Theoretical kinetics study of the $F(^2P) + NH_3$ hydrogen abstraction reaction

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Abstract

The hydrogen abstraction reaction of fluorine with ammonia represents a true chemical challenge because it is very fast and is followed by secondary abstraction reactions which are also very fast, and it presents experimental/theoretical controversy about the rate constants. Using a full-dimensional analytical potential energy surface previously developed, we found that the $F + NH_3 \rightarrow HF + NH_2$ system is a barrierless reaction with intermediate complexes in the entry and exit channels. In order to understand the reactivity of the title reaction thermal rate constants were calculated using ring polymer molecular dynamics and compared with available experimental data for the common temperature range 276–327 K. The theoretical results obtained show behaviour practically independent on the temperature, reproducing the Whalter-Wagner's experiment, but in contrast with the more recent Persky's experiment. However, quantitatively, our results are one order of magnitude larger that those of Whalter-Wagner and reasonably agree with the Persky at the lowest temperature, questioing so the older Whalter-Wagner's data. At this moment the reason of this discrepancy is not clear, although we point out some possible reasons on the light of the present theoretical calculations.

1. INTRODUCTION

The F + NH_3 reaction is difficult to study experimentally because it is very fast, followed by extremely fast secondary atom/radical reactions, F + NH_2 → HF + NH. It is also difficult to study theoretically because the accurate description of low-energy barriers requires very high levels of quantum chemistry theory.

The title reaction has been studied theoretically in the past a few times[1-6] although recently its study has presented a renewed interest.[4-6] These theoretical studies contrast with the extensive experimental literature,[1,4,7-18] both kinetics and dynamics. From the dynamics point of view, Sloan et al.[1,12,14] and Wategaonkar and Setser[13] reported an inverted vibrational distribution of the HF product, and they suggested that it could be caused by a strongly hydrogen-bonded FH…NH_2 complex in the exit channel, which causes a randomization of the reaction exoergicity among all available product degrees of freedom. In addition, Goddard et al.[1] found this complex theoretically using high-level ab initio calculations with energy 8.1 kcal mol^{-1} lower than the products. More recently, Misochko et al. [16,17] based on their infrared and EPR spectroscopic studies, observed for the first time this intermediate complex, FH…NH_2. From the kinetics point of view, there is controversy about the positive/negative activation energy for the forward reaction. Thus, while the experiment of Walther and Wagner[18] reported conventional temperature dependence, and consequently positive activation energy, the more recent Persky's experiment[15] in the temperature range 276-327 K reported inverse temperature dependence, and they are one order of magnitude larger. To explain this behaviour Persky suggested the existence of an intermediate complex in the entry channel. Therefore, intermediate complexes in the entry and exit channels may affect the reaction kinetics and dynamics, and their influence or not becomes an important issue.

Recently, Xiao et al.[4] and Feng et al.[5] using very high-level ab initio calculations investigated some complexes in the entry and exit channels for the title reaction. However, the multiple electronic states due to the open-shell character of the system were not taken into account.

Finally, in 2011 some of us[6] performed a dynamics study on the title reaction using quasi-classical trajectory (QCT) calculations based on a full-dimensional analytical potential energy surface PES-1997 developed in our research group.[3] This PES is the only analytical surface proposed for this reaction, and it is basically a valence-bond molecular-mechanics (VB-MM) surface with adjustable parameters. It presents high exothermicity, -25.80 kcal mol^{-1}, in excellent agreement with the recent high-level ab initio calculations,[4] -25.77 kcal mol^{-1}. In addition, it presents a F… H_3N van der Waals complex in the entry channel (face

configuration), stabilized by 6.11 kcal mol^{-1} with respect to the reactants, and an $H_2N\ldots HF$ hydrogen bond complex in the exit channel, stabilized by 6.25 kcal mol^{-1} with respect to the products, in reasonable agreement with high-level ab initio calculations,[4] 12.28 and 9.94 kcal mol^{-1}, respectively, given the semiempirical character of the PES and that in that time (1997) these complexes were not determined and therefore not included in the fitting procedure.[3] In that work[6] we found that recent crossed-beam experiments reported by Xiao et al.[4] at 4.5 kcal mol^{-1} are reproduced, providing confidence to the PES-1997 surface.

