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Rate Coefficients for the Gas Phase Reactions of CF_3CH_2F (HFC-134a) with Chlorine and Fluorine Atoms: Experimental and ab Initio Theoretical Studies

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The first direct measurements of rate coefficients for the hydrogen abstraction reactions from CF_3CH_2F by chlorine or fluorine atoms in gas phase are reported as a function of temperature using the discharge flow/mass spectrometric technique (DF/MS). The reactions were investigated under pseudo-first-order conditions with Cl or F atoms in large excess with respect to the haloethane. The temperature dependence of the rate coefficients is expressed in the Arrhenius form. For the reaction Cl + CF_3CH_2F, the Arrhenius expression over the temperature range 298−423 K was found to be $(3.2 \pm 0.3) \times 10^{-12} \exp[-(2300 \pm 70)/T]$ and for the reaction F + CF_3CH_2F over the range 296−381 K, $(6.5^{+2.1}_{-1.6}) \times 10^{-11} \exp[-(1100 \pm 100)/T]$. The units of the rate constants are cm^3 $molecule^{-1}$ s^{-1}, and the quoted uncertainties are within the 95% confidence range. Ab initio molecular orbital calculations for the H-abstraction from CF_3CH_2F by F and Cl were performed. The characteristics (energies, structural parameters, and frequencies) of the reactants, products, and transition states were determined at the MP2/6-31G(d,p) level of theory. Single-point energy calculations have been performed at MP4/6-31G(d,p), MP2/6-311G(d,p), and MP2/6-311G(2d,2p) levels. ISO-M energy corrections have been applied leading to reaction enthalpies and activation energies in a good accord with experimental findings. Calculated rate constants at room temperature including one-dimensional tunneling are in agreement with experiment.

Introduction

Because they retain many of desirable properties of CFCs and have a zero ozone depletion potential (ODP), hydrofluorocarbons (HFCs) are considered as the most promising long-term alternatives of chlorofluorocarbons (CFCs). Among the HFCs proposed as substitutes for replacing CFCs in industrial applications, HFC-134a (1,1,1,2-tetrafluoroethane) is now largely used as a substitute of CFC-12 (CCl_2F_2) and HCFC-22 ($CHClF_2$) in domestic refrigeration systems, automotive air conditioning, and aerosol applications. Its total cumulative production for years 1990 through 1994 for dispersive use is about 8.5×10^4 t.[1] Recent measurements of HFC-134a from air samples collected from sites across the globe have shown the presence of this species in the atmosphere at 1.6 ppt in mid-1995.[2] Its average lifetime in troposphere, defined with respect to the reaction with OH radicals, which initiates its tropospheric degradation processes, can be estimated in the range of 10−25 years.[3]

In the framework of most laboratory studies devoted to the assessment of the environmental acceptability of HFC-134a, initiation reactions using Cl or F atoms as surrogate of OH radicals were currently used. However, if a number of recent rate coefficient measurements on the initiation reactions with Cl or F atoms have been performed at room temperature using various methods,[4−7] limited experimental data is available on the temperature dependence of these reactions. In earlier studies, we have reported ab initio theoretical and experimental results on the kinetic parameters of the reactions of Cl atoms with halomethanes[8,9] and with haloethanes of type $CH_3CCl_{3-x}F_x$[10](x = 0, 1, and 2). In this paper, we report the first direct measurements of rate coefficients as a function of temperature for the reactions of CF_3CH_2F (HFC-134a) with chlorine and fluorine atoms:

$$Cl + CF_3CH_2F \xrightarrow{1} HCl + CF_3CHF \qquad \Delta H_1^\circ \cong +0.0 \text{ kcal mol}^{-1}$$

$$F + CF_3CH_2F \xrightarrow{2} HF + CF_3CHF \qquad \Delta H_2^\circ \cong -33.1 \text{ kcal mol}^{-1}$$

both used in laboratory studies as sources of primary radical CF_3CHF. The above reaction enthalpies have been calculated at 298 K using the experimental formation enthalpies reported by DeMore et al.[11] To the best of our knowledge, the temperature dependence of rate coefficients for reactions 1 and 2 was only measured by Kaiser[12] and Maricq et al.,[13] respectively, with both groups using the relative rate method. Furthermore, we have performed ab initio calculations in order to gain insight into the reactivity differences between Cl and F atoms reacting with the same haloalkane. Transition state structures are determined and calculated kinetic parameters (activation energies and Arrhenius *A*-factors) are compared with the experimental values determined in this work. Reactivity differences between Cl and F atoms with the studied compound are inspected and discussed.

