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Publication Date

1975-03-01

0 0 0 0 4 3 0 7 0 4 5
Submitted to Journal of Chemical Physics

LBL-4002
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March 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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CROSSED MOLECULAR BEAM STUDY OF

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ABSTRACT

The reaction of $F + CH_3I \rightarrow IF + CH_3$ has been studied at two relative collision energies of 2.6 and 14.1 kcal mole⁻¹ using the crossed molecular beam technique. Angular and velocity distributions of the reactively scattered IF products have been measured. At the lower collision energy the distributions are consistent with reaction occurring through a complex for which the lifetime is many rotational periods. At the higher collision energy, the complex lives only a fraction of a rotational period. The energy distributions measured for these systems are shown to be fairly consistent with RRKM and phase space statistical models; in order to make a more reliable statistical calculation on this system, the stability of the intermediate complex, CH_3IF , has been determined in independent measurements of the threshold for the reaction

$$F_2 + CH_3I \rightarrow CH_3IF + F.$$

Introduction

The crossed molecular beam technique has been demonstrated to provide valuable information concerning the dynamics of decomposition of radicals produced in bimolecular association reactions. Many of the recent molecular beam experiments performed in this laboratory¹⁻⁶ and elsewhere⁷⁻⁹ have been concerned with testing theories of unimolecular reactions, particularly with regard to the validity of the hypothesis in RRKM theory¹⁰ that energy randomization is rapid compared to chemical reaction. In crossed molecular beam experiments, the extent of energy randomization of chemically activated radicals is assessed from the angular and velocity distributions of product molecules in contrast to recent chemiluminescence experiments in which internal state distributions of product molecules are measured.¹¹ In addition to the energy distributions of product molecules, information on the lifetime of the chemically activated complex is most valuable in assessing the extent of energy randomization before the decomposition of the complex. Measurements of complex lifetimes are rather difficult in general since these times may be as short as 10^{-13} sec. The technique of chemical activation, developed extensively by Rabinovitch and co-workers,¹² provides some information on the rapidity of energy randomization in the decomposing molecule. A study of the ratio of decomposition rate to stabilizing rate of activated molecules from collisions with bath gases as a

function of total pressure can effectively change the time scale of a measurement to the time between collisions, provided one assumes that large amounts of energy are removed from activated molecules in single collisions. The chemical activation technique has generally provided data supporting the rapid energy randomization hypothesis, although the recent work of Rynbrandt and Rabinovitch¹³ concerning CH_2 and CD_2 addition to hexafluorovinylcyclopropane suggests that randomization may not occur rapidly compared to chemical reaction in this case.

The crossed molecular beam method can yield some information regarding complex lifetimes under certain well-specified conditions: the "clock" in a molecular beam experiment is essentially the rotational period of the bimolecular species "synthesized" as the reactants scatter from one another. Chemical reactions have conveniently been classified as "direct" or "complex" depending on the ratio of the collision lifetime to the rotational period. Reactions which proceed through a complex live many rotational periods and the center of mass (c.m.) angular distribution exhibits symmetry about $\theta = \pi/2$. The observation of forward-backward symmetry in angular distributions, although providing information that the lifetime of the complex is longer than a rotational period, typically 10^{-12} sec, will not tell us anything about the actual lifetime. If a reaction proceeds through a long-lived complex at some collision energy which is significantly less than the binding energy of the complex E_0 , then as the collision energy is increased toward E_0 , one expects some asymmetry to appear in the c.m. angular distribution as the lifetime of the collision complex becomes comparable to or shorter than the rotational period, since the decrease of the

rotational period is expected to be much smaller than the decrease of the complex lifetime when the collision energy is increased. Consequently, it is possible to obtain some information on the complex lifetime by controlling experimental conditions such that the lifetime of the complex becomes comparable to the rotational period which can be estimated easily. An experimental problem arises in producing beams of sufficiently high energy when the complex is bound by ~ 50 kcal mole⁻¹ as in the C₂H₄F complex formed from F + C₂H₄, but for many systems, this method should be feasible. Herschbach and co-workers have observed "sticky" collisions in the reactions of Br and I with halogen molecules¹⁴ and in the reactions of alkali atoms with thallium halides,¹⁵ where binding energies are considerably smaller and the lifetimes of the complexes are found to be comparable to the rotational period in their thermal energy experiments.

