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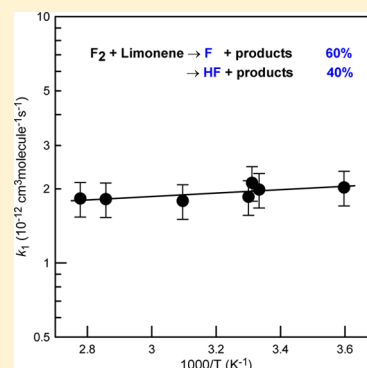
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Reaction of Limonene with F₂: Rate Coefficient and Products

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ABSTRACT: The kinetics of the reaction of limonene (C₁₀H₁₆) with F₂ has been studied using a low pressure ($P = 1$ Torr) and a high pressure turbulent ($P = 100$ Torr) flow reactor coupled with an electron impact ionization and chemical ionization mass spectrometers, respectively: $F_2 + \text{Limonene} \rightarrow \text{products}$ (1). The rate constant of the title reaction was determined under pseudo-first-order conditions by monitoring either limonene or F₂ decay in excess of F₂ or C₁₀H₁₆, respectively. The reaction rate constant, $k_1 = (1.15 \pm 0.25) \times 10^{-12} \exp(160 \pm 70)/T$ was determined over the temperature range 278–360 K, independent of pressure between 1 (He) and 100 (N₂) Torr. F atom and HF were found to be formed in reaction 1, with the yields of 0.60 ± 0.13 and 0.39 ± 0.09 , respectively, independent of temperature in the range 296–355 K.



1. INTRODUCTION

Compared with reactions involving free radicals, the kinetic and mechanistic data on the elementary reactions between closed-shell molecules are very limited. Generally, these reactions exhibit significant energy thresholds and, consequently, are very slow at moderate temperatures. In this respect, the F₂ molecule, manifesting relatively high reactivity with respect to some stable molecules, seems to be an exception of the rule. For example, crossed molecular beam experiments supported by ab initio calculations have demonstrated that reactions of molecular fluorine with organosulfur compounds, DMS (CH₂SCH₃) and DMDS (CH₃SSCH₃), are barrierless reactions.^{1–3} An unexpectedly high value, $1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, was reported for the rate constant of the reaction of F₂ with DMS.⁴

Reactions of F₂ with alkenes represent another interesting class of reactions of molecular fluorine, which were shown to proceed with a relatively low barrier. Experimental crossed beam data give a threshold in collision energy of 5.5⁵ and 2.4 kcal mol⁻¹⁶ for F₂ reactions with C₂H₄ and C₃H₆, respectively, while F₂ reaction with double methyl-substituted ethylene is expected to be barrierless according to the theoretical predictions.⁷ Concerning the products of the reactions of F₂ with C₂H₄, C₃H₆, and C₄H₈, in recent crossed molecular beam studies only the F atom formation channel was observed.^{5–7} It should be noted that despite recent interesting experimental (basically cross beam data) and theoretical findings, there are virtually no quantitative kinetic data (in particular, on the temperature dependence of the rate constants) on the reactions of F₂ with closed-shell molecules. More studies are needed in order to eliminate some existing discrepancies between experiment and theory,⁸ and to better understand the nature of the specificity of F₂ molecule regarding its reactivity toward stable molecules.

In addition to general interest, the information on the reactions between closed-shell molecules is of practical interest for the flow tube and smog chamber kinetic and mechanistic investigations of the gas phase reactions, where the reactions between closed-shell molecules can act as unexpected and surprisingly rapid side processes. For example, we have observed the reaction between F₂ and limonene (the title reaction) upon experimental study of the reaction of limonene with OH radicals, where reaction $F + H_2O$ was used as a source of OH.⁹

In the present work we report the results of the kinetic and mechanistic study of the reaction of F₂ with limonene (C₁₀H₁₆), a monoterpene, containing a cyclohexene ring and ethylene tailing group:



The rate constant of the reaction as well as the reactive pathways were determined over the temperature range 278–360 K.

2. EXPERIMENTAL SECTION

Two experimental setups were used: low pressure discharge flow reactor combined with an electron impact ionization mass spectrometer (EIMS)^{10–13} and high pressure turbulent flow reactor with chemical ionization mass spectrometry (CIMS) as a detection method.¹⁴

2.1. Low Pressure Flow Tube/EIMS. The low pressure flow tube, shown in Figure 1 along with the movable injector of the reactants, consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (water or ethanol). The walls of the reactor as well as of the