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Experimental Section

Method. The experiments were carried out using the conventional discharge flow/mass spectrometric technique (DF/MS). The apparatus has been already described in detail elsewhere[14,15] and is only briefly described here.

Chlorine or fluorine atoms were generated by a microwave discharge (2450 Mhz, 40W) in a mixture of Cl_2 (or F_2)/He through a fixed sidearm located in the upstream part of the flow tube. More specifically for the generation of fluorine atoms, the discharge was achieved through a 0.5-cm internal diameter alumina tube[16,17] in order to reduce the wall reactions of F atoms. The wall loss of Cl or F atoms on all internal surfaces of the flow tube surfaces made of Pyrex was minimized by coating with pure orthophosphoric acid. Concentrations of chlorine atoms were determinated by mass spectrometric measurement on the extent of Cl_2 to Cl conversion and occasionally by titration with C_2H_3Br as proposed by Park et al.,[18] with both methods leading to results in good agreement. Concentration of fluorine atoms along the reaction distance were determined by using the fast reaction titration of F + Cl_2 as proposed by Clyne et al.[19]

Flow rates of different gases were regulated by calibrated mass flow controllers. Average flow velocities were over the range 2−9 m s^{-1}. The pressure in the flow tube (range: 1−5 Torr) was measured upstream and downstream by a capacitance manometer.

Monitoring of the Reactions. All experiments were carried out under pseudo-first-order conditions with chlorine or fluorine atoms in large excess with respect to the initial concentration of the studied haloethane. Kinetic measurements were performed by monitoring the temporal decay of the intensity of the base peak (CH_2F^+) detected at the mass/charge ratio $m/e = 33$. This fragment ion (detected at 40 eV) is specific to the initial reactant.

Purities. The purities of HCFC-134a supplied by Elf Atochem was > 99.7%. This haloethane was used without further purification. The source of Cl_2 (or F_2) was a commercial mixture (Alphagaz) constituted of 2% of Cl_2 (>99.99%) (or 5% of F_2, >99.99%) in helium (>99.9995%). As an additional diluent, helium (Air Liquide, purity >99.995%) was purified by circulating through a liquid nitrogen trap.

Treatment of Kinetic Data. The bimolecular rate coefficients k_1 for the reaction

$$Cl + CF_3CH_2F \xrightarrow{1} HCl + CF_3CHF$$

were determined using the same procedure as described in our latest papers.[9,10] This procedure takes into account the variation of Cl concentration along the flow tube due to the wall and homogeneous recombination reactions of Cl atoms generated at high concentrations (in the order of 10^{15} atoms cm^{-3}). The variation of Cl introduces a systematic error when the treatment of kinetic data without Cl loss is used. Such a treatment of kinetic data is not necessary for the reaction

$$F + CF_3CH_2F \xrightarrow{2} HF + CF_3CHF$$

since the recombination reactions of F atoms on the wall and in gas phase along the reaction distance are observed to be not significant due to the use of relatively low concentrations for fluorine atoms (in the order of 10^{13} atoms cm^{-3}). This low level of F concentrations is made possible because the reaction F + CF_3CH_2F is much faster than the reaction Cl + CF_3CH_2F. Hence, the conventional treatment of kinetic data obtained under pseudo-first-order conditions has been used for the determination of the bimolecular rate coefficients k_2.

