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Crossed Molecular Beam Studies and Dynamics of

Decomposition of Chemically Activated Radicals

Introduction

The power of the crossed molecular beams method in the investigation of the
dynamics of chemical reactions lies mainly in the direct observation of the consequences
of single collisions of well controlled reactant molecules. The primary experimental
observations which provide information on reaction dynamics are the measurements of
angular and velocity distributions of reaction products. Recently, the improved
sophistication of experimental methods has allowed investigators to further analysis of
product rotational[1] and vibrational[2,3] state distributions by various methods, and to study
the effect of orientation of reactant molecules.[4,5] Most of the crossed molecular beams
studies of chemical reactions reported so far, however, including the recent studies of
methyl radicals with halogen molecules,[6,7] are rather primitive, typically, two
effusive beams with Maxwell–Boltzmann velocity distribution has been crossed and the
laboratory angular distribution measurements are the only experimental data avaliable.
The number of experiments which have used velocity selected molecular beams and for
which measurements of both angular and velocity distributions have been carried out[8,9]
is relatively small. Very often, the selection of the velocity of reactant atoms or
molecules is sacrificed in order to obtain higher product intensity. The results of
these primitive experiments which forego velocity selection of reactant molecules are
sometimes very useful in obtaining qualitative information. For example, in the
classic study of the $K + CH_3I$ reaction,[10] the rebound mechanism was deduced from the
analysis of the laboratory angular distribution, and more recently the experiments of
methyl radicals with halogen molecules have shown the similarity of these reactions to
those of hydrogen atoms with halogen molecules.[6,7] When detailed information on reac-
tion dynamics is suggested from these primitive experiments by fitting experimental
angular distributions with assumed angular and velocity distributions in the center-of-
mass coordinate system, one should receive these conclusions with great caution. If
the velocity spread of the beams is wide, the distributions of both the magnitude and

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orientation of the relative velocity vector are

ditions, especially, the relative motions are ι

divergences of both beams are small.   Conseq

or product angular and velocity distributions l

relative velocity, it is almost impossible to d(

dynamics just from a laboratory angular distril

tion does not depend on relative velocity of r

of the reaction is much larger than the spread

information obtained from the additional anal

could be quite reliable.   However, when an (

cross section is expected, because of an acti\

the experiment with velocity selected molecu

velocities are analyzed in great detail, relial

difficult to derive.   Future investigations of r

emphasis on selection of velocities of reactan

Although the use of the molecular be(

of radicals is still very limited, it is expectec

technology should enable us to investigate m(

near future.   The studies of reactions with po

reactants are still in the primitive stage, but

decomposition of chemically activated radica

in recent years. [11,12,9a,b,c]   Our following discussion wi

The chemical activation method has b

investigation of unimolecular decompositions. [1]

in the fact that radicals formed by the additic

excitation energies.   The information on effi(

energy transfers are derived from the ratios ol

various experimental conditions.   The study o

and molecules by the method of crossed mole(

the conventional chemical activation method.

velocities of the colliding atoms and molecul

complex can be defined to better than 1 kcal,

periment one observes the consequences of sir

significant and experimental con-

ll defined even if the angular

if the reaction cross sections

n appreciable dependence on

'correct" information on reaction

alone.   If the reaction cross sec-

it molecules and if the exoergicity

relative kinetic energies, the

velocities of product molecules

iable energy dependence of the

energy, it is necessary to perform

ams; otherwise, even if product

ormation on reaction dynamics is

n dynamics should place more

ns whenever possible.

hod in the investigation of chemistry

the progress of molecular beam

ementary reactions of radicals in the

ic radicals such as CH_3 and C_2H_5 as

s of radical reactions, namely, the

s been investigated rather extensively

imited to this type of reaction.

ied extensively and fruitfully in the

advantage of this method lies mainly

itoms to molecules have well defined

es of intra-and intermolecular

lization and decomposition under

lecular addition reactions of atoms

eams has several advantages over

t, by controlling the spread of

total energy of the activated

Second, in a crossed beam ex-

ollisions.   There is no intermolecular

energy transfer after the collision complex is formed, so that the experimentally
observed product angular and velocity distributions and the relative reaction rates
for competing decomposition channels can only reflect the efficiency of intra-
molecular energy transfer prior to decomposition of the activated complex.