In the present work, thermal rate constants using the ring polymer dynamics molecular (RPMD) approach are calculated based on the analytical PES-1997 surface, and compared with the available experimental values. Given that the PES-1997 presents a complex in the entry channel, this calculation represents an excellent opportunity to test the Persky's hypothesis that the inverse temperature dependence is due to the presence of this complex.

2. METHODS AND COMPUTATIONAL DETAILS

2.1. Potential Energy Surface

The analytical PES-1007 function was developed in the previous study[3] and therefore will be only briefly described here. It is basically a valence bond-molecular mechanics (VB-MM) surface, given by the sum of three terms: a stretching potential, $V_{stretch}$, a harmonic bending term, V_{harm}, and an anharmonic out-of-plane potential, V_{op},

$$V = V_{stretch} + V_{harm} + V_{op} \qquad (1)$$

and it was designed to describe exclusively the hydrogen abstraction reaction.

The stretching potential is the sum of three London-Eyring-Polanyi (LEP) terms, each one corresponding to a permutation of the three ammonia hydrogens,

$$V_{\text{stretch}} = \sum_{i=1}^{3} V_3\left(R_{\text{NH}_i}, R_{\text{NF}}, R_{\text{H}_i\text{F}}\right), \qquad (2)$$

where R is the distance between the two subscript atoms, and H_i stands for one of the three ammonia hydrogens. Note that 14 fitting parameters are required to describe this stretching potential.

The V_{harm} term is the sum of three harmonic terms, one for each bond angle in ammonia,

$$V_{\text{harm}} = \frac{1}{2}\sum_{i=1}^{2}\sum_{j=i+1}^{3} k_{ij}^{0} k_i k_j \left(\theta_{ij} - \theta_{ij}^{0}\right)^2 \quad , \tag{3}$$

where k_{ij}^{0} and k_i are force constants, and θ_{ij}^{0} are the reference angles. The k_{ij}^{0} force constants are allowed to evolve from their value in ammonia, k^{NH_3}, to their value in the amidogen radical, k^{NH_2}, corresponding to two parameters of the fit, by means of switching functions. In total, 16 parameters need to be fitted for the calibration of the V_{harm} potential.

The V_{op} potential is a quadratic-quartic term whose aim is to correctly describe the out-of-plane motion of ammonia,[3]

$$V_{\text{op}} = \sum_{i=1}^{3} f_{\Delta_i} \sum_{\substack{j=1 \\ j\neq i}}^{3} \left(\Delta_{ij}\right)^2 + \sum_{i=1}^{3} h_{\Delta_i} \sum_{\substack{j=1 \\ j\neq i}}^{3} \left(\Delta_{ij}\right)^4 \quad . \tag{4}$$

The force constants, f_{Δ_i} and h_{Δ_i}, have been incorporated into a switching function which is such that V_{op} vanishes at the amidogen radical limit. Δ_{ij} is the angle that measures the deviation from the reference angle,

$$\Delta_{ij} = \text{acos}\left(\vec{N}_i \frac{\vec{r}_j}{\left\|\vec{r}_j\right\|}\right) - \theta_{ij}^{0} \quad , \tag{5}$$

where N_i is a unit vector normal to the plane defined by the three hydrogen atoms of the ammonia and θ_{ij}^{0} is the reference angle. The vector N_i is given by

$$\vec{N}_i = \frac{(\vec{r}_k - \vec{r}_j) x (\vec{r}_l - \vec{r}_j)}{\left|(\vec{r}_k - \vec{r}_j) x (\vec{r}_l - \vec{r}_j)\right|} \quad \text{i=1,2,3} \tag{6}$$

where $\vec{r}_j$, $\vec{r}_k$, and $\vec{r}_l$ are vectors going from the nitrogen atom to the j, k, and l hydrogen atoms, respectively, in ammonia. To correctly calculate Δ_{ij}, the motion from j to l has to be clockwise. In total, 4 parameters need to be fitted for the calibration of the V_{op} potential.