Herman et al.⁹ have studied the decomposition of C₄H₈⁺ produced in the crossed beam reaction of C₂H₄⁺ + C₂H₄ and have observed increasing anisotropy in the angular distribution as the collision energy increases to ~ 4 eV. Their results have been interpreted in terms of a statistical model of the RRKM form^{16,17} and suggest incomplete participation of all vibrations in the decomposition.

In this paper, we present results of a study of the dynamics of the reaction F + CH₃I → CH₃ + IF which is found to proceed through a long-lived complex at collision energies of ~ 2 kcal mole⁻¹ and asymmetry in the angular distribution begins to appear at a higher translational energy of 14 kcal mole⁻¹. The reaction is exothermic by ~ 11 kcal mole⁻¹ but the uncertainty of this value is ± 3 kcal. The production of IF in the reaction of CH₃I in fluorine supported flames was first observed by

Durie¹⁸ who observed emission from IF attributed to the $A^3\Pi_o^+ \rightarrow X^1\Sigma$ band system. The spectroscopic constants for IF were determined from these data. Interestingly, IF was the last interhalogen compound to be observed although its dissociation energy is nearly 70 kcal mole⁻¹. IF has also been produced by the crossed molecular beam method in the reaction $F + I_2$ studied in this laboratory and in the Grice lab in Cambridge.¹⁹

Tal'roze²⁰ has made a mass spectrometric study of the three reactions which can occur in this system

and although the latter two reactions are quite exoergic, the first reaction is found to be the dominant one. The last reaction, an example of the "Walden inversion", was found to proceed with a very small rate, if at all.

The discussion of the question of whether the energy is randomized in the complex before decomposition is only possible if we have knowledge of the stability of the complex. In the reaction of $CH_3I + F \rightarrow IF + CH_3$, the reaction "intermediate", CH_3IF , has not been identified previously and we do not have a reliable estimate of how strongly F is bound to the I atom on this "molecule". On the other hand, if we assume the energy of the complex is fully randomized before the decomposition, it is possible to estimate the stability of CH_3IF based on information regarding the complex lifetime obtained in our experiment. In order to pursue a more meaningful discussion, in a separate

experiment we have obtained information concerning the stability of the CH_3IF complex through an endoergic molecular reaction

$\text{CH}_3\text{I} + \text{F}_2 \rightarrow \text{CH}_3\text{IF} + \text{F}$.²¹ We present results concerning the partitioning of energy in the reaction $\text{F} + \text{CH}_3\text{I}$ and indicate how the data can be interpreted in terms of statistical models at low collision energy and an "osculating complex"¹⁵ model at high energy.

Experimental Procedure

The experimental arrangement is similar to that described previously.¹⁻⁶ The CH_3I beam was produced by supersonic expansion: reagent grade CH_3I (J. T. Baker) was maintained at 25°C by a water bath (CH_3I vapor pressure ~ 400 torr). The CH_3I vapor passed through a gas handling system of copper and stainless steel tubing to a 0.1 mm nozzle which was heated to 220°C . The molecular beam source design was that of Parson.²² The velocity distribution of the CH_3I beam was determined by the time-of-flight (TOF) method with a resolution of $\sim 15\%$ FWHM. The beam distribution was characterized by Mach number 10 and specific heat ratio $\gamma = 1.31$. Beams of F atoms and F_2 molecules are produced by seeding $\sim 2\%$ of F_2 in either He and Ar and expanding the mixture through a 0.1 mm nozzle in a nickel oven operated up to a temperature of 800°C where partial dissociation to atoms occurs. Collision energies are controlled by both the average mass number of the mixture and the oven temperature.

The reactively scattered IF molecules from $\text{F} + \text{CH}_3\text{I}$ were detected in the plane of the beams using the rotatable mass spectrometer detector described earlier.²³ Four angular scans consisting of 40 second counts

were performed for the low energy experiment; typical counting rates were $250\text{--}300\text{ sec}^{-1}$ at the angle of maximum intensity. Two 20 second counts were adequate for the high energy reaction where the counting rate was 2200 sec^{-1} at the most intense angle. A signal at mass 161 attributed to formation of CH_3IF in the reaction $\text{F}_2 + \text{CH}_3\text{I}$ was measured by counting at each angle for 20 seconds and performing two angular scans: the maximum counting rate was 500 sec^{-1} .

