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THE QUESTION OF ENERGY RANDOMIZATION
IN THE DECOMPOSITION OF CHEMICALLY
ACTIVATED $C_2H_4F^*$

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ABSTRACT

The question of whether energy randomization occurs in the decomposition of chemically activated C_2H_4F is further examined with the crossed molecular beam technique by measuring the collision energy dependence of the C_2H_3F product recoil energy distributions for the reaction $F+C_2H_4$. The effect of the exit channel barrier becomes less important at higher collision energies since the fraction of the total energy associated with the barrier becomes smaller as the collision energy increases. The experimental recoil velocity distributions yield average product translational energies which remain almost constant at ~50% of the total available energy: these results are shown to be inconsistent with phase space theory and the recent "Tight Transition State" theory of Marcus. If the energy is completely randomized and quasi-equilibrium is established between the complex and the transition state, most of the additional energy deposited in activated C_2H_4F at higher collision energies should remain as product internal

excitation. Consequently, a much smaller fraction of the total energy should appear as translational energy. The symmetric angular distributions of product molecules indicate that the lifetime of C_2H_4F remains longer than the rotational period even at higher collision energies. This implies that the features of the kinetic energy distributions observed in this system do not arise from the partial activation of available vibrational degrees of freedom throughout the reaction, but rather, the energy transfer to the reaction coordinate prior to reaching the critical configuration must be slow.

INTRODUCTION

Among the general classifications of gas phase chemical reactions, perhaps the most studied and best understood branch is that of unimolecular decompositions. The Lindemann mechanism,¹ which postulates collisional activation of the reactive species by bath gas molecules followed by decomposition of the activated molecule to products, is quite well accepted and a host of unimolecular decompositions have been demonstrated to obey the general low- and high-pressure behavior implicit in such a mechanism. The emphasis in unimolecular kinetics has generally shifted toward an examination of the dynamics of decomposition of collisionally activated species, that is, determination and interpretation of the k_3 term in the Lindemann mechanism:

The Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular decomposition² addresses itself to the calculation of k_3 and verification of the assumptions in RRKM theory has been a major effort in gas phase chemical kinetics in the past 15 years. The central assumption of RRKM theory, that intramolecular energy transfer in the activated species is rapid on the time scale of chemical reaction, has received considerable support through the studies of Rabinovitch and co-workers³ and Kistiakowsky⁴ as well as other investigators. These tests of RRKM theory involve chemical activation, however, instead of thermal

(collisional) activation of reacting molecules.

Conventional tests of the energy randomization hypothesis in RRKM theory have involved determining the ratio of chemical reaction rate to deactivation of A^* by bath molecules M assuming that $k_2[M] = \omega$, the collision frequency. This assumption states that deactivating collisions occur with unit probability. Many chemical activation³ tests of RRKM theory have suggested that energy randomization in the complex is rapid compared to reaction. A classic example is provided by the experiments of Butler and Kistiakowsky⁴ who prepared activated methylcyclopropane by two distinct processes and found that the composition of butenes to which the activated species decomposed was identical in both cases.

Chemical activation tests of RRKM theory are valuable in the sense that the time scale of a measurement is effectively $1/k_2[M]$, inversely proportional to the deactivating collision frequency and therefore one can determine, as Butler and Kistiakowsky did, if energy randomization has taken place in this characteristic time period. While many experiments indicate that randomization takes place in this time, Rynbrandt and Rabinovitch⁵ have studied the insertion reactions of CH_2 and CD_2 with substituted cyclopropanes and present evidence against energy randomization in this reaction:

Reversal of the deuterium label has also been performed and the experiments demonstrate in both cases that as the pressure increases, the newly formed ring cleaves in preference to the original one; at low pressures, however, both products are formed in equal amounts. In these experiments knowledge of the nature of collisional energy transfer has yielded information on the characteristic time of intramolecular relaxation. Although a study of the nature of intermolecular energy transfer can be quite enlightening, particularly in view of the Lindemann assumption that deactivating collisions must remove very large amounts of energy with high efficiency,⁶⁻⁷ tests of the energy randomization hypothesis, central to nearly all unimolecular decay theories, require information on intramolecular energy transfer prior to deactivation. In recent years, the crossed molecular beam technique has provided valuable information regarding the dynamics of intramolecular energy transfer. This technique has become important in the study of unimolecular chemical dynamics since the discovery by Herschbach and co-workers⁸⁻⁹ that reactions of the type $M + M'X \rightarrow MX + M'$, where M and M' are alkali atoms and X is a halogen, often proceed through a collision complex [MXM'] which lives long compared to a rotational period. One therefore expects that the products of such a chemical reaction should provide information about the dynamics of intramolecular energy transfer in the complex. Statistical theories have been developed⁸ which can correlate these data quite readily.

Although thermal beams are used in these experiments and the internal energy of the complex is defined only within a few kcal mole⁻¹, considerable dynamical information can be obtained. The dynamics of complex formation of these systems are dominated by the centrifugal barrier arising from the strong long range force between the highly dipolar salt molecule and the polarizable alkali atom: the disposal of the total angular momentum as orbital angular momentum leads to center of mass (c.m.) angular distributions which are strongly forward-backward peaked. The single collision conditions of these experiments allow one to study intramolecular energy transfer in the absence of collisional deactivation; more recent work concerning halogen atom addition to unsaturated hydrocarbons has extended the scope of studies on intramolecular energy transfer and improved techniques have allowed for the production of chemically activated radicals with only a 1 kcal mole⁻¹ energy spread.

Herschbach and co-workers¹⁰ have studied the addition of Cl and Br atoms to various olefins, but thermal beams were again employed. As part of a series of studies on the addition of fluorine atoms to olefins and other organic molecules, some 30 systems have been studied in this laboratory¹¹⁻¹⁷ in which the F atom replaces hydrogen, CH₃ or a halogen atom: by employing a velocity selected atomic source, the velocity distribution of the F atoms was reduced to 20% FWHM and use of a free jet molecular beam provides the narrow energy dispersion for producing radicals of well-known energy. The angular and energy distributions of the unimolecular decomposition products of the

chemically activated radicals have provided a wealth of dynamical information and systematic variation of hydrocarbon chain length and substituent placement have led to a somewhat clearer picture of intramolecular energy transfer.

