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**Kinetic study of the  $F_2+C_2H_4$  reaction: disagreement between theory and experiment resolved?**

**Yuri Bedjanian\***

Institut de Combustion, Aérodynamique, Réactivité et Environnement (ICARE), CNRS  
45071 Orléans Cedex 2, France

\* Corresponding author. E-mail: [yuri.bedjanian@cnrs-orleans.fr](mailto:yuri.bedjanian@cnrs-orleans.fr)

## ABSTRACT

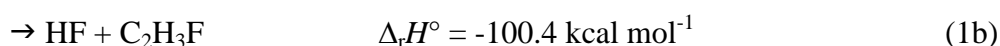
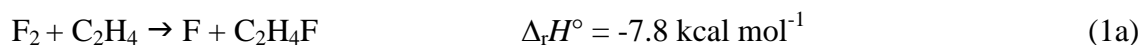
Reaction  $F_2 + C_2H_4 \rightarrow F + C_2H_3F$  (1) has been studied using a discharge flow reactor combined with an electron impact ionization mass spectrometer. The reaction rate constant was determined either from kinetics of the reaction product, F-atom, formation or from the kinetics of  $F_2$  consumption in excess of  $C_2H_4$ :  $k_1 = (7.94 \pm 2.06) \times 10^{-12} \exp(-(3867 \pm 120)/T)$   $cm^3 molecule^{-1} s^{-1}$  at  $T = 297-833$  K. The reaction activation energy,  $7.7 \pm 0.3$  kcal  $mol^{-1}$ , is consistent with current theoretical prediction for the reaction barrier height and seems to solve the long-standing problem of the divergence between theory and experiment.

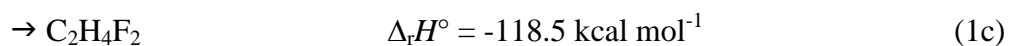
**Keywords:** Fluorine, Ethylene, Kinetics, Rate constant, Activation energy, Reaction barrier.

## 1. Introduction

Elementary reactions of F<sub>2</sub> molecules exhibit certain specific features and represent an interesting research topic both for theorists and experimentalists. So, on the one hand, molecular fluorine relatively slowly reacts with chemically active species, such as halogen and oxygen atoms and, on the other hand, it manifests relatively high reactivity with respect to some closed-shell molecules [1]. Fluorination of alkenes is an interesting class of reactions of molecular fluorine, which were shown to proceed with a relatively low barrier. Experimental crossed beam data provide a threshold in collision energy of 5.5 [2] and 2.4 kcal mol<sup>-1</sup> [3] for F<sub>2</sub> reactions with C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, respectively, while F<sub>2</sub> reaction with double methyl-substituted ethylene is expected to proceed with very low barrier of less than 1 kcal mol<sup>-1</sup> according to the theoretical predictions [4]. It should be noted that despite recent interesting experimental (basically crossed beam data) and theoretical findings, there are virtually no quantitative kinetic data on the reactions of F<sub>2</sub> with alkenes. In particular, temperature dependent kinetic studies are needed in order to resolve the long-standing general problem of the disparity between the high level theoretical calculations and experimental barriers of the F<sub>2</sub> reactions with C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> [5,6]. For example, theoretical barrier for the reaction of F<sub>2</sub> with the simplest alkene, C<sub>2</sub>H<sub>4</sub>, is higher by (1.6-2.5) kcal mol<sup>-1</sup> compared with the experimentally observed reaction threshold in collision energy. As noted by Feng and Allen [6], "the perplexing disparity between the state-of-the-art theoretical and experimental barriers for the C<sub>2</sub>H<sub>4</sub>+F<sub>2</sub> reaction elevates this system as an important testing ground for chemical physics."

In the present work we report the results of an experimental kinetic study of the reaction of molecular fluorine with C<sub>2</sub>H<sub>4</sub> in an extended temperature range (from 297 to 833 K):





The reaction enthalpies are from ref. [1]. We show that the activation energy determined from temperature dependence of the reaction rate constant is consistent with theoretical prediction for the reaction barrier height.