Determination of the velocity distributions of the products was accomplished using the TOF technique described earlier:² a channel width of 15 μsec was used for these experiments. Counting times ranged from one to two hours and flight times were 300–400 μsec . In performing the TOF experiments at the lower collision energy where the counting rate is fairly low, the signal statistics were improved by cooling the collision chamber to liquid nitrogen temperature. A nickel plated OFHC copper lining in the main collision chamber was attached to a 25-liter liquid nitrogen reservoir for this purpose. The main chamber pressure with the beams running was 1×10^{-7} torr.

Results and Analysis

The experimental angular and velocity distributions are shown in Figures 1-4. The angular distributions show bimodal character associated with the formation of a complex with lifetime greater than or comparable to a rotational period.

Because the fluorine beam contains an appreciable component of molecular fluorine ($\sim 30\%$), it was necessary to correct the IF signal

for contributions from products of molecular F_2 reactions, CH_3IF , which fragment in the mass spectrometer to IF . At the lower collision energy, the molecular reaction was not observed, but at the higher collision energy, a substantial IF signal was observed even when the oven temperature was reduced to arrest F atom production. A study of the mass spectrum of the product of the molecular reaction revealed the parent ion to be associated with $m/e = 161$ formed from the reaction $F_2 + CH_3I \rightarrow CH_3IF$. This product was found to fragment to mass 146 (IF) in the electron-bombardment ionizer. The angular distribution of CH_3IF is shown in Figure 5: in order to correct for IF arising from fragmentation of this product, the IF and CH_3IF angular distributions were measured successively under the same detection conditions in order to normalize the data. The fragmentation ratio was then determined by reducing the fluorine oven temperature where the F/F_2 ratio decreased and finally a temperature was reached such that the measured mass 146/mass 161 ratio became constant; at this point the IF signal was assumed to come exclusively from CH_3IF fragmentation. This limiting ratio was found to be essentially unity, implying 50% fragmentation of CH_3IF to IF . This value was used to correct the high energy data: the data of Figures 3 and 4 were corrected for this fragmentation. The largest correction was necessary at $\theta = 50^\circ$ where the apparent IF signal contained a 30% component ascribed to this fragmentation.

The apparent threshold for CH_3IF production was determined by monitoring the mass 161 signal as a function of the fluorine oven temperature, and thus of the kinetic energy. The shape of the lab angular distribution for CH_3IF remained essentially unchanged as the kinetic

energy was reduced and thus the intensity at the maximum can be used as a measure of the relative total cross section for the reaction. The "total cross section" data for CH_3IF production are shown in Figure 6 in which the data have been extrapolated to a threshold of 11 kcal mole⁻¹. This value implies that the CH_3IF complex is stable by at least 25 kcal mole⁻¹ relative to $\text{F} + \text{CH}_3\text{I}$ since the F_2 bond energy is 36 kcal mole⁻¹. This value for the stability of CH_3IF will be useful in later discussions of RRKM theory for this system.

The experimental data were analyzed using a least squares kinematic analysis procedure similar to that employed in other works from this laboratory.²⁴ A c.m. cross section function separable in recoil energy and scattering angle was used in the analysis:

$$I(E', \theta) = f(E') g(\theta)$$

The c.m. function was transformed to the laboratory by averaging over a 25 Newton diagram grid to yield a velocity averaged lab cross section for comparison with the data. The form chosen for $f(E')$ was the generalized RRK form:

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

where the parameters α , s , and V_a were varied. The angular distribution function was formulated as an expansion in Legendre polynomials with the coefficients chosen by a least square fit to the data:

$$g(\theta) = \sum_{\ell=0}^N a_\ell P_\ell(\cos\theta)$$

The low energy data were fitted using the first two even- ℓ functions since the data exhibited symmetry about $\theta = \pi/2$ in the c.m. system. The high energy experiment required the use of the first three

polynomials ($\ell = 0, 1, 2$) since the data were not perfectly symmetric about $\pi/2$; the significance of this point is discussed further, later in the paper. The best-fit energy and angular distribution parameters are listed in Table 1 and the fits which these functions provide are shown in Figures 1 to 4. The fits to the high energy data are satisfactory in light of the uncertainties in the correction for CH_3IF fragmentation. It was found that the angular distribution was not extremely sensitive to this correction but the opposite was true for the time-of-flight data. Center of mass contour maps for IF formation are shown in Figure 7.