Two of the more completely studied systems are the F + ethylene reaction forming vinyl fluoride¹¹ and F + C₄H₈¹² in which both hydrogen and methyl emission products have been observed. In the former case, comparison with RRKM² and phase space theory¹⁸⁻²⁰ (which provide essentially identical results when angular momentum conservation is considered in RRKM) suggests that the translational energy distributions for C₂H₃F are in accord with theory only if a small number of oscillators in the complex are activated. The implication of this statement is that energy randomization is not rapid compared with chemical reaction: microcanonical equilibrium in the reaction complex is not achieved before fragmentation to products occurs. Similar results are obtained in the translational distributions of product molecules for the F + C₄H₈ case: it is interesting to note, however, that extensive redistribution of the energy must take place before chemical reaction occurs because bonds far removed from the site of initial excitation are observed to break before those at the site of F-atom addition if the remote bond is weaker. In many of the other beam experiments performed in this laboratory involving fluorine atom substitution reactions, the product recoil energies were found to be much higher than the predictions based on exoergicities and the number of vibrational modes. An interesting correlation was found with

average product kinetic energy and exit channel barrier height: the experimental data suggested that the exit channel barrier was largely disposed of as product translational energy and these observations were supported by trajectory studies.

Marcus²¹ has objected to the manner in which these conclusions of incomplete energy randomization have been made. The RRKM assumption of quasi-equilibrium between A^* , the complex, and A^+ , the critical configuration, essentially removes dynamical considerations from the rate constant calculation: the only problem to be solved is the trivial one of translation over a length δ on the potential energy surface. The translational distribution of reaction products can only be related to the density of states of the critical configuration when certain additional assumptions are made. One such assumption requires that exit channel interactions, that is, coupling between the reaction coordinate and internal motion beyond the critical configuration, must be small. This criterion is rigorously fulfilled only for "loose" critical configurations in which all incipient product rotations in the complex are free, implying that the reverse association reaction has no activation energy.²² Under such circumstances, the partitioning of the total angular momentum into product orbital and rotational angular momentum can be incorporated into the calculation as well, modifying the recoil distribution so as to include both the statistical factor plus angular momentum effects. In the case where $L' \gg J'$ as appropriate for the alkali-atom-alkali halide exchange reactions, Safron et al.²³ have given an expression for the product recoil

distribution including the above-mentioned "centrifugal prohibition" modulation of the statistical term. Marcus has also provided a general treatment²⁴ for including the dynamics between the critical configuration and products in the cases of "loose" and "tight" critical configurations for conversion of the total angular momentum J primarily into L' or into J' . This model will be discussed in greater detail later in this paper.

Further experimental work on the $F + C_2H_4$ system has been done by McDonald and co-workers²⁵ who have recently detected infrared chemiluminescence to study $F + C_2H_4$, C_2H_3Br , and C_2H_3Cl in which vinyl fluoride + H, Br, or Cl are the products. Their results show that C_2H_3F resulting from Br or Cl emission from the complex possesses a statistical distribution of internal energy while C_2H_3F from the reaction of ethylene does not. The difference is attributed to the absence of an exit channel barrier in the C_2H_3Br and C_2H_3Cl reactions (as inferred from kinetic data for the reverse addition reactions of Br and Cl to vinyl halides) whereas $F + C_2H_4$ possesses an exit channel barrier. Only that fraction of the total energy in excess of the barrier is available for statistical redistribution while energy released in descending the barrier is channeled into specific modes. The initially randomized energy distribution in the complex can then be destroyed by preferential population of modes in accordance with the nature of the potential barrier.

Thus, the question of whether energy randomization in the $[C_2H_4F]$ complex is rapid with respect to decomposition to $C_2H_3F + H$ is not

satisfactorily answered although evidence remains suggesting that such is not the case. Recent infrared chemiluminescence measurements²⁶ on halogen substitution in the related systems

indicate that nonstatistical behavior is observed to the extent that the populations of one particular vibrational mode of the products are enhanced. These results are of particular significance because the exit channel barriers for halogen emission should be quite small and thus the recoil distributions should reflect the distribution of energy at the critical configuration. In an effort to provide additional experimental data to test the hypothesis of energy randomization we have studied the energy dependence of the angular and energy distributions of the product of the $\text{F} + \text{C}_2\text{H}_4$ reaction. Use of a seeded supersonic F atom beam with diluent gases such as argon and helium provides a convenient method for varying the relative kinetic energy of the reactants and further enables the energy of the complex to be well-defined.

A study of the energy dependence of the product recoil energy and angular distributions in this system should provide important information regarding the dynamics of unimolecular decomposition for several reasons. The recoil distribution of products should reflect the manner in which the energy in excess of the exit channel potential barrier is distributed at the critical configuration; as the collision

energy increases, the energy which is liberated in descending the exit channel barrier (and is unrelated to the assumptions of RRKM theory regarding energy randomization) becomes a much smaller fraction of the total energy. Thus, the contribution of the barrier to the recoil distribution becomes smaller and any assumptions regarding its disposition become less important. As the collision energy is increased, the lifetime of the complex becomes closer to a rotational period and if the complex stability is not too great compared to the collision energy, one expects some asymmetry to appear in the angular distribution. This effect has been seen in $F + CH_3I \rightarrow IF + CH_3$,²⁷ but as we shall see later, no change in the angular distributions is noted over a sixfold change in the collision energy in the present study. Finally, the $F + C_2H_4$ system provides very favorable kinematic relations which effectively remove angular momentum constraints on the form of the recoil distribution. Since the formation of products involves emission of a hydrogen atom which carries away very little orbital angular momentum, the total angular momentum of the complex becomes rotational excitation of C_2H_3F which is calculated to be quite small. This system contrasts with others in which the emission of a heavier particle removes a large amount of orbital angular momentum, thus requiring the product recoil distribution to be consistent with this fact.

Group contributions to the heat of formation of vinyl fluoride provide an estimate of the exoergicity of the $F + C_2H_4$ reaction as $\sim 11 \text{ kcal mole}^{-1}$ although further discussion of this point is included later. As indicated in earlier work¹¹ this reaction is well known to

produce C_2H_4F which has an estimated stability of $\sim 50 \text{ kcal mole}^{-1}$ with respect to the reactants and additional experimental data from this laboratory confirm the existence of C_2H_4F as produced in the reaction $F_2 + C_2H_4 \rightarrow C_2H_4F + F$. The latter reaction is known to proceed with an activation energy of $\sim 6 \text{ kcal mole}^{-1}$.²⁸

Abstraction of a hydrogen atom by fluorine is another channel which proceeds readily and has been studied in the previous work. The present work is concerned with the dynamics of complex formation and subsequent unimolecular decay and hence further work on the abstraction reaction was not done.