Received: September 19, 2014

Revised: October 16, 2014

Published: October 20, 2014

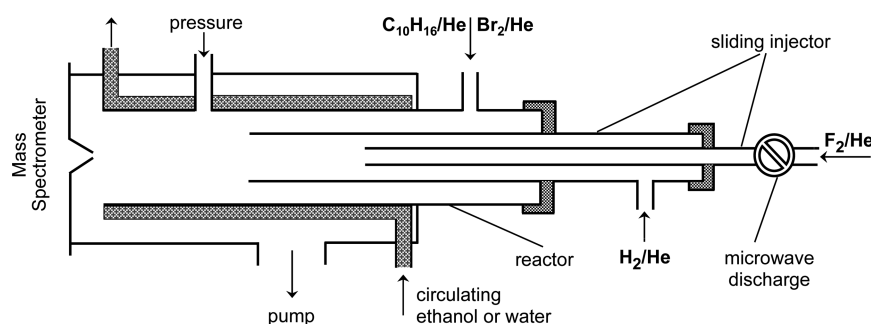


Figure 1. Diagram of the flow reactor.

injector were coated with halocarbon wax in order to minimize the heterogeneous loss of active species.

The limonene vapor was introduced into the flow reactor by passing helium through a thermostated glass bubbler containing liquid limonene or from a 10 L flask with known limonene/He mixture. In the low pressure experiments, all species were detected by mass spectrometry at their parent peaks $m/z = 136$ ($C_{10}H_{16}^+$), 38 (F_2^+), 20 (HF^+), 98/100 (FBr^+), 160 (Br_2^+). The concentrations of the stable species (including limonene) in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of mixtures of the species with helium in calibrated volume flasks. For limonene, similar (within 10%) results were obtained when absolute calibration of the mass spectrometer was performed by injecting known amounts (a few μL) of liquid limonene inside the flow tube and integrating the area of the mass spectrometric signals of $C_{10}H_{16}$ at $m/z = 136$.

F atoms and HF were observed as the products of the title reaction. Fluorine atoms were detected at $m/z = 98/100$ (FBr^+) after being scavenged with Br_2 :



This reaction was also used for the determination of the absolute concentrations of FBr via conversion of F atoms to FBr in reaction 2 with an excess Br_2 : $[FBr] = \Delta[Br_2]$, i.e., concentration of FBr was determined from the consumed fraction of $[Br_2]$. In the calibration experiments, F atoms were formed in the microwave discharge of F_2/He mixtures. In order to reduce F atom reactions with glass surface inside the microwave cavity, a ceramic (Al_2O_3) tube was inserted in this part of the injector. For the absolute calibration of HF signals, the reaction of F atoms with hydrogen was applied:



Two different approaches were used. In the first one, the absolute concentration of HF was determined via complete conversion of H_2 to HF with an excess of F atoms: $[HF] = [H_2]_0$. In another approach, F atoms were successively converted to HF and HBr in reactions with excess H_2 and Br_2 , respectively:



In this case, $[F]_0 = [HF] = \Delta[Br_2]$, i.e., concentration of HF, could be determined from the consumed fraction of $[Br_2]$. Two methods of HF calibration gave similar (within 10%) results.

2.2. CIMS Apparatus. A turbulent flow reactor (TFR) coupled to a quadrupole mass spectrometer with chemical ionization was described earlier.¹⁴ In the present study, the

reactor was operated at $T = 302$ K and pressure of 100 Torr of N_2 with a flow velocity of 2080 cm s^{-1} (Reynolds number $Re \approx 4100$). For the introduction of the reactants into the reactor the configuration similar to that described above for the low pressure flow system was used.

The reactive mixture, sampled from the TFR through a Teflon cone, was ionized in the ion–molecule reactor (stainless steel, 20 cm length and 4 cm i.d., 0.9 Torr total pressure of Ar). Primary Ar^+ ions were produced by electron impact ionization, the electrons being emitted by a heated filament (thoriated iridium) and accelerated with 20 V potential. The primary negative ions, SF_6^- , were formed via electron attachment to SF_6 . F_2 was detected in a negative mode as F_2^- ($m/z = 38$) formed by electron transfer from SF_6^- . Limonene molecules were detected in a positive mode as $C_{10}H_{16}^+$ ions ($m/z = 136$), formed via electron impact ionization.

Nitrogen, used as the bath gas in CIMS experiments, was obtained by evaporation of liquid nitrogen (Air Liquide). The purities of other gases used were as follows: He >99.9995% (Alphagaz), argon >99.9995% (Alphagaz), passed through liquid nitrogen traps; limonene >98% (Fluka), degassed before use; Br_2 >99.99% (Aldrich); F_2 , 5% in helium (Alphagaz).

3. RESULTS

3.1. Reaction Rate Constant. 3.1.1. EIMS Measurements.

The measurements of the rate constant of reaction 1 were carried out at 1 Torr total pressure of helium under pseudo-first-order conditions in excess of fluorine over limonene. The initial concentration of limonene was $(0.5\text{--}0.8) \times 10^{12} \text{ molecules cm}^{-3}$. The range of the concentrations of F_2 as well as the flow velocities in the reactor are presented in Table 1. The concentrations of both limonene and F_2 were simultaneously measured as a function of reaction time. Consumption of F_2 was negligible as a result of its sufficient excess over limonene.

