Ab initio calculations of the rate constants Reaction $F^- + CH_3F = F...CH_3...F^-$

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Absolute rate theory within rigid rotor—harmonic oscillator approximation was used for evaluation of the rate constant of the title reaction. In calculations of energy barrier extended basis set (DZ + P) was used with correlation effects included using the fourth-order many-body perturbation theory. Zero point energies and vibration partition functions were computed at the SCF 4-31G level. Solvent effect was estimated by means of simple electrostatic continuum model. Reliability of both activation enthalpy at T=0 K and rate constants is discussed using extrapolation of experimental results for similar reactions.

Теория абсолютных скоростей в приближениях жесткого волчка и гармонического осциллятора была применена для определения константы скорости заглавной реакции. При расчете энергетического барьера использовался расширенный базис (DZ + P), включая корреляционные эффекты, рассчитанные с помощью многочастичной теории возмущений четвертого порядка. Энергии в нулевых точках и колебательные суммы состояний были рассчитаны для SCF 4-31G уровня. Эффект растворителя был оценен посредством простой электростатической континуальной модели. Достоверность значений энтальпии активации при T=0 K и значений констант скоростей показана, используя экстраполяцию экспериментальных величин для подобных реакций.

Among problems studied by quantum chemical methods *ab initio* approaches to equilibrium and rate constants of chemical reactions belong to the most difficult tasks. The complexity of the problem is a reason that only few papers devoted to this topic appeared in the last decade, *e.g.* [1--6].

The aim of this contribution is to present results of *ab initio* calculations on the model system for the gas-phase $S_N 2$ reaction

$$F^{-} + CH_{3}F = F...CH_{3}...F^{-}$$
 (A)

and to note some preliminary results of this reaction in solution. Our choice of this reaction was due to the following facts:

i) The activation barrier of the system was studied theoretically by several authors [7-13], but without statistical thermodynamical treatment, *i.e.* the partition functions and the rate constants were not calculated.

ii) The system is relatively simple and symmetric, so that the use of DZ + P basis set in SCF and correlation energy calculations is free of great computational difficulties.

iii) The reactions of this type were also studied experimentally by one of us [14, 15].

Let us note briefly some basic information concerning this reaction as it was obtained from the literature:

i) Reaction path involving back side attack passes through the activated complex of the D_3h symmetry [9] and is accompanied with the familiar Walden inversion.

ii) Ab initio SCF calculations have shown that activation barrier ΔE^{\pm} is relatively small [10, 11, 16] (20–30 kJmol⁻¹) and that it is very sensitive to the basis set used. The use of DZ or smaller basis sets leads to a negative barrier [7, 9]. From comparison with other similar reactions (H⁻ + CH₃F, Cl⁻ + CH₃F, CN⁻ + CH₃F) it follows that it is necessary to augment the DZ basis with polarization *d* functions on heavy atoms at least.

iii) It is possible that ZPE correction and correlation energy contribution may modify the barrier height significantly, because of its small value. More complete information concerning correlation energy contribution to activation barrier will be published elsewhere [17].

Calculations

Following Eyring's absolute rate theory (ART) for the rate constant of bimolecular reaction in the gas phase

$$A + B = [A...B] \rightarrow C \tag{B}$$

we have

$$k = l^{*} \varkappa \frac{k_{\rm B} T Q^{*}}{h Q_{\rm A} Q_{\rm B}} \exp\left[-\Delta H_{0}^{*}/RT\right]$$
⁽¹⁾

where l^* is statistical factor [18-20], \varkappa transmission coefficient, Q^* , Q_A , Q_B are partition functions of activated complex and reactants, respectively, and ΔH_0^* activation enthalpy at T=0 K. For evaluation of the rate constants we used standard statistical thermodynamical treatment within approximation rigid rotor—harmonic oscillator.

