

Calculated RRKM Rate Constants for Competitive Reactions

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Neste trabalho foram calculadas as energias críticas e os fatores pré-exponenciais para a decomposição e a isomerização unimoleculares do 1-metil-2,2,3,3-tetrafluorociclopropano.

Também foram modeladas as reações de adição e inserção de metileno a hidrocarbonetos e comparou-se a razão das constantes calculadas com o valor experimental.

RRKM calculations are used to compute the critical energies and pre-exponential factors for the unimolecular decomposition and isomerization reactions of 1-methyl-2,2,3,3-tetrafluorocyclopropane.

Also the addition and insertion of methylene to hydrocarbons is modelled and the ratio of the constants is compared with the experimental values.

Key words: *RRKM calculations; competitive reactions.*

Introduction

It is well known that gem-difluorocyclopropanes undergo decomposition reactions to yield $:CF_2$ plus the corresponding olefin. However, thermochemical calculations suggest that this process should occur in competition with structural isomerization, involving a hydrogen atom migration. In spite of that, this process has never been experimentally observed in thermal studies^{1,2}. In this type of reactions, the deposition of energy in reactants molecules is left to the chance of molecular encounters. The state of the reacting system can be macroscopically described by its temperature; on the microscopic level, it represents an infinite collection of states with all possible values of E , the total internal energy, in excess of zero-point energy, and of J , the rotational quantum numbers, between zero and (in principle) infinite. This represents a very considerable collection of states, with the result that the thermal distribution function, $P(E)_e$, is very broad at temperatures where the reaction proceeds at a convenient rate.

At practical temperatures, that is below 900K, the maximum of $P(E)_e$ is always below the critical energy for reaction. This implies that $k(E)$ the microcanonical rate constant for unimolecular reaction, is averaged over the tail of the distribution function. In most of the experimental systems, which might present competitive reactions paths, only the path of lower critical energy is observed.

By contrast-in the chemical activation technique the energy is deposited in the reactant molecules during the course of their production by a large exothermic chemical reaction,

at relatively low temperature. The activated molecule has a distribution of energies, $F(E)$, that begins and reaches its maximum at energies which are generally much greater than the critical energy for unimolecular reaction. In spite of that, the two functions are not very different: in essence $F(E)$ is similar to the function $P(E-E_0^{\text{cr}})_e$, that is $P(E)$ shifted along the energy axis by E_0^{cr} , the critical energy of the reverse of the activation reaction in the chemical activation system. That means that the formation of the activated molecule proceeds at low temperature with a narrow distribution of energies, while the maximum of the function corresponds to a temperature about five times higher. Thus the averaging of $k(E)$ is done over the entire range of $F(E)$. The two functions are qualitatively compared in Figure 1.

In addition, due to the high energies obtained, more than one channel of reaction can be available, allowing the observation of high energy path which are not attainable in a thermal system. As a consequence, in the experimental study of the unimolecular reaction of chemically activated 1-methyl-2,2,3,3-tetrafluorocyclopropane (MTFC), two paths of reaction were observed: isomerization and decomposition with elimination³ of $:CF_2$.

While conventional thermal studies have provided most of the available information on the Arrhenius parameters, the chemical activation method has been mainly used to obtain data on collisional energy transfer through the comparison of the experimental data with the calculated values using the RRKM theory and a suitable model for the energy transfer probabilities⁴⁻⁷.

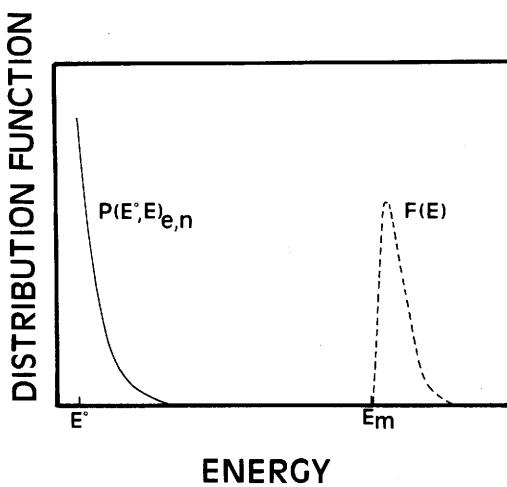


Figure 1. Comparison of thermally and chemically activated systems. The distribution functions $P(E_0, E, n)$ and $F(E)$ refer to the distribution of energies of the vibrational excited molecule formed by the thermal and chemical activation processes, respectively.