Table 1. Experimental Conditions and Results of the Measurements of the Rate Constant of the Reaction $F_2 + \text{Limonene}$ at 1 Torr Total Pressure of Helium

No./exp. ^a	T, K	flow velocity ^b	$[F_2]^c$	k_1^d
6	278	2440–3120	0.38–5.05	2.03
11	298	1280–1660	0.12–1.65	1.99
6	323	1370	0.04–0.65	1.79
7	350	1980–2410	0.11–1.58	1.82
6	360	2000–2160	0.16–2.00	1.83

^aNumber of kinetic runs. ^bUnits of cm s^{-1} . ^cUnits of $10^{14} \text{ molecules cm}^{-3}$. ^dUnits of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, estimated uncertainty on k_1 is nearly 15%.

As could be expected for the bimolecular reaction carried out under pseudo-first order conditions in excess of molecular fluorine, the exponential decays of limonene were observed (Figure 2).

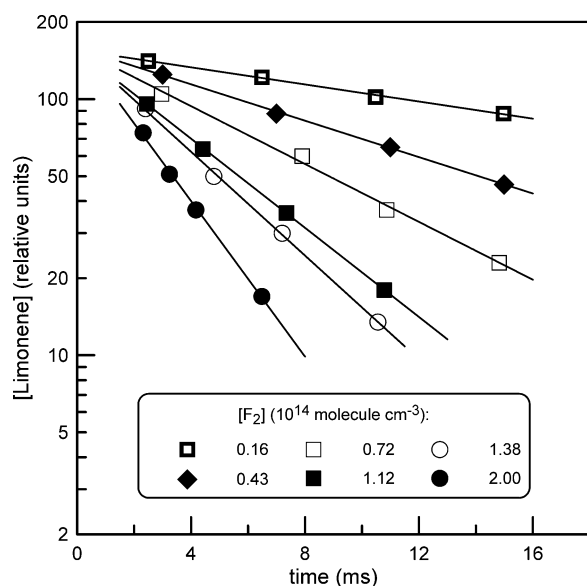


Figure 2. Examples of the limonene consumption kinetics in reaction 1 observed with different concentrations of F_2 : $T = 360$ K, $P = 1$ Torr.

Figure 3 shows the pseudo-first-order rate constant, $k_1' = k_1[F_2]$, as a function of the concentration of fluorine. All the

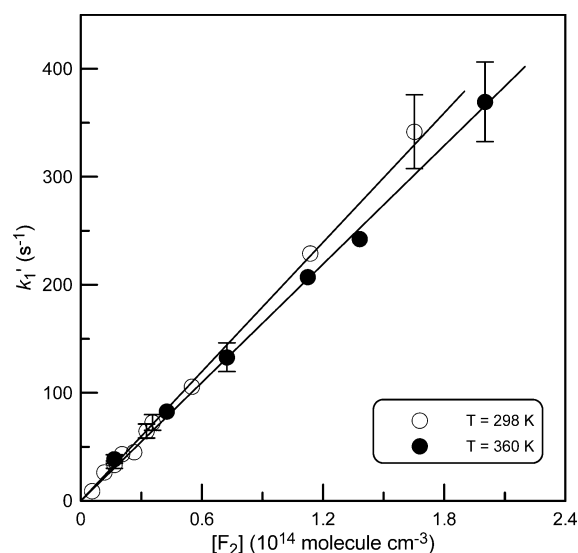
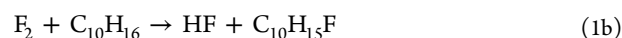
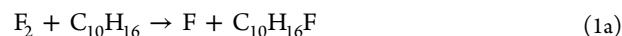


Figure 3. Example of pseudo-first-order plots obtained from limonene decay kinetics in excess of F_2 ($T = 298$ and 360 K).

measured values of k_1' were corrected for axial and radial diffusion¹⁵ of limonene. For the diffusion coefficient of limonene in He we have used that of benzene, $D_0 = 460$ Torr $cm^2 s^{-1}$ at $T = 423$ K¹⁶ with $T^{3/2}$ -dependence on temperature. Corrections were generally less than 5%, being higher (up to 12%) in a few kinetic runs only. The straight lines in Figure 3 represent linear through origin (no consumption of limonene was observed in the absence of F_2 in the reactor) fits to the experimental data. Their slopes give the values of k_1 at

respective temperatures. All the results obtained for k_1 within the described approach and at different temperatures are shown in Table 1. At lower temperatures in the reactor, we have observed an abnormal increase of the reaction rate constant, which might be related to the surface adsorbed limonene. The possible impact of the wall reaction on the results obtained in this section is discussed below, based on the data observed in a high pressure turbulent flow reactor.