EXPERIMENTAL METHOD

Most of the previous reactive scattering studies of fluorine atoms with organic molecules in this laboratory have employed a thermal dissociation source in which a slotted disc velocity selector^{29,30} produces a beam with a velocity distribution of 20% FWHM. In an attempt to increase intensity in reactive scattering experiments while maintaining the narrow velocity dispersion necessary to perform well-defined experiments, we have attempted to produce supersonic atomic fluorine beams by expanding mixtures of 2% fluorine in argon or helium carrier gas through a resistively heated nickel oven in which a 0.1 mm diameter hole has been drilled. This technique produces high intensity supersonic nozzle beams of fluorine atoms with narrow velocity distributions (~10% FWHM) typical of nozzle beams used in earlier works from this and other laboratories.^{31,32}

The C_2H_4 beams were produced by supersonic expansion also; in order to vary the collision energy, both pure and seeded C_2H_4 gas mixtures were employed. The velocity distribution measured by TOF analysis indicated that for pure ethylene (Matheson CP grade) the Mach number was 9 with specific heat ratio $\gamma=1.29$. A 45% C_2H_4/He mixture (Linde) was also used and the velocity distributions of beams produced by isentropic expansion were found to be much narrower with Mach numbers near 20. The various combinations of seeded atomic and molecular beams allowed us to vary the initial kinetic energy from 2.2 to 12 kcal mole⁻¹. Four different collision energies were chosen for experiments: 2.2, 4.4, 10.4, and 12.1 kcal mole⁻¹.

The remainder of the crossed molecular beam apparatus has been discussed numerous times in the literature.³³ Angular distribution measurements were performed by detecting the vinyl fluoride product every 2.5° in the laboratory system using a rotatable mass spectrometer detector. Signal counting rates ranged from 500 sec⁻¹ at the lowest collision energy to 2000 sec⁻¹ at the highest attainable energy: two angular scans consisting of 20 sec counts yielded angular distributions for which the standard deviation of a single count at the maximum was $\lesssim 1\%$. A much weaker signal at mass 47 corresponding to the reaction $F_2 + C_2H_4 \rightarrow C_2H_4F + F$ was measured by 3 to 5 scans consisting of 200 sec counts.

The velocity distributions of the reactively scattered products of the chemical reaction can be determined by measuring the distribution of flight times of detected products. A large aluminum disc of radius 8.5 cm into which four 3 mm slots have been cut modulates the scattered beam at a high frequency, typically 1500 Hz for these experiments. A burst of molecules enters the detector chamber at time T_0 for a period of 15 μ sec: simultaneously a light pulse from a lamp-photoFET arrangement initiates the counting cycle of a 40-channel multiscaler which determines the arrival times of ions which have been detected at some time $t = L/v$ later than T_0 , where L is the flight path length and v is the particle velocity. The accumulated data are stored in a NOVA 1220 minicomputer.

Time of flight velocity distributions of reactively scattered C_2H_3F were measured at the laboratory angle corresponding to the direction of the center of mass at each of the four collision energies employed. As indicated in the next section, the reaction proceeds through a long-lived complex; the separable energy and angular distributions which are thereby implied can thus be determined by a single velocity distribution at each energy. Counting times were typically one to three hours.

RESULTS AND ANALYSIS

The experimental C_2H_3F angular and velocity distribution data are shown in Fig. 1. The symmetry of the angular distributions about the center of mass direction provides support for the assumption that the reaction proceeds through a long lived complex⁸ at all collision energies studied here. Because the angular distributions do not show any asymmetry at higher energies, we can only state that the lifetime of the complex must exceed many rotational periods of the complex.

Information regarding the center of mass energy and angular distributions was obtained using standard techniques of kinematic analysis^{34,35} in which the c.m. cross section is represented as a function separable in energy and scattering angle:

$$I_{c.m.}(E, \theta) = f(E) g(\theta)$$

This separability has been assumed for many kinematic analyses of direct and complex reactions, and although evidence exists against its validity in the former case, separability should be valid for reactions proceeding through long-lived complexes. The form for $g(\theta)$ is the following:

$$g(\theta) = a_0 + a_2 P_2(\cos\theta)$$

where $P_2(\cos\theta)$ is the usual Legendre polynomial of order two. This function possesses symmetry about $\theta = \pi/2$ as it should for reactions proceeding through long-lived complexes. For an assumed recoil energy distribution $f(E')$, the kinematic analysis program determines the

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coefficients a_0 and a_2 through a least squares fit to the data. The functional form for $f(E')$ is the following:

$$f(E') = (E' - V_a)^\alpha (E_{\text{tot}} - E')^s$$

where V_a , α , and s are parameters which are varied to provide a fit to the data. The parameter V_a is related to the height of the exit channel barrier (but is not numerically equal to it) and α is related to the dimensionality of the reaction coordinate.

For assumed parameters V_a , α , and s , Legendre coefficients a_0 and a_2 were determined by least squares and the recoil distribution parameters were varied until a fit to the data was achieved. The assumed center of mass cross sections were averaged over a 5×5 grid of Newton diagrams appropriate to the beam conditions discussed in the previous section. In analyzing the velocity distribution data, three resolution effects were considered: the variation in path length (~ 17 cm) caused by the finite ionization length (≤ 2.5 cm), the finite open time of the shutter ($\tau_{1/2} = 15$ μsec) and the finite channel size used in time space. The first effect was found to be the most significant at velocities $v \lesssim 1.6 \times 10^5$ cm sec^{-1} . At higher velocities, the latter two effects began to become important. In all cases, however, these averaging procedures did not significantly affect the position or width of peaks under the experimental conditions employed here.

In performing the kinematic calculations, it was necessary to consider the value of ΔD_0 used which determines the total energy distributed between translational and internal degrees of freedom of the products. The initial value used, -11 kcal, was determined from group contributions to the heat of formation of C_2H_3F .³⁶ However, the group values for the $=C\begin{smallmatrix} \nearrow H \\ \searrow F \end{smallmatrix}$ moiety are rather uncertain and hence the error limits on ΔH_f for vinyl fluoride are large. An analysis of the angular and velocity distributions for these reactions indicated that products with a high degree of translational energy must be formed in order to produce the observed wide spread in value. In order to produce such wide angular distributions, particularly at the lowest collision energy where most of the total energy comes from ΔD_0 , large recoil velocities were required and imposing a ΔD_0 value of -11 kcal mole⁻¹ produced a sharp unphysical cutoff in the recoil distribution. Accordingly, it was decided to increase the exoergicity to 14 kcal to produce smooth recoil distributions. The fit to experiment was correspondingly improved and the value used is within quoted error limits for the group method.