The recoil distributions suggest that for the low energy reaction, approximately 70% of the total energy is channeled into internal excitation of the molecular fragments, while at the higher energy only ~55% of the energy appears in internal excitation. Rotational excitation of the fragments should be relatively low since the products separate along a line which passes through or close to the product centers of mass. Consequently, energy released in association with any repulsive bond rupture should remain primarily translational. Further discussion of the energy partitioning is found later. The c.m. angular distribution functions, plotted in Figure 8, demonstrate that the distributions show forward-backward peaking, the mechanism for which can be understood in terms of angular momentum disposal. Although the geometry of the CH_3IF complex is unknown, the well-known polyvalency of iodine along with Walsh diagram considerations suggests that the CH_3IF complex should be highly prolate. Although the complex contains 15 valence electrons (treating CH_3 as an H-atom) and thus Walsh's rules²⁵ do not allow a prediction of geometry, the fact that CH_3I is a highly prolate symmetric top ($I_{\perp}/I_{\parallel} \approx 20$) indicates that bonding of a fluorine atom to iodine should

maintain this general prolate structure even if C-I-F angle is slightly less than 180° . Because the CH_3I reactant is produced in a supersonic expansion, $J \approx 0$ and the orbital angular momentum $\underline{L}$ becomes the total angular momentum $\underline{J}$. Prior to separation of the complex to products, the rotational angular momentum of the complex equals $\underline{J}$ and the highly prolate nature of the complex requires that K , the projection of $\underline{J}$ on the symmetry axis, must be very small. Under these circumstances the complex rotates in a plane perpendicular to $\underline{J}$ and isotropic product emission occurs in this plane. Since the mass of the departing CH_3 is comparable to that of the F atom which attaches to the heavy I atom, one would expect a large fraction of the total angular momentum to be disposed of primarily as product orbital angular momentum $\underline{L}'$. This fact, coupled with the azimuthal distribution of $\underline{L}$ about $\underline{V}$ creates the $1/\sin\theta$ form factor consistent with forward-backward peaking. Miller, Safron, and Herschbach⁷ have shown that this model is characterized by a parameter $X = L_m/K$ where L_m is the average product angular momentum and K is the projection of $\underline{J}$ on the complex symmetry axis: X thus specifies the mean tilt of $\underline{J}$ with respect to $\underline{V}'$. K is quite small in our case and thus X is large: as the collision energy increases, L_m becomes larger while K remains small thus producing the stronger peaking observed at higher energy. The asymmetry observed at higher energy is attributed to the fact that the complex forms but decomposes before one full rotational period elapses. This process has been described by the "osculating complex" model proposed by McDonald, Fisk, and Herschbach¹⁵ to account for similar behavior observed in the reactions of alkali atoms with thallium halides. They have shown that the deviation from forward-backward

symmetry starts to appear when the complex lifetime becomes comparable to the rotational period and the ratios of backward to forward peaks become 0.81, 0.43, and 0.2 when the complex lifetime is 1.0, 0.5, and 0.3 times the rotational period, as shown in Figure 9. In the present case, we observe $I(\pi)/I(0) \approx 0.6$ and thus the osculating model predicts $\tau/\tau_r \approx 0.6$. Thus, if a reasonable estimate of the rotational period, τ_r , can be made, the osculating complex model can tell us the complex lifetime. The data analysis indicates that the observed $I(\pi)/I(0)$ ratio depends quite weakly on the fitting procedure and the precise recoil distribution parameters and thus τ_r and therefore τ should be determined with fair accuracy.

Statistical Models

As in previous works concerned with the decomposition of radicals produced by addition of fluorine atoms to organic molecules, the results can be compared with existing statistical theories to provide insight into the dynamics of unimolecular decomposition. Two theories have been used extensively in such comparisons: RRKM theory,¹⁰ parameterized in terms of the long-lived collision complex and critical configuration, and phase space theory,²⁶⁻²⁸ whose application depends on the asymptotic energy levels of the products. It is interesting to note, however, that the phase space theory requires a high degree of parameterization in determining the limits of the "strong-coupling" complex and in the disposal of the rotational energy of the critical configuration in descending an exit channel barrier. Considerations of such criteria have

led to a variety of assumptions⁵ in implementing phase space theory so that this model is parameterized nearly as much as RRKM under certain circumstances.