As it will be shown below, F atoms and HF were found to be the primary products of reaction 1



Additional F atoms could be produced in reactions of F_2 with fluorinated organic radicals formed in reaction 1a. In this respect, the possible impact on the measurements of k_1 of the secondary reactions of F atoms with limonene



was explored in separate series of experiments at $T = 298$ K, where the rate constant of reaction 1 was measured with fixed concentration of F_2 (4.0×10^{13} molecules cm^{-3}) and concentration of limonene varied in the range $(0.4\text{--}22.3) \times 10^{12}$ molecules cm^{-3} . The results of these measurements are shown in Figure 4.

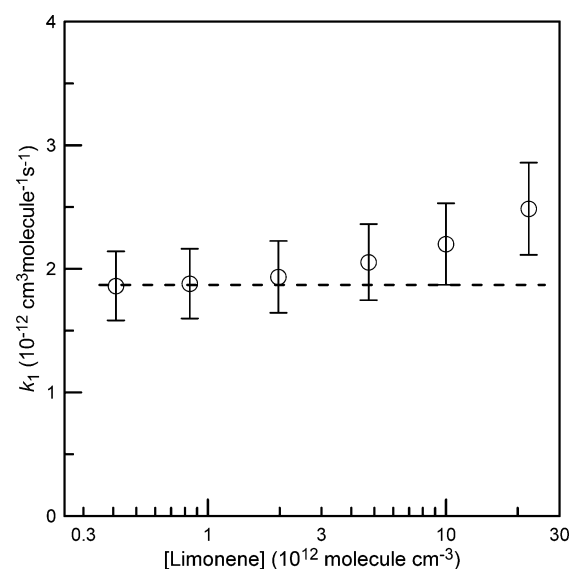


Figure 4. Dependence of the rate coefficient of reaction 1 on the initial concentration of limonene: $T = 298$ K, $[F_2] = 4.0 \times 10^{13}$ molecules cm^{-3} . Error bars correspond to estimated 15% uncertainty on the measurements of k_1 .

At low concentrations of limonene ($\leq 2 \times 10^{12}$ molecules cm^{-3}), the measured rate constant ($k_1 = 1.87 \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1} , dotted line in Figure 3) was found to be independent (within a few %) of the initial concentration of limonene, indicating the negligible contribution of the secondary chemistry to the limonene loss under the experimental conditions used in the measurements of k_1 : $[Limonene]_0 = (0.5\text{--}0.8) \times 10^{12}$ molecules cm^{-3} . A trend toward an increase with increasing $[C_{10}H_{16}]_0$ is observed for k_1 at higher initial concentrations of limonene. Unfortunately, these data do not allow for estimation of the rate constant of

the reaction 5, since neither F atom sources (reactions of F_2 with radicals produced in reaction 1a) nor loss processes (wall loss, reactions with fluoro organic radicals—products of reaction 1 are well characterized).

3.1.2. CIMS Measurements. All the values of k_1 measured in a low pressure flow tube (Table 1) were obtained from the kinetics of limonene consumption in excess of F_2 . The attempts to measure k_1 monitoring decays of F_2 in excess of limonene led to systematically higher values of the rate constant. This made us think of possible contribution of the heterogeneous reaction of F_2 with surface adsorbed limonene. In order to verify if the low pressure measurements are affected by heterogeneous chemistry we have carried out the measurements of the rate constant of reaction 1 in a high pressure turbulent flow reactor, which can be considered as a wall-free reactor due to limited mass exchange between turbulent core (central portion of the flow) and laminar sublayer (the region near the wall).¹⁷

Two series of experiments were conducted: k_1 was determined from both limonene ($[Limonene]_0 \sim 5 \times 10^{11}$ molecules cm^{-3}) and F_2 ($[F_2]_0 \leq 10^{12}$ molecules cm^{-3}) decays monitored in excess of F_2 ($[F_2] = (0.07\text{--}1.20) \times 10^{14}$ molecules cm^{-3}) and limonene ($[C_{10}H_{16}] = (0.14\text{--}1.21) \times 10^{14}$ molecules cm^{-3}), respectively. The measurements were carried out at near room temperature and 100 Torr total pressure of N_2 in the reactor, the flow velocity in the reactor was 2080 $cm\ s^{-1}$. Figure 5 shows the experimental data observed for the pseudo-first-order rate constants k_1' .