The best fit energy distribution parameters for the experiments performed here are listed in Table 1. Although a thorough discussion of these parameters follows in a later section, it is interesting to note that these calculations yield parameters whose values change very little as the collision energy is varied.

The c.m. angular distribution parameters are also rather interesting. Figure 2 shows the c.m. angular distributions determined for these reactions: the distributions are nearly isotropic, but the

slight sideways peaking observed has been noted in the previous work¹⁷ and is worthy of additional comment. From the viewpoint of angular momentum disposal, sideways peaking can be explained in terms of decomposition of an oblate complex along the symmetry axis.⁹ The C_2H_4F complex is nearly a symmetric top but quite prolate with $I_{\perp}/I_{\parallel} \approx 7$ and the explanation of sideways peaking is more subtle: the details are shown in Fig. 3. The F atom must approach the C_2H_4 molecule in the direction along the p_z orbital of the carbon atom involved in the π -bond. Since $J \approx 0$, the total angular momentum must be the initial orbital angular momentum; since the emitted H atom is light and if the C-H bond is extended, the C-C-F framework can define a plane perpendicular to $\underline{J}$ and the complex rotates in this plane. This dominance of the total angular momentum by the C-C-F framework rotation requires that the emitted H-atom, which cannot remove much orbital angular momentum, exit along $\underline{J}$ and therefore perpendicular to $\underline{V}'$ since $\underline{J}$ is converted to $\underline{J}'$ of the C_2H_3F as H leaves. A more isotropic distribution should be generated if the emitted group is heavy: in that case the heavy atoms are not in one plane and hence the total angular momentum is not dominated by rotation in a plane perpendicular to the initial angular momentum.

Heavy particle emission can create $\underline{L}'$ and $\underline{J}'$, the sum of which will approximate $\underline{L}$ as required by angular momentum conservation, but the individual components may be large compared with $\underline{L}$. In such a case the product emission direction bears little relationship to $\underline{L}$, but only to molecular orientation at the moment of product separation.

This mechanism for $F+C_2H_4$ sideways peaking seems to remain valid over the entire range of kinetic energies studied: the anisotropy remains essentially constant with $g(0)/g(\pi/2) \sim 0.7-0.9$. This observation suggests that the slight tendency for sideways peaking reflects the fact that the breaking C-H bond maintains a near perpendicular geometry with respect to the plane defined by C_2H_3F . If this were not the case and slight rotational motion of the reactant C_2H_4 were to provide a range of initial orientations tending to reduce the anisotropy of emission angles, then the increasing dominance of L as the collision energy is increased should produce stronger sideways peaking. Such an increase in anisotropy does not appear to be observed here.

The total cross section for reaction is frequently determined by integrating the differential reactive scattering cross section and normalizing to small angle elastic scattering of the reactants, the absolute cross section for which can be calculated from the C_6 constant.⁴⁷ Because of the large flow of rare gas carrier and proximity of the F-atom source to the collision region, it was impossible to measure elastic scattering cross sections at angles small enough to observe the limiting $\theta^{-7/3}$ slope characteristic of a $1/r^6$ potential. Consequently, we were unable to determine the absolute total reactive cross section. However, in the previous work, such a determination was made yielding $\sigma_r = 2.2 \text{ \AA}^2$. This value should not be especially energy dependent since complex formation appears to depend on the geometric factors consistent with F-atom approach perpendicular to the plane of the C_2H_4 molecule. The value of $2.2 \text{ \AA}^2$ was thus used in all calculations

where its value was required in elucidating reaction dynamics. However, the results inferred from those analyses do not depend strongly on the value used.

The angular distributions at higher energies show "tails" near the fluorine beam whose significance is ascribed to the reaction of F_2 with C_2H_4 . This reaction has been studied in fluorine flames²⁸ and is found to have an activation energy of ~ 6 kcal mole⁻¹. The shoulder is especially pronounced in the raw data at the highest collision energy; Figure 4 shows the angular distribution of the mass 47(C_2H_4F) product formed via the molecular mechanism. The mass 46 shoulders in Fig. 1 presumably comes from fragmentation of C_2H_4F in the mass spectrometer ($\gtrsim 90\%$ efficiency). By normalizing these data appropriately, the shoulder has been removed from the C_2H_3F data at $\bar{E} = 12.1$ kcal mole⁻¹. Center of mass angular and energy distributions have not yet been fitted to these data from the molecular reaction.

STATISTICAL MODELS FOR REACTIONS PROCEEDING THROUGH A LONG-LIVED COMPLEX

As discussed earlier, bimolecular chemical reactions producing long lived chemically activated radicals can be considered as examples of unimolecular dissociations. Several theories have been advanced to explain such behavior and two of the most widely used models are the Rice-Ramsperger-Kassel-Marcus (RRKM) theory² and phase space theory.¹⁸⁻²⁰ In the former theory, energy randomization is assumed and absolute rate theory is applied to an unobservable "critical configuration" of the complex which usually corresponds to an energy

maximum, either created by an activation energy or by centrifugal force.³⁷ In the phase space model, the cross sections are determined by the asymptotic eigenstates of products and conservation of angular momentum is specifically included in the dynamics of complex formation and subsequent decay to products. A discussion of this model follows in a later section: the present section is devoted to a discussion of the RRKM theory.

As noted earlier, the RRKM theory addresses itself to a determination of a single rate constant in the generally accepted Lindemann mechanism. This calculation assumes that the rate constant depends upon the energy of the complex or energized reactant. Whereas the Lindemann mechanism assumes that decomposition of the energized molecule A^* proceeds with rate constant k_3 , the Marcus treatment divides the process into two parts:

where $+$, as usual, denotes the critical configuration. The rate constant k_a is calculated assuming a quasiequilibrium between the energized species A^* and the critical configuration A^+ and k^+ is calculated by considering the frequency of passage over the critical configuration. By assuming a quasiequilibrium between activated molecules and the critical configuration, Marcus showed that the energy-dependent rate constant k_E for unimolecular decomposition is the ratio of the number of states of the internal modes of the critical configuration (with the one-dimensional translational contribution of the reaction coordinate integrated over) to the total

density of states of the energized complex. The critical assumption of RRKM theory thus reduces to the assumption of a microcanonical distribution of bound state configurations at the surface in phase space separating reactants and products. Such an assumption implies that intramolecular energy exchange in the complex is rapid with respect to chemical reaction: the random lifetime assumption is an equivalent statement of the microcanonical equilibrium hypothesis. Since lifetime measurements are rather difficult to perform, the recoil distributions of reactively scattered products provide us with the most direct evidence regarding the distribution of energy at the critical configuration. Recoil distributions of fragments of molecules ionized by electron impact, for example, have been discussed in terms of a transition state theory called the Quasi-Equilibrium Theory (QET).^{38,39} This theory is identical to RRKM theory.

