Ab inito investigation of the H_2O_2+F elementary reaction

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Abstract

Elementary gas phase reaction of hydrogen peroxide with fluorine atom has been investigated theoretically using ab initio quantum chemistry methods. Two possible reaction paths are considered: the H-abstraction path leading to HO_2 and HF products and the OH-abstraction one leading to OH and HOF products. The optimized structures and the harmonic vibrational frequencies of all the involved molecular systems are calculated using the CCSD(T) approach with the jun-cc-pvtz basis set. For the H-abstraction path, the reaction is found to be barrier less with a ZPE corrected classical barrier height equals to -2.5 kcal mol^{-1}. A reactant complex (RC) is located at the entrance channel with relative stabilities about 3.8 and 1.3 kcal.mol^{-1} compared to the reactants (H_2O_2 + F) and the transition state (TS), respectively. These results suggest that the reaction according to this path is very fast, which can explain the remarkable lack in the corresponding kinetic experimental data. For the OH-abstraction path, the barrier height including ZPE correction is found to be 14.6 kcal mol^{-1}. The corresponding rate constants k evaluated by means of the transition state theory TST over the temperature range of 200-2500 K shows that this path has no significant contribution to the title reaction.

Keywords: Hydrogen peroxide; Fluorine atom; Ab initio-TST.

1. Introduction

The emission of the chlorofluorocarbons CFCs in the atmosphere led to two harmful environmental impacts: the depletion of the stratospheric ozone layer and the global warming. Therefore, international efforts have been made to phase out these compounds and replace them progressively by the hydrofluorocarbons HFCs and the hydrochlorofluorocarbons HCFCs. All these species represent the main sources of the atmospheric fluorine atom. The high reactivity of this atom has attracted significant attention from many researches. Numerous experimental and theoretical studies dealing with the mechanism and the kinetics of the fluorine atom reactions with CH_4, H_2, H_2O, O_3, CF_3O_2 and CH_3O_2 were carried out [1-12]. Unfortunately, there are scarce experimental kinetic data for the reaction of this atom with the hydrogen peroxide H_2O_2. The single reported value of the thermal rate constant as a function of temperature k(T) is that measured at T=298K by Walther and Wagner [13] (k = 5 10^{-11} cm^3 $molecule^{-1}$ s^{-1}). Besides, no theoretical investigation has been yet reported on this reaction.

In this work, we attempt to elucidate the mechanism of the title reaction by assuming that it can proceed via two paths:

the H-abstraction path $\qquad H_2O_2 + F \rightarrow HF + HO_2$ and

the OH-abstraction path $\qquad H_2O_2 + F \rightarrow HOF + OH$

To reach our aim, ab initio electronic structure calculations relative to the stationary points on the potential energy surface of this reaction were performed. For the OH-abstraction path, the obtained ab initio results were employed in conjunction with the transition state theory (TST) to study its kinetic behavior over a wide temperature range of 200-2500 K and to examine the importance of its contribution to the studied reaction.

2. Computational methods

For Both H and OH abstraction paths of the H_2O_2 + F reaction, all the involved molecular systems are taken in their ground state. The minimum energy structures and the harmonic vibrational frequencies of the reactants (H_2O_2 and F), intermediate (RC), products (HO_2, HF, OHF and OH) as well as transition states (TS) were evaluated at the singles and doubles coupled cluster with a perturbative treatment of triple excitations CCSD(T) level of calculation [14] implemented in the GAUSSIAN 09 program [15] using the jun-cc-pvtz basis set [16].

For the OH abstraction path, conventional transition state theory TST was employed to evaluate theoretical rate constants over a temperature range of 200-2500 K on the basis of the

obtained ab initio electronic structures and energy information, by means of the GAUSSRATE 9.1 program [17]. Quantum effects were neglected because the fluorine atom abstracts a hydroxyl group, which is too heavy to tunnel. Variationel effects were not considered here since same deduction about the contribution of the OH path can be provided with high limit TST values of the thermal rate constant.