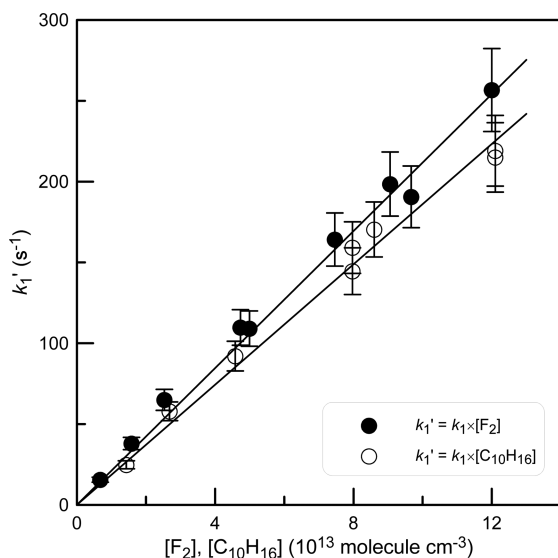


Figure 5. Pseudo-first-order plots obtained in turbulent flow reactor ($P = 100$ Torr of N_2) from limonene decay kinetics in excess of F_2 ($T = 302$ K, filled symbols) and from F_2 decays in excess of limonene ($T = 303$ K, open symbols).

The slopes of the linear through origin dependencies in Figure 5 provide the following values for the rate constant: $k_1 = 2.12 \times 10^{-12}$ at $T = 302$ K and 1.86×10^{-12} $cm^3\ molecule^{-1}\ s^{-1}$ at $T = 303$ K, measured in excess of F_2 and limonene, respectively. These results are in good agreement (within estimated 15% uncertainty of the measurements) with each other, as well as with the value of $k_1 = 1.99 \times 10^{-12}$ $cm^3\ molecule^{-1}\ s^{-1}$ measured with EIMS at $T = 298$ K and 1 Torr total pressure in the reactor. These results indicate that the low pressure measurements were not affected by possible

heterogeneous complications, when F_2 is in excess, and that the rate constant of reaction 1 is pressure independent in the range 1–100 Torr.

3.1.3. Temperature Dependence of k_1 . All the results obtained for k_1 at different temperatures are shown in Figure 6.

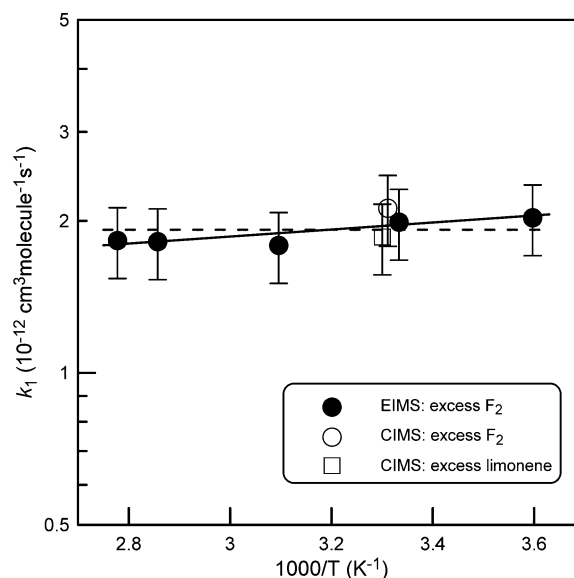


Figure 6. Temperature dependence of the rate constant of the reaction $F_2 + Limonene$: EIMS, electron impact ionization mass spectrometry, $P = 1$ Torr; CIMS, chemical ionization mass spectrometry, $P = 100$ Torr.

The combined uncertainty on the measurements of the rate constant was estimated to be in the range 15–20%, including statistical error and those on the measurements of the flows, pressure, temperature, and the absolute concentrations of the relevant species. The unweighted exponential fit to the present data for k_1 yields the following Arrhenius expression:

$$k_1 = (1.15 \pm 0.25) \times 10^{-12} \exp(160 \pm 70)/T \text{ cm}^3\ molecule^{-1}\ s^{-1}$$

where the cited uncertainties are 1σ statistical ones. The experimental results for k_1 can also be well represented with temperature independent value (dotted line in Figure 6) of

$$k_1 = (1.92 \pm 0.30) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } T = 278\text{--}360\ K$$

3.2. Reaction Products. Experiments on the identification and quantification of the reaction products were carried out in a low pressure flow tube/EIMS system. Significant increase in the peak intensity at $m/z = 20$ was observed upon reaction of limonene and F_2 , that was attributed to the formation of HF as a reaction product. In addition, we have observed (but not quantified) the appearance of the signal at $m/z = 154$, which could correspond to $C_{10}H_{15}F$, coproduct of HF in reaction 1b. In order to check for the formation of another possible reaction product, F atom, Br_2 was added in the reactive system: if F atoms are formed in reaction 1 they could be scavenged in a rapid reaction with Br_2 forming FBr molecules. Indeed, the formation of FBr at $m/z = 98/100$ (FBr^+) was observed upon addition of Br_2 , showing the presence of F atom in the reaction products. Another observation was that HF signal decreased

upon addition of Br₂, indicating that in Br₂-free system, HF was partly formed in secondary reactions of F atoms.