Note that in the original expression, the V_{op} term was added to obtain a correct description of the umbrella mode of ammonia. Although recently Yang and Corchado[19] noted that this term yields non-physical behaviour along the ammonia inversion path (which was not taken into account originally), this problem is of no importance in the present case because only the hydrogen abstraction reaction is being considered.

The PES-1997 is symmetric with respect to the permutation of the three equivalent ammonia hydrogens, a feature which is especially important in dynamics calculations. It depends on 34 parameters: 14 for the stretching, 16 for the harmonic term, and 4 for the out-of-plane potential. These 34 parameters endow the PES with great flexibility, while keeping the VB/MM functional form physically intuitive.

Once the functional form was available, the 34 parameters describing the PES-1997 were fitted by using as input information a combination of theoretical and experimental data. In this sense therefore, the surface is semi-empirical.

2.2. Kinetics calculations. The thermal rate constants calculations of the title reaction were performed using the analytical PES-1997 surface[3] and ring polymer molecular dynamics (RPMD) calculations.[20,21] The RPMD method exploits the isomorphism between the statistical properties of the quantum system and those of a classical fictitious ring polymer consisting of many copies of the original system connected by harmonic springs.[22] This isomorphism enables the automated inclusion of quantum effects via classical molecular dynamics simulations in an extended phase space. Application of RPMD to gas phase bimolecular chemical reactions[23-32] has demonstrated that it provides systematic and consistent performance across a wide range of system dimensionalities. In all systems considered so far, the RPMD rate coefficient captures almost perfectly the ZPE effect, and is usually within a factor of 2-3 of accurate results at very low temperatures in the deep quantum tunnelling regime when compared to rigorous quantum mechanical results available for these systems. Most chemical reactions can be studied using RPMD with only about 1-2 order of magnitude higher computational costs than conventional QCT calculations.

The RPMD calculations were carried out using the RPMDrate code developed by one of us;[29] the working equations of the RPMD rate theory can be found in Refs. 24,27. The title system has one bond that forms and breaks in the reaction and three equivalent product arrangement channels. The transition state dividing surface was placed at intermediate saddle point between the two complexes in the entry and exit channels of the PES-1997 and was defined in the same way as previously for thermally activated reaction in terms of the bond-breaking and bond-forming distances as discussed in Ref. 29. Number of beads of the ring polymer was set to 128 for all temperatures considered. The transmission coefficients were computed at the maximum of the potential of mean force which occurred before the reactant intermediate complex. For these calculations, the child trajectories were propagated for 0.3 ps where the transmission coefficients reached plateau values. All other parameters can be found

in the Table I of the RPMDrate manuscript.[29] It is interesting to note that the present study is one of the first applications of this method to polyatomic barrierless reactions (see also Ref. 31).

3. RESULTS AND DISCUSSION

In the hydrogen abstraction mechanism, the F atom approaches the NH_3 molecule through a very stabilized complex in the entry channel and it is a barrierless process. In this section we report the rate constants calculations for this reaction using the RPMD/PES-1997 approach. Table 1 lists the forward rate constants in the temperature range 276-327 K and experimental values[15,18] are included for comparison as well. Figure 1 shows these results.

Quantitatively, the theoretical results are one order of magnitude larger than those of Whalter-Wagner's[18] and show a reasonable agreement with the Persky's values[15] at the lowest temperature (276 K). In addition, they show that the rate constants are practically independent of temperature. This behaviour agrees with the Whalter-Wagner's experiments,[18] but disagrees with the more recent Persky's experiment,[15] which presents a strong variation in this small temperature range. Given that the PES-1997 surface presents a well in the entry channel, and the theoretical study does not report sudden changes, it can not be the cause of the variation with the temperature suggested by Persky.