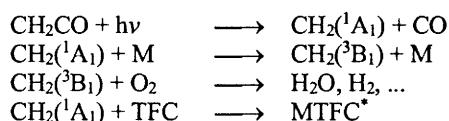
The main aim of this work is to show how critical energies and preexponential factors for two competitive paths of reaction can be estimated through a careful computational work and a comparison with the chemical activation data. Here, the experimental results of Reference 3 were used for comparison.

Two aspects must be pointed out. First, the Arrhenius parameters for the isomerization of MTFC can not be obtained from a conventional thermal study, while the parameters for the decomposition via were only crudely estimated because of the experimental difficulties of this system³. Second, chemical activation calculations involve an extensively parameterization. In any case, some of the parameters can be estimated from experimental data and from the knowledge of related systems. Care must be taken in this choice to obtain reliable results. Also it must be kept in mind that these calculations can provided only a reasonable estimation of the results within the limitations of the involved parameters.

We also calculate in this work, the relative velocities of insertion and addition of singlet methylene to hydrocarbons, using the concepts of the RRKM theory and equilibrium and compare these results with experimental ones⁸.

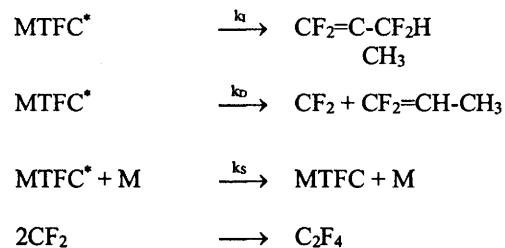
Calculation of the unimolecular constants

Chemically activated 1-methyl-2,2,3,3-tetrafluorocyclopropane (MTFC^{*}) can be formed by the insertion of singlet methylene to the C-H bond of 1,1,2,2-tetrafluorocyclopropane (TFC):



Singlet methylene is formed in-situ by the UV photolysis of ketene and oxygen is added in order to remove triplet methylene⁸⁻¹⁰.

It was determined that MTFC^{*} reacts according to the following mechanism³:



Isomerization, decomposition and collisional stabilization are competitive processes and experimental data has been obtained for the isomerization/decomposition (I/D) isomerization/stabilization (I/S) and decomposition/stabilization (D/S) ratios³.

In this work the theoretical D/S and I/S ratios were computed by adopting the matrix formulation of Hoare¹¹, originally proposed for a one-channel system:

$$D/S = (1/\omega) \sum_i \{ k_D[(I - P) + (k_D/\omega + (k_i/\omega)]^{-1} f \}_i$$

here ω is the collisional frequency, k_D is a diagonal matrix with elements $k_D(E)$ the microcanonical rate constants for the decomposition reaction, k_i is a diagonal matrix with elements $k_i(E)$ the microcanonical rate constants for the isomerization path, I is the unit matrix, P is a matrix with elements P_{ij} , the collisional transition probabilities from state i to j , and f is a vector with elements $f(E)$, the energy distribution function of MTFC^{*}. A similar expression was found for the ratio I/S.

The collisional frequency, ω , can be evaluated from the product ($P k_M$). The collision number k_M is computed from the collision diameter, s_{AM} , the reduced molar mass and the temperature¹². In order to calculate the collision diameter, the molecular diameters, σ , the Lennard Jones parameters, ϵ/k , and the collisional integrals $\theta^{2,2}(T^*)$ are needed^{13,14}. The following relations were used:

$$k_M = s_{AM}^2 (8\pi kT/\mu_{AM})^{1/2}$$

$$s_{AM} = \sigma_{AM} [\theta^{2,2}(T^*)]^{1/2}$$

$$\sigma_{AM} = (\sigma_A + \sigma_M)/2$$

$$\epsilon_{AM}/k = [(\epsilon_A/k)(\epsilon_M/k)]^{1/2}$$

The microcanonical constants were computed from the RRKM theory^{12,15,16}.

$$k(E) = (L^{\#}/h)(Q_1^+/Q_1) \{ \sum P(E_{vr}^+) / N^*(E^*) \}$$

$k(E)$ is the rate constant at a specific energy E , $L^{\#}$ is the statistical factor, Q_1^+ and Q_1 are the partition functions for the adiabatic rotations in the complex and the molecule, respectively, $P(E_{vr}^+)$ is the sum of the numbers of vibrational-rotational quantum states of the activated complex at all the energy levels of energy less than or equal to E^+ and $N^*(E^*)$ is the density of quantum states of the energized molecule at energy E^* .