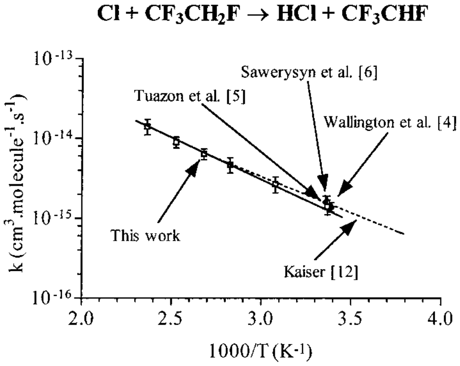

Figure 1. Arrhenius plot for the reaction of Cl + CF_3CH_2F determined in this work and compared with the previous determinations ($k \times 10^{15}$ in cm^3 $molecule^{-1}$ s^{-1} at room temperature: 1.38 ± 0.18 in ref 4, 1.6 ± 0.3 in ref 5, and 1.6 ± 0.3 in ref 6).

Results and Discussion

Cl + CF_3CH_2F → HCl + CF_3CHF (k_1). In a previous study,[6] we have measured for k_1 a value equal to (1.6 ± 0.3) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1}at 297 ± 2 K without corrections for $[Cl]_o$ in a very good agreement (Figure 1) with the one obtained by Wallington et al.[4] and Tuazon et al.[5] using a relative rate method. The correction due to the diffusion effect for k_1 was very small (<2%). As previously indicated, we have estimated the systematic error due to the homogeneous and heterogeneous recombinations of Cl along the reaction distance. Consumption of Cl between 17 and 26% can be predicted at 298 K by modeling at the end of the flow tube. The kinetic data accounting for the Cl recombination reactions leads to a corrected value $k_{1,c}$ for k_1 very close to the uncorrected value:

$$k_{1,c}\,(298\text{ K}) = (1.4 \pm 0.3) \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$$

Table 1 gives the results obtained for this reaction at various temperatures and relevant experimental conditions. By a least squares treatment of the plot ln $k_{1,c}$ vs $1/T$, we obtain the following Arrhenius expression:

$$k_{1,c}\,(298{-}423\text{ K}) = (3.2 \pm 0.3) \times 10^{-12} \exp[-(2300 \pm 70)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$$

This Arrhenius expression is plotted in Figure 1. Our result is in a very good agreement with the only earlier determination of Kaiser[12] using the relative rate method ($k = 1.8 \times 10^{-12}$ $\exp[-(2100/T)]$ over the 262−348 K temperature range).

F + CF_3CH_2F → HF + CF_3CHF (k_2). As the concentrations of F atoms used in this study are much lower than the Cl concentrations used in the determination of k_1, systematic error due to homogeneous and heterogeneous recombinations of F atoms along the reaction distance becomes very small (<2%). Therefore the conventional treatment of kinetic data is used for the determination of k_2. The plot of the pseudo-first-order rate constant k_{obs} as a function of $[F]_o$ along the reaction zone is shown in Figure 2. Least-squares linear regression gives the following value for the bimolecular rate constant with corrections due to radial and axial diffusion effects (<1%):

$$k_{2,c}\,(296\text{ K}) = (1.5 \pm 0.2) \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$$

Indicated errors are only statistical uncertainties within the 95% confidence range for the fit of experimental data. This value

TABLE 1: Summary of the Relevant Experimental Conditions and Values of the Rate Coefficients k_1(Uncorrected) and $k_{1,c}$ (with Corrections) as a Function of Temperature for the Reaction Cl+ CF_3CH_2F

T (K)	P (Torr)	expts	$[CF_3CH_2F]_o^a \times 10^{-13}$	$[Cl]_{o,o}^a \times 10^{-14}$	$(k_1 \pm 2\sigma)^b \times 10^{15}$	$(k_{1,c} \pm 2\sigma)^b \times 10^{15}$
297	2.8−4.8	6	1.27−2.02	12.90−30.30	1.6 ± 0.3	1.4 ± 0.3
325	2.7−3.8	5	0.83−2.26	6.77−17.20	2.8 ± 0.5	2.7 ± 0.6
354	2.1−3.8	5	0.85−2.14	7.19−17.80	5.1 ± 0.8	4.7 ± 1.0
373	2.5−3.9	6	0.92−2.13	7.05−16.01	7.0 ± 0.9	6.4 ± 1.0
396	3.6−4.3	6	0.98−1.93	8.31−22.40	9.8 ± 1.2	9.0 ± 1.4
423	2.0−4.7	6	0.64−1.91	6.83−22.10	15.2 ± 2.6	14.1 ± 3.1

[a] Concentrations are expressed in molecule cm^{-3}. [b] Units are cm^3 $molecule^{-1}$ s^{-1}.