3. Results and discussion

3.1. H abstraction path

In this section, we report our results of the ab initio calculation relative to the geometries, the harmonic vibrational frequencies and the energies of all the stationary points, containing the reactants, reactant complex, transition state and products (HO_2 and HF), as well as the potential energy profile which connects them.

The optimized geometric parameters of H_2O_2, RC, TS, HO_2 and HF are shown in Fig.1 along with the available experimental data. For the reactant and product species, it is apparent that the obtained values match well with the experimental data with a maximum error which doesn't exceed 0.4% for the bond lengths and 1.6% for the angles. This excellent accord supports our choice of the CCSD(T)/ jun-cc-pvtz method.

The inspection of the TS structure in Fig.1 reveals that, in order that the reaction takes place via the H-abstraction channel:

- The breaking O1···H3 bond length must be elongated by 2.5% compared with its homologous in H_2O_2 molecule and the forming H3···F bond must be longer than the equilibrium bond length in the isolated HF molecule by 72.2%. This indicates that the TS is reactant-like which is a characteristic of an "early" transition state on the minimum energy path.

- The preferred bringing together of H_2O_2 molecule and F atom is when the bending θ(FH3O1) and dihedral α(O2O1H3F) angles are 104° and -99.3°, respectively.

Fig.1 shows also that the intermediate CR is a van der Waals type complex which has a five membered cyclic structure. The F-H3 and F-H4 bond lengths are predicted to be 2.113 and 2.221 Å, respectively.

Table 1 presents calculated and available experimental harmonic vibrational frequencies of different species implied in the considered path. As can be seen, the agreement between calculated and measured values for H_2O_2, HO_2 and HF is good with a relative deviation lying between 0.1 and 6.2%. The activated complex is characterized by one and

only one imaginary normal mode having a frequency with a magnitude equals to 656.5 cm^{-1}. This mode is animated using MOLDEN package [26] to ensure that we have located the adequate transition state according to the H-abstraction reaction hypothesis.

The frequency value of $\gamma(OH)$ mode in the reactant complex RC increases from 380.5 cm^{-1} in H_2O_2 to 508.2 cm^{-1}. In the IR or Raman spectrum of the pure gaseous H_2O_2 and of a (H_2O_2, F) gaseous mixture, such a significant shift toward a higher frequency can be a possible experimental proof of the existence of the RC stable complex.

The calculated CCSD(T)/jun-cc-pvtz total energies of the reactants, RC, TS and products are listed in Table 2. These total energy values and the ZPE corrections are used to draw the potential energy diagram. This latter is shown in Fig. 2. As can be seen, the predicted reaction energy (E_r= -48.4 kcal/mol) agrees well with the experimental value. The studied path is exothermic which is in accordance with the reactant-like character of the transition state found in the stationary points section and subsequently with the Hammond's postulate [27]. It can also be seen that the transition state lies 2.5 kcal/mol below the reactants, which implies that the H-abstraction path is a barrier-less one. In another word, if the H_2O_2 molecule and the F atom collide in the preferred direction leading to the formation of the TS, the reaction proceeds without requirement of activation.

Collisions between the H_2O_2 molecule and the F atom can lead to the formation of the reactant complex (RC) which is predicted to be more stable than the reactants and the transition state by 3.8 and 1.3 kcal/mol, respectively. This latter value, which represents the barrier when the reaction proceeds via the formation of the RC, has the same order of magnitude as the calculation error (1 kcal/mol) and so it can be considered as a small value. This means that the RC should not have a significant contribution to the kinetic of the considered path.

Therefore, for the two mentioned types of collision between H_2O_2 molecule and F atom, our calculation predicts that no significant barrier is required for the reaction according to the H-abstraction path. Accordingly, the rate constant will not exhibit a significant temperature dependence which is in line with the experimental finding of an only value of the rate constant k(T) [13].