In earlier work,¹¹ we have shown that for a one-dimensional reaction coordinate in which the density of states can be defined, the recoil distribution function at energy E' is equal to the density of states of the critical configuration evaluated at $E_{\text{tot}} - E'$, where E_{tot} is the total available energy, the initial collision energy plus the exoergicity of the reaction. Since the dynamics connecting the critical configuration to products are ignored, as well as angular momentum conservation, this treatment does not allow a direct comparison with experiment. However, in a system such as the decomposition of $\text{C}_2\text{H}_4\text{F}$, the departing hydrogen atom is so light that the dynamics connecting the critical configuration to the products primarily involve the conversion

of the exit channel potential energy to translational energy, and the conservation of angular momentum is taken care of in the phase space theory. Thus, the conclusion that energy randomization is not achieved during the lifetime of C_2H_4F based upon comparisons of observed and theoretical (phase space) recoil energy distributions¹⁷ seems reasonable. Marcus' recent work²⁴ on the application of RRKM theory to recoil distributions of products formed from unimolecular decomposition includes such exit channel effects with the inclusion of coupling of the total angular momentum to the product rotation and orbital angular momentum. The critical added assumption to canonical RRKM theory which accounts for modifications to the statistical recoil energy factor is as follows: the reaction probability for the reverse association reaction is assumed to be a function of the translational energy in excess of the barrier. The barrier is the sum of any potential energy barrier present in the decomposition of a "tight" complex, plus a centrifugal term. In a tight complex, such as C_2H_4F , incipient product rotations are not free, but rather correspond to bending vibrations. The conversion of these bending vibrations to product rotations can release energy into translation. If one assumes that these bending modes in the complex and their corresponding rotations in the reaction products are statistically adiabatic, then the energy deficit associated with the difference in vibrational and rotational level spacings can be compensated for by translational energy. Such a statistical adiabaticity coupled with the particular assumption of reverse reaction probability yields recoil distributions which reflect a higher fraction of the

total energy in translation than one might initially expect. The experimental recoil distributions do indeed show that the fraction of the total energy in translation is larger than one expects from simple statistical arguments and furthermore, the widths of the distributions are substantial compared to the total energy available. We wish to discuss the applicability of this model to our experimentally observed recoil distributions. The most significant feature of the experimental recoil distributions is derived from the fact that as the collision energy is increased from 2.2 to 12.1 kcal mole⁻¹ and thus the total energy available for product molecules nearly doubles from 16 kcal mole to 26 kcal mole⁻¹, the fraction of the total energy appearing in translation remains very high and essentially constant. The tight transition state theory of Marcus predicts, as does any statistical theory, that as the total energy increases, the fraction of the total energy appearing in translation should decrease in a system which has many vibrational degrees of freedom. In the case of the complex C₂H₄F, the bending vibrational energy of selected modes is converted into rotational excitation of products. Since the emitted H-atom is so light, most of the total angular momentum appears in rotational excitation of the products. The reaction cross section is basically determined by the approach of the F-atom along the π -bonding p_z-orbital on the C-atom and is thus reasonably insensitive to the initial collision energy. Even at the lowest collision energy, the orbital angular momentum between F and C₂H₄ is much larger than the molecular angular momentum of C₂H₄, which is essentially zero because of rotational relaxation in the

isentropic expansion. Thus the total angular momentum increases approximately as $\sqrt{E}$. Since the total angular momentum appears primarily as product rotational excitation, we expect E'_{rot} to vary linearly with E , which varies over a factor of nearly six in our experiments. In contrast, the energy which appears in the bending excitations of the complex is a given fraction of the total non-fixed energy which varies by a factor of two in this system. Therefore, if the bending vibrations and their corresponding product rotations are statistically adiabatic (i.e., their quantum numbers remain the same), the fraction of the energy defect to be accounted for by translation will decrease as the collision energy increases and thus the recoil distribution normalized to total energy should shift toward lower values (i.e., smaller fraction of the total energy) as the collision energy increases.

To show this fact more quantitatively, we have performed some simple calculations using the "tight" transition state theory of Marcus.²⁴ The theory calculates the recoil energy dependent correction to the statistical factor in the product recoil energy distribution:

$$P(E') = A(E') \rho(E_{\text{tot}} - E')$$

where $\rho(E_{\text{tot}} - E')$ is the density of states of reaction products. Marcus has shown for the case that $J' \gg L'$ that the $A(E')$ can be calculated as follows:

$$A(E') = \frac{1}{2\pi i} \int_{C-i\infty}^{C+i\infty} \frac{Q_J^\dagger(s)}{sQ(s)} e^{sE'} ds$$

where the inverse Laplace transform is calculated along a contour with C chosen to lie to the right of all singularities of the integrand in the complex s -plane. $Q_J^\ddagger(s)$ and $Q(s)$ are partition functions for the activated complex and products, respectively, with the following definitions

$$Q_J^\ddagger(s) = \int_0^\infty \rho^{\ddagger J}(y - B_{1J}^\ddagger) e^{-sy} dy$$

$$Q(s) = s^{-\frac{m_r}{2}} \int_0^\infty \rho^{J'}(y) e^{-sy} dy$$

$\rho^{\ddagger J}$ denotes the density of states of the complex with total angular momentum J and $B_{1J}^\ddagger$ is the exit channel barrier associated with the potential energy V_a plus the rotational energy of the complex, $J(J+1)\hbar^2/2I_1^\ddagger$. $\rho^{J'}$ is the density of product states with a fixed value of J' and m_r denotes the number of product rotations arising from complex bending vibrations. We have thus assumed that the partition function for these rotations is classical.

The densities of states $\rho^{\ddagger J}$ and $\rho^{J'}$ are taken to be the Schlag-Sandmark expressions:⁴⁰

$$\rho(E_v) = C_1(E_v + E_z)^m + C_2(E_v + E_z)^{m-2} + C_3(E_v + E_z)^{m-4}$$

where C_1 , C_2 , and C_3 are functions of the vibrational frequencies and zero point energies E_z , m is the number of vibrational modes, and

$$\rho^{J'}(E) = \rho(E - E_{J'})$$

Conservation of angular momentum requires that virtually all of the total angular momentum, which becomes rotational angular momentum of the complex reappears as product rotational excitation. We thus find that the J' dependence of the $A(E')$ term is quite weak.

