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

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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 ± 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_2 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^{-1} [3] for F_2 reactions with C_2H_4 and C_3H_6, respectively, while F_2 reaction with double methyl-substituted ethylene is expected to proceed with very low barrier of less than 1 kcal mol^{-1} 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_2 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_2 reactions with C_2H_4 and C_3H_6 [5,6]. For example, theoretical barrier for the reaction of F_2 with the simplest alkene, C_2H_4, is higher by (1.6-2.5) kcal mol^{-1} 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_2H_4+F_2 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_2H_4 in an extended temperature range (from 297 to 833 K):

$$F_2 + C_2H_4 \rightarrow F + C_2H_4F \qquad \Delta_r H° = -7.8 \text{ kcal mol}^{-1} \qquad (1a)$$

$$\rightarrow HF + C_2H_3F \qquad \Delta_r H° = -100.4 \text{ kcal mol}^{-1} \qquad (1b)$$

$\rightarrow C_2H_4F_2$ $\Delta_r H° = -118.5$ kcal mol^{-1} (1c)

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 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, F_2 and C_2H_4, were detected at m/z = 38 (F_2^+) and 26 ($C_2H_2^+$), respectively. C_2H_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 (C_2H_4, F_2, 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 (FBr^+) upon their chemical conversion to bromine fluoride, FBr, in reaction with excess Br_2:

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

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

The absolute concentration of FBr was determined from the fraction of [Br_2] consumed in reaction (2), [BrF] = Δ[Br_2]. F atoms in the calibration experiments were produced in the microwave discharge of F_2/He mixtures. In order to reduce F atom reactions with Pyrex surface inside the microwave cavity, a ceramic (Al_2O_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; C_2H_4 >99.99% (Phillips); F_2, 5% in helium (Alphagaz); Br_2 >99.99% (Aldrich).

3. Results and Discussion

3.1. Rate constant of reaction (1).

The rate constant of reaction F_2 + C_2H_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 F_2 consumption in excess of C_2H_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 (F_2 and C_2H_4) was negligible (less than 5 % at all temperatures of the study). Under experimental conditions where concentration of C_2H_4 and F_2 are constant, the F-atom formation is governed by zeroth order kinetics, $d[F]/dt = k_{1a}\times[C_2H_4]\times[F_2]$ = const, and linear increase of the concentration of F atoms with reaction time is expected. Experiments were carried out in the presence of Br_2 in the reactor ([Br_2] = $(1.0\text{-}6.4)\times10^{14}$ molecule 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:

$$d[FBr]/dt = d[F]/dt = k_{1a}\times[C_2H_4]\times[F_2] \quad (I)$$

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[F]/d*t* (in molecule $cm^{-3}s^{-1}$). The rate of F-atom production measured as a function of product of the concentrations of C_2H_4 and F_2 at different temperatures is shown in Figs. 2 and S2-S3 (Supplementary Material). The slopes of the observed linear dependences of d[F]/d*t* on $[F_2]\times[C_2H_4]$ 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.