The collisional transition probabilities were computed using the step-ladder model, where the down-transition element P_{ij} , from state i to j , are defined as follows¹⁷⁻¹⁹:

$$\begin{aligned} P_{ij} &= 1.0 - P_{ij} & \text{for } i - j = \langle \Delta E \rangle_d \\ P_{ij} &= 0 & \text{for } i - j / \langle \Delta E \rangle_d \end{aligned}$$

$\langle \Delta E_d \rangle$ is the mean down-energy loss. The up transitions were calculated from detailed balance:

$$P_{ij}/P_{ji} = (g_j/g_i) \exp(-(E_i - E_j)/kT)$$

g_i and E_i are the degeneracies and energies of the i^{th} element. As usual, the condition $\sum_i P_{ij} = 1.0$ was imposed on the transition probability matrix column by column.

The distribution function of the chemical activated system was derived from the expression²⁰:

$$f(E) \delta E = \frac{k_a'(E) K(E) \delta E}{\int_{E_m}^{\infty} k_a'(E) K(E) dE}$$

which is obtained using the principle of detailed balance applied to the reverse process of reforming CH_2 and TFC from MTFC* with a rate constant $k_a'(E)$. It is assumed that all the species are in thermal equilibrium and that the fraction of molecules with energy between E and $E + \delta E$ is the Boltzmann equilibrium population $K(E) \delta E$.

Calculated results for the unimolecular paths

The calculations were performed using a VAX 8810 (Núcleo de Computação Eletrônica of the UFRJ) and FORTRAN programs.

Normal mode frequencies for the molecule which are needed for the evaluation of $N^*(E^*)$, have not been reported in the literature, so they were estimated from the assignments for 1,1,2,2-tetrafluorocyclopropane²¹ and propene²². Several models were constructed for the activated complexes of the isomerization, decomposition and reverse reaction. The entropy of activation was calculated using the vibrational frequencies for each model. Then, from this value and the statistical factor, the preexponential factor for each via was computed. In order to reduce the time of computation, seven groups of degenerated frequencies were artificially constructed. This method have proved to be very good and accurate enough¹².

The sum and density of quantum states were calculated by exact count up to 20 kcal/mol and then by direct inversion of the partition function²³. In most calculations a step-size of integration of 1 kcal/mol was used. Some calculation were performed with a graining of 0.25 kcal/mol, and by couting exactly the vibrational states up to the maximum energy. No noticeable differences were found.

The statistical factors were calculated by numbering the atoms and counting the equivalent but distinct complexes for each via of reaction and the Q_i^+/Q_i ratio was arbitrary set as unity¹³. In fact, the value calculated from the inertia moments of the molecule and the assumed activated complexes, was not so far different from unity.

In this kind of calculation the needed parameters are the critical energies and preexponential factors for unimolecular reactions, the minimum energy of the energization, (E_m),

and the mean energy loss for deactivating collisions. In well characterized systems, the only unknown is $\langle \Delta E \rangle_d$ and an adequate use of the theory and the experimental results, permits to obtain this value for different bath gases. If E_m is also unknown, a careful computation can provide both values within reasonable limits²⁴. As has just been discussed, for the present system, the Arrhenius parameters for the isomerization reaction have not been obtained and the parameters for the decomposition via have only been estimated with a considerable error³. Since the main aim of this work is determining these parameters, a different approach was adopted.

The $\langle \Delta E \rangle_d$ value can be reasonable estimated in 6 ± 2 kcal/mol (See Figure 6 of Reference 7). The relation between the mean energy loss for deactivating collisions and the complexity of the activated molecule, was first proposed by Carr²⁵ on the basis of the data for many chemical activation systems and latter was extended and re-discussed for a variety of systems, including the results of direct techniques for azulene, toluene, substituted cycloheptatrienes and substituted cyclopropanes⁷.

The E_m value can be estimated from the heat of formation of $\text{CH}_2(^1\text{A}_1)$, 101 ± 1 kcal/mol²⁴, and the difference of -7 kcal/mol between the heats of formation of 1-methyl-2,2,3,3-tetrafluorocyclopropane and 1,1,2,2-tetrafluorocyclopropane calculated from group additivity rules²⁶.

$$\Delta H^0 f_0(\text{MTFC}) - \Delta H^0 f_0(\text{TFC}) = \Delta H^0 f_0(\text{CH}_2(^1\text{A}_1)) - E_m$$

In this manner E_m can be estimated as 108 kcal/mol, with an error which depends on the uncertainty in the heat of formation of the $\text{CH}_2(^1\text{A}_1)$ and the uncertainty in the -7 kcal/mol value. This last error is inknown, but should be about ± 4 kcal/mol. That means that E_m can be reasonably estimated as 108 ± 5 kcal/mol. These figures were used, in combination with the values of critical energy and entropy of activation obtained from the aroximately Arrhenius parameters, as the initial set of parameters. Then, iterative calculations were made in order to obtain the best fit to the experimental data and in such manner get a reasonable estimation of the kinetic parameters for both vias of reaction.