Basis sets

Vibrational modes for ZPE correction and vibrational partition function were calculated with 4-31G basis set. As shown by $\check{C}\acute{a}rsky$ and Zahradník [1], the use of this basis set for this purpose is quite satisfactory. Energy barrier was calculated using two basis sets. Both were constructed from Dunning's [4s2p] basis [21] augmented by one diffuse p function on fluorine atoms according to *Keil* and *Ahlrichs* [11]. This basis was further extended as follows:

Basis set SP+BF

One s function was placed on each C—H bond, two s functions on C—F bond. In the first case distance from carbon atom was 1.7×10^{-10} m, exponent 1.1, in the second case the distances of the bond functions from C and F atoms were equal to 1.7×10^{-10} m, exponent 1.3. The exponents of the bond functions were optimized for CH₃F.

Basis set SPD

On both C and F atoms a complete set of d functions was placed with exponents according to [11]. More precisely, for F atom we have [431] basis set, because the p set is extended by diffuse function, for C atom we have the [421] basis set.

Vibrational modes

For the reference geometry we adopted the geometry determined by *Keil* and *Ahlrichs* [11] by means of the CEPA method. The force constants were evaluated numerically by a three-point fit to parabola, distorted structures we obtained by changing the bond lengths by 0.01×10^{-10} m and bond angles by 1.5° with respect to the reference geometry. Symmetry coordinates for CH₃F were taken from Ref. [22], for FCH₃F⁻ from Ref. [23].

Resulting force constants are presented in Table 1. Vibrational modes were calculated using standard Wilson's FG-matrix method. Computed wavenumbers for both CH_3F and FCH_3F^- are in Tables 2 and 3, respectively.

Activation enthalpy ΔH_0^{\ddagger}

Activation enthalpy at T=0 K we obtain as

$$\Delta H_0^* = \Delta E^* + \Delta Z P E \tag{2}$$

Numerical values of force constants of CH₃F and FCH₃F⁻ calculated with 4-31G basis set

Symmetry	f _i ,		Symmetry	f _i ,	
CH ₃ F					
A_1	f_{11} (S)	6.002	E	f44 (S)	5.697
	f_{22} (S)	5.667		f55 (B)	0.727
	f_{33} (B)	0.809		f (B)	0.935
	f_{12} (S—S)	0.264		f_{45} (S—B)	-0.208
	f_{13} (S—B)	0.138		f46 (S-B)	0.072
	f_{23} (S—B)	-0.620		f56 (B-B)	-0.054
FCH ₃ F ⁻					
A'_1	f_{11} (S)	6.513	E'	f55 (S)	6.357
	f_{22} (S)	1.946		f (B)	0.458
	f_{12} (S—S)	0.199		f77 (B)	0.972
				f56 (S-B)	-0.136
A_2''	f_{33} (S)	0.584		f ₅₇ (S-B)	-0.163
	f44 (S)	0.544		f.7 (B-B)	-0.037
	f ₃₄ (S-B)	0.958			
			E''	$f_{\rm ss}$ (B)	0.479

a) S — stretching mode, B — bending mode; stretching force constants in 10^2 Nm⁻¹, bending force constants in 10^{-8} Nrad⁻¹, interaction force constants in 10^{-18} Nmrad⁻².

Table 2

Symmetry		CH ₃ F			CD ₃ F		$\omega_{H}{}^{d}$
of the mode	4-31G ^ª	SWB*	expʻ	4-31G	SWB	exp	ω
$\omega_1(A_1)$	3217.9	2878.0	2910.0	2307.3	2114.0	2110.0	1.39
$\omega_2(A_1)$	1065.2	1164.0	1048.6	1011.2	1076.0	992.3	1.05
$\omega_3(A_1)$	1647.7	1562.0	1460.9	1263.1	1241.0	1134.8	1.30
<i>ω</i> ₄ (<i>E</i>)	3253.2	2970.0	3006.2	2411.7	2286.0	2258.5	1.35
ω ₅ (E)	1676.6	1577.0	1467.8	1213.6	1149.0	1071.3	1.38
$\omega_{\rm e}(E)$	1230.5	1247.0	1182.3	945.4	960.0	911.3	1.30