## 2. Experimental

Experiments were carried out in a low pressure discharge flow reactor using a modulated molecular beam mass spectrometer with electron impact ionization as the detection method [7-9]. The flow reactor operated at temperatures  $T = 297 - 833 \text{ K}$  and nearly 2 Torr total pressure of Helium and consisted of an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled extremities (Fig. S1, Supplementary Material) [10]. Temperature in the reactor was measured with a *K*-type thermocouple positioned in the middle of the reactor in contact with its outer surface. Temperature gradients along the flow tube measured with a thermocouple inserted in the reactor through the movable injector was found to be less than 1% [10].

The configuration of the flow reactor used in the experiments is shown in Figure S1. Reactants,  $\text{F}_2$  and  $\text{C}_2\text{H}_4$ , were detected at  $m/z = 38$  ( $\text{F}_2^+$ ) and 26 ( $\text{C}_2\text{H}_2^+$ ), respectively.  $\text{C}_2\text{H}_4$  was detected at its fragment peak, since the parent peak at  $m/z = 28$  was perturbed by contribution of the unavoidable traces of molecular nitrogen. The absolute concentrations of all the stable species used ( $\text{C}_2\text{H}_4$ ,  $\text{F}_2$ ,  $\text{Br}_2$ ) were calculated from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in calibrated volume flasks. Fluorine atoms formed in reaction (1a) were monitored at  $m/z = 98/100$  ( $\text{FBr}^+$ ) upon their chemical conversion to bromine fluoride,  $\text{FBr}$ , in reaction with excess  $\text{Br}_2$ :



$$k_2 = (1.28 \pm 0.20) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 299 - 940 \text{ K}) [11]$$

The absolute concentration of FBr was determined from the fraction of  $[\text{Br}_2]$  consumed in reaction (2),  $[\text{BrF}] = \Delta[\text{Br}_2]$ . F atoms in the calibration experiments were produced in the microwave discharge of  $\text{F}_2/\text{He}$  mixtures. In order to reduce F atom reactions with Pyrex surface inside the microwave cavity, a ceramic ( $\text{Al}_2\text{O}_3$ ) tube was inserted in this part of the injector.

The purities of the gases used were as follows: He >99.9995% (Alphagaz), passed through liquid nitrogen trap;  $\text{C}_2\text{H}_4$  >99.99% (Phillips);  $\text{F}_2$ , 5% in helium (Alphagaz);  $\text{Br}_2$  >99.99% (Aldrich).

### 3. Results and Discussion

#### 3.1. Rate constant of reaction (1).

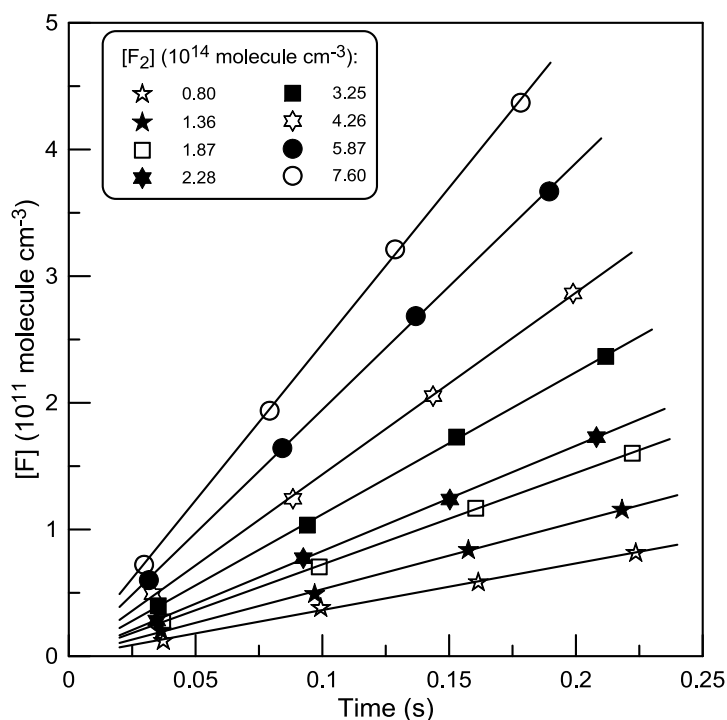
The rate constant of reaction  $\text{F}_2 + \text{C}_2\text{H}_4$  was determined using two different methods. In the first one, used in most experiments under conditions where reaction (1) is relatively slow and consumption of the reactants is too low to be measured accurately, the rate constant was determined by monitoring the kinetics of the reaction product, F-atom. The second approach used at higher temperatures ( $T = 590, 728$  and  $833$  K), consisted in a direct monitoring of the kinetics of  $\text{F}_2$  consumption in excess of  $\text{C}_2\text{H}_4$ .