From the experimental high pressure rate constants³, $k^\infty_1 = 4.85 \cdot 10^8 \text{ s}^{-1}$ and $k^\infty_D = 1.52 \cdot 10^9 \text{ s}^{-1}$, the isomerization path can be neglected, in a first approximation, in order to obtain a rough estimation of the other parameters. So, some exploratory calculations were initially performed setting the rate constant for the insomerization path to zero and varying E_m between 98 and 114 kcal/mol, $\langle \Delta E \rangle_d$ between 5 and 13 kcal/mol, E_D^0 between 43 and 48 kcal/mol and $\log A_D$ between 13.0 and 15.0, that is, all the parameters were varied beyond their limits of uncertainty. Because of the need of checking the sensitivity of the results to the choice of the parameters, about 120 calculations were carried out. By this method, it is not determined a unique transition state, since different models may reproduce the frequency factor A_D and activation energy E_D . Nevertheless, RRKM rate constants are not particularly sensitive to the choice of vibrational frequencies and moments of inertia, as long as the critical energy is used in agreement with the activation energy and $\Delta S^\#$ agrees with the A factor.

The $\log A_D = 13.0$ and $\log A_D = 15.0$ values can be reproduced using the same high vibrational frequencies, while

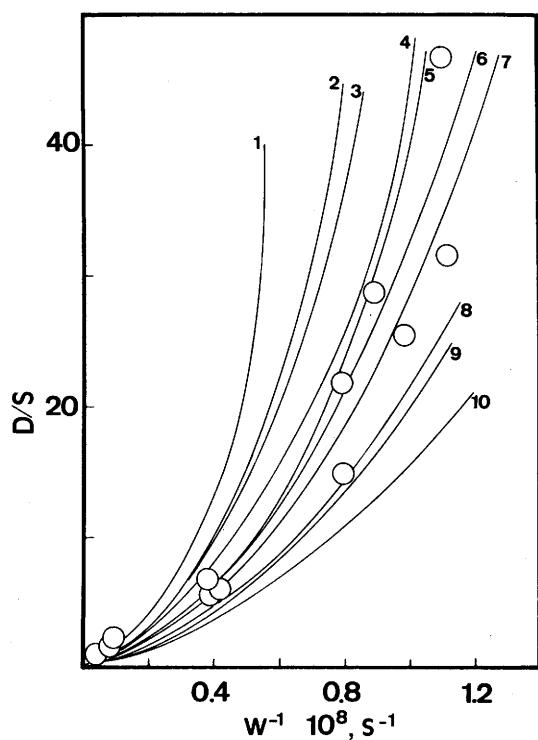


Figure 2. Comparision of experimental data for the decomposition via with RRKM calculations, using different sets of parameters and setting the isomerization constant equal to zero. Energy values are in kcal/mol.

Curve	E_m	$\langle \Delta E \rangle_d$	E_D^0	$\log A_D (s^{-1})$
1	104	5	44	13.2
2	108	6	46	13.2
3	105	8	46	13.6
4	108	10	44	13.2
5	105	6	45	13.2
6	110	8	46	13.2
7	104	8	44	13.2
8	105	8	46	13.4
9	111	8	46	13.0
10	110	8	46	13.0

choosing different values for the frequencies equal or lower than 500 cm^{-1} . If all these "low frequencies" are added, the sum $\sum v_i$ is nearly 25% lower for the $\log A_D = 15.0$ value. The uncertainty of the estimated value 13.1 ± 0.3 , correspond to error of $\pm 33\%$ in the three lower frequencies (375 cm^{-1}).

It was assumed that there were no active rotations. Also, some calculations were made considering the internal rotations of the methyl group. This approach, as well as other improvements for the calculations, were finally not considered because the considerable scattering of the chemical activation data used for comparision. Each of the calculations gives the D/S values for all the collision frequency interval. It was found that the results can be fitted with $E_D^0 = 46 \pm 2 \text{ kcal/mol}$, $\log A_D/s^{-1} = 13.1 \pm 0.3$ using the previous selected values: $E_m = 108 \pm 5 \text{ kcal/mol}$ and $\langle \Delta E \rangle_d = 6 \pm 2 \text{ kcal/mol}$. Some of the results are shown in Figures 2 and 3.