However, to try to understand this difference with Persky's experiment we have considered the following two issues:

a) Comparison with similar fast reactions. We have analyzed recent bibliography on similar very fast reactions, and have not found the behaviour observed in the Persky's experiment in a so small temperature range. For instance, Bahng and Macdonald[33] determined the rate constants for the OH+OH reaction over the temperature range 203-373K, which were practically independent of the temperature, $2.7\text{-}2.2*10^{-12}$ cm^3 $molecule^{-1}s^{-1}$. Jasper et al.[34] found that the capture coefficient for the CH_3+OH reaction was nearly independent of the temperature, suggesting that the discrepancies with experiment is a result of falloff in the experimental results. For the ClO self-reaction, important above the ambient temperature, Ferracci and Rowley,[35] found that the temperature dependence obtained over the temperature range 298-323 K is considerably less pronounced than those previously reported. Finally, the kinetics of the OH + CO reaction has been extensively studied[36-40] revealing that the rate constant remains almost invariant at low temperature, only increasing sharply with temperature above 500 K.

b) Effect of the secondary reaction in the title reaction. As it was indicated in the Introduction, the title reaction is very fast, followed by the even faster secondary reaction, $F + NH_2 \rightarrow HF + NH$. We propose the following hypothesis: could the temperature dependence be due to the presence of fast secondary reactions in the experiment?

To analyze this supposition we have considered two similar fast hydrogen abstraction reactions followed by very fast secondary reactions, $OH + NH_3/NH_2$ and $O(^3P) + NH_3/NH_2$ reactions, whose experimental rate constants are well-known[41-43] (Table 2). In both reactions, the secondary reactions are faster than the primary ones, by factors of 10.44 and $2.51.10^5$, respectively, at 300 K. However, more interesting is the variation of this increase with temperature. So, taking as a reference the highest temperature analyzed, 400 K (value unity), in the $OH + NH_3/NH_2$ reactions, the secondary reaction is ~3 times faster at 250 K; while in the $O(^3P) + NH_3/NH_2$ reactions, the secondary reaction is ~16 times faster at 300 K. In sum, the lower the temperature, the faster is the secondary reaction. Assuming similar behaviour for the title reaction $F + NH_3/NH_2$, if in the experiment the secondary reaction $F + NH_2 \rightarrow HF + NH$ occurs (in whole or in part), its faster rate constants could contaminate the primary one, more strongly as the temperature decreases.

Therefore, further studies should be carried out to solve the disagreement between theory and experiment on the title reaction. In this context new experiments on the system over a larger range of temperatures would be of great help. From the theory point of view a possible further step to this work would be to explicitly evaluate of the s-o coupling along the reaction path, and constructing more accurate global analytical PES for further dynamics studies with such advanced techniques as RPMD.

4. CONCLUSIONS

By using an analytical full-dimensional potential energy surface, PES-1997, we have investigated the gas-phase reaction $F + NH_3 \rightarrow HF + NH_2$. We found that when the fluorine atom approaches to NH_3 the reaction evolves without barrier, with stabilized intermediate complexes in the entry and exit channels.

Based on this surface, we have calculated the thermal rate constant using the ring polymer molecular dynamics (RPMD) approach. The theoretical results, RPMD/PES-1997, present a behaviour practically independent of the temperature. In the common temperate range, 276-327 K, this behaviour agrees with the Whalter-Wagner's experimental measures, although quantitatively our results are higher by one order of magnitude. In contrast, our

results show a reasonable agreement with the more recent Persky's values[15] at the lowest temperature (276 K), which seems to suggest that the old Whalter-Wagner's values could be underestimated. However, the theoretical value disagree with the variation with temperature reported by Persky, which show a sudden change of behaviour in this very small temperature range, to our knowledge, never reported for similar fast reactions. To explain this behaviour Persky suggested an intermediate complex in the entry channel. The PES-1997 shows a van der Waals complex in the entry channel, but it is not associated with any sudden changes in the kinetics results. Therefore, further theoretical and experimental studies are needed to understand this discrepancy.

Acknowledgments

This work was partially supported by Gobierno de Extremadura, Spain, and FEDER (Project No. IB10001). YVS acknowledges the support of a Combustion Energy Research Fellowship through the Combustion Energy Frontier Research Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0001198. AFR thanks Xunta de Galicia through Grant No. 2012/314 para a consolidación e a estruturación de unidades de investigación competitivas do Sistema Universitario de Galicia, 2012.