Since the C-F bond is stronger than any other single bond with a carbon atoms,
it is expected that fluoro-olefin complexes formed by addition of fluorine atoms to
olefin molecules in single collisions should have sufficient excitation energy to break
C-C, C-H or C-halogen bonds. An energy diagram of various decomposition channels
for substitution reactions of F atoms is illustrated in Fig. 1,
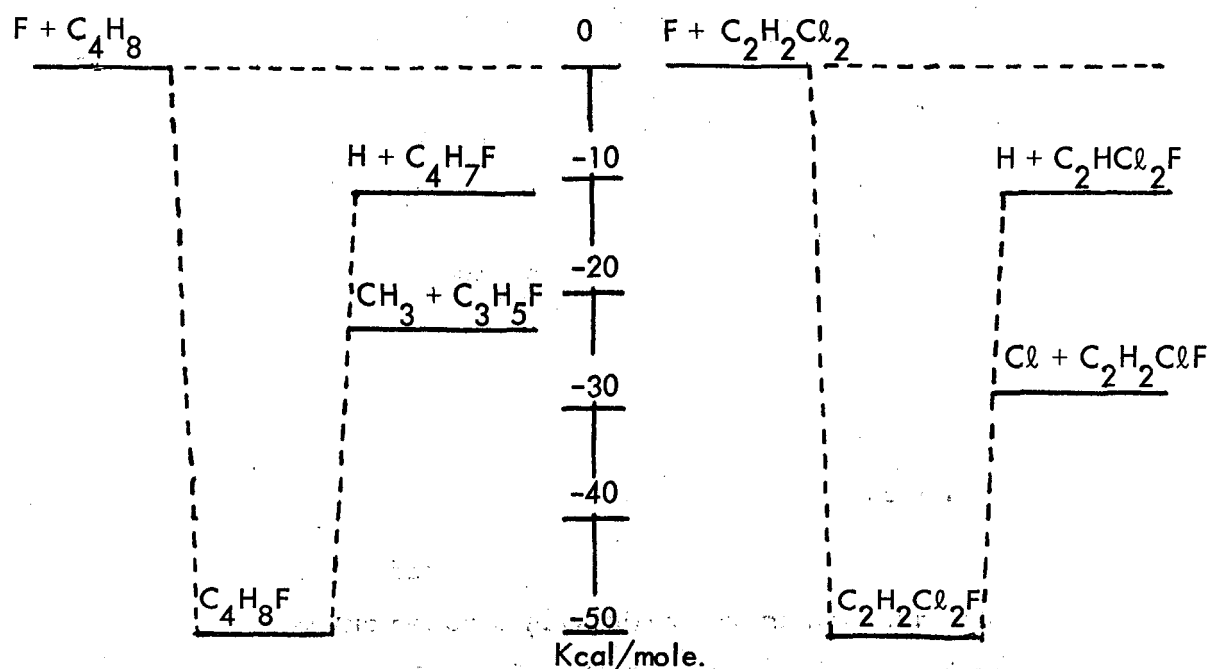
Fig. 1. Schematic energy diagrams of $F + C_4H_8$ and $F + C_2H_2Cl_2$.

By systematically selecting more than thirty different olefin molecules, we have in-
vestigated the velocity and angular distributions of product molecules, the competition
between different channels and their relation to the location of initial activation. In
addition to our studies with fluorine atoms, the reactions of Cl with several brominated
olefins have been studied by Herschbach and co-workers at Harvard University.[10]

Experimental Arrangement

A schematic diagram of a typical experimental arrangement is shown in Fig. 2.