***Kinetics of F-atom production in reaction (1).*** In this series of experiments, the rate constant of reaction (1) was determined in the temperature range 297 - 809 K from the kinetics of the reaction product, F-atom, formation under conditions where consumption of reactants ( $\text{F}_2$  and  $\text{C}_2\text{H}_4$ ) was negligible (less than 5 % at all temperatures of the study). Under experimental conditions where concentration of  $\text{C}_2\text{H}_4$  and  $\text{F}_2$  are constant, the F-atom formation is governed by zeroth order kinetics,  $d[\text{F}]/dt = k_{1a} \times [\text{C}_2\text{H}_4] \times [\text{F}_2] = \text{const}$ , and linear increase of the concentration of F atoms with reaction time is expected. Experiments were carried out in the presence of  $\text{Br}_2$  in the reactor ( $[\text{Br}_2] = (1.0-6.4) \times 10^{14}$  molecule  $\text{cm}^{-3}$ ), which led to a rapid

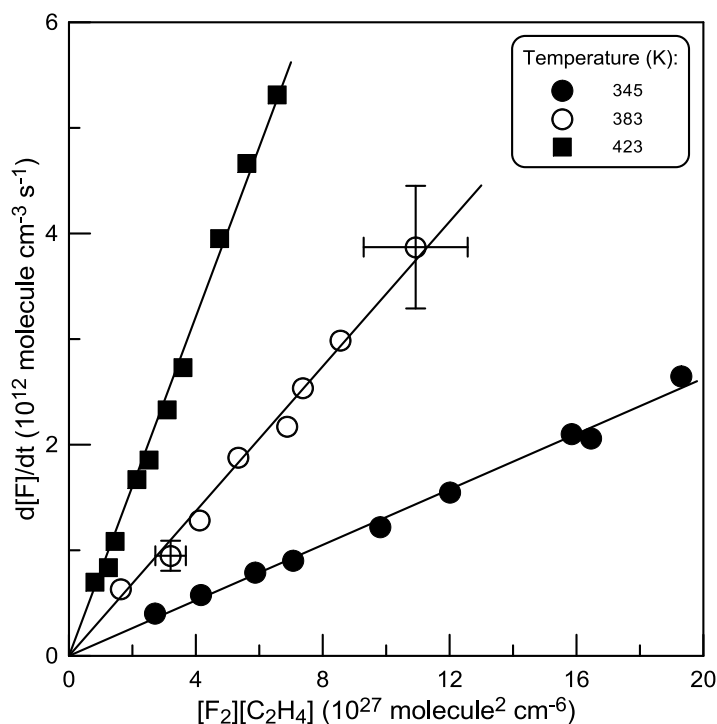
conversion of the fluorine atoms, formed in reaction (1a), to FBr through reaction (2). The kinetics of FBr formation corresponded to the following equation:

$$d[\text{FBr}]/dt = d[\text{F}]/dt = k_{1a} \times [\text{C}_2\text{H}_4] \times [\text{F}_2] \quad (\text{I})$$