3.2. OH abstraction path

Since the reactants are common to both considered paths, the related results are not repeated in this section.

The optimized structures of the transition state and the products are depicted in Fig. 3. The available experimental data for OHF and OH are also listed for comparison. A good agreement can be noted between the evaluated values and the measured ones, with a maximum deviation within 0.4% for the bond lengths and 1.1% for the angles.

For the TS, the breaking O1···O2 bond is stretched by 19.7% with respect to its homologous in the isolated H_2O_2 molecule and the forming O1···F bond is longer than the equilibrium value in OHF molecule by 11.2%. That is, the relative elongation of the breaking bond is greater than that of the forming one. Hence, the OH–abstraction reaction proceeds via a late transition state and it is expected to be endothermic.

The obtained CCSD(T)/jun-cc-pvtz harmonic vibrational frequencies as well as the available experimental values are given in Table 3. It is clear that the calculated results for OHF and OH are in a good accord with the experimental ones and the relative error is between 2.4 and 6.3%. Besides, the transition state is confirmed to have only one imaginary frequency which has a magnitude of 835.1 cm^{-1}. To ensure that the imaginary normal mode corresponds to the reaction coordinate, the MOLDEN package is used.

Table 4 summarizes the energies of various species involved in the OH-abstraction path. Accordingly, the ZPE corrected barrier height $V^{\neq}$ and reaction energy E_r are 14.6 and 1 kcal/mol, respectively. Compared to the H-abstraction path, the OH abstraction one possesses a positive and high value of the activation energy. Thus, the contribution of the OH-abstraction path to the reaction is expected to be negligible. The obtained value of E_r indicates that this reaction is slightly endothermic as it was expected previously.

The obtained TST values of the rate constants over the temperature range from 200 to 2500 K are listed in Table 5. Fig 4 presents the plot of the logarithm of the modeled rate constants versus 1000/T (K) along with the unique experimental point.

It can easily be seen that, even for high temperatures, the experimental point remains far beyond the theoretical curve. This allows us to predict that the OH-abstraction path has no significant contribution to the title reaction for all considered temperatures.

4. Conclusion

In this paper, the CCSD(T)/jun-cc-pvtz method has been employed to study the reaction of the hydrogen peroxide with the fluorine atom. Two paths are considered.

For the H-abstraction path, the reaction is found to be barrier less and a reactant complex is located in the entrance channel with a slight relative stability of 3.8 and 1.3 kcal/mol compared to the reactants and the TS, respectively. These results suggest that the

rate constant will not exhibit a significant temperature dependence which is in line with the experimental finding of an only value of the rate constant.

For the OH abstraction path, the barrier height is found to have a high value (14.6 kcal/mol). The corresponding theoretical rate constants are calculated in the temperature range from 200 to 2500 K by conventional transition state theory and compared to the available experimental value. No significant contribution of this path to the reaction is detected.

Therefore, our calculation predicts that the H_2O_2+F reaction is a purely H-abstraction one and takes place without requirement to any activation.

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Relative energy (kcal/mol)

H_2O_2+F — 0

−2.5
−3.8 — RC

TS

HO_2+HF

−48.4
(−51.2)[a]