Fig. 2.   Top view of beam arrang

F atoms were produced by thermal dissociatior

velocity selected to 20% full width at half ma

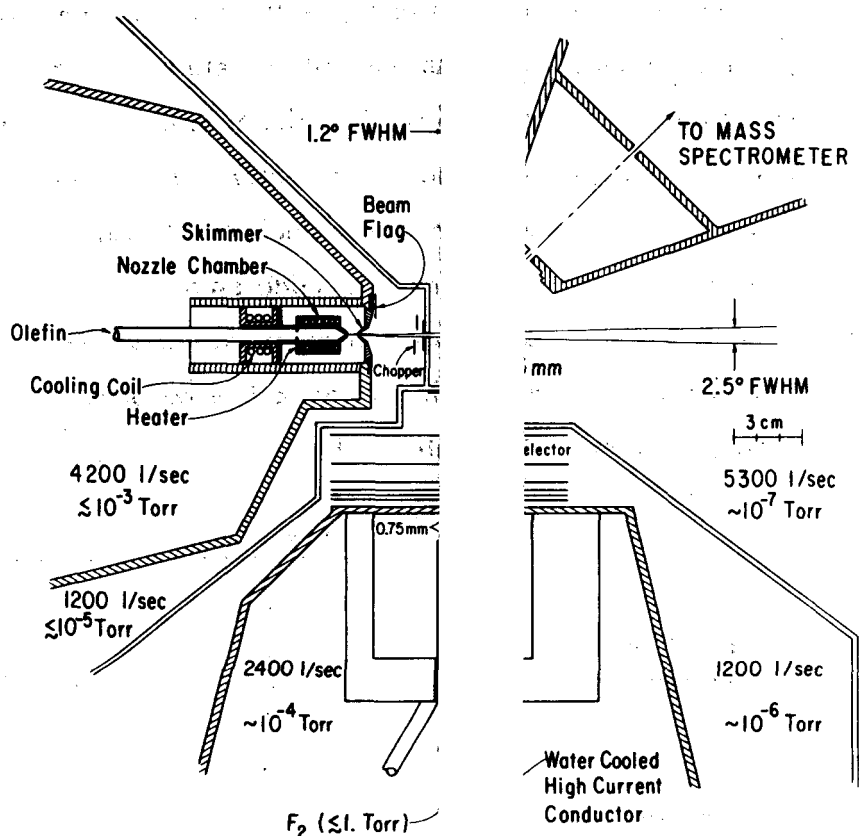molecules were formed into a supersonic beam

source pressures in the range 400–700 Torr bef

distribution of the olefin molecules has a typi

maximum.   The peak velocities were always f

indicating that some of the vibrational degree

tional degrees of freedom, have relaxed durin

were collimated to 1.2 and 2.5° for F and the

tions of products were measured with a rotatab

detector, and other details of the experimentc

where.[9a,12] The velocity distributions of product i

flight method with a resolution of approximate

of-flight data were controlled by a minicompu

0°C, formed into a beam, and

by a slotted disk selector.   Olefin

w from a free jet source using

0.1 mm diameter nozzle.   The velocity

ige of ~15–20% full width at half

o be slightly larger than $(8kT/m)^{1/2}$

eedom, in addition to all the rota-

isentropic expansion.   The beams

ns respectively.   The angular distribu-

ss spectrometer detector.   This

ngement, have been described else-

les were measured by a time-of-

6; collection and processing of time-

Experimental Results[9 a, b, c, 12]

Some interesting features of the experimental results will be described below:

1. $F + C_2H_4 \rightarrow C_2H_3F + H$
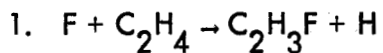
The contour map of the center-of-mass flux density distribution of C_2H_3F derived from laboratory angular and velocity distribution measurements is shown in Fig. 3.

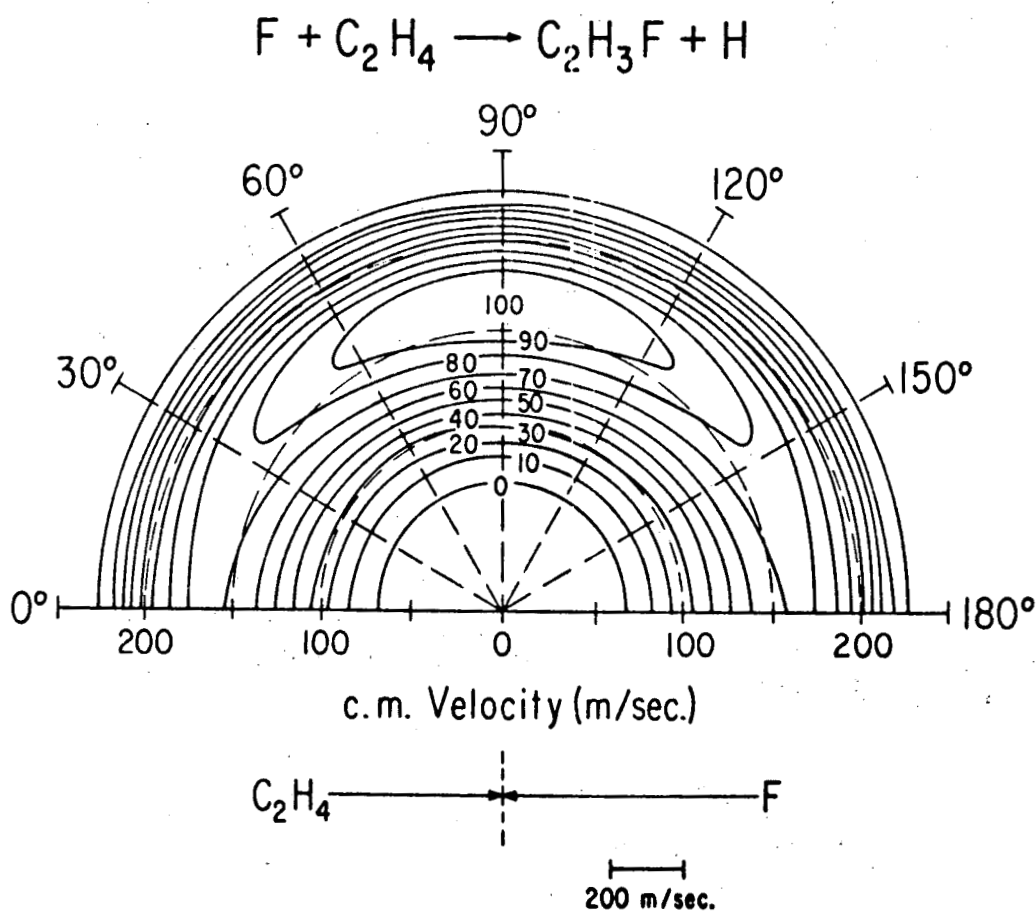Fig. 3.   Contour map of C_2H_3F flux density distribution in the center-of-mass system of coordinates produced in the reaction $F + C_2H_4$. These contours are obtained by fitting the laboratory angular and velocity distributions.