Vibrational wavenumbers $(\tilde{\nu}/cm^{-1})$ for CH₃F and CD₃F

a) This paper; b) Ref. [35]; c) experiment: Ref. [36, 37]; d) ratio of 4-31G wavenumbers.

		a preside people
FCH ₃ F ⁻	FCD ₃ F ⁻	ω _н / ω _ъ
3311.9	2341.8	1.41
416.3	416.3	1.00
-437.5	-371.6	1.18
1872.2	1602.4	1.17
3472.5	2604.3	1.33
2202.0	1615.4	1.36
255.4	238.6	1.07
1202.4	855.9	1.40
	FCH ₃ F ⁻ 3311.9 416.3 - 437.5 1872.2 3472.5 2202.0 255.4 1202.4	FCH ₃ F ⁻ FCD ₃ F ⁻ 3311.9 2341.8 416.3 416.3 -437.5 -371.6 1872.2 1602.4 3472.5 2604.3 2202.0 1615.4 255.4 238.6 1202.4 855.9

Vibrational wavenumbers $(\tilde{\nu}/cm^{-1})$ for FCH₃F⁻ and FCD₃F⁻

a) Decay vibration.

where

$$\Delta E^{\dagger} = E^{\dagger} - (E_{\rm A} + E_{\rm B}) \tag{3}$$

and ΔZPE is defined similarly as ΔE^{\pm} . For the sake of completeness we also note that for our reaction no direct experimental evidence on the energy of activation is available [24].

SCF and correlation energy calculations

In the SCF step two programs have been used: GAUSSIAN 70 [25] for calculation of the vibrational modes and POLYATOM/2 [26] for other calculations. Correlation was calculated using the Many-Body energy Rayleigh-Schrödinger Perturbation Theory (MB-RSPT) up to the fourth order, including double excitations in the second and third order $(E_{D}^{(2)})$ and $E_{D}^{(3)}$ and double and quadruple excitations with the renormalization term $(E_{DOR}^{(2)-(4)})$ in the fourth order. We have used our set of computer programs [27]. The details of our approach were published in [28, 29]. The relation of MB-RSPT to other approaches as CEPA (Coupled Electron Pair Approximation) and CI (Configuration Interaction) the results of which have been used in this work may be found elsewhere [30-32].

Results and discussion

The results of activation barrier calculations with different basis sets and related values ΔH_0^{\pm} are summarized in Table 4. Using these data, the wavenumbers from Tables 2 and 3, and the optimum geometry, the rate constants of the title reaction were calculated for six temperatures. The plot of $[\log k - \log(k_B T/h)]$ vs. 1/T is presented in Fig. 1.

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Basis set	Method	F⁻	CH ₃ F	FCH ₃ F ⁻	∆E *	$\Delta H_0^{\star a}$
SPD	SCF"	-99.4014	- 139.0256	-238.4203	+ 0.0067	
	CEPA [*]	- 0.2009	- 0.3509	- 0.5444	+0.0074	+46.1
SP + BF	SCF	-99.4423	- 139.0620	-238.5027	+0.0016	
	$E_{D}^{(2)}$	- 0.1460	- 0.2235	- 0.3783	-0.0088	- 9.9
SPD	SCF	-99.4433	- 139.0719	-238.5066	+0.0086	
	E ⁽²⁾	- 0.2074	- 0.3140	- 0.5259	-0.0045	+ 19.9
	$E_{D}^{(2)-(3)}$	- 0.1988	- 0.3262	- 0.5251	-0.0001	+31.8
	$E_{DOR}^{(2)(4)}$	- 0.2029	- 0.3301	- 0.5334	-0.0004	+ 31.0

Numerical values of SCF and correlation energies of reactants and activated complex, appropriate contributions to the activation barriers E/E_{h} , and activation enthalpies at T=0 K in kJ mol⁻¹

a) Activation enthalpy at T=0 K obtained as a sum of SCF, correlation contributions, and ZPE correction; b) results from Ref. [11].