The Schlag-Sandsmark expression is not as accurate as the Whitten-Rabinovitch expression^{41,42} for $\rho(E)$, but the use of the former yields an analytic expression for $Q_J^\ddagger$ and Q and casts the integrand of $A(E')$ as a ratio of polynomials in s . The Schlag-Sandsmark expression overestimates the density of states at low energies, but since we take the $Q^\ddagger/Q$ ratio, we expect some cancellations of inaccuracies. The vibrations for the product are taken from the literature⁴³⁻⁴⁵ while those of the complex are estimated from those of the product. We can then invert the Laplace transform by finding the poles of the integrand. In our calculation we include 14 vibrations of the complex, 12 for the products, and 2 product rotations. The partition function ratio then yields a second order pole at the origin, the residue of which yields a term of the form $A(E') = (E' - V_a)$, a result expected for classical vibrational partition functions. Other poles provide higher order corrections to $A(E')$. We thus see that $A(E')$ shifts the recoil distribution to higher translational energies. We have plotted the results of our "tight" transition state calculations in Fig. 5. These calculations were performed with the vibrational frequencies listed in Table 2. The vibrational modes to which these frequencies correspond are also listed with assignments based upon their precursor frequencies in C_2H_3F .

We have also calculated recoil distributions using the phase space theory of Light and co-workers.¹⁸⁻²⁰ Once the criteria for formation and decomposition of a "strong-coupling" complex are formulated, cross sections and hence recoil distributions follow from considerations of the number of product states accessible from a complex whose total energy, total angular momentum and projection on a space-fixed axis are given. The usual criterion for formation of the collision complex considers a step "opacity" function which is unity for $L \leq L_{\max}$ and zero for $L > L_{\max}$ where L is the initial orbital angular momentum. In earlier work,¹⁹ $L_{\max}$ was chosen according to the criterion that the complex would form so long as the energy was large enough to allow passage over the centrifugal barrier formed by the R^{-6} dispersion term plus the angular momentum term. In the case of $F + C_2H_4$, however, the formation of the complex probably depends on geometric factors governed by perpendicular approach of the F atom to the C_2H_4 molecule. Hence, we use the value of the total cross section determined from previous work in this laboratory, $2.2 \text{ \AA}^2$, to generate an impact parameter $b_{\max}$, and thus $L_{\max} \approx \mu v b_{\max} \approx 18\hbar$. This value for the lowest collision energy compares favorably with $15\hbar$ calculated using one-half the carbon-carbon double bond length in C_2H_4 ; we thus use $L_{\max} \approx J_{\max}$. Similar arguments must be applied regarding the orbital angular momentum of the products separating from the complex: since kinetic data for H-atom addition to olefins suggest a barrier of $\sim 3 \text{ kcal}^{46}$ we can apply the treatment of phase space theory to reactions with activation energy, considering the complex dissociation to be the

reverse of the association reaction $H + C_2H_3F$ with barrier V_0 . In such a case, Light and Lin²⁰ have assumed that for a reactive channel, there must exist a maximum impact parameter D beyond which complex formation does not occur. The simple collision theory concept that the energy along the line of centers at D must exceed V_0 to promote reaction allows one to relate angular momentum, collision energy, and V_0 thus giving the maximum L' for given D :

$$L'_{\max} = \frac{1}{h} \sqrt{2\mu D^2 (E' - V_0)}$$

Since V_0 is small relative to typical values of E' in our experiments, we can neglect the effects of product internal excitation lowering the effective barrier below V_0 . Parson et al.¹² have used this model for $F + C_4H_8$ and have shown the dependence upon choice of D . As D is increased, L' increases thereby increasing the density of rotational states. The increase in J' states is most noticeable when $E' \approx V_0$ and increased values of J' make the recoil distribution rise from zero more rapidly. As $D \rightarrow \infty$, the total angular momentum must be disposed of as orbital angular momentum and the recoil distribution reflects only the vibrational density of states. The choice of D is rather arbitrary and for purposes of calculation, we have chosen $D = 2 \text{ \AA}$. The values of $L'_{\max}$ are quite consistent with those calculated neglecting V_0 and assuming that the bound on L' obtains from the requirement that the products surmount the centrifugal barrier. The Slater-Kirkwood⁴⁷ estimate for C_6 yields $L'_{\max} \approx 15$ for $E' = 6 \text{ kcal mole}^{-1}$ at the lowest collision energy.

Figure 6 compares phase space recoil distribution calculations with $D = 2 \text{ \AA}$ for the four collision energies employed in these experiments. Two different calculations were carried out to demonstrate the extent to which the vibrational density of states plays a role in this reaction. The 12-oscillator model includes all the vibrations of $\text{C}_2\text{H}_3\text{F}^{43-45}$ while the 5-oscillator calculation reflects, in a heuristic manner, the possibility of incomplete vibrational activation. The choice of oscillator frequencies for such a calculation is quite arbitrary, since one has no a priori knowledge of which vibrations to exclude. The C-H stretches must participate since this mode is effectively the reaction coordinate. Since formation and decomposition of the complex requires $\text{sp}^2 \rightarrow \text{sp}^3 \rightarrow \text{sp}^2$ hybridization changes, one expects the out-of-plane C-H and C-F motions to be involved. The C = C stretch must be activated since the π -bond must be partially broken and reformed. Thus the following vibrational modes were included: $3080(\nu_{10})$, $3115(\nu_{11})$, $3150(\nu_{12})$, $940(\nu_5)$, and $1654(\nu_9) \text{ cm}^{-1}$. $\text{C}_2\text{H}_3\text{F}$ is nearly a symmetric top with the two largest moments of inertia equal to $48.3 \text{ amu \AA}^2$ and $56.1 \text{ amu \AA}^2$. We have taken their average to perform the phase space calculations. The 12-oscillator model calculations consistently produce distributions which peak at low E' values: the 5-oscillator calculations, while in somewhat better agreement with experiment, still yield energy distributions for the products with too much internal excitation.