The symmetry of the angular distribution of product molecules with respect to 90° in the center-of-mass coordinate indicates that the lifetime of the fluoro-ethylene

complex is much longer than the rotational pe   ·f the complex. The angular distribu-

tion of product molecules is almost isotropic,   ie slight sideways peaking is very

interesting; it reveals the nature of the poten·   iergy surface and the role played by

the conservation of angular momentum. The i   nism for causing sideways peaking
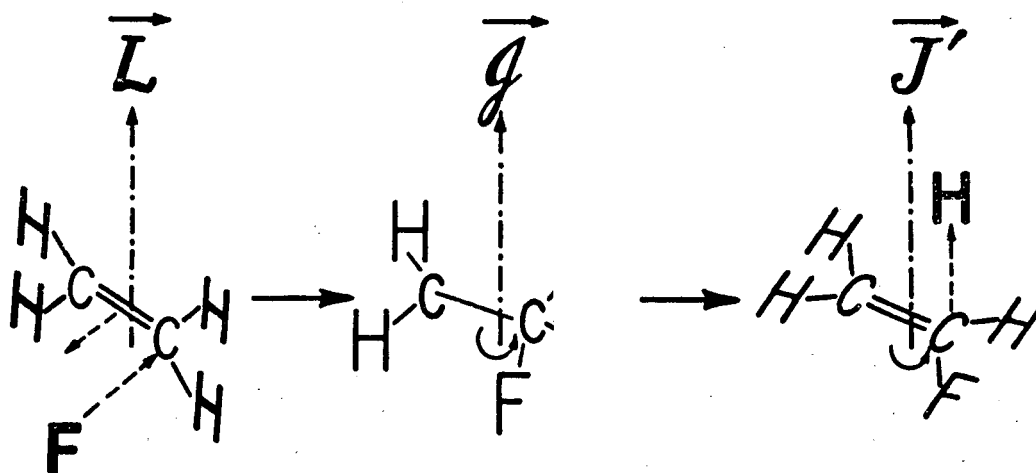
is portrayed in Fig. 4.

Fig. 4. Mechanism of F + C_2H_4
relation between the angular moi
of the product separation.

$\cdot_3$F + H reaction illustrating the
n and the preferred orientation

If a fluorine atom must approach a C_2H_4 molϵ approximately perpendicular to the

plane of the molecule in order to form the C_2 omplex, and since the angular momentum

$\underset{\sim}{J}$ of C_2H_4 is very small because of nearly cor   rotational relaxation during isentropic

expansion in the formation of the supersonic (beam, the average rotational angular

momentum $\underset{\sim}{L}$ is much larger than $\underset{\sim}{J}$ and the tl   eavy atoms in C_2H_4F wil' rotate in a

plane roughly perpendicular to $\underset{\sim}{L}$. If the tran   state for hydrogen atom emission has a

geometry with the CH bond considerably exte   then the rest of the molecule will be

relaxed to an almost planar geometry. Conse   ly, the hydrogen atom must leave the

complex perpendicular to the plane determinϵ the C-C-F arrangement, and the final

relative velocity $\underset{\sim}{V}'$ will be approximately parallel or antiparallel to $\underset{\sim}{L}$ and thus perpendicular to initial relative velocity vector $\underset{\sim}{V}$. Most of the initial orbital angular momentum will then remain as product angular momentum of C_2H_3F.