TS
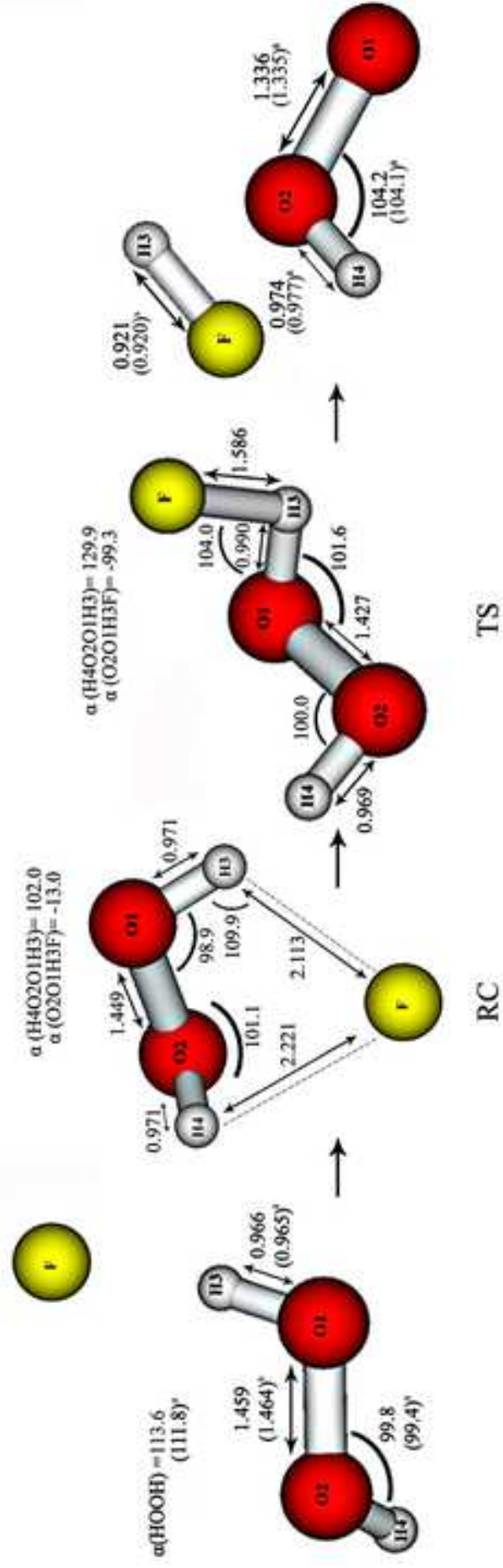