TABLE 2: Summary of the Relevant Experimental Conditions and Values of the Rate Coefficients k_2 (Uncorrected) and $k_{2,c}$ (with Corrections) as a Function of Temperature for the Reaction F + CF_3CH_2F

T (K)	P (Torr)	expts	$[CF_3CH_2F]_o^a \times 10^{-12}$	$[F]_o^a \times 10^{-13}$	$(k_2 \pm 2\sigma)^b \times 10^{12}$	$(k_{2,c} \pm 2\sigma)^b \times 10^{12}$
296	1.0−1.3	18	3.5	3.5−12.9	1.5 ± 0.2	1.6 ± 0.2
318	1.0−1.3	6	3.3	4.0−10.1	1.9 ± 0.2	2.1 ± 0.2
333	1.0−1.3	6	3.1	4.1−9.8	2.2 ± 0.2	2.4 ± 0.2
348	1.0−1.3	5	3.0	2.8−6.7	2.6 ± 0.4	2.9 ± 0.4
355	1.0−1.1	6	1.1	2.5−6.7	2.8 ± 0.2	3.0 ± 0.2
381	1.1−1.2	6	1.4	2.3−4.9	3.4 ± 0.2	3.6 ± 0.2

[a] Concentrations are expressed in molecule cm^{-3}. [b] Units are cm^3 $molecule^{-1}$ s^{-1}.

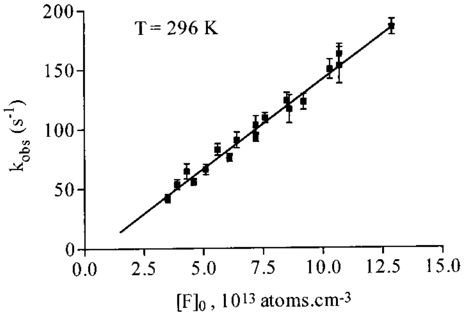

Figure 2. Pseudo-first-order rate constants k_{obs}; plotted vs $[F]_o$ for the reaction F + CF_3CH_2F at 296 K.

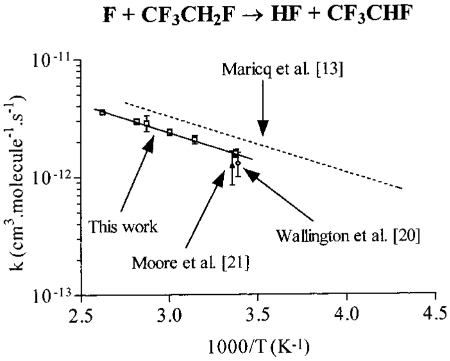

Figure 3. Arrhenius plot for the reaction of F + CF_3CH_2F determined in this work and compared with the previous determinations ($k \times 10^{12}$ in cm^3 $molecule^{-1}$ s^{-1} at room temperature: 1.4 ± 0.3 in ref 20; 1.25 ± 0.4 in ref 21).

is in very good agreement with the value obtained by Wallington et al.[20] using a relative rate method and a laser flash photolysis and the one of Moore and Smith[21] using a relative method. Table 2 gathers the results obtained for this reaction at different temperatures and relevant experimental conditions. By a least-squares treatment of the plot ln $k_{2,c}$ vs $1/T$ (Figure 3), we obtain the following Arrhenius expression:

$$k_{2,c}\,(296-381\text{ K}) = (6.5^{+2.1}_{-1.6}) \times 10^{-11} \exp[-(1100 \pm 100)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

This expression is consistent with only the Arrhenius expression previously reported by Maricq et al.[13] ($k = (9.8^{+9}_{-5} \times 10^{-11} \exp[-(1130 \pm 190)/T]$ over the 210−363 K temperature range), with both studies reporting a large range of uncertainty.