Examples of the kinetics of F-atom (FBr) production are shown in Fig. 1. The slopes of the straight lines in Fig. 1 provide the rate of F-atom production,  $d[\text{F}]/dt$  (in molecule  $\text{cm}^{-3}\text{s}^{-1}$ ). The rate of F-atom production measured as a function of product of the concentrations of  $\text{C}_2\text{H}_4$  and  $\text{F}_2$  at different temperatures is shown in Figs. 2 and S2-S3 (Supplementary Material). The slopes of the observed linear dependences of  $d[\text{F}]/dt$  on  $[\text{F}_2] \times [\text{C}_2\text{H}_4]$  provide, in accordance with equation (I), the values of  $k_{1a}$  at respective temperatures. All the data obtained in this way for the rate constant of reaction (1a), as well as initial concentrations of the reactants used in these experiments, are shown in Table 1. The combined uncertainty on the measurements of  $k_{1a}$  was estimated to be of nearly 20 %, including statistical error and those on the measurements of the flows, pressure, temperature and absolute concentrations of the three species involved.



**Fig. 1.** Kinetics of F-atom production in reaction (1a) observed at  $T = 345\text{K}$  with  $[\text{C}_2\text{H}_4] = (2 - 3) \times 10^{13}$  molecule  $\text{cm}^{-3}$  and different initial concentrations of  $\text{F}_2$ . Continuous lines represent linear fit to the experimental data.



**Fig. 2.** Examples of the dependence of the rate of F-atom production in reaction (1a) on the product of the concentrations of  $F_2$  and  $C_2H_4$ . Selectively shown error bars represent the estimated typical 15% uncertainties on the measurements of the corresponding values.

**Table 1**

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

$T$ (K)	No./exp <sup>(a)</sup>	$[F_2]$ <sup>(b)</sup>	$[C_2H_4]$ <sup>(b)</sup>	$[Br_2]$ <sup>(b)</sup>	$k$ <sup>(c)</sup>	method <sup>(d)</sup>
297	8	3.2-23.3	0.25-0.62	5.5-6.4	0.0016	F kinetics
345	9	0.80-7.6	0.25-0.34	4.0-4.7	0.013	F kinetics
383	8	0.71-4.6	0.23-0.25	4.0-4.6	0.034	F kinetics
423	10	0.33-3.1	0.21-0.25	3.5-3.9	0.080	F kinetics
491	7	0.17-2.3	0.086-0.10	2.0-3.0	0.286	F kinetics
590	7	0.030-0.040	2.7-28		1.04	$F_2$ kinetics
618	7	0.088-0.91	0.069-0.078	1.9-2.2	1.40	F kinetics
728	8	0.030-0.040	0.80-10		3.81	$F_2$ kinetics
809	8	0.024-0.23	0.070-0.088	1.0-1.2	6.04	F kinetics
833	9	0.030-0.040	0.20-6.5		9.85	$F_2$ kinetics

<sup>(a)</sup> Number of kinetic runs

<sup>(b)</sup> Units of  $10^{14}$  molecule  $cm^{-3}$ .

<sup>(c)</sup> Units of  $10^{-14}$   $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>.

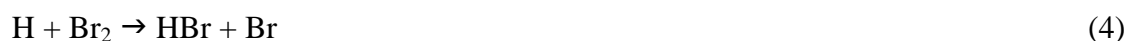
<sup>(d)</sup>  $k$  derived from kinetics of F-atom formation (F kinetics,  $k_{1a}$ ) or  $F_2$  consumption ( $F_2$  kinetics, total rate constant,  $k_1$ ).