Typical experiments on the determination of the yields of the reaction products, F and HF, consisted of the measurements of the concentration of limonene consumed and concentrations formed of the products in excess of F₂ ($[F_2] = (2.5\text{--}5.0) \times 10^{13}$ molecules cm⁻³) and in the presence of relatively high concentrations of Br₂ ($[Br_2] = (1.5\text{--}4.3) \times 10^{14}$ molecules cm⁻³) in the reactor. Reaction time was approximately 0.03 s in all the experiments and initial concentration of limonene was varied in the range $(0.76\text{--}8.30) \times 10^{12}$ molecules cm⁻³. Under these experimental conditions, more than 80% of limonene was consumed in the reaction with F₂. The concentrations formed of the reaction products, HF and F, were detected at $m/z = 20$ (HF⁺) and 98 (FBr⁺) as a function of the concentration consumed of limonene. Example of the experimental data observed at $T = 323$ K is shown in Figure 7.

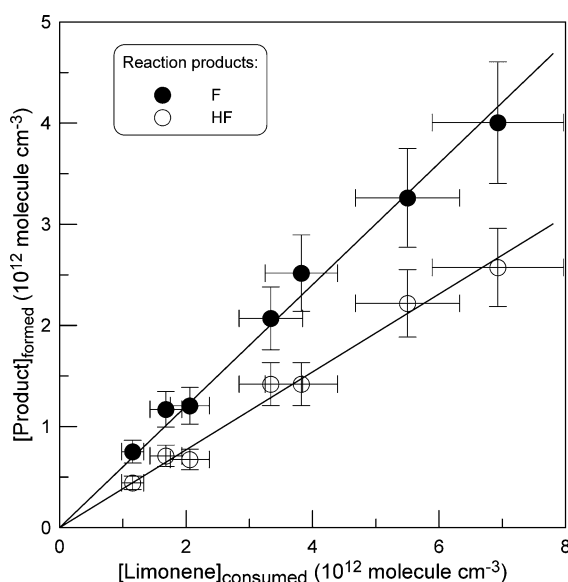


Figure 7. Concentrations of F atoms and HF formed in reaction 1 as a function of the consumed concentration of limonene: $T = 323$ K. Error bars correspond to 15% uncertainties on the determination of the absolute concentrations of the relevant species.

The slope of the straight line in Figure 7 provides the branching ratios for the fluorine atoms and HF forming channels of reaction 1: 0.601 and 0.385, respectively. All the results obtained in this way for k_{1a}/k_1 and k_{1b}/k_1 at different temperatures are shown in Table 2.

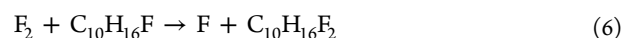
The reactive system limonene/F₂/Br₂ being rather complex, the possible impact of the secondary and side reactions on the results of the measurements of the product yields should be discussed. First, it should be noted that Br₂ did not react with either limonene or F₂, despite the high concentrations of bromine used. This was verified in separate experiments with Br₂/limonene and Br₂/F₂ mixtures. F atoms, formed in reaction 1, were scavenged with Br₂, but they could also participate in secondary reactions with limonene and products of reaction 1. However, the possible impact of these reactions can be neglected, considering the very high value of the rate constant of the reaction $F + Br_2$, $k_2 = (2.2 \pm 1.1) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at $T = 299$ K,¹⁸ and high $[Br_2]$ to $[limonene]_0$ ratio (≥ 20) used in these experiments. Another issue, which should be considered, is possible formation of additional F atoms in

Table 2. F Atom and HF Yields in the Reaction of F₂ with Limonene As a Function of Temperature

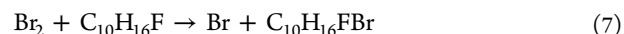
No./exp. ^a	<i>T</i> (K)	k_{1a}/k_1^b	k_{1b}/k_1^b
5	296	0.568	0.428
5	315	0.607	0.411
7	323	0.601	0.385
5	333	0.627	0.420
6	338	0.611	0.354
5	343	0.585	0.351
5	355	0.631	0.403
mean: ^c		0.604 ± 0.022	0.393 ± 0.031

^aNumber of experimental runs. ^bAll data were obtained in excess of F₂ over limonene, except $T = 338$ K, where excess of limonene over F₂ was used. ^cUncertainty is 1 σ statistical one.

secondary reactions of F₂ with fluoroorganic radicals produced in reaction 1.