2. Translational energies of product molecules.

The fractions of total energy appearing in translational motion of the product molecules varies considerably for different channels. When H atoms or CH_3 radicals are replaced by F atoms, ~40-50% of the total energy available appears as translational motion; on the other hand, when $C\ell$ atoms are replaced by F atoms by breaking C-Cℓ bonds, only ~10-15% of the energy is in translation. Appearance of the large fraction of energy in translational motion in H and CH_3 emission reactions seem surprising in view of the large number of internal degrees of freedom available in the long-lived fluoro-olefin complex studied. But this large translational energy release actually reflects the nature of the potential energy hypersurface of bond breakage. It is well known that the reverse reactions, namely, the additions of $C\ell$, H and CH_3 to olefins, have activation energies of 0, 2~3 and 6~8 kcal/mole, because of the differences in the potential energy barriers. The same potential energy barriers also have to be overcome in the processes of decomposition.

When the average translational energies of decomposition are compared with the activation energies of the reverse reactions, we arrive at an interesting conclusion: the potential energy of the barrier with respect to the product molecules seems to be trans-formed mainly into translational motion of the product molecules in the emission of H or CH_3 from activated complexes. The dynamics of decomposition of activated complexes after passing over the barrier seems to be in qualitative agreement with what would be expected from ITFITS half collision model. When the emitting particle is a light particle, most of the potential energy is expected to be transformed into translational motion. Our results also imply that the coupling of motion along the reaction coordinate with other internal degrees of freedom after passing over the potential energy barrier must be quite small in H and CH_3 emissions. In Fig. 5, the translational energy distributions of the reactions $F + C_4H_8 \rightarrow C_3H_5F + CH_3$ and $F + C_2H_2C\ell_2 \rightarrow C_2H_2C\ell F + C\ell$ are shown.
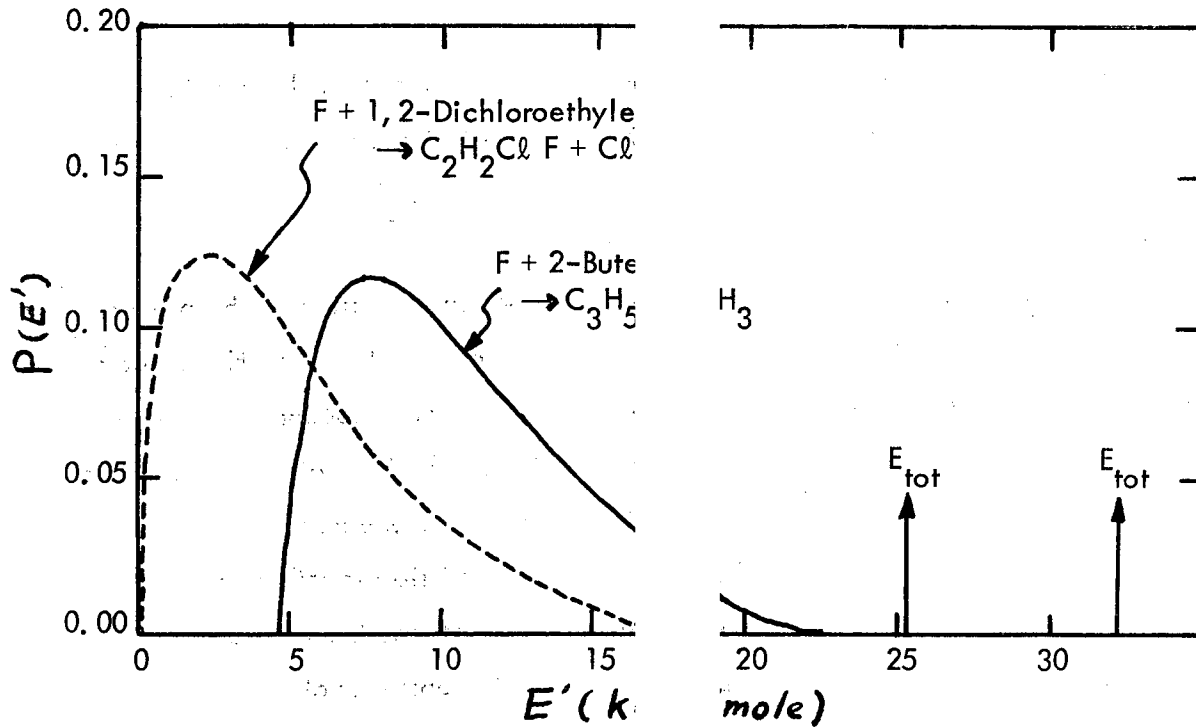
Figure 5. --The translational energy di