Then, several computations were performed using these selected values and with different pairs of E_D^0 and A_I for the

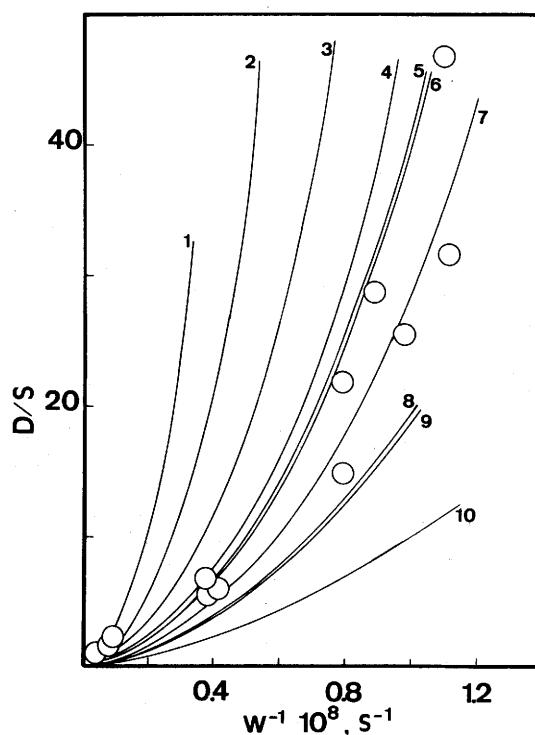


Figure 3. Comparision of experimental data for the decomposition via with RRKM calculations, with the rate constant for the isomerization path equal to zero, $E_m = 108 \text{ kcal/mol}$ and $\langle \Delta E \rangle_d = 6 \text{ kcal/mol}$.

Curve	$E_D^0, \text{kcal/mol}$	$\log A_D(s^{-1})$
1	43	13.2
2	43	13.0
3	45	13.2
4	47	13.4
5	46	13.2
6	45	13.0
7	46	13.1
8	47	13.2
9	46	13.0
10	47	13.0

isomerization reaction. The D/S ratios were as expected, the same as those calculated considering only one reaction path, at least within the significant figures of our calculations.

A first adjustment was made by evaluating the D/I ratio for different pairs of E_m and $\langle \Delta E \rangle_d$. It was found that the difference between the critical energies of the decomposition and isomerization path is $(E_D^0 - E_I^0) = -7.5 \pm 2.0 \text{ kcal/mol}$ and the A_D/A_I ratio is 0.20 ± 0.15 , for any value of E_m and $\langle \Delta E \rangle_d$, and also for any reasonable value for the kinetic parameters for the decomposition via.

Then the experimental results I/S in function of the collisional frequency were adjusted to found the best values, using the selected ones for E_m , $\langle \Delta E \rangle_d$ and E_D^0 , that is 108, 6 and 46 kcal/mol, respectively, and $\log A_D = 13.1$. Nearly 60 calculations were done, giving $E_I^0 = 54 \pm 2 \text{ kcal/mol}$ and $\log A_I = 13.8 \pm 0.3$ (see Figure 4).

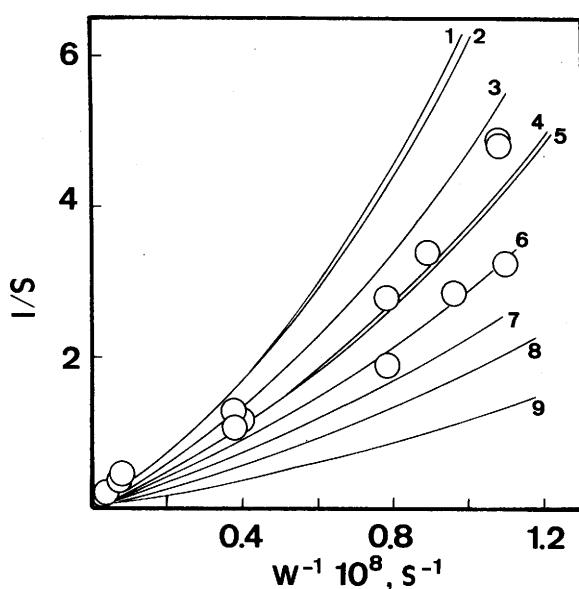


Figure 4. Comparison of the experimental data for the isomerization via with RRKM calculations, using $E_m = 108$ kcal/mol, $\langle \Delta E \rangle_d = 6$ kcal/mol, $E^o_D = 46$ kcal/mol and $\log A_D = 13.1$.