The assumption of quasiequilibrium between activated species A^* and critical configuration A^+ coupled with the separability of a one-dimensional reaction coordinate leads to the following expression for the unimolecular rate constant k_E describing conversion of activated species to products under the influence of the vibrational potential:

$$k_E = \sum_{E_{vr}^+ = 0}^{E^+} P(E_{vr}^+) / hN(E_{vr}^*) \quad (1)$$

where the numerator is the sum of all levels of the critical configuration (excluding the reaction coordinate) with energy $\leq E^+$, $N(E_{vr}^*)$ is the density of states of the complex at energy E_{vr}^* and h is Planck's constant. The appropriate energies are portrayed in Figure 10 where the energy assignments are those consistent with the observed stability of CH_3IF and the exothermicity of the reaction. The random lifetime assumption, implicit in the RRKM theory, relates the average lifetime of the complex to k_E : $\tau = (k_E)^{-1}$. By assuming structures for the energized complex CH_3IF and the critical configuration, the lifetime can be calculated from equation (1). The derivation of equation (1) assumes that rotations are inactive, a likely assumption if the moment of inertia of the complex varies little from that of the critical configuration. Because we have assumed that there is no exit channel potential energy barrier, centrifugal effects may be expected to reduce the calculated

lifetimes. Appropriate methods for averaging k_E over angular momentum have been given in the excellent review of Waage and Rabinovitch.²⁹ Corrections to k_E made with these methods generally increase the rate by $\lesssim 20\%$ and become smaller as the complex and critical configuration moments of inertia become more nearly equal. For our purposes, such small corrections will be ignored. Three models for calculation are employed: model A in which the CH_3 group is considered structureless and only the vibrations associated with the C-I-F framework are included. The IF bond strength in CH_3IF is roughly a factor of 3 lower than free IF: to lowest order, then, by assuming that a Morse potential describes IF and the potential curvature remains constant, we assume the IF frequency in the complex is a factor of $\sqrt{3}$ lower than that of the IF molecule, or, 350 cm^{-1} . The C-I frequency was reduced to 80% of its value in CH_3I ³⁰ or 400 cm^{-1} . The C-I-F bending frequency was assigned a value of 250 cm^{-1} . In the complex, the C-I stretch is associated with bond rupture, the IF frequency is increased to 550 cm^{-1} and the C-I-F bending frequency is decreased to 200 cm^{-1} . Using these values and ignoring the internal rotation of the CH_3 group since its reduced moment of inertia is quite small, the RRKM theory allows us to calculate τ . The results for model A are shown in Figure 11. A similar calculation was performed assuming activation of vibrations in the methyl fragment (model B), using the following frequencies taken from those of CH_3I : 2933, 1252, 3060, 3060, 1437, 1437, 882, 882, 400, 250, 350, 400 cm^{-1} . The results of this calculation are also shown in Figure 11, along with a lifetime calculation assuming the only vibration activated in CH_3 group is the umbrella bending mode ν_2 (model C). One expects

this mode to be active in the products because of geometry changes as the reaction occurs.

The rotational period of the complex can be calculated approximately if the angular momentum of the complex and its moment of inertia can be calculated. Since the total angular momentum is essentially equal to the initial orbital angular momentum, we can write $\tau_r = 2\pi(I/L)$. The reaction appears to proceed without large activation energy and thus we can calculate the orbital angular momentum from the condition that the kinetic energy exceeds the effective potential given by the long range attraction plus the centrifugal term.

$$\text{Thus } L_{\max} = [(2C_6)^{1/6} E^{1/3} (3\mu)^{1/2}] \quad (2)$$

$$V_{\text{eff}} = \hbar^2 L^2 / 2\mu R^2 - C_6/R^6$$

The C_6 constant was calculated using the Slater-Kirkwood³¹ expression: the F atom polarizability was taken as $0.6 \text{ \AA}^3$ ³² and that of CH_3I as $7.3 \text{ \AA}^3$.³³ We thus calculate $L_{\max}$ and $\tau_r \geq 2\pi(I/L_{\max})$: the moment of inertia of the complex was calculated assuming a bent structure with bond angle 150° . The I-F distance was chosen to be 25% longer than in free IF¹⁸ yielding $2.4 \text{ \AA}$; the C-I distance was assigned a value of $2.3 \text{ \AA}$, 10% longer than the C-I distance in CH_3I . This structure yields $I_{\perp} = 176 \text{ amu \AA}^2$: combined with $L_{\max} = 200 \hbar$ for the reaction at the higher collision energy, we calculate the rotational period of be $\tau_r \geq 8 \times 10^{-13} \text{ sec}$. This value is to be compared with RRKM lifetimes calculated at $E^+ = 25 \text{ kcal mole}^{-1}$ recalling that the osculating complex model predicts $\tau \approx 0.6 \tau_r$ or $5 \times 10^{-13} \text{ sec}$. The prediction of the osculating model appears to be in good accord with RRKM theory if only