A simple, at first glance, chemical system (consisted of three stable molecules, C<sub>2</sub>H<sub>4</sub>, F<sub>2</sub> and Br<sub>2</sub>) used in the measurements could, in fact, generate a number of side and secondary reactions, which should be discussed. First, F-atoms, formed in primary reaction (1a) and scavenged in reaction (2) with Br<sub>2</sub>, could also react with C<sub>2</sub>H<sub>4</sub>:



Reaction (3) was studied in a recent work from this group [8] where the independent of temperature total rate constant  $k_3 = (1.78 \pm 0.30) \times 10^{-10}$  and partial rate constants for two reactive channels,  $k_{3a} = (0.80 \pm 0.07) \times 10^{-10} \exp(189 \pm 37/T)$  and  $k_{3b} = (1.26 \pm 0.13) \times 10^{-10} \exp(-414 \pm 45/T)$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> were recommended in the temperature range (298 – 950) K. Due to high [Br<sub>2</sub>]/[C<sub>2</sub>H<sub>4</sub>] ratios used in the present experiments (Table 1), correction on the impact of the reaction (3) applied to the measured rate of F atom formation was rather low (generally < 10%, up to 14 % for a few points). It can be noted that H-atoms and C<sub>2</sub>H<sub>3</sub> radicals formed in the secondary reaction (3) are rapidly removed through respective reactions with Br<sub>2</sub> [1] and do not interfere with the kinetic measurements:



Another reaction which can potentially impact the observed kinetics of FBr is reaction of F<sub>2</sub> with Br<sub>2</sub>, which can proceed through two reaction pathways in the temperature range of the study:



The rate constant of FBr formation in this reactive system was measured in a recent study from this group:  $k_{6a} + 2 \times k_{6b} = (9.23 \pm 2.68) \times 10^{-11} \exp(-(8373 \pm 194)/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at T = 500-960 K [7]. Contribution of this reaction to the measured profiles of FBr was

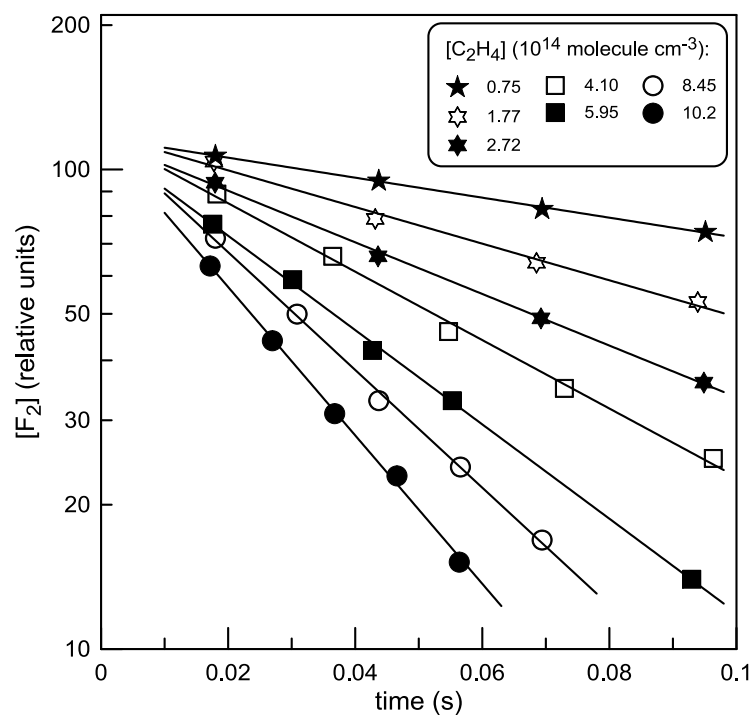
negligible at lower temperatures of the study. However, at the highest temperature ( $T = 809$  K) of the study it reached 40%. In this case, the concentration of FBr formed in reaction  $F_2 + Br_2$  was directly monitored in the absence of  $C_2H_4$  in the reactor and was extracted from that measured in the presence of  $C_2H_4$  in the reactive system. Finally, Br atoms formed, mainly, in the reaction (2) were present in the reactive system in concentrations close to those of FBr. Reaction of Br atoms with  $F_2$  is another potential additional source of FBr [7]:



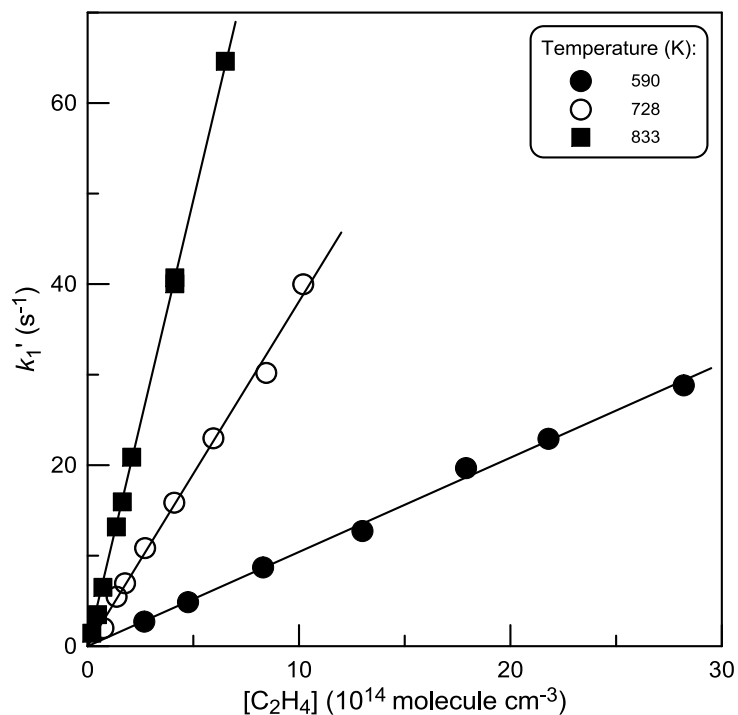
$$k_7 = (4.66 \pm 0.93) \times 10^{-11} \exp(-4584 \pm 86/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 300-940 \text{ K})$$

The contribution of this reaction to the measured rate of FBr formation, significant only at highest temperatures (up to 18% at  $T = 618$  and  $809$  K) of the study, was taken into account.

***Kinetics of  $F_2$  consumption in excess of  $C_2H_4$ .*** Reaction (1) is relatively slow; for this reason the experiments on the determination of  $k_1$  from  $F_2$  decays were conducted at three temperatures,  $T = 590, 728$  and  $833$  K, at high temperature limit of the temperature range used. The measurements were carried out under pseudo-first order conditions in excess of  $C_2H_4$  over  $F_2$ : initial concentrations of the reactants are shown in Table 1. The flow velocity in the reactor was in the range  $(320-400) \text{ cm s}^{-1}$ . Examples of the exponential decays of the concentration of  $F_2$ , in accordance with  $d[F_2]/dt = -k_1[F_2][C_2H_4]$ , are shown in Fig. 3. Consumption of  $C_2H_4$  was negligible in all the experiments due to its high excess over  $F_2$ . Fig. 4 shows the pseudo-first order rate constants,  $k_1' = k_1[C_2H_4]$ , measured as a function of the concentration of  $C_2H_4$ . All measured values of  $k_1'$  were corrected for axial and radial diffusion [12] of  $F_2$ . The corrections on  $k_1'$  ( $\leq 20\%$ ) were calculated using diffusion coefficient of  $F_2$  in He,  $D_0 = 427 \times (T/298)^{1.75} \text{ Torr cm}^{-2} \text{ s}^{-1}$  (estimated with Fuller's method) [13]. The slopes of the straight lines in Fig. 4 (linear through origin fit to the experimental data) provide the values of  $k_1$  at  $T = 590, 728$  and  $833$  K, shown in Table 1.



**Fig. 3.** Examples of  $F_2$  consumption kinetics in reaction with excess  $C_2H_4$  at  $T = 728$  K.



**Fig. 4.** Pseudo-first order rate constant,  $k_1' = k_1[C_2H_4]$ , as a function of the  $C_2H_4$  concentration at  $T = 590, 728$  and  $833$  K.