Curve	$E^0, \text{kcal/mol}$	$\log A_I(\text{s}^{-1})$
1	54	14.02
2	53	13.80
3	53	13.75
4	55	14.02
5	54	13.80
6	53	13.70
7	55	13.90
8	56	13.75
9	55	13.80
7	54	13.70
8	56	13.90
9	56	13.75

This uncertainty in the A_I factor means and uncertainty of $\pm 10\%$ in the lower frequencies of the isomerization complex (250 cm^{-1}).

Calculation of bimolecular constants

The RRKM theory has been applied in ways that go beyond the scope of unimolecular reactions.

Here, we use the results of RRKM theory to estimate the rate constants for the insertion and the addition of CH_2 to hydrocarbons.

The chemical activated species (MTFC*) is formed and stabilized through the mechanism:

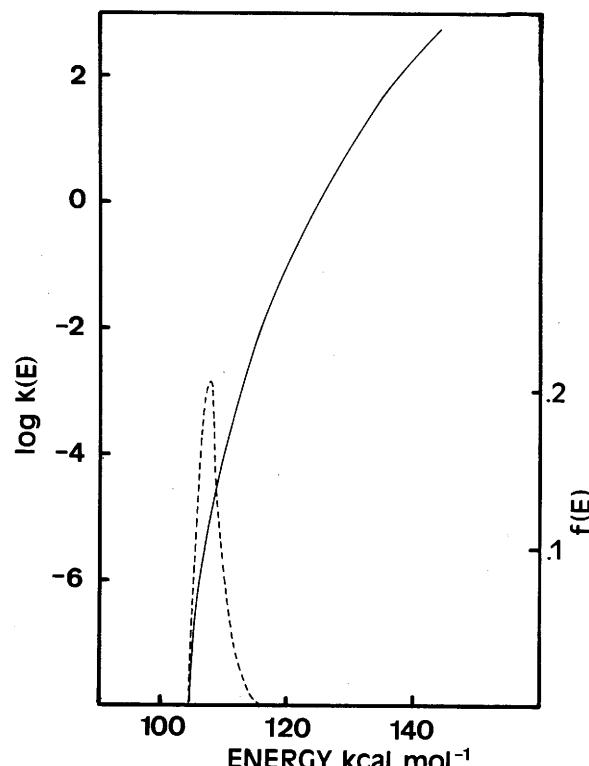
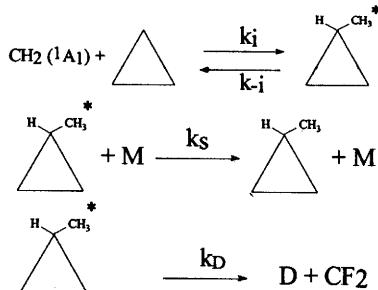
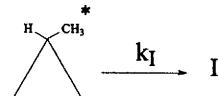


Figure 5. Energy distribution function of chemically activated MTFC and microcanonical rate constant (s^{-1}) for decomposition to TFC + CH_2 . The calculations were performed considering $E^o = 104$ kcal/mol

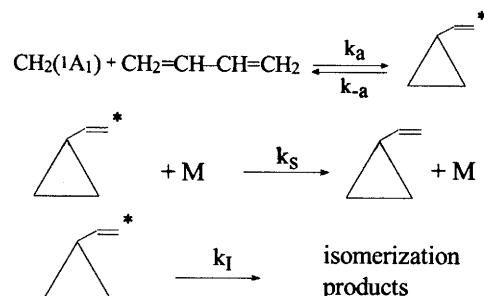


where D stands for the decomposition product and I for the isomerization product.

In this mechanism, a quasi-equilibrium is assumed to exist between the reactants and the activated molecule. This approach is similar to that of the atom-atom scattering theory developed by Smith²⁷ and that of the atom-molecule recombination theory of Bowman²⁸. From this mechanism the quasi-equilibrium constant can be calculated from the partition functions of the reactants and the activated MTFC²⁹.

$$K_I(T) = Q^*(T)/Q_{\text{react}}(T)$$

Similarly for an addition reaction such as the formation of vinylcyclopropane (VCP) the following mechanism can be proposed^{30,31}.



and also a quasi-equilibrium constant can be calculated:

Table 1. Summary of molecular and transition state models for the unimolecular reactions of MTFC. The values given for the activated complexes are the ones for the preferred models.