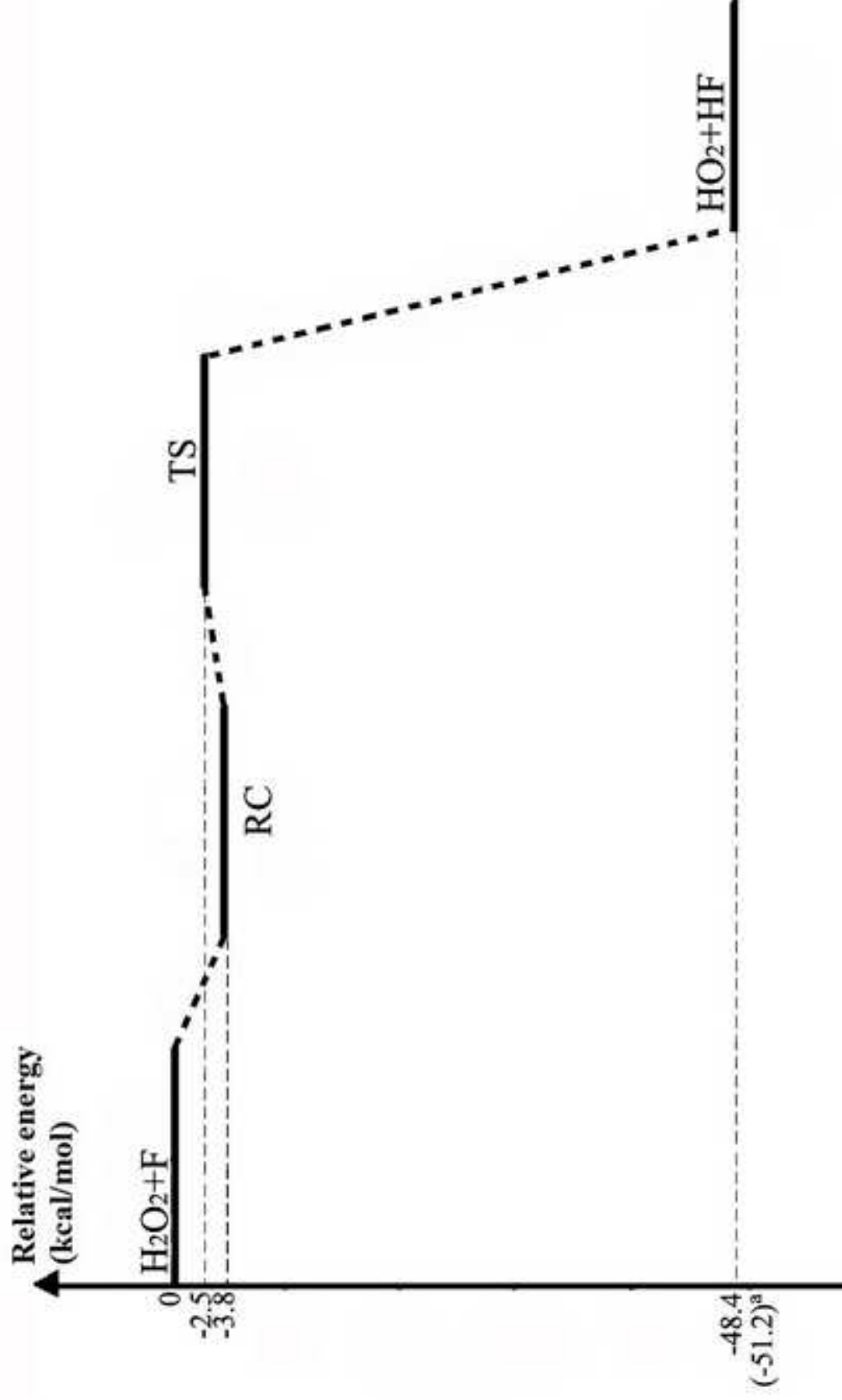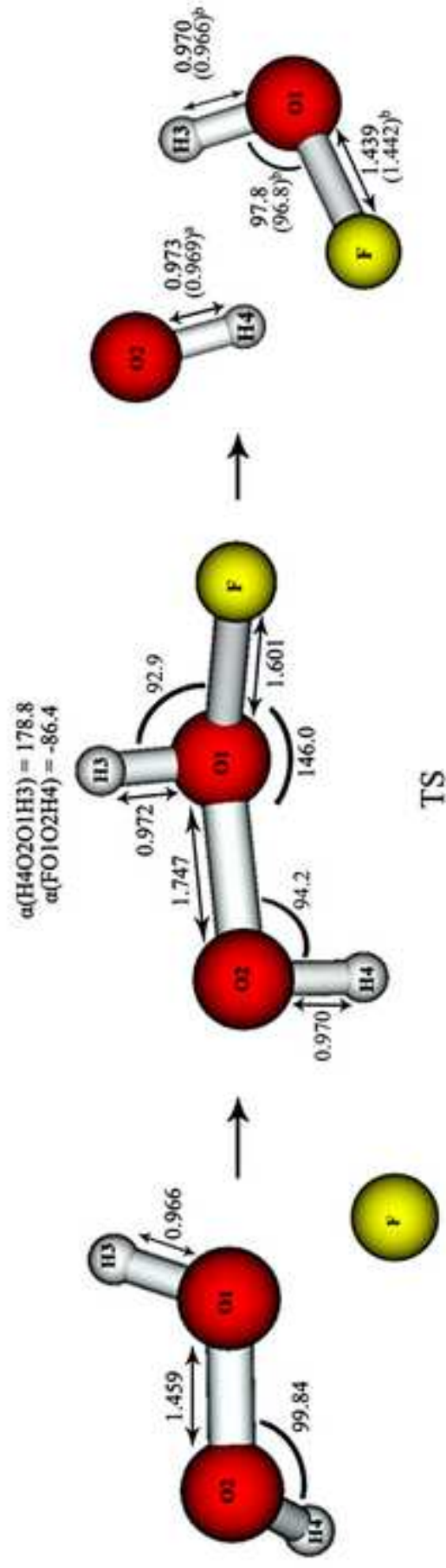