Theoretical Study

Method. Ab initio molecular orbital calculations have been performed using the GAUSSIAN 94 package of programs.[22] Critical points of the surfaces and equilibrium and saddle point geometries were optimized at the MP2/6-31G(d,p) level. Vibrational frequencies and zero-point energies were calculated at this level using analytical second-order derivatives of the potential. It is admitted that the transition state corresponds to the saddle point along the reaction path. Energies have been improved either by using the fourth-order Moller−Plesset perturbation theory[23] including all single, double, triple, and quadruple excitations (MP4SDTQ/6-31G(d,p)) or by adding polarization functions in the basis set. For the open-shell structures, the spin contamination has been taken into account by the spin-projected method proposed by Sosa and Schlegel[24] and available in the program (noted PMP2 and PMP4 in the Tables).

Finally, the energies have been corrected empirically using the ISO-M method described in ref 8. In this method, the reaction enthalpy ΔH_r(ISO) is corrected using the isodesmic reaction, $CH_3 + CF_3CH_2F \rightarrow CH_4 + CF_3CHF$, and the experimental HCl and HF dissociation energies at 298 K. The activation energies E_a are then improved by using Marcus quadratic relationship[25] between activation energies and reaction enthalpies.

Results and Discussion

No long-range intermediate complex has been found for reactions 1 and 2. We have then studied the H-abstraction from CF_3CH_2F by chlorine (reaction 1) and fluorine (reaction 2) atoms. Geometrical structures and vibrational frequencies along with zero-point energies and thermal corrections are reported in Tables 3 and 4, respectively. The atoms are labeled as in Figure 4.

The transition state (TS-Cl) related to the Cl reaction resembles the products more than the reactants with a significant elongation of the C-H bond (0.284 Å) and a smaller elongation of the H−Cl bond (0.166 Å) with respect to the bond distance in the product H−Cl. On the opposite, the transition state TS−F related to the F reaction is more reactant-like than TS-Cl, with

TABLE 3: MP2/6-31G(d,p) Optimized Geometries[a]

	CF_3CH_2F	TS-Cl	TS-F
$r(C_1-H_1)$	1.088	**1.372**	**1.151**
$r(H_1-X)$		**1.435**	**1.336**
$r(C-F)$	1.346	1.346	1.346
$r(C-C_1)$	1.508	1.507	1.510
$r(C_1-F_1)$	1.382	1.340	1.365
$r(C-H)$	1.088	1.087	1.088
$\theta(XH_1C_1)$		174.4	155.4
$\theta(FCC_1)$	108.6	109.1	109.5
$\theta(FCF)$	111.6	110.7	110.5
$\theta(F_1C_1C)$	108.7	112.0	109.9
$\theta(HC_1C)$	108.9	115.7	111.6
$\theta(H_1C_1C)$	108.9	104.0	107.1
dih (F_1C_1CF)	180.0	174.9	179.3
dih (HC_1CF_1)	119.8	132.2	124.4
dih $(H_1C_1CF_1)$	−119.8	−115.6	−118.3

$r(H\text{-}Cl) = 1.269$ Å $r(H\text{-}F) = 0.921$ Å

[a] For the transition states TS-Cl and TS-F, the lengths of C_1-H_1 breaking and H_1-X forming bonds are written in bold type. Distances are in angströms and angles in degrees.

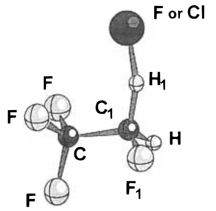

Figure 4. Drawing of the transition state $F_3CHF-H-X$.

a much smaller elongation of the C−H bond (0.063 Å) and a much larger one for the H−F bond (0.415 Å). This behavior agrees well with Hammond's postulate[27] which predicts a product-like character of the transition state when the reaction is endothermic (here, Cl reaction is almost thermoneutral) and a reactant-like character with an exothermic reaction (in this case F reaction is significantly exothermic).