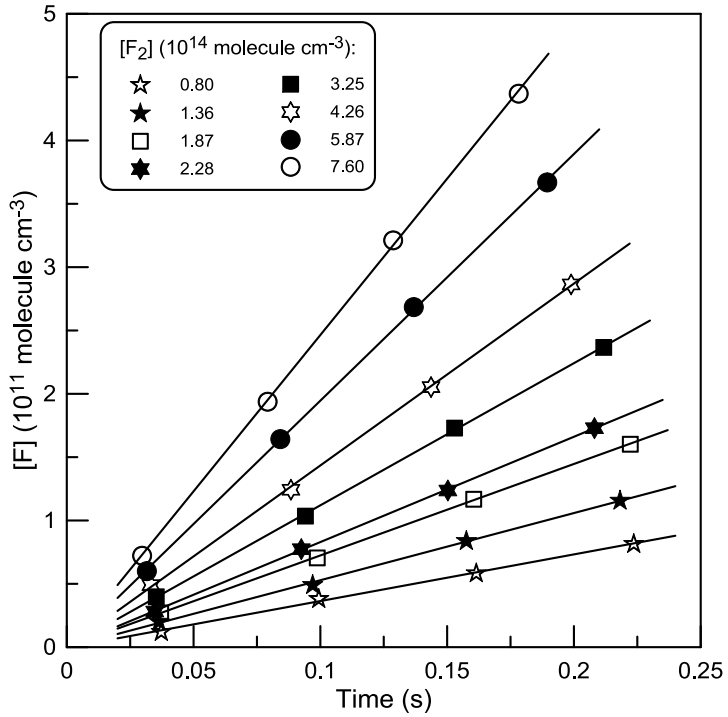

Fig. 1. Kinetics of F-atom production in reaction (1a) observed at T = 345K with $[C_2H_4] = (2 - 3)\times10^{13}$ molecule cm^{-3} and different initial concentrations of F_2. Continuous lines represent linear fit to the experimental data.

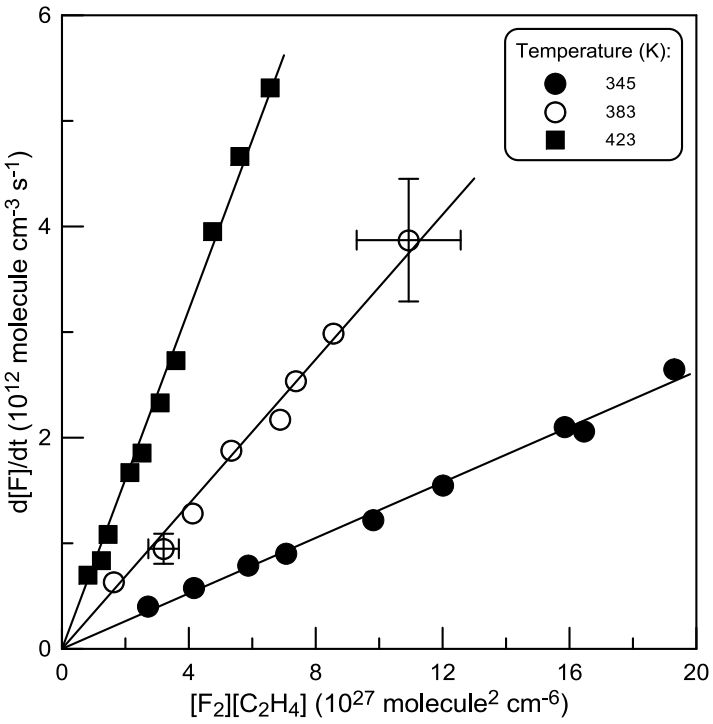

Fig. 2. Examples of the dependence of the rate of F-atom production in reaction (1a) on the product of the concentrations of F_2 and C_2H_4. Selectively shown error bars represent the estimated typical 15% uncertainties on the measurements of the corresponding values.

Table 1

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

T (K)	No./exp[(a)]	$[F_2]$[(b)]	$[C_2H_4]$[(b)]	$[Br_2]$[(b)]	*k*[(c)]	method[(d)]
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

[(a)] Number of kinetic runs

[(b)] Units of 10^{14} molecule cm^{-3}.

[(c)] Units of 10^{-14} $cm^3 molecule^{-1} s^{-1}$.

[(d)] *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_2H_4, F_2 and Br_2) 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_2, could also react with C_2H_4:

$$F + C_2H_4 \rightarrow H + C_2H_3F \quad (3a)$$

$$\rightarrow HF + C_2H_3 \quad (3b)$$

Reaction (3) was studied in a recent work from this group [8] where the independent of temperature total rate constant $k_3 = (1.78 \pm 0.30)\times10^{-10}$ and partial rate constants for two reactive channels, $k_{3a} = (0.80 \pm 0.07) \times 10^{-10} \exp(189 \pm 37/T)$ and $k_{3b} = (1.26 \pm 0.13) \times 10^{-10} \exp(-414 \pm 45/T)$ $cm^3 molecule^{-1} s^{-1}$ were recommended in the temperature range (298 – 950) K. Due to high $[Br_2]/[C_2H_4]$ 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_2H_3 radicals formed in the secondary reaction (3) are rapidly removed through respective reactions with Br_2 [1] and do not interfere with the kinetic measurements:

$$H + Br_2 \rightarrow HBr + Br \quad (4)$$

$$C_2H_3 + Br_2 \rightarrow C_2H_3Br + Br \quad (5)$$

Another reaction which can potentially impact the observed kinetics of FBr is reaction of F_2 with Br_2, which can proceed through two reaction pathways in the temperature range of the study:

$$Br_2 + F_2 \rightarrow F + Br_2F \quad (6a)$$

$$\rightarrow FBr + FBr \quad (6b)$$

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^3 $molecule^{-1}$ s^{-1} 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]:

$$Br + F_2 \rightarrow FBr + F \qquad (7)$$

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

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) 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, $D_0 = 427 \times (T/298)^{1.75}$ Torr cm^{-2} 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.

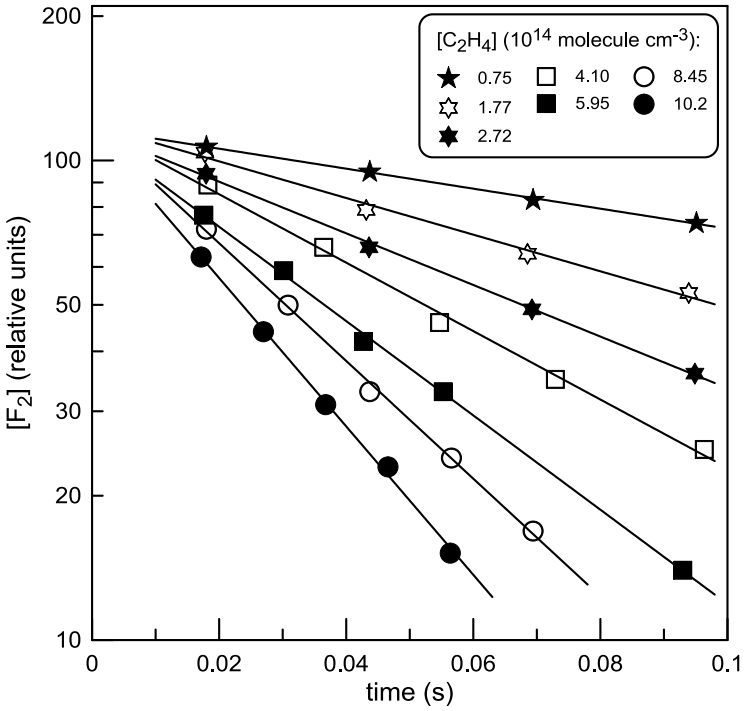

Fig. 3. Examples of F_2 consumption kinetics in reaction with excess C_2H_4 at T = 728 K.

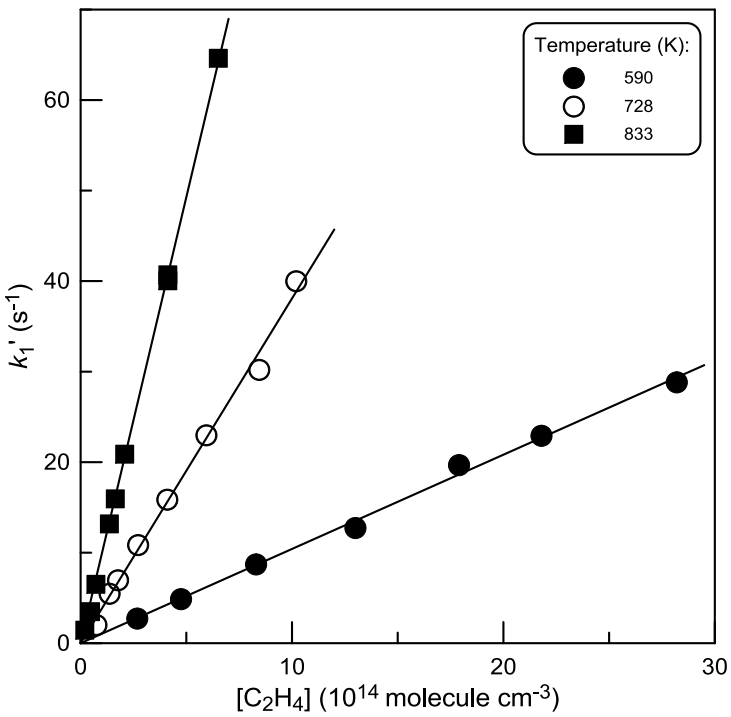

Fig. 4. Pseudo-first order rate constant, $k_1' = k_1[C_2H_4]$, as a function of the C_2H_4 concentration at T = 590, 728 and 833 K.