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Table 1. Thermal forward rate constants (cm^3 $molecule^{-1}$ s^{-1}) for the $F+NH_3$ reaction.

T(K)	RPMD/PES-1997	Exp. [a]	Exp. [b]
276	5.67E-10	3.60E-10	2.34E-11
298	5.69E-10	1.00E-10	2.85E-11
327	6.05E-10	9.00E-11	3.37E-11

a) Ref. 15
b) Ref. 18

Table 2. Experimental rate constants (cm^3 $molecule^{-1}s^{-1}$) for the OH + NH_3/NH_2 and $O(^3P)$ + NH_3/NH_2 reactions, and relative increase for each reaction.

T(K)	OH+NH_2 [a]	OH+NH_3 [b]	Quotient	Relative quotient
250	1.48E-12	0.865E-13	17.11	2.80
275	1.57	1.21	12.97	2.12
300	1.67	1.60	10.44	1.71
325	1.77	2.03	8.72	1.43
350	1.88	2.49	7.55	1.24
375	2.00	2.97	6.73	1.10
400	2.12	3.47	6.11	1.00
T(K)	**$O(^3P)$+NH_2 [a]**	**$O(^3P)$+NH_3 [b]**	**Quotient**	**Relative quotient**
250	1.19E-11	-	-	-
275	1.18	-	-	-
300	1.18	0.469E-16	2.51E05	16.00
325	1.18	1.09	1.08	6.88
350	1.19	2.26	0.526	3.35
375	1.19	4.30	0.276	1.76
400	1.20	7.62	0.157	1.0