$C_3H_5F + CH_3$ and $F + C_2H$

tions of the reactions $F + C_4H_8 \rightarrow$

$\rightarrow C_2H_2ClF + Cl$.

Although substitutions of Cl and CH_3 |
differences in product translational energy dis
formed by the substitution of Cl atoms have av
in comparison with the 17 kcal/mole by substi
differences in internal excitation are mainly c
barriers.

It is also interesting to compare measu
what would be expected from statistical theory
forward, since an additional assumption has to
energy distribution of the product molecules m
$F + C_2H_4 \rightarrow C_2H_3F + H$ is compared with thos
assuming that the interaction between the reac
freedom is negligible and the potential energy
into the translational mode of motion. This as
reasonable for the emission of a light H atom.
calculated by using phase space theory, if act

ave similar exoergicities, marked
on are observed. The fluoro-olefins
internal energies of 27 kcal/mole
of CH_3 group. These significant
by the difference of exit channel

inslational energy distributions with
ese comparisons are not straight-
ide. In Fig. 6, the translational
id in the reaction of
ulated by using phase space theory
oordinate and the internal degrees of
e exit barrier is mainly transformed
on does not seem to be too un-
ranslational energy distributions
brational modes of motion are limited

$$F + C_2H_4 \rightarrow C_2H_3F + H$$

Normalized P (E')

E', Kcal/mole
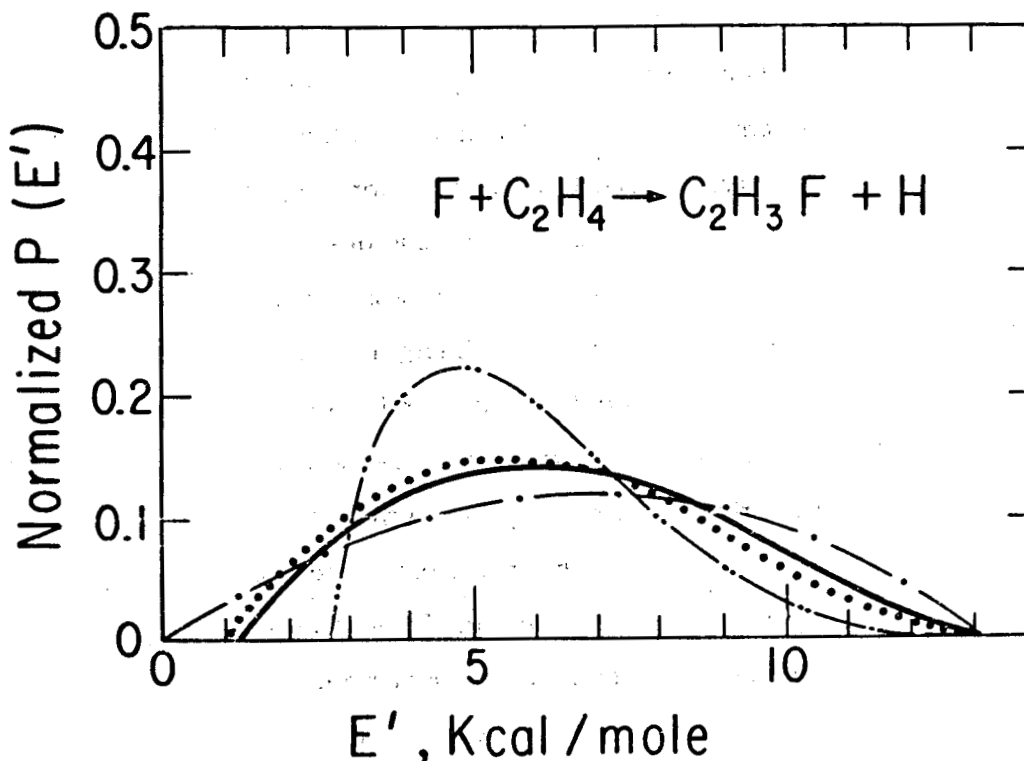
Figure 6. --Product translational energy distributions for the reaction
F + C₂H₄ — C₂H₃F + H ———, Best fit energy distribution obtained
from experimental results; —.—.—.—, Best fit energy distribu-
tion obtained by only fitting laboratory angular distribution assuming
an isotropic angular distribution in the center-of-mass system of
coordinates; ..—..—, energy distribution calculated from 12-
oscillator phase-space theory model; ...., energy distribution cal-
culated from 5 oscillator model. Potential barriers for the product
channel are adjusted, each of the last two calculations to best match
the width of laboratory angular distribution.