Fig. 1. Temperature dependence of the rate constant of the reaction $F^- + CH_3F = FCH_3F^-$ The rate constants in units of cm³ mol⁻¹ s⁻¹.

1. Calculated with $\Delta H_0^{\star} = 31.9 \text{ kJ mol}^{-1} (\text{SCF})$; 2. calculated with $\Delta H_0^{\star} = 19.9 \text{ kJ mol}^{-1} (\text{SCF} + E_D^{(2)})$; 3. calculated with $\Delta H_0^{\star} = 31.0 \text{ kJ mol}^{-1} (\text{SCF} + E_{D_{\text{C}}}^{(2)})$.

Let us focus our attention on two aspects of the problem studied:

- i) effect of basis set on SCF barriers;
- ii) effect of basis set on the ZPE correction.

The role of the correlation energy is discussed in detail elsewhere [17]. Here we shall mention it only briefly (see below).

As we have noted in the introduction, activation barrier of reaction (A) at the SCF level is relatively small: with the basis set SP + BF it is equal to 4.2 kJ mol⁻¹, with the basis set SPD to 22.6 kJ mol⁻¹. The respective difference is however rather large and it shows that bond functions (at least in the form used in this paper) cannot substitute polarization functions properly. The use of smaller basis set leads to qualitatively incorrect results. Schlegel et al. [9] in their study of possible reaction paths of reaction (A) at the 4-31G and STO-3G levels have shown that 4-31G potential energy curve of the F⁻...CH₃F system has a small local maximum in the region of the transition state, though ΔE^{*} value is negative, while STO-3G fails completely in this case predicting a stable intermediate. These findings are in close agreement with studies of chemical equilibria in the gas phase [33, 34], namely, that for "chemically" accurate reaction heats calculation at least a DZ + P basis set for the first-row atoms is necessary.

The most computer time consuming step is the calculation of energies required for the vibrational analysis and the ZPE correction. For this part of calculations we selected the 4-31G basis set. It is assumed that 4-31G potential hypersurface is not significantly different from the DZ + P one, at least in the proximity of equilibrium geometry of reactants and optimum geometry of activated complex (see also the work of *Schlegel et al.* [9]). In Table 2 in addition to our results we present wavenumbers calculated by *Schlegel et al.* [35] and experimental results of *Dedieu* and *Kohlrausch* [36, 37]. Overall agreement between theoretical and experimental data for CH₃F and CD₃F is satisfactory. Small differences are mostly due to basis set deficiency and absence of correlation energy and vary from 2 to 14% both for CH₃F and CD₃F, all theoretical values being overestimated. In Table 3 similar results are displayed for FCH₃F⁻ and FCD₃F⁻ As a justification of use of 4-31G basis for this activated complex may serve :

1. Comparison of related vibrational modes between CH_3F and FCH_3F^- (increase of C—H stretches and CH_3 bends, decrease of C—F stretches). These trends are supposed when passing from reactants to transition state (*cf.* also related force constants in Table 1).

2. Presence of imaginary frequency ω_3 (A_2'') which corresponds to the decay vibration of F...CH₃...F⁻

3. Comparison of ratios $\omega_{\rm H}/\omega_{\rm D}$, in both cases these vary between 1.0—1.4 having no abnormal values for activated complex.

Finally, the correlation energy contribution to the activation barrier of reaction (A) should be mentioned. Up to date only two papers concerning correlation energy contribution to the barrier in reaction (A) appeared. Limited CI calculations with partial inclusion of single and double excitations (CI—SD) performed by

Dedieu et al. [16] yielded negligible contribution of the correlation energy, 0.1 kJ mol⁻¹. This result must be taken with caution, however, because CI-SD is not a size-extensive method [38, 39]. As noted by Keil and Ahlrichs [11], the correction for size-extensivity may be as large as about 60 kJ mol⁻¹ for our reaction. The reason why Dedieu et al. did not obtain so large contribution to the activation barrier may be probably attributed to two further approximations applied in their work: they used only limited number of polarization d functions on C and F atoms and no p functions on hydrogen atoms and in CI, excitations from both 1s and 2s orbitals of the C and F atoms were not considered.