The absolute energies are listed in Table 5 for different levels of calculations. Enthalpies of reactions and activation energies at 298 K are listed in Table 6. MP2 level of calculation and use of polarization functions in the basis set are necessary to obtain a good description of parts of the potential energy surface especially for the transition states where bonds are elongated. Due to the large number of electrons in the systems studied, the largest level of calculation used for the search of stationary states is the MP2/6-31G(d,p) level. Single-point energies have then been calculated on the optimized structural parameters. For each level of theory, the ISO-M correction has been done, leading to values of the reaction enthalpies in excellent agreement with the available experimental ones. Whatever the level of calculation is, both activation energies E_a(ISO-M) for reactions 1 and 2 are, within a precision of roughly 2 kcal mol^{-1}, in a good accord with experimental ones presented in the first part of this paper.

Using the conventional transition state theory, the preexponential A factors for both reactions have been obtained from calculated molar entropies (Table 4). As seen from Table 7, the A_{Cl} factor is lower than the A_F one in agreement with the experiment, but the difference is not so large.

The resulting rate constants have been calculated for the values of the activation energies obtained at PMP2/6-31G(d,p) level (energy and geometry at the same level) after ISO-M correction. Moreover, the tunneling effect has been taken into account by modeling the reaction energy profile by an unsymmetrical Eckart potential and calculating the ratio Γ^{*28-31} between the quantal and classical expression of the thermal rate constant in the same way as in ref 8. The resulting rate constants listed in Table 7 are in a good agreement with the experimental findings.

Conclusions

Arrhenius expressions for the hydrogen abstraction reactions from CF_3CH_2F (HFC-134a) by chlorine or fluorine atoms in

TABLE 4: Calculated MP2/6-31G(d,p) Values

CF_3CH_2F	114, 216, 358, 412, 530, 549, 668, 865, 1021, 1147, 1246, 1247, 1360, 1363, 1508, 1563, 3170, 3245[a,e]	ZPE = 29.42,[b] STE = 32.82,[c] S = 75.39[d]
CF_3CHF	86, 213, 352, 419, 517, 556, 673, 724, 884, 1211, 1229, 1254, 1340, 1505, 3325	ZPE = 20.42,[b] STE = 23.89[c]
HCl	3119	ZPE = 4.46,[b] STE = 5.94[c]
HF	4192	ZPE = 5.99,[b] STE = 7.47[c]
TS-Cl	i1411	
	51, 69,141, 217, 305, 415, 491, 538, 555, 685, 877, 959, 1017, 1171, 1225, 1270, 1284, 1341, 1475, 3241[a,e]	ZPE = 24.77,[b] STE = 29.36,[c] *S* = 89.50[d]
TS-F	i1479	
	21, 73, 110, 217, 316, 406, 521, 544, 667, 715, 867, 979, 1184, 1257, 1267, 1345, 1413, 1447, 1641, 3219[a,e]	ZPE = 26.03,[b] STE = 30.60,[c] *S* = 89.95[d]

[a] Vibrational frequencies (cm^{-1}). [b] ZPE: zero-point vibrational corrections (kcal mol^{-1}). [c] STE: sum of thermal energies at 298 K including ZPE (SPE in kcal mol^{-1}). [d] Entropies (cal mol^{-1} K^{-1}). [e] Comparaison with experimental values and assignment of all 18 fundamentals for CF_3CH_2F were recently reported by Papasavva et al.[26]

TABLE 5: Absolute Energies[a] for the Different Species Involved in the Reactions