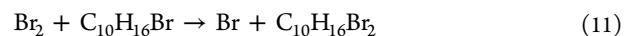
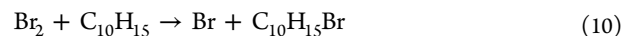
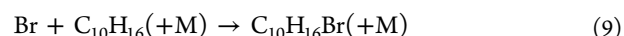
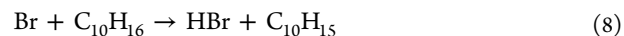


It can be assumed that in the reactive system used, C₁₀H₁₆F radicals react preferentially with Br₂, considering high reactivity of hydrocarbon radicals toward Br₂^{19,20} (although halogen substitution somewhat reduces the reactivity)²¹ and excess of Br₂ over F₂ in the present experiments:



This interpretation seems to be supported by the experimental observation of the invariance of the branching ratio data, obtained with $[Br_2]/[F_2]$ ratio varied from 4 to 16.

Finally, we have carried out another series of measurements, this time, in excess of limonene over F₂. The concentrations of the reaction products were monitored as a function of the consumed concentration of F₂. Initial concentration of fluorine was varied in the range $(0.7\text{--}5.0) \times 10^{12}$ molecules cm⁻³. Reaction time and concentration of limonene being ~ 0.04 s and $\sim 10^{13}$ molecules cm⁻³, respectively, nearly half of F₂ was consumed in reaction 1 under these experimental conditions. It was observed that addition of Br₂ ($(2\text{--}5) \times 10^{14}$ molecules cm⁻³) into the reactive limonene/F₂ mixture led to significant decrease of the limonene concentration, most probably due to possible secondary (chain) reactions of limonene with Br atoms initially formed in reactions of Br₂ with F atoms and organic radicals - products of reaction 1:



In the context of the measurements of k_{1a}/k_1 and k_{1b}/k_1 ratios, it is important to note that this secondary chemistry does not impact the concentration of F₂ and those of the reaction products, F (detected as FBr⁺) and HF. Results of these experiments are shown in Figure 8.

The yields of F atoms and HF, defined by the slopes of the linear dependencies in Figure 8, are 0.611 and 0.354, respectively. These data are very close to those obtained in excess of F₂ over limonene. Similarity of the results obtained under different experimental conditions is an indication of the limited impact of the uncontrolled side chemistry on the measurements of the product yields. In particular, it indicates

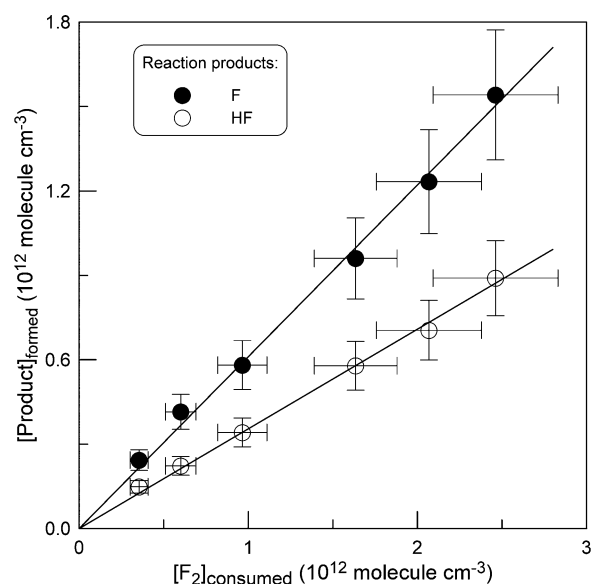


Figure 8. Concentrations of F atoms and HF formed in reaction 1 as a function of the consumed concentration of F_2 ; $T = 338$ K. Error bars correspond to 15% uncertainties on the determination of the absolute concentrations of the relevant species.

that in excess of F_2 , the possible secondary reaction of F_2 with the coproduct of HF, $C_{10}H_{15}F$, which is a closed shell molecule with two double bonds, does not affect the results of the measurements of F and HF yields in reaction 1.

Finally, the k_{1a}/k_1 and k_{1b}/k_1 ratios (Table 2) were found to be independent of temperature between 296 and 355 K, and the mean values

$$k_{1a}/k_1 = 0.60 \pm 0.13$$

$$k_{1b}/k_1 = 0.39 \pm 0.09$$

can be recommended from this study, with estimated uncertainty of nearly 20%.