the v_2 umbrella mode of CH_3 is included in evaluating densities of states. Worth noting in Figure 11 is the fact that the complex lifetime varies by only a factor of eight in moving from the "atomic CH_3 " representation to the fully-activated picture. This fact, showing the vibrational motions associated with light H atom in a atom-molecule transfer reaction involving heavier atoms are statistically insignificant, coupled with numerous approximations required to compare experimental and theoretical lifetimes, suggests that one cannot conclude the precise degree of activation of the complex, but only that RRKM theory combined with the osculating complex model gives reasonable lifetime results. A somewhat more quantitative assessment of the validity of statistical models can be made by discussing product recoil distributions calculated using phase space theory.

The phase space theory of Light and co-workers can be applied to this system readily: the particular model we have chosen assumes no activation barrier in the exit channel and thus the limits on the statistical theory are those of surmounting the centrifugal barrier. Our kinematic analysis of the data does not suggest an exit channel barrier and experimental studies of the related reaction $\text{CH}_3 + \text{I}_2$ ³⁴ indicate no activation energy. In this case the angular momentum restrictions are given by an equation of the form (2) where C_6 , E , and μ are the values appropriate to the exit channel. The Slater-Kirkwood theory was used to estimate C_6 : polarizabilities for the products were determined from a variety of sources. Such data are not available for IF but one can add the polarizabilities of F and I atoms as a first

approximation. The value for α_I was taken from the value for the negative ion³²; the atom and ion should have similar polarizabilities. Bond polarizability values³⁵ were used to compute α_{CH_3} . A consideration of the reactive cross section energy dependence indicates that the entrance channel centrifugal barrier is not the feature dominating complex formation. In such a case one expects the cross section to decrease as $E^{1/3}$; however, integration of the differential cross section data at the two energies indicates that the cross section increases by a factor of two as the energy increases from 2.6 kcal/mole to 14.1 kcal/mole. For purposes of calculation we have assumed cross sections of $25 \text{ \AA}^2$ and $50 \text{ \AA}^2$ at the two collision energies respectively. These values are quite consistent with the rate constant measured by Tal'roze.²⁰ Given the total cross section, we estimate L_{max} as follows:

$$L_{\text{max}} \approx (\mu v / \pi \hbar) (\sigma)^{1/2}.$$

Parameters used in these calculations are listed in Table 2. The phase space theory was used to calculate the cross section for forming products with recoil energy E' from reactants with initial kinetic energy E . In implementing the phase space theory readily the CH_3 group can be treated either approximately as a structureless particle as in the CH_3 emission studies from olefins or the vibrational degrees of freedom can be included in a more complete treatment. The latter case was considered appropriate here because of the number of states of CH_3 relative to IF. However, only the rotational motion of IF was included, partly because the coupling of three angular momenta necessary to describe rotational excitation of both fragments is difficult to formulate for calculations, and partly because rotational excitation of CH_3 should be small since the moment of inertia of CH_3 is small and

the products separate along a line which very nearly passes through their centers of mass. Phase space calculations were performed with two models: in model C, only the umbrella mode ν_2 of CH_3 is excited. This vibration is expected to be excited because of the change in geometry from tetrahedral to trigonal planar in proceeding from reactants to products. In model D, six vibrations of CH_3 are included which are those appropriate to D_{3h} symmetry. The frequency values are chosen in accordance with the precursor frequencies in CH_3I except for experimental values of ν_2 .³⁶ The following values were used: 2969, 607, 3060 (2), and 1440 (2), where (2) indicates these vibrations are doubly degenerate. The results of the phase space calculations with these models are shown in Figure 12. For computational ease, the Whitten-Rabinovitch approximation³⁷ for the vibrational level density was used for all calculations since the number of states is reasonably large where the recoil distribution is large. The phase space results at low energy provide a picture quite consistent with that given by the RRKM calculation. Model C, which only includes the ν_2 mode of CH_3 , appears to give slightly better overall fits to experimental angular and energy distributions as shown in Figures 1 and 2. The difference between Model C and Model D is rather small because the additional phase space volume provided by the remaining CH_3 vibrations not included in Model C do not make a significant contribution in this system as discussed earlier. The derived best-fit translational energy distribution lies somewhere between Model C and Model D. This comparison suggests that the statistical distribution of the energy in the complex holds to a large extent at the lower collision energy.