	Molecule	Transition	Transition
		state (decomposition)	state (isomerization)
Vibrational frequencies (degeneracies), cm^{-1}	3009 (4) 1421 (5) 1226 (3) 969 (5) 685 (3) 494 (5) 226 (5)	3009 (4) 1421 (5) 931 (5) 647 (4) 500 (5) 410 (3) 375 (3)	2973 (3) 1521 (4) 1336 (4) 1018 (6) 683 (4) 499 (5) 250 (5)
calculated preexponential factors, s^{-1}		$1.26 \cdot 10^{13}$	$6.31 \cdot 10^{13}$
calculated critical energy, kcal/mol		46 ± 2	54 ± 2
I^*/I^*		1	1
σ		2	2
collisional diameter, S_{AM} , Å		5.5576	
collision number, k_M , $\text{s}^{-1} \text{Torr}^{-1}$		1.014 $\cdot 10^7$	

$$K_a(T) = Q^*(T)/Q_{\text{reac}}(T)$$

If the quasi-equilibrium constants are computed as well as the unimolecular decomposition constants, k_i and k_a , for the activated molecules, the bimolecular constants k_i and

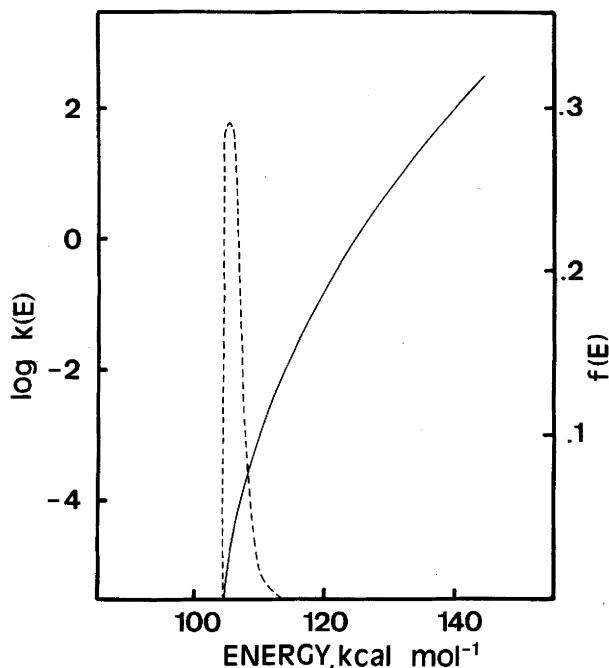


Figure 6. Energy distribution function of chemically activated VCP and microcanonical constant (s^{-1}) for decomposition to butadiene + CH_2 . The calculations were performed considering $E^{\circ} = 104 \text{ kcal/mol}$.

k_a can be calculated. In spite of that, the error in the absolute value of the bimolecular constants may be considerably high due to the parameterization needed for the calculation of the unimolecular rate constants (see below) and the uncertainties in the computation of the partition functions. Also, as was suggested by the referee, the validity of the quasi-equilibrium assumption may be questionable. The reagents are in their fundamental states with a Boltzmann distribution of energy, and the MTFC and VCP molecules are vibrationally excited with a distribution function similar to the $P(E)$ shifted along the energy axis by E_m . However, if the ratio k_i/k_a is calculated these errors are cancelled in part, and a reasonable value is obtained. Anyway, this value should be considered as a rude estimation of the true one.

Calculated results for the bimolecular rate constants.

The k_i/k_a ratio was computed from the relation:

$$k_i/k_a = \{K_i(T)k_i\}/\{K_a(T)k_a\}$$

The unimolecular rate constants were computed using the RRKM theory and the same equations and programs as in the previous sections. For the insertion via the same activated complex as in the previous calculations was assumed. For the addition reaction, the vibrational frequencies using in the modelling of References 30 and 31 for the chemical activation study of vinylcyclopropane, were adopted (Table 2). The microcanonical rate constants as well as the energy distribution functions, $f(E)$, are shown in Figures 5 and 6. The mean constants were obtained by averaging over the $f(E)$ for each system.

Calculations for MTFC were done for different critical energies in the range $108 \pm 5 \text{ kcal/mol}$. Here the results for 104 kcal/mol, which is in the range of uncertainty of E_m , are shown, for a better comparison with the results for VCP.

Partition functions were calculated as usual²⁴. Spectroscopic data needed for the computation were taken from the bibliography^{21,22,30,32-34}.

Table 2. Parameters used for the RRKM calculation of the rate constants k_i and k_a for the inverse processes of insertion and addition.

