolute and relative measurements, respectively.

Wagner et al. [6] used mass spectrometry to monitor the species involved in the F + CH_4 reaction system, where F atoms were generated in the reaction of NF_2 with excess nitrogen atoms. The rate constant of reaction (1) was determined at three temperatures (253, 286 and 352 K) both from F atom decays and from the kinetics of HF and HCN formed in reactions (1) and (5), respectively:

$$F + CH_4 \rightarrow HF + CH_3 \quad (1)$$

$$N + CH_3 \rightarrow HCN + \text{products} \quad (5)$$

The original rate constant data shown in Fig. 4 were kindly provided by Cornelius Zetzsch. Although these largely scattered data show a steeper temperature dependence, in absolute terms they agree well with the present work, at least at T = 253 and 286 K. Moore and Smith [7] derived the rate constant of reaction (1) by monitoring the chemiluminescence of the reaction product, HF, formed upon pulsed laser photolysis of F_2 in the presence of CH_4. The measurements were carried out at four temperatures (294, 218, 179, and 139 K) and shown rather negative temperature dependence of the rate constant: the reported values of k_1 were $(5.3\pm 0.3)\times10^{-11}$ at T = 294 and 218 K increasing to 7.4 and 8.0×10^{-11} $cm^3molecule^{-1}s^{-1}$ at T = 179 and 139 K (not shown in Fig.4), respectively. The k_1 data at T = 294 and 218 K agree with the present measurements in the range of the reported experimental uncertainties (Fig. 4). One can note an excellent agreement between the present data and those reported by Persky [8,9]. The comparison could be limited to this statement; however, further analysis shows that the perfect agreement between two studies seems to be fortuitous. Persky [8] using a discharge-flow-mass spectrometric technique measured the temperature dependence of k_1 by a relative rate method using reaction (4) as a reference one. To place the rate constant of reaction (1) on an absolute basis, a rather complicated approach was applied. First, the measured k_1/k_4 ratios were combined with the data available for the kinetic isotope effect, k_6/k_4, to calculate the k_1/k_6 ratios, which were subsequently multiplied by the recommended on that date values for k_6 to finally determine the absolute values of k_1:

$$F + H_2 \rightarrow HF + H \quad (6)$$

In a recent study from this group, we reported a new self-consistent kinetic dataset for the reactions of F atoms with H_2 and D_2 [20]. The rate constants of the reactions of F atoms with

H_2 and D_2 have been directly measured in a wide temperature range T = 220 – 960 K. In addition, the kinetic isotope effect, which was determined independently, was found to be in excellent agreement (within a few percent) with the ratio of k_1 to k_2 calculated with the Arrhenius expressions for k_1 and k_2 determined in the study [20]. The original data of Persky on k_1/k_4 ratio [8], when combined with k_4 = (8.47± 0.42)×10^{-11} exp(-(670 ± 16)/T) $cm^3molecule^{-1}s^{-1}$ [20], provide the absolute values of k_1 (gray filled squares in Fig. 4) which are by a factor of 1.3-1.4 lower than the current measurements. In fact, one of the reasons for the seemingly good agreement between the present data for k_1 and the data reported by Persky [8,9], where the reaction rate constant was calculated as $k_1 = k_1/k_4 \times k_4/k_6 \times k_6$, can be the compensating effect of the first two terms, k_1/k_4 and k_4/k_6. Indeed, the k_1/k_4 ratios measured in the present work, k_1/k_4 = 1.47×exp(454/T) (T = 230-720 K), are by approximately 20% higher than those reported by Persky, k_1/k_4 = 1.21×exp(420/T) (T = 184-406 K) [8] (Fig. S4, Supplementary Material). On the other hand, the values of k_4/k_6 = 0.96×exp(-186/T) (T = 184-406 K) [21], used by Persky in the calculations of k_1 [8,9] are significantly higher than recently reported, k_4/k_6 = 0.63×exp(-131/T) (T = 220-960 K) [20].

Concerning the results of the current study, one can note an excellent agreement between the absolute and relative (with two reference reactions) measurements of k_1. The unweighted exponential fit to the present data (solid line in Fig. 4) yields the following Arrhenius expression:

k_1 = (1.28 ± 0.04) × 10^{-10} exp(-(219 ± 9)/T) $cm^3molecule^{-1}s^{-1}$

at T = 220-960 K, where the cited uncertainties are 2σ statistical ones.

Figure 4 shows also the results of some theoretical calculations of k_1. Espinosa-Garcia et al. [5] developed a semiempirical potential energy surface (PES) for the F + CH_4 reaction and using variational transition-state theory calculated the thermal rate constants over the temperature range 180-500 K. The calculations are in very good agreement with experiments. However, it should be noted that the developed PES was calibrated to reproduce the experimental data of Persky [8,9]. The calculations of Wang and Czakó [4], realized on an ab initio potential energy surface, are also in fair agreement with the experimental data. Both theoretical calculations predict some curvature in the Arrhenius plot. Although this effect was not clearly observed in the current experiments, the present data do not exclude the possible, however, statistically insignificant in the range of the experimental uncertainty, curvature of the temperature dependence of k_1.

In conclusion, the rate constant of the title reaction was measured in a wide temperature range, T = 220 -960 K (for the first time at temperatures above 406 K). The measurements provide a new reliable dataset for practical use (atmospheric modeling, laboratory studies) and an experimental basis for further theoretical developments.

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Declaration of interest statement

No conflicts of Interest.

Appendix A. Supplementary data

Supplementary data related to this article can be found at ...

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