In order to assess the predictions of the various statistical models, we have computed angular and velocity distributions for the

lowest and highest collision energies using a c.m. angular distribution with $g(0)/g(\pi/2) = 0.7$. The absence of low velocities coupled with recoil distributions which rise sharply from zero at $E' = V_0$ produces significant dips in the angular and velocity distributions. The phase space results are shown in Fig. 7 while the Marcus "Tight Transition State" calculations are shown in Fig. 8. An overall assessment of the model calculations and their comparison with experiment can be obtained by the examining the average product translational energy calculated from the various expressions for $P(E')$. These calculations are shown in Table 3: one notes immediately that the average observed values exceed the calculated values and furthermore, the variation in $\bar{E}'$ with initial kinetic energy is significantly smaller for the model calculations than for experiment. The "Tight Transition State" and 12 oscillator phase space calculations yield very similar results while the 5 oscillator phase space calculations vary over a slightly wider range. Further discussion of this point is found in the next section.

Finally, to demonstrate that kinematic resolution arising from hydrogen emission is not a limiting feature in our deductions about energy disposal in this reaction, we have calculated the angular and velocity distributions corresponding to an average translational energy of 2 kcal mole^{-1} for the $\text{C}_2\text{H}_3\text{F}$ product at the highest collision energy. This result corresponds to the recoil energy expected for classical distribution of the total energy among the oscillators of the complex. These results, shown in Fig. 9 indicate that although the H-atom

0 0 0 0 4 4 0 6 9 2 4

-33-

emission should place some kinematic restrictions on the information derived from these experiments, such a restriction is not serious.

DISCUSSION

Past work from this laboratory has been interpreted in terms of the validity of various statistical models of decomposition of activated reactants. In many cases, evidence has been presented which mitigates against such statistical theories but the presence of an exit channel barrier complicates the interpretation. Clough *et al.*⁴⁸ have shown that the decomposition of chemically activated CF_3CH_3^+ , in which 30 kcal can be distributed statistically and 42 kcal released in descending a barrier, produces HF^+ whose vibrational excitation must be attained in the latter process. Although this is a rather special case in which two atoms are ejected simultaneously from different sites and vibrational motion of HF is not simply related to the reaction coordinate of decomposition, it is not difficult to imagine that under certain kinematic restrictions, the product internal energy distribution is sensitive to dynamics beyond the transition state. McDonald's infrared chemiluminescence studies of $\text{F}+\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_3\text{Br}$, and $\text{C}_2\text{H}_3\text{Cl}$ to produce $\text{C}_2\text{H}_3\text{F}$ suggest that a non-statistical distribution obtains only when H-atom emission occurs:²⁵ this is the only case in which an exit channel barrier is likely to be found. However, we have indicated that some of his recent results²⁶ for halogen substitutions show nonstatistical behavior even in the absence of an exit channel barrier.

By studying the energy partitioning in the $\text{F}+\text{C}_2\text{H}_4$ reaction as a function of collision energy, the effect of the non-random energy partitioning from descending the barrier can be isolated. As the collision energy is increased, the available energy is consistently

partitioned with 50% in translation. The remaining energy can be separated into vibrational and rotational contributions quite easily by considering the conservation of angular momentum. Since the emitted H-atom removes so little angular momentum because of kinematic restrictions, one can assume that the initial orbital angular momentum becomes product rotation. Since the product is quite prolate we expect small values of the projection quantum number, K' , to predominate: we thus estimate that rotational excitation accounts for $\leq 5\%$ of the total energy in all case, ranging from $0.3 \text{ kcal mole}^{-1}$ at $E_{\text{rel}} = 2.2 \text{ kcal mole}^{-1}$ to $1.6 \text{ kcal mole}^{-1}$ at $E_{\text{rel}} = 12.1 \text{ kcal mole}^{-1}$.

Because the light H-atom emission may be influenced by quantum-mechanical tunneling through the barrier, we cannot make an accurate estimate of the magnitude of V_a . We can, however, isolate its influence because as the collision energy increases, one expects the nonrandom energy partitioning arising from descent of this barrier to play a much smaller role in determining $P(E')$. The fact that the $P(E')$ function shows no tendency toward more statistical behavior at higher energies strongly suggests that the complex does not decay in accordance with a statistical model.

The origin of such nonstatistical behavior is quite interesting and also quite speculative at this point. If the complex is formed and rapid energy randomization occurs such that all 15 oscillators in the complex are excited, a non-random recoil distribution results if only a few of these modes couple to the reaction coordinate just prior to reaching the critical configuration. Conventional lifetime measurements performed by determining decomposition-stabilization ratios as a function

of pressure will not provide this information. Rowland⁴⁹ has recently studied this reaction in a hot-atom ¹⁸F experiment: the measured half-stabilization pressure for C₂H₄F produced in the hot atom experiment corresponds to a lifetime of 10⁻⁹ seconds. An RRKM calculation⁵⁰ in which all modes in C₂H₄F are activated predicts a lifetime of ~4×10⁻¹⁰ seconds at the energy of this experiment. A similar calculation in which only six modes of the complex are activated, that is, those corresponding to our five-oscillator phase space calculations plus one C-H stretch of the reaction coordinate, yields much shorter lifetimes, typically 10⁻¹³ seconds. The results of these lifetime calculations are shown in Fig. 10 where the abscissa E* is the excitation energy of the complex. While phase space calculations suggest heuristically that a reduction in the number of active oscillators produces recoil distributions in closer accord with experiment, the lifetimes calculated are less than a rotational period of the complex, estimated to be 1 to 3×10⁻¹² seconds over the range of experimental collision energies employed here.

In our earlier work on the F + C₂H₄ reaction, significant conclusions regarding the nature of the unimolecular decay were drawn from the shapes of observed and model recoil distributions at a single collision energy. In this paper we have shown that by varying the collision energy by a factor of six and the total energy twofold, the average product translational energy increases by a factor of two also. Furthermore the average kinetic energy of the products remains at about 50% of the total available energy, irrespective of initial conditions. This

observation is not in accord with statistical predictions in which one expects the average recoil energy to increase quite slowly with total energy while the fraction of the total energy appearing in translation decreases. The effect of the exit channel barrier should be isolated in these experiments and its role becomes smaller as the magnitude of the barrier compared to the available energy decreases. These observations suggest that deviations from statistical behavior are occurring which are not entirely caused by the presence of an exit channel barrier. The phase space calculations performed with only 5 product oscillators activated seem to behave more qualitatively correctly in placing more of the total energy in product translation, but the lifetime calculated with so few active product oscillators is less than one rotational period, in contradiction to our experimental results. Rowland's experiment, however, indicates that the lifetime of the complex (the minimum of the reaction coordinate) is consistent with full vibrational activation. One thus must conclude that substantial energy randomization in the C_2H_4F complex is likely achieved, but some (as yet unspecified) energy transfer process preferentially populates the lower frequency modes or depopulates higher frequency modes of the products while also directing large amounts of the total energy into the reaction coordinate before the critical configuration is reached. Such a mechanism may also be operative in the reaction $Cl + CH_3CH = CHBr \rightarrow CH_3CH = CHCl + Br$ studied by McDonald in which one particular product vibrational mode is overpopulated compared to statistical predictions.