The high energy results calculated from phase-space theory do not give as good an agreement with experimental data as shown in Figures 3 and 4. The experimental data appear to be fitted better with a model in which more energy appears in translational modes than either model predicts, but the derived best-fit product energy distribution does not deviate significantly from those of both statistical models.

Discussion

The present results have demonstrated that additional valuable information regarding the energetics and dynamics of unimolecular decomposition can be obtained from molecular beam experiments when the collision energy of the reactants is increased to values comparable to the well-depth of the chemically activated intermediate species such that complex lifetimes become comparable to a rotational period. In the case of $F + C_2H_4$ ^{1,38}, for example, the C_2H_4F radical is bound by ~ 50 kcal mole⁻¹ and collision energies high enough to break up this complex are difficult to achieve by seeded molecular beam techniques. The $F + CH_3I$ system is especially favorable for studies employing the complex rotational period as a "clock" because the structure of the complex coupled with the partitioning of angular momentum produces strongly bimodal angular distributions at high energy and the disappearance of forward-backward symmetry can be detected easily. If no information on the energetics of the complex is available, by assuming that RRKM theory applies to the decomposition of the complex, a lower bound on the stability of the complex can be estimated from the total energy available

to the complex and the complex lifetime. For CH_3IF , the stability estimated from the preceding dynamic arguments is indeed in reasonably good agreement with the value obtained from the threshold behavior of the $\text{F}_2 + \text{CH}_3\text{I}$ reaction forming CH_3IF . Since a reliable value for the binding energy has been measured independently in our experiments, the complex lifetime and translational energy distribution will provide us an opportunity to carry out a more meaningful discussion. Such favorable conditions have led us to conclude that RRKM calculations for the complex lifetime and phase space calculations of the product recoil distribution are in reasonable accord with the data at the lower collision energy of $2.6 \text{ kcal mole}^{-1}$. The high energy results suggest that while the lifetime is in good accord with RRKM theory, the recoil distribution is not very statistical. At the higher collision energy of $14.1 \text{ kcal mole}^{-1}$, the lifetime of the complex may be reduced to the extent that energy randomization cannot occur in this time period. Statistical theories make no assumptions regarding the dynamics of intramolecular energy transfer which are only assumed to be rapid compared to the chemical reaction time. Bunker³⁹ has performed trajectory calculations to examine the time required for energy randomization to occur and has found that for covalent systems, microcanonical equilibrium is achieved within $\sim 10^{-11}$ sec and RRKM theory seems to be valid for most polyatomic systems except a few bent triatomic molecules. Conversely, Rabinovitch⁴⁰ has shown, using the chemical activation technique, that energy randomization takes place in less than 2×10^{-13} sec in butyl radicals undergoing decomposition to methyl radicals plus propylene. Thus a wide time scale has been shown to characterize energy randomization. The

efficiency of intramolecular energy transfer for a given molecule depends on the details of the potential energy hypersurface. In general, if the stability of the complex is large in comparison with the excess energy available beyond that required for the decomposition, the lifetime of the complex is expected to be long compared to a rotational period and the energy randomization assumption of RRKM theory should be reasonable. On the other hand, if the total energy available to the reaction is much larger than the binding energy of the complex, the reaction will be more "direct", especially for systems containing a small number of atoms, and the reaction may be essentially complete before the energy is fully randomized in the molecule.

For a given system, when the energy of the complex is increased, although anharmonicity of vibrational motion, i.e., the coupling between various modes, is expected to be more important and may facilitate the randomization of energy, a decrease of the lifetime from the excess energy available is expected to be more drastic. Consequently, it is not surprising to find that when the energy of a system is increased substantially, the characteristics of the dynamics of the decomposition of the complex change from statistical to nonstatistical. This transition is gradual both as the total energy of the system changes and as the structural and chemical characteristics of the complex are varied. From our experience in the investigation of substitution reactions of fluorine atoms and unsaturated hydrocarbons, it is fair to say that if the binding energy of the complex is several times the exoergicity, even if some evidence of a nonstatistical energy distribution is observed, such a feature will not dominate the reaction dynamics and

the energy randomization assumption of RRKM theory will be good first approximation for estimating the lifetime of the complex to derive information on the rate of decomposition. We have also observed previously when a barrier in the decomposition channel is present, the potential energy is usually released entirely as translational motion of product molecules. The decomposition of many fluoro-olefin, emitting H and CH₃, are good examples.