a) Ref. 40

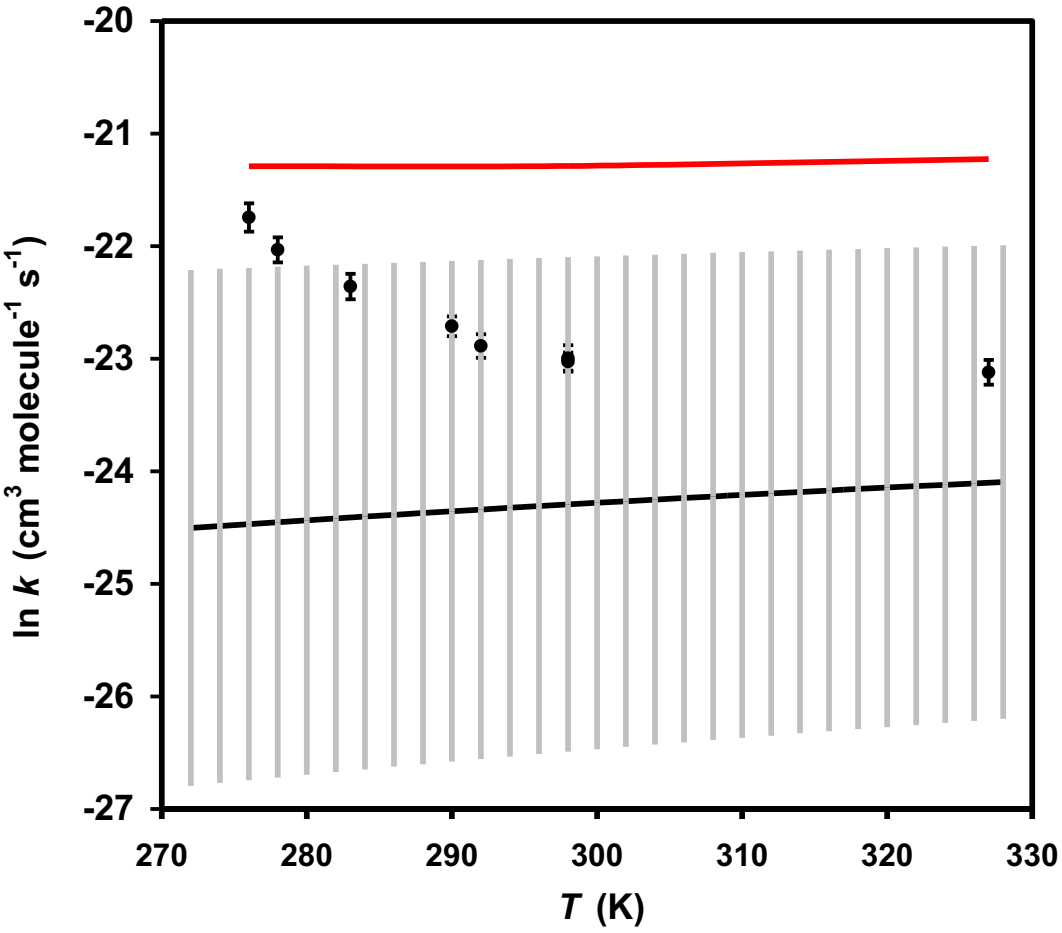
b) Ref. 41

c) Ref. 42

FIGURE CAPTIONS

Figure 1. Plot of ln k (cm^3 $molecule^{-1}$ s^{-1}) against the temperature (K) in the range 276-327 K. Solid black circles: Persky's experimental values; black line: Walther and Wagner's experimental values (the uncertainity region is shown shaded); red line: RPMD calculation on PES-1997.

Figure 1


-20
-21
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-23
-24
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ln k (cm3 molecule-1 s-1)
270
280
290
300
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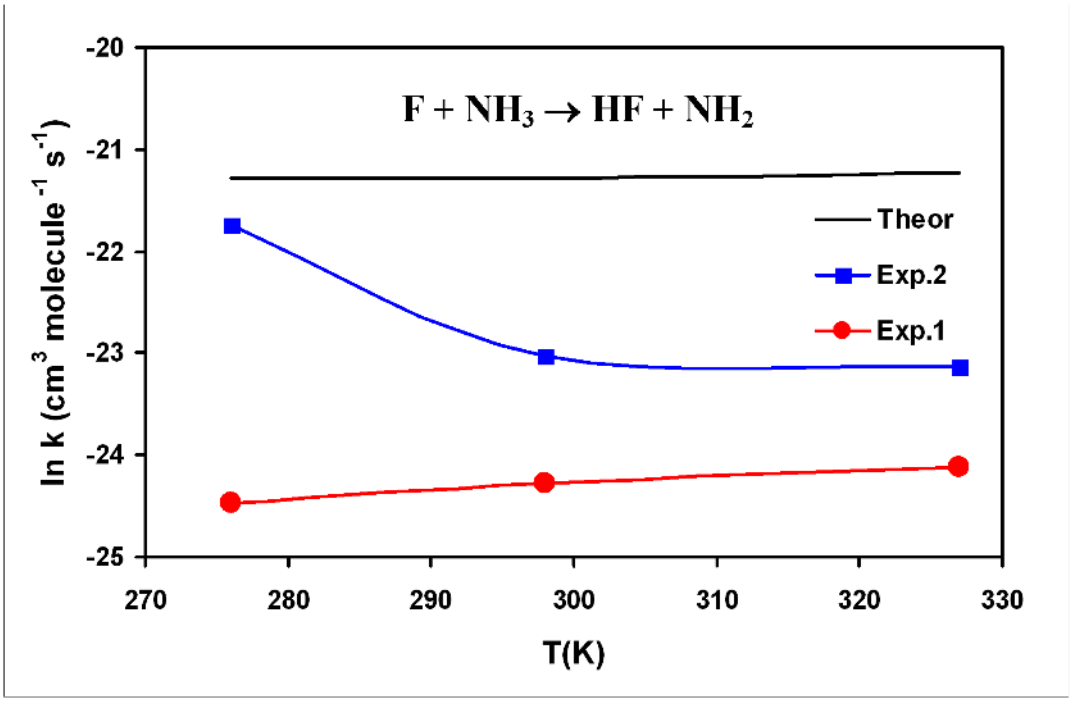
320
330
T (K)

TOC


F + NH3 → HF + NH2
ln k (cm3 molecule-1 s-1)
-20
-21
-22
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-24
-25
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300
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320
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T(K)
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Exp.2
Exp.1