In order to check for the possible impact of a secondary chemistry on the results of these measurements, the rate of reaction (1) was measured at  $T = 833$  K with fixed concentration of

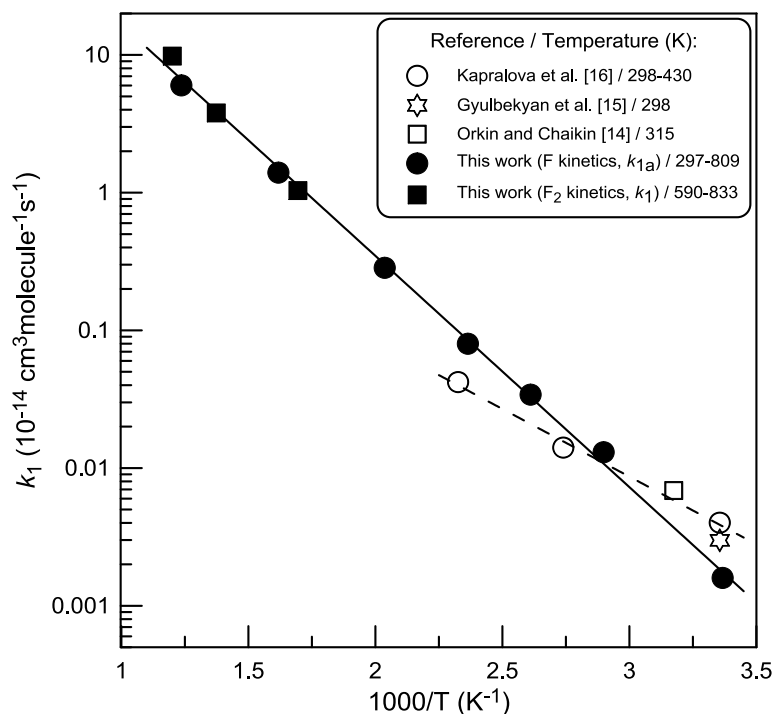
$C_2H_4$  ( $2.1 \times 10^{14}$  molecule  $cm^{-3}$ ) and initial concentration of  $F_2$  varied in the range (1.3 – 18.5)  $\times 10^{12}$  molecule  $cm^{-3}$ . The pseudo-first order rate constant of  $F_2$  loss was found to be independent of  $[F_2]_0$  with mean value of  $k_1' = (20.9 \pm 0.9) s^{-1}$  from five measurements. The independence of the reaction rate of the initial concentration of  $F_2$  indicates the negligible contribution of the secondary chemistry to  $F_2$  loss under experimental conditions of the study.

### 3.2. Comparison with previous studies.

All the results obtained for  $k_1$  at different temperatures in the present study are shown in Fig. 5 in line with literature data. The unweighted exponential fit to the present data for  $k_1$  yields the following Arrhenius expression:

$$k_1 = (7.94 \pm 2.06) \times 10^{-12} \exp(-3867 \pm 120)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the cited uncertainties are  $2\sigma$  statistical ones.



**Fig. 5.** Summary of the experimental data for the rate constant of the  $F_2+C_2H_4$  reaction. Uncertainty on the values of  $k_1$  from the present study (nearly 20%) corresponds to the size of the symbols.