Vibrational frequencies (degeneracies), cm^{-1} for insertion reaction	MTFC	transition state
	3009 (4)	3048 (3)
	1421 (5)	1441 (5)
	1226 (3)	1273 (3)
	969 (5)	1002 (5)
	685 (3)	750 (3)
	494 (5)	457 (4)
	226 (5)	223 (6)
for addition reaction	VCP	transition state
	3050 (8)	3048 (7)
	1417 (6)	1441 (6)
	1000 (11)	1100 (11)
	750 (4)	800 (4)
	425 (1)	500 (1)
	310 (2)	350 (2)
	80 (1)	200 (1)A
critical energy for reaction, kcal/mol	insertion	addition
	108 ± 5	104 ± 2
mean constants for inverse reaction, s^{-1}	$1.46 \cdot 10^{-4}$	$1.49 \cdot 10^{-4}$
K_i/K_a		0.138

In this manner the ratio k_i/k_a was calculated as 0.17 per bond, considering the indistinguishable sites of addition and insertion and critical energies for reaction of 104 kcal/mol. If a critical energy of 108 kcal/mol is considered for the inverse of the insertion reaction, the k_i/k_a is about 0.10.

Discussion

The experimental evidence of a structural isomerization path, in addition to the decomposition via³, seems particularly relevant since the occurrence of both processes in gem-difluorocyclopropanes has only been observed in MTFC and 1,1-difluorocyclopropane³⁵. Nevertheless, the chemical activation results were not able to provide direct information about the kinetic parameters for both vias of reaction. As was just been discussed, most of the chemical activation works deal with the calculation of the mean energy loss by collision, $\langle \Delta E \rangle_d$ and the characterization of the collisional energy transfer process²⁴. In all these systems the Arrhenius parameters for reaction are known, and can be used in computing the RRKM rate constants. In this manner, the experimental results, which are always obtained as the ratio decomposition (or isomerization)/stabilization, are compared with the computed values for which the only unknown is $\langle \Delta E \rangle_d$, which is used as an adjustable parameter.

For the present system, due to the lack of thermochemical data, only a phenomenological characterization could be done and the usual approachment for the calculation of E_m and $\langle \Delta E \rangle_d$ could not be realized³. In the present work the experimental date were re-analyzed and the RRKM theory together with the stepladder model for collisional deactivation, was used to estimate the kinetic parameters.

The usual unknowns, $\langle \Delta E \rangle_d$ and E_m , were obtained from the knowledge of many chemical activation systems, which seems to behave in a previsible way. The adopted value of $\langle \Delta E \rangle_d$ is undoubtedly good since the correlation of Carr²⁵ has proved to be followed by a variety of systems. The value for E_m is subject to the pertinence of extending the use of Benson's rules²⁶ for this type of compounds and then using the difference of -7 kcal/mol obtained for cyclic hydrocarbons. In the estimation of the heats of formation of cyclic hydrocarbons, the agreement with experimental is generally in the range ± 0.5 kcal/mol. Both experimental and theoretical calculations give a difference of -7 kcal/mol for cyclobutane, cyclopentane, cyclohexane and the corresponding methyl-compounds. With halogen-containing compounds the experimental data are somewhat sparse and conformational corrections differ from those applicable to hydrocarbons. Nevertheless, in general the calculated ΔH_f agree to ± 2 kcal/mol with the experimental value. In addition, we only need, for present purpose the difference between the heat of formation of MTFC and TFC and so is quite probably that the difference is within -7 ± 4 kcal/mol.

The critical energies and pre-exponential A factors calculated in this way are a reasonable estimation of these values, which can not be experimentally obtained. The fact that A factors are relatively small could be an evidence for postulating that the transition states are cyclic. These processes if occur in a concerted mechanism also explain the relatively low energy of activation compared with unfluorinated cyclopropanes.

The difference between the critical energies for both vias of reaction can be determined with reasonable confidence as 8 ± 4 kcal/mol. This difference is high enough to explain why the structural isomerization path way, which takes

place in competition with the decomposition reaction, can not be observed in a conventional thermal study. With the parameters of Table 1, it can be calculated that at 500 K the isomerization would represent less than 0.5% of the total, while at 700 K it would be $\approx 13\%$. However, at this temperature the reaction would be too fast to be studied by conventional methods³. In the chemical activation system the distribution function has its maximum at approximately 57 kcal/mol above the critical energy for isomerization.

Finally, the calculated insertion/addition ratio is in good agreement with the conventional experimental value for hydrocarbons of 0.12⁸. It also confirms the hypothesis proposed by Boaglio *et al.*⁷, who obtained a value of 1.7 by extrapolation of the chemical activation results for a system which presents non-RRKM behavior at high pressures. Clearly, this new calculated value demonstrates that, as it was just claimed, the discrepancy found in Reference 7 is due to experimental error because of the impossibility of reaching the true high-pressure region.

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