to the selected seven, give better agreement with experimental results than when all vi-
brational modes are considered to be active, implying that the rate of decomposition is
faster than the rate of energy randomization in fluoroethylene complexes. For the re-
actions which emit Cl atoms, the translational energy distributions of product molecules
measured are in good agreement with thos calculated by using statistical phase space
theory.

   3. Relative rates for competitive decompositions.

   For almost all of the systems studied so far, if there is more than one decomposi-
tion channel available, the weaker bonds are broken more easily than the stronger bond
just as would be expected from statistical theory of unimolecular decomposition. For re-
actions of a fluorine atom with symmetric molecules such as cis-2-butene, 1,2-
dichloroethylene, and tetramethylethylene, a meaningful comparison for the relative
rates of decomposition between RRKM prediction and experimental results can be made.
In these systems, there is no complication because of possible preferential attachment of

a fluorine atom to a special carbon atom, anc elative rates of decomposition will be a good indication of the extent of energy ization before the decomposition of an activated complex. The relative rates of I itution for CH_3 and H in F + Cis-2- butene and F for Cℓ and H in F + Cis-1,2-dic thylene are 22 to 1 and larger than 540 to 1 respectively. These experimental vc re in reasonable agreement with RRKM predictions in view of the uncertainties energetics of these reactions and the analysis of the experimental results. On her hand, in the reaction of F + tetramethylethylene, the experimentally dete I cross section ratio of F for CH_3 and H is found to be much smaller than that calculat RRKM theory. Of course, the calculated reaction cross sections are depend the estimated exothermicities and exit channel potential barrier, Va. In Fig. 7, ensitivity of cross section ratio $\sigma(CH_3)/\sigma(H)$ to changes in the number of acti rational modes, for two choices of the number of contributing rotations and H-en exit channel potential barrier, is shown.
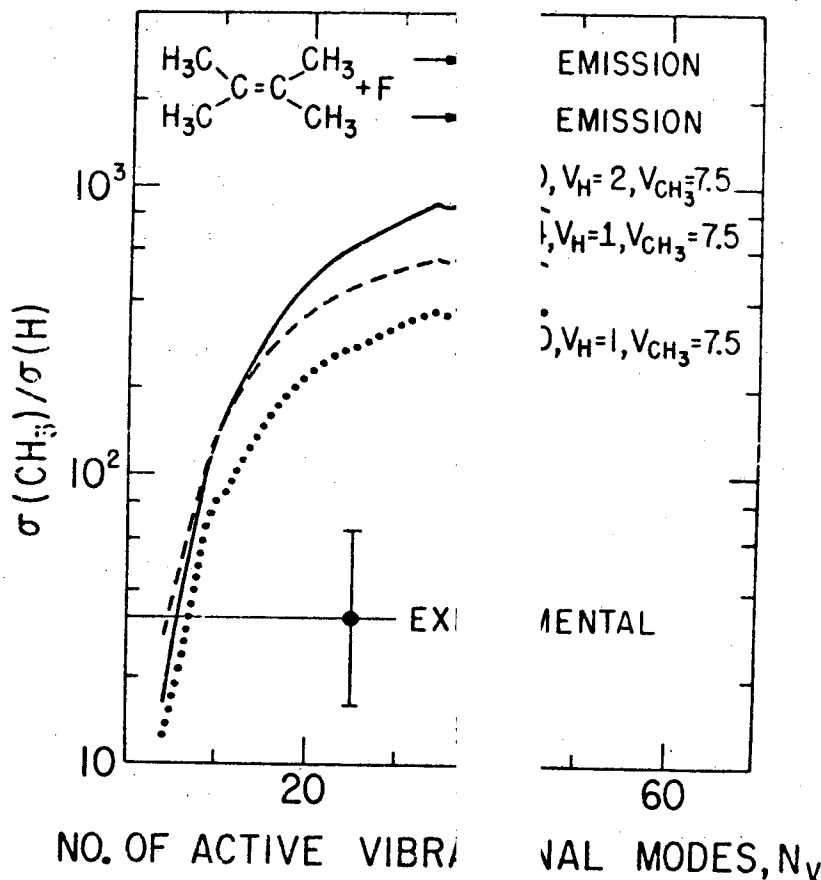

Figure 7. --$\sigma(CH_3)/\sigma(H)$ as a func f number of active vibrational modes in F + tetramethylethylene on calculated by using RRKM theory. Experimental result is al vn for comparison.