Second calculation of the correlation correction to the activation barrier of reaction (A) comes from *Keil* and *Ahlrichs* [11], who obtained the correlation contribution of 19.4 kJmol^{-1} with the CEPA method.

Our MB-RSPT calculations in the approximate fourth order, including double and quadruple excitations lead to the correlation contribution to the barrier of -1.0 kJ mol^{-1} . Taking into account the relative similarity (in the physical sense) of both methods, our value is surprisingly low (and even of opposite sign) in comparison to CEPA. Both these methods are size-consistent, both take into account double excitations (but MB-RSPT only to the fourth order) and both take into account quadruple excitations (MB-RSPT correctly in the fourth order, whereas CEPA only approximately). The different inherent limitations of fourth order MB-RSPT and CEPA may lead to slightly different results, together with the effect of the different basis set. Specifically, we used basis set without polarization pfunctions on hydrogen atoms in contrast to Keil and Ahlrichs. Our preliminary calculations with these p functions and with complete fourth-order MB-RSPT suggest that rather very low correlation contribution is most probable. This opinion is supported also by experimental results (see the last section).

Solvent effect in reaction (A)

One of the first quantum chemical attempts to account for solvent effect in the title reaction was a CNDO calculation by *Cremaschi et al.* [13]. They used a supermolecule approach with several possible arrangements of water molecules around reactants and activated complex. The contribution of solvation to gas phase activation barrier $\Delta E^{\pm} = -369.7$ kJ mol⁻¹ (CNDO fails badly here giving a large negative barrier) varied from 267.5 to 421.7 kJ mol⁻¹ according to the number and arrangement of water molecules in the supermolecule and ΔE^{\pm} reached in the latter case 52.3 kJ mol⁻¹.

The continuum solvaton model (again at CNDO level) leads to similar results [40], inclusion of solvent increased originally negative barrier to value of 72.2 kJmol^{-1} .

In our work we used continuum model, too, utilizing Chalvet—Jano equation (CJ) [41] with modification proposed by *Miertuš* and *Kysel* [42]

$$-\Delta G_{\rm s} = \frac{N_{\rm A}}{4\pi\varepsilon_0} (1 - 1/\varepsilon_{\rm r}) \frac{1}{2} \sum_{ij} \frac{Q_i Q_j}{R_{ij}}$$
(4)

where N_A is Avogadro's constant, ε_0 permittivity of vacuum, ε_r relative permittivity, Q_i , Q_j are fractional charges, R_{ij} interatomic distance plus van der Waals radius of atom *j*, R_{ii} is van der Waals radius. In order to compare our solvent effect with *Daudel's* calculation [43] we assume acetone as a solvent, $\varepsilon_r = 20.49$. Daudel used the known values of activation energy for Cl⁻ and Br⁻ in acetone

$$Br^{-} + CH_3Br = CH_3Br + Br^{-}$$
 $E_a = 66.9 \text{ kJ mol}^{-1}$
 $Cl^{-} + CH_3Cl = CH_3Cl + Cl^{-}$ $E_a = 83.7 \text{ kJ mol}^{-1}$

to estimate activation energy for reaction with fluorine by means of extrapolation. Table 5 summarizes results of estimates of the solvent effect. As expected, theoretical and experimental contributions of the solvent differ significantly, by 62.6 kJmol^{-1} . When analyzing this difference we have to keep in mind shortcomings of this simple approach (eqn (4)):

i) Our estimate of solvent effect includes only coulombic part of the interaction between solute and solvent.

ii) Continuum model cannot account for specific interactions, *e.g.* hydrogen bonds, which are important in this system.