	PMP2/6-31G(d,p)// MP2/6-31G(d,p)	PMP4/6-31G(d,p)// MP2/6-31G(d,p)	PMP2/6-311G(d,p)// MP2/6-31G(d,p)	PMP2/6-311G(2d,2p)// MP2/6-31G(d,p)
CF_3CH_2F	-475.605 755	−475.655 514	−475.878 362	−475.994 401
Cl	−459.553 533	−459.570 274	−459.586 248	−459.604 170
F	−99.488 229	−99.499 076	−99.555 189	−99.574 357
CF_3CHF	−474.940 328	−474.987 669	−475.217 139	−475.325 524
HCl	−460.205 447	−460.223 936	−460.244 012	−460.265 875
HF	−100.194 639	−100.201 430	−100.267 133	−100.292 867
TS-Cl	−935.137 605	−935.202 935	−935.446 790	−935.584 668
TS-F	−575.083 593	−575.144 291	−575.422 646	−575.559 979
CH_3	−39.694 621	−39.715 890	−39.709 104	−39.720 989
CH_4	−40.364 626	−40.388 640	−40.379 174	−40.393 487

[a] In Hartrees.

TABLE 6: Reaction Enthalpies and Activation Energies

	reaction 1 (Cl)				reaction 2 (F)			
level of theory	ΔH_r	ΔH_r (ISO)	E_a	E_a (ISO-M)	ΔH_r	ΔH_r (ISO)	E_a	E_a (ISO-M)
PMP2/6-31G(d,p)//MP2/6-31G(d,p)	4.60	−0.46	9.85	7.14	−28.07	−33.06	4.01	2.81
PMP4/6-31G(d,p)//MP2/6-31G(d,p)	5.00	−0.67	9.99	7.24	−24.00	−33.27	3.95	1.82
PMP2/6-311G(d,p)//MP2/6-31G(d,p)	−1.71	−5.15	7.43	5.05	−34.18	−35.74	4.33	3.95
PMP2/6-311G(2d,2p)//MP2/6-31G(d,p)	0.62	0.13	4.97	4.71	−33.49	−32.47	3.00	3.22
exptl	+ 0.0		4.6		−33.1		2.2	

[a] ΔH_r for the level of theory given on the left and ΔH_r(ISO) including isodesmic correction. [b] E_a for the level of theory given on the left and E_a(ISO-M) including ISO-M correction method, see text. [c] All the values are calculated at 298 K and given in kcal mol^{-1}.

TABLE 7: Preexponential *A*-factors, E_a Activation Energies, Γ* Transmission Factors, Calculated Rate Constants with Included Tunneling at 298 K, Ratio of Experimental and Calculated Values for the Rate Constants at 298 K

	A^a	$E_a{}^b$	Γ*	$k_{calc}{}^c$	k_{exp}/k_{calc}
Cl-reaction	5.0×10^{-12}	7.14	8.6	2.4×10^{-16}	5.4
F-reaction	1.4×10^{-11}	2.81	7.6	9.1×10^{-13}	1.6

[a] In cm^3 molecule^{-1} s^{-1}. [b] In kcal mol^{-1}. [c] In cm^3 molecule^{-1} s^{-1}.

gas phase have been determined using the discharge flow/mass spectrometric technique (DF/MS). The reactions were investigated under pseudo-first-order conditions with Cl or F atoms in large excess with respect to the haloethane, as opposed to conventional excess reactant molecule. Wall and homogeneous recombination reactions of atomic chlorine generated at high concentrations were taken into account in the calculation of the rate coefficients for the reaction Cl + CF_3CH_2F. In contrast, the conventional treatment of kinetic data was applied to the calculation of the rate coefficients for the reaction F + CF_3CH_2F due to the use of F concentrations much lower than the one of Cl atoms. At room temperature, the values of rate constant measured for both reactions are in good agreement with literature data. The corresponding kinetic parameters (*A*-factor and activation energy) are also in good agreement with the ones previously reported and obtained using the relative method. The ab initio calculations which have been performed for both abstraction reactions show that energies including electronic correlation (MP2, MP4) and corrected with means of ISO-M method, lead to thermodynamic and kinetic parameters in a very good agreement with experiment. In particular, the very different thermodynamic properties between both reactions are well reproduced. Moreover, the structural and energetic parameters of the transition states are shown to be product-like for the Cl-reaction and reactant-like for the F-reaction in accord with the each exothermicity. All these results show that the method ISO-M coupled with high-level ab initio calculations is reliable and can be used for the determination of other reactions characteristics, which are still unknown.

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