In Fig. 8, the systematic dependence of $\sigma(CH_3)/\sigma(H)$ and V_H and V_{CH_3} for two sets of active vibration-rotation modes: (a) Nv = 46, Nv = 4 and (b) Nv = 7, Ñv = 0 are presented.
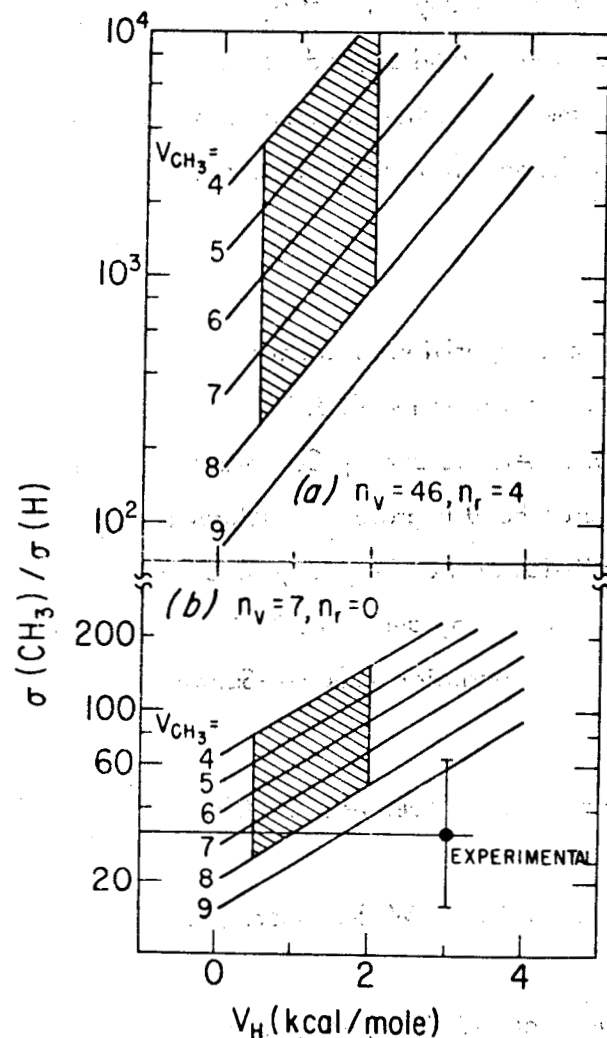
Figure 8. --Dependence of $\sigma(CH_3)/\sigma(H)$ on the magnitude of the exit channel potential barrier in the reaction of F + tetramethylethylene. RRKM theory is used for the calculation (a) 46 vibrations and 4 rotations are assumed to be active. (b) 7 vibrations and no rotations are assumed to be active.

Taking into account the uncertainties in the activation energies for the reverse methyl radical addition to trimethylethylene (V_{CH_3} = 4 ~ 8 kcal/mole; most probable value ~6 kcal/mole) and hydrogen atom addition to tetramethylethylene (V_H = 0.5~2.0 kcal/mole; most probably value ~1 kcal/mole), it is concluded that vibration-rotation set (a) while taking all internal degrees of freedom into account does not lead to an acceptable range of calculated cross section ratios, but the set (b) assuming only a fraction of vibrational modes available at the transition state are active in accepting the available energy in the complex does give acceptable cross section ratios for the case V_H small and V_{CH_3} large.

Concluding Remark

The study of unimolecular decomposi   f chemically activated complexes
discussed above is one of the few radical re(; which have been studied by the
crossed molecular beams method. The dynar   ʼ many interesting and important
radical reactions are yet to be explored. A: method of production of beams of
radicals and the sensitivity of the detection   d further develop, crossed molecular
beams will no doubt provide valuable new ir   tion on radical chemistry in the
near future.

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complexes presented here are the results of c   iration with J. M. Parson, K. Shobatake
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