We performed also a supermolecule 4-31G calculation of the process

$$CH_{3}F + [F...H_{2}O]^{-} = [FCH_{3}F...H_{2}O]^{-}$$
 (C)

Table 5

Comparison of numerical values of activation energies for title reaction in the gas phase and in the solution

values in Komor				
Activation energy	Gas phase	Contribution of the solvent	Total	
E. theoretical	35.9°	29.4*	65.3	_
E. experimental ^d	12.6	30.4° 92.0	66.3 104.6	

Values in kJ mol⁻¹

a) Taken as ΔH_0^{\bullet} from Table 4, $(E_{\text{DOR}}^{c_2-(4)} \text{ row})$ corrected for room temperature, $E_* = \Delta H_0^{\bullet} + 2RT$; b) obtained from eqn (4), action solution ($\epsilon_r = 20.49$); c) obtained from eqn (4), aqueous solution ($\epsilon_r = 78.36$); d) obtained by extrapolation, gas phase: Ref. [24], solution: Ref. [43].

	$E_{ m SCF}/E_{ m h}$	$\Delta E_{\rm scf}/{\rm kJmol^{-1}}$
F ⁻	- 99.247 82	
CH ₃ F	- 138.858 59	
FCH ₃ F ⁻	-238.129 60	-60.9"
[FH ₂ O] ⁻	- 175.217 60	
[FCH ₃ FH ₂ O] ⁻	- 314.074 46	+ 4.5"

Activation barrier with and without hydration calculated by supermolecule approach 4-31G basis set

a) $\Delta E_{\rm SCF} = E_{\rm FCH_3F^-} - (E_{\rm CH_3F} + E_{\rm F^-});$

b) $\Delta E_{\text{SCF}} = E_{\text{IFCH}_3\text{F}...\text{H}_2\text{O}\text{I}^-} - (E_{\text{CH}_3\text{F}} + E_{\text{IF}...\text{H}_2\text{O}\text{I}^-}).$

with O—F distance 2.5×10^{-10} m in linear hydrogen bond configuration in both supermolecules (Table 6). Contribution of the solvent, +65.4 kJmol⁻¹, is much higher in comparison with CJ result for water.

More accurate and complete information about solvent effect on reaction (A) can be obtained from some kind of simulation technique (Monte Carlo, molecular dynamics). Work of this kind is in progress in our laboratory.

Conclusion

In this part we would like to comment on the reliability of our theoretical calculations in the gas phase. Experimental rate constants of our reaction in the gas phase as well as in the solution are unknown. Only rate constants of related gas phase S_N2 reactions CH₃Cl+F⁻ (log{ k_{297K} } = 15.04, k_{297K} in cm³mol⁻¹s⁻¹) and $CH_3Br + F^-$ (log { k_{297K} } = 14.84) are at our disposal [24]. These data are very different from our value of $\log \{k_{298K}\} = 6.38$. Probably the difference is mainly due to differences in activation barriers. Again, experimentally measured activation energies are known only for the above-mentioned reactions, with CH₃Cl and CH₃Br being 0.6 and 1.3 kJmol⁻¹. Fortunately, the cited authors made an extrapolation from a series of reactions with different nucleophiles and arrived to the value of E_a (Arrhenius activation energy) 12.6 kJ mol⁻¹. Using this E_a and our calculated preexponential factor we can obtain the "experimental" value of $\log\{k\}$ which should lie within 9-10. This is in qualitative agreement with the observation [24] that the gas phase S_N2 reactions with CH₃F do proceed at least 100 times slower than with CH₃Cl and CH₃Br. The fact that our purely theoretically predicted rate constant is by several orders lower than the extrapolated "experimental" one, is connected with the result that our activation energy is more

than twice larger than experimental E_a . Our results suggest that the barrier is not so large as it follows from preceding theoretical calculations [11]. This leads to better agreement with extrapolated experimental value, although the barrier still seems to be too high. Further calculations with more extended basis set and complete fourth-order correlation energy will lead probably to more reliable results. Work along these lines is in progress in our laboratory.

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