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 (2.1×10^{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 2σ statistical ones.

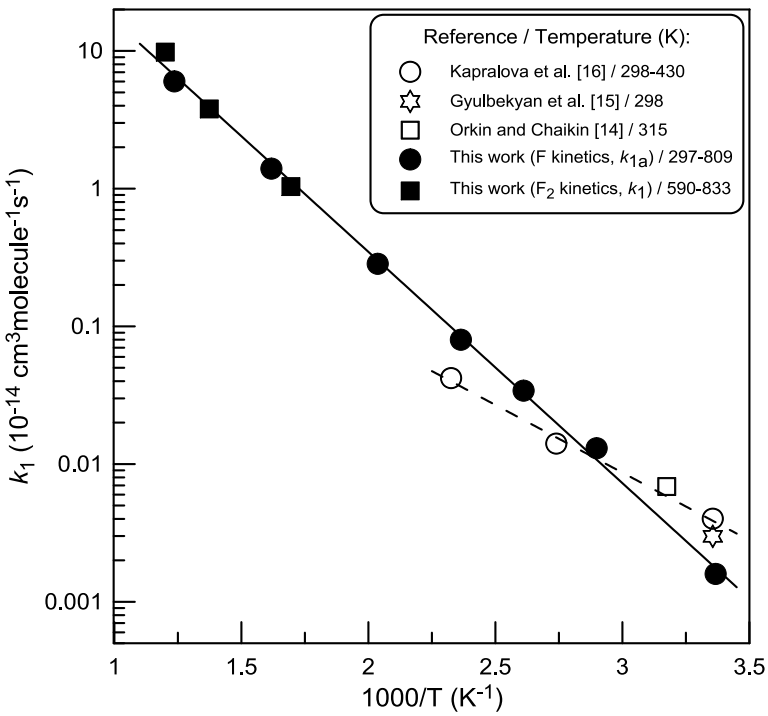

Fig. 5. Summary of the experimental data for the rate constant of the F_2+C_2H_4 reaction. Uncertainty on the values of k_1 from the present study (nearly 20%) corresponds to the size of the symbols.

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_2 with C_2H_4 in the temperature range T = 298–430 K and pressure range 11-43 Torr (mainly C_2H_4) using diffusion flame method combined with temperature measurements in the reaction zone and reported the following expression for the rate constant: $k_1 = 8\times10^{-14}$ exp(-4600/*R*T) $cm^3molecule^{-1}s^{-1}$. 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 $k_1 = 3\times10^{-17}$ $cm^3molecule^{-1}s^{-1}$ 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 $C_2H_6/F_2/O_2$ mixtures. Orkin and Chaikin [14] have derived the rate of formation of fluorine atoms in the reaction $F_2 + C_2H_4$, $k_1 = (6.9\pm0.7)\times10^{-17}$ $cm^3molecule^{-1}s^{-1}$, 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_2 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^{-1}, only one, $F+CH_2CH_2F$ 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 $CH_2F–CH_2$ 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 ± 0.5 kcal mol^{-1}, i.e. slightly higher than the activation energy of 4.6 kcal mol^{-1} reported by Kapralova et al. [16] and lower than the activation energy determined in the present work (7.7 ± 0.3 kcal mol^{-1}). 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_2 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^{-1} [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_2 with C_2H_4, 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_2+C_2H_4, 7.7 ± 0.3 kcal mol^{-1}, 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_2 with C_3H_6, for which the experimentally determined threshold of 2.4 ± 0.3 kcal mol^{-1} is lower than the calculated ones by 2.0 or 2.8 kcal mol^{-1} [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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