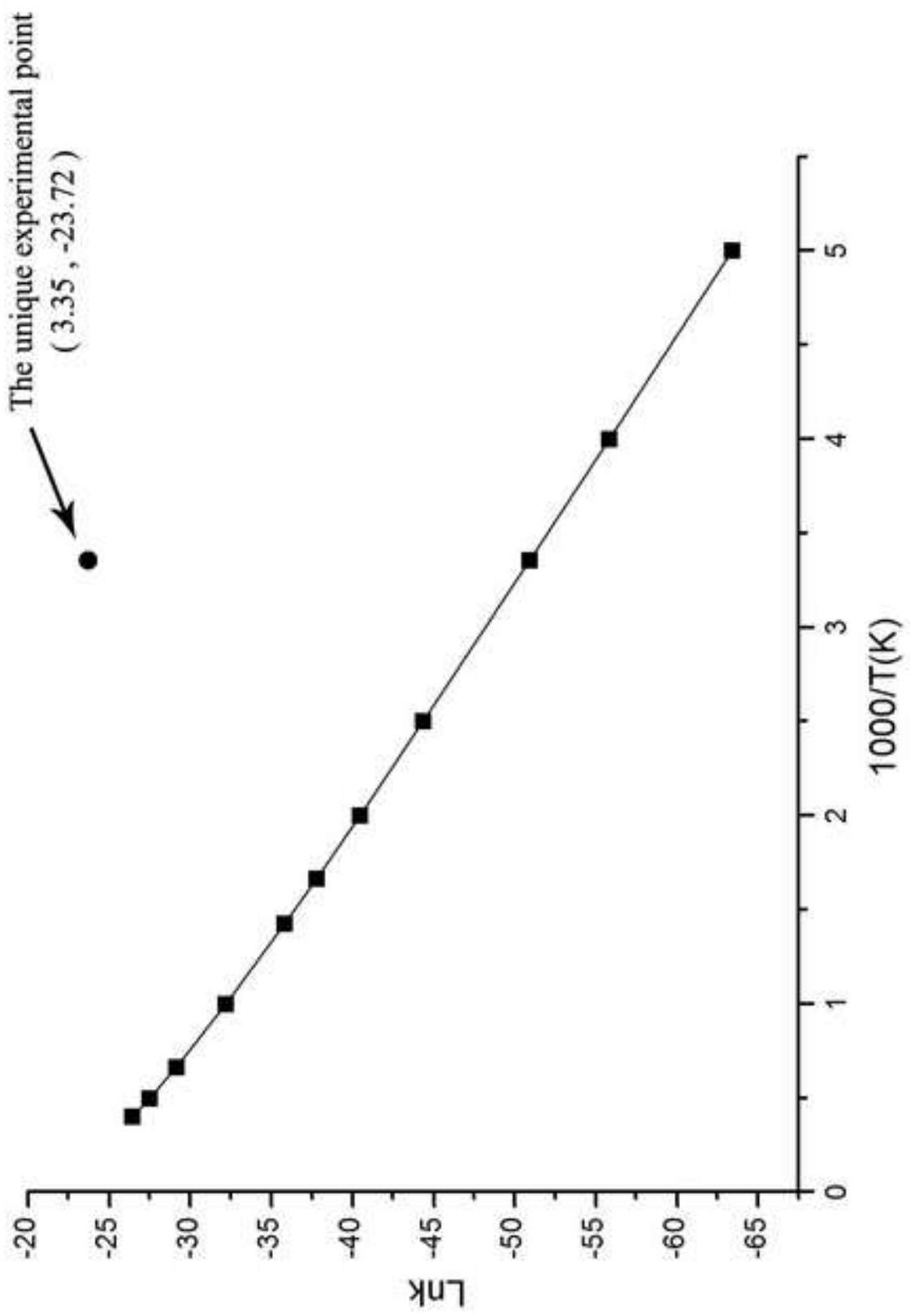
Tables