The recent work of Baer and collaborators⁵¹ on the decomposition of $C_4H_6^+$ ions formed by photoionization of 1,3-butadiene, 1,2-butadiene, cyclobutene, 2-butyne, and 1-butyne also provides valuable and consistent insight into the discussion of the decomposition of C_2H_4F . Rate constants measured as a function of ion internal energy showed very strong deviations at low excess energies, consistent with measured lifetimes shorter than those predicted from statistical models. The shorter lifetime is indicative of incomplete sharing of vibrational energy among the modes. At low excitation energies where the greatest deviations from statistical behavior are observed, the formation of localized states may occur, trapping some of the energy in modes which couple to the reaction coordinate while remaining isolated from other modes in the molecule whose participation is required to lengthen the lifetime. At higher excitation energies, the closer correlation with statistical expectations is in accord with the calculations of Nordholm and Rice,⁵²⁻⁵⁴ who noted such a transition from localized to stochastic behavior in model systems of coupled oscillators.

While it is likely that rapid energy randomization has been substantially achieved in the complex of C_2H_4F , the quasiequilibrium with the critical configuration, central to RRKM theory, has not been established. Rather, the dynamics connecting the complex and the critical configuration, which RRKM explicitly ignores by invoking quasiequilibrium, must be considered in explaining our observed recoil distributions.

That the products of the $F + C_2H_4$ reaction show deviations from statistical behavior has been known since the initial work on this system by Parson and the results have been corroborated by McDonald. Prior to this work, however, the point at which such deviations occur was thought by some to be beyond the critical configuration where exit channel interactions place energy in specific modes in accordance with the dynamics dictated by the potential barrier; quasiequilibrium between the complex and the critical configuration was believed to be valid. The present work shows the nonstatistical behavior of the energy distribution in C_2H_4F must already exist in the critical configuration. An explanation of the recoil distribution, then, requires dynamical arguments considering the coupling of the normal modes of C_2H_4F as the F enters and the emitted H-atom separates. A theoretical understanding of this interesting unimolecular decomposition, then, likely awaits development of a coupled oscillator formalism describing the population of specified modes upon bond cleavage.

Recent experimental results adequately illustrate that the formation of a "long lived" complex does not assure complete energy randomization. It is not really surprising to see nonstatistical behavior in a small system consisting of light atoms such as C_2H_3F . For many larger systems or systems with heavier atoms, if the "activation" energy is sufficiently high, i.e., the complex is very stable, the stronger coupling and the higher density of states are likely to establish more complete energy randomization in the complex before chemical reaction as suggested in RRKM theory.

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Table 1. Energy Distribution Parameters.

E_{rel}	V_a	α	s
2.2 kcal	0.25 kcal	0.6	0.5
4.4	0.25	0.5	0.4
10.4	0.15	0.5	0.4
12.1	0.15	0.5	0.4

Table 2. Vibrational Frequencies for Marcus Tight Transition State Theory Calculation.

$\nu^\ddagger$ (Crit. Config.)			ν (Product)
2800 cm^{-1}	(3)	C - H stretch	3200 (3)
1500 cm^{-1}		C = C stretch	1600
800 cm^{-1}		bend	800
483 cm^{-1}		ν_1	483
1100		C - F stretch	1200
929		ν_6	929
1306		ν_7	1306
1380		ν_8	1380
711		ν_2	711
863		ν_4	863
800		CH_2F bend	... ^a
800		CH_2F bend	... ^a

^arotations derived from critical configuration bending vibrations.

Table 3. Average Product Translational Energy^a

E_{rel}	$\bar{E}'_{\text{obs.}}$	$\bar{E}'_{\text{TTST}}$	$\bar{E}'_{12 \text{ osc.}}$	$\bar{E}'_{5 \text{ osc.}}$
2.2 kcal	7.87 kcal	7.58 kcal	7.33 kcal	7.82 kcal
4.4	9.50	7.98	7.67	8.44
10.4	12.64	9.06	8.61	10.16
12.1	13.50	9.40	8.87	10.65

^aThe barrier height of 3 kcal/mole is used in all model calculations.

FIGURE CAPTIONS

- Fig. 1. C_2H_3F angular and velocity distribution data. The nominal Newton diagram for each energy indicates the circle corresponding to C_2H_3F formed with maximum translational energy.
- Fig. 2. C. M. angular distributions:
 ———, $\bar{E} = 2.2 \text{ kcal mole}^{-1}$
 ·····, $\bar{E} = 4.4 \text{ kcal mole}^{-1}$
 -·-·-·, $\bar{E} = 10.4 \text{ kcal mole}^{-1}$
 - - -, $\bar{E} = 12.1 \text{ kcal mole}^{-1}$
- Fig. 3. Schematic diagram of $F + C_2H_4 \rightarrow C_2H_3F + H$ reaction mechanism.
- Fig. 4. C_2H_4F angular distribution data, highest collision energy.
- Fig. 5. "Tight Transition State" product recoil distribution functions, $f(E)$, at each collision energy.
- Fig. 6. Recoil distribution functions, $f(E)$, for the $F + C_2H_4 \rightarrow C_2H_3F + H$ reaction.
- Fig. 7. Phase space calculations compared with experiment. Calculations and data as noted.
- Fig. 8. Marcus "Tight Transition State" calculations compared with experiment as noted.
- Fig. 9. Calculation to illustrate kinematic resolution, $\bar{E} = 12.1 \text{ kcal mole}^{-1}$ experiment.
 ———, experimental fit.
 -·-·-·, calculation with $\bar{E}' = 2 \text{ kcal mole}^{-1}$.
- Fig. 10. RRKM lifetime vs. E^* for two models of C_2H_4F complex. Arrows denote values of E^* corresponding to these experiments.

Fig. 1

XBL 7512-9967

XBL 7512-9969

Fig. 2

Fig. 3

XBL 7512 - 9971

Fig. 4

Fig. 5

XBL 7512 -9973

XBL 7512 -9974

Fig. 6

Fig. 7

XBL 7512-9975

Fig. 8

XBL 7512-9976

Fig. 9

XBL 7512-9972

Fig. 10

XBL 7512-9970

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