One notable difference between $F + CH_3I \rightarrow IF + CH_3$ and $F + C_2H_4 \rightarrow C_2H_3F + H$ studied previously^{1,38} concerns the disposal of the rotational energy of the complex. For both cases, part of the translational energy will become rotational energy of the complex as a consequence of the conservation of angular momentum of the system. In the decomposition of C₂H₄F into C₂H₃F+H, since the H atom is a light particle, it will not carry away significant fraction of the total angular momentum and the rotational energy of the complex will mainly appear as rotational excitation of the product. In the decomposition of CH₃IF, however, a significant fraction of the angular momentum will be carried away by the departing CH₃ radical, since the departing CH₃ has a mass similar to an F atom which attaches to I, and thus the rotational energy of the CH₃IF complex will mainly appear as translational energy of the product. The larger fraction of energy appearing as translational energy in both statistical calculations and experiment at the higher collision energy in contrast with those of low collision energy arises primarily from the fact that a larger fraction of the total energy is deposited as rotational energy of the complex and reappears as translational energy of product molecules.

The determination of the binding energy of CH_3IF from the threshold behavior of the endoergic reaction of CH_3I and F_2 , represents a promising new general method for probing stabilities of radicals. This method, which is unique to the crossed molecular beam technique, is expected to provide much new information on the stability of radical molecules which have eluded chemists for a long time.

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* Work performed under the auspices of U.S. Energy Research and Development Administration and Office of Naval Research.

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TABLE 1. Energy and Angular Distribution Parameters

E(kcal/mole)	V _a (kcal/mole)	α	s	a ₀	a ₁	a ₂
2.60	0.	.5	2.6	1.00	0.00	0.444
14.1	0.5	1.2	1.4	1.00	0.528	1.193

TABLE 2. Phase Space Parameters

Parameter	Value
α_{IF}	$6.6 \text{ \AA}^3$
α_{CH_3}	$1.9 \text{ \AA}^3$
$(\text{C}_6')_{\text{CH}_3} - \text{IF}^a$	$3769 \text{ kcal \AA}^6$
Model C	
β^b	0.5000
E_z^b	1.72 kcal/mole
Model D	
β	1.0551
E_z	19.75 kcal/mole

^a Slater-Kirkwood values^b Whitten-Rabinovitch parameters

Figure Captions

Fig. 1. IF angular distribution, $\bar{E} = 2.60$ kcal/mole. Phase space calculations as noted.

Fig. 2. IF flux distributions vs. lab velocity for various θ . —, experimental fit; — —, phase space model C; - · - ·, phase space model D. $\bar{E} = 2.60$ kcal/mole.

Fig. 3. IF angular distribution, $\bar{E} = 14.1$ kcal/mole.

Fig. 4. IF flux distributions for various θ . —, experimental fit; — — —, phase space model C; - · - ·, phase space model D. $\bar{E} = 14.1$ kcal/mole.

Fig. 5. CH₃IF angular distribution, $\bar{E} = 25.1$ kcal/mole.

Fig. 6. CH₃IF production vs. kinetic energy.

Fig. 7. IF center of mass contour maps for $F + CH_3I \rightarrow IF + CH_3$ at two collision energies. Equal intensity contours shown in arbitrary units.

Fig. 8. C.M. angular distributions. —, $E = 2.60$ kcal/mole. - · - ·, $\bar{E} = 14.1$ kcal/mole.

Fig. 9. Osculating model falloff function for various ratios of lifetime to rotational period.

Fig. 10. Symbolic reaction coordinate diagram for $F + CH_3I$ reaction. Energies defined in the text.

Fig. 11. RRKM complex lifetime calculations. Model A, structureless CH₃. Model B, CH₃ fully activated. Model C, ν_2 mode of CH₃. Arrows denote energies of experiments.

Fig. 12. $F + CH_3I$ product recoil energy distributions.

Fig. 1

XBL 756-1496

Fig. 2

XBL 756-1497

Fig. 3

XBL 756-1498

NBL 756-1499

Fig. 4

Fig. 5

XBL 756-1500

XBL 756-1501

Fig. 6

XBL 755-2913

Fig. 7

XBL 756-1502

Fig. 8

XBL 756-1503

Fig. 9

XBL 756-1504

Fig. 10

XBL 756-1505

Fig. 11

NBL 756-1506

Fig. 12

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