Table 1 Harmonic vibrational frequencies (cm^{-1}) of the reactant (H$_2$O$_2$), the reactant complex (RC), the activated complex (TS) and the products (HO$_2$ and HF) for the H-abstraction path. The values in the parentheses are the experimental ones.

Mode	H$_2$O$_2$	RC	TS	HO$_2$	HF
1	3788.9(3619[a])	3721.9	3758.0	3648.9(3436.2[e])	4134.0(4138.3[f])
2	3788.2(3610[a])	3711.2	3330.8	1427.8(1391.8[e])	
3	1428.2(1394[b])	1414.5	1479.4	1129.1(1097.6[e])	
4	1314.9(1274[c])	1325.4	1272.4		
5	905.1(878[d])	899.6	925.1		
6	380.5(371[a])	508.2	350.9		
7		320.7	309.9		
8		305.2	154.5		
9		178.4	656.5 I		

[a] Ref. [20].

[b] Ref. [21].

[c] Ref. [22].

[d] Ref. [23].

[e] Ref. [24].

[f] Ref. [25].

Table 2 Total energies (a.u) of the reactants (H_2O_2 and F), the reactant complex (RC), the activated complex (TS) and the products (HO_2 and HF) for the H-abstraction path.

System	Total energy
H_2O_2	-151.3672671(16.6)
F	-99.6244923
RC	-250.9995225(17.7)
TS	-250.9956561(16.6)
HO_2	-150.7203846(8.9)
HF	-100.3455829(5.9)

Values in parentheses are the ZPE corrections (kcal/mol)

Table 3 Harmonic vibrational frequencies (cm^{-1}) of the activated complex (TS) and the products (OHF and OH) for the OH-abstraction path. The values in the parentheses are the experimental ones.

Mode	TS	OHF	OH
1	3767.5	3758.8(3537.1[a])	3730.1(3570[b])
2	3759.0	1391.7(1359[a])	
3	1209.5	918.3(886[a])	
4	984.7		
5	552.7		
6	497.9		
7	277.7		
8	243.3		
9	835.1I		

[a] Ref. [29].

[b] Ref. [30].

Table 4 Total energies (a.u) of the activated complex (TS) and the products (OHF and OH) for the OH-abstraction path.

System	Total energy
TS	-250.9677966(16.1)
HOF	-175.3434155(8.7)
OH	-75.6426757(5.3)

Values in parentheses are the ZPE corrections (kcal/mol)

Table 5 Calculated ab initio-TST rate constant (in cm^3 molecule^{-1} s^{-1}) as function of temperature for the OH- abstraction path. (Power of 10 in parentheses).

T(K)	k_{TST}
200	2.77 (-28)
250	5.28 (-25)
298.15	7.20 (-23)
400	5.18 (-20)
500	2.64 (-18)
600	3.82 (-17)
700	2.68 (-16)
1000	1.02 (-14)
1500	2.12 (-13)
2000	1.10 (-12)
2500	3.20 (-12)

Figures captions

Fig. 1 Optimized geometries of reactant (H_2O_2), reactant complex (RC), saddle point (TS) and products (HO_2 and HF). The values in the parentheses are the experimental ones. Bond lengths are in angstroms and angles are in degrees. [a] Ref. [18], [b] Ref. [19].

Fig. 2 ZPE corrected potential energy profile of the H-abstraction path. The experimental value of the reaction energy is given in parentheses. [a] Ref. [13]

Fig. 3 Optimized geometries of saddle point (TS) and products (HOF and OH). The values in the parentheses are the experimental ones. Bond lengths are in angstroms and angles are in degrees. [a] Ref. [18], [b] Ref. [28].

Fig. 4 Plot of logarithm of the modeled rate constants (cm3 molecule-1 s-1) versus 1000/T(K) for the OH-abstraction path.

Supplementary Materials