4. DISCUSSION

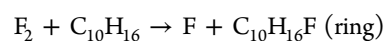
F atoms and HF molecules were observed as products of reaction 1 with the sum of their yields corresponding to nearly 100% of the fluorine mass balance. In order to verify the thermochemistry of the reaction pathways leading to the formation of these products, we have conducted density functional theory (DFT) calculations. All of the corresponding conformer structures were obtained by performing geometry optimization calculations at the B3LYP/6-31+G(d) level of theory, with the Gaussian 09 program suite.²² Thermochemical parameters were obtained from the calculations of vibrational frequencies, at the same level of theory. Three different pathways, all resulting from the initial interaction of F_2 with one of the double bond of limonene, were considered in the calculations:



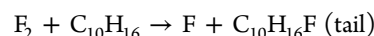
$$\Delta H = -108 \text{ kcal mol}^{-1} \quad \Delta G = -107 \text{ kcal mol}^{-1}$$



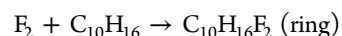
$$\Delta H = -104 \text{ kcal mol}^{-1} \quad \Delta G = -103 \text{ kcal mol}^{-1}$$



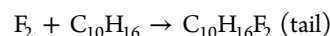
$$\Delta H = -15.8 \text{ kcal mol}^{-1} \quad \Delta G = -14.3 \text{ kcal mol}^{-1}$$



$$\Delta H = -14.8 \text{ kcal mol}^{-1} \quad \Delta G = -14.6 \text{ kcal mol}^{-1}$$



$$\Delta H = -123 \text{ kcal mol}^{-1} \quad \Delta G = -111 \text{ kcal mol}^{-1}$$



$$\Delta H = -121 \text{ kcal mol}^{-1} \quad \Delta G = -109 \text{ kcal mol}^{-1}$$

The first channel concerns the formation of HF and the corresponding ring or tail monofluoro-limonene, with $\Delta H \approx -108$ and ≈ -104 kcal mol⁻¹, respectively. The second pathway corresponds to the attack of F_2 to one of the double bonds of limonene leading to the formation of F atoms and the corresponding ring or tail fluorinated radical with $\Delta H \approx -15.8$ and ≈ -14.8 kcal mol⁻¹, respectively. Finally, the last channel (not observed in our experiments) represents the addition of F_2 to limonene double bonds forming the ring or tail difluoro-limonene with $\Delta H \approx -123$ and ≈ -121 kcal mol⁻¹, respectively. These calculations show that the reaction channels leading to the formation of the observed products, F and HF, are exothermic, as one could expect considering the absence of the reaction barrier, indicated by the observed slightly negative temperature dependence of the total rate constant of reaction 1. Besides, the observed negative temperature dependence of the rate constant seems to point to the addition/elimination mechanism. It should be noted that to get accurate energies, single point calculations should be performed at higher levels of theory, which demonstrate small deviations in comparison with experimental values of energies and enthalpies of formation.^{23,24} However, in the case of heavy molecules (e.g., limonene) single point calculations are time-consuming, require high computer power, and were beyond the scope of this work.

To our knowledge, the present study is the first one reporting the experimental measurements of the rate constant for reaction of F_2 with unsaturated organic compound. The previous crossed molecular beam studies of F_2 reactions with alkenes^{5–7} provided the information on the reaction threshold, but not on the reaction rate constant.

In the present study, the limonene fluorination channel (HF forming channel) was found to proceed with the branching ratio of nearly 40%. This strongly differs from the results observed previously for reactions of F_2 with alkenes: HF was not observed in crossed molecular beam studies of the reactions of F_2 reactions with C_2H_4 , C_3H_6 , and isomers of C_4H_8 .^{5–7} At this stage, it is difficult to assign the reason for the difference in the mechanisms of the interaction of F_2 with double bonds in limonene and simple alkenes. More detailed experimental (kinetic and mechanistic) and theoretical studies are needed to better understand the dynamics of the reactions of F_2 with unsaturated organic compounds.

5. CONCLUSION

In this work, we investigated the kinetics and products of the reaction between two closed-shell molecules, F_2 and limonene ($C_{10}H_{16}$), using two experimental setups: a low pressure ($P = 1$ Torr) and a high pressure turbulent ($P = 100$ Torr) flow reactor coupled with an electron impact ionization and

chemical ionization mass spectrometers, respectively. The reaction rate constant determined either from limonene or from F₂ loss kinetics was found to be independent of pressure between 1 and 100 Torr and to slightly decrease with increase of temperature in the range 278–360 K. Two major reaction pathways leading to production of F atom and HF were identified and the corresponding branching ratios were measured to be 0.60 ± 0.13 and 0.39 ± 0.09 , respectively, independent of temperature in the range 296–355 K. Density functional theory (DFT) calculations showed that the reaction channels leading to the formation of the observed products, F and HF, are exothermic, as one could expect considering the absence of the reaction barrier, indicated by the observed slightly negative temperature dependence of the total rate constant. Similar experimental studies of the reactions of F₂ with smaller alkenes in combination with high level calculations would be very useful to better understand the dynamics of the reactions between these closed-shell molecules.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J. M. is very grateful for his PhD grant from CAPRYSSES project (ANR-11-LABX-006-01) funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir).

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