Three previous studies [14-16] reported indirect measurements of the rate constant of reaction (1). Kapralova et al. [16] have studied the reaction of F<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> in the temperature range T = 298–430 K and pressure range 11-43 Torr (mainly C<sub>2</sub>H<sub>4</sub>) using diffusion flame method combined with temperature measurements in the reaction zone and reported the following expression for the rate constant:  $k_1 = 8 \times 10^{-14} \exp(-4600/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The mean values of the rate constant obtained by Kapralova et al. [16] at three temperatures are shown in Fig. 5. Gyulbekyan et al. [15] have reported the value of  $k_1 = 3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at T = 298 K which was derived from analysis of a complex mechanism of fluorination of ethane in presence of oxygen at room temperature and 0.5 Torr total pressure of C<sub>2</sub>H<sub>6</sub>/F<sub>2</sub>/O<sub>2</sub> mixtures. Orkin and Chaikin [14] have derived the rate of formation of fluorine atoms in the reaction F<sub>2</sub> + C<sub>2</sub>H<sub>4</sub>,  $k_1 = (6.9 \pm 0.7) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , from the measurements of the temperature rise upon chain fluorination of hydrogen in flow tube experiments at T = 315K and P = 3-10 Torr. Although the Arrhenius expression for  $k_1$  reported by Kapralova et al. differs significantly from that of the present study, the agreement of the absolute values of  $k_1$  from current and previous studies (within a factor of 2.3) can be considered as satisfactory given the non-direct nature of the measurements in refs. [14-16].

One can note good agreement between the values of  $k_{1a}$  and total rate constant  $k_1$  measured in the present work from kinetics of F-atom production and F<sub>2</sub> consumption, respectively. This experimental observation indicates that F-atom forming channel of the reaction (1) is the main one ( $k_{1a}/k_1 = 0.8-1.0$ , considering uncertainty on the measurements of the rate constants), if not unique, in the temperature range of the study and is in agreement with previous experimental and theoretical findings [2,6,14,17]. For instance, in crossed molecular beam experiments of Lu et al. [2] carried out with collision energies up to 11 kcal mol<sup>-1</sup>, only one, F+CH<sub>2</sub>CH<sub>2</sub>F forming, reaction channel was observed. Wang et al. [17] studied the reaction with DFT calculations and proposed a two-step reaction mechanism with

initial formation of diradical intermediate, followed by dissociation of the F–F bond, to produce CH<sub>2</sub>F–CH<sub>2</sub> and F-atoms. However, Lu et al. [2], in their crossed molecular beam study, observed a strongly backward angular distribution of the reaction products and suggested a typical rebound reaction mechanism discriminating mechanisms involving a stable intermediate.

The experimental threshold for reaction (1) determined by Lu et al. [2] was  $5.5 \pm 0.5$  kcal mol<sup>-1</sup>, i.e. slightly higher than the activation energy of 4.6 kcal mol<sup>-1</sup> reported by Kapralova et al. [16] and lower than the activation energy determined in the present work ( $7.7 \pm 0.3$  kcal mol<sup>-1</sup>). The source of disagreement between the reaction threshold measured by Lu et al. [2] and activation energy determined in the present work is not clear. The possible impact of vibrational excitation of F<sub>2</sub> in molecular beams was analyzed and reported to be negligible [2]. The experimental data can be compared with calculated reaction barriers of 7.1 [2] and 8.0 kcal mol<sup>-1</sup> [6] reported in the most recent theoretical studies. The theoretical potential energy barriers were substantially higher than the available experimental data for reaction threshold and activation energy. This discrepancy between the computed and experimental barriers for the reaction of F<sub>2</sub> with C<sub>2</sub>H<sub>4</sub>, simplest alkene, posed a general problem for the understanding of the mechanism of fluorination of alkenes. In this respect, the present study, where the activation energy of the reaction F<sub>2</sub>+C<sub>2</sub>H<sub>4</sub>,  $7.7 \pm 0.3$  kcal mol<sup>-1</sup>, is derived from the direct absolute measurements of the reaction rate constant as a function of temperature in an extended temperature range and is well consistent with computed barrier data, appears to solve the problem of the discrepancy between theory and experiment. It can be noted that a similar theory/experiment problem also exists for the reaction of F<sub>2</sub> with C<sub>3</sub>H<sub>6</sub>, for which the experimentally determined threshold of  $2.4 \pm 0.3$  kcal mol<sup>-1</sup> is lower than the calculated ones by 2.0 or 2.8 kcal mol<sup>-1</sup> [3]. It would be interesting to conduct similar kinetic measurements

for this reaction too, especially, considering that kinetics of propene fluorination has never been studied.

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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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