Computer Simulation of Some Reactions of Energetic Tritium and Fluorine Atoms

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A six body atom + tetrahedral molecule model of hot atom reactions is described and used to study the reactions of hot T and F atoms with CH_4 and CF_4. Excitation functions for all observed reactions are given for the energy range 0-30 eV. The functions are compared with the data available from recoil atom studies and found to be qualitatively consistent with the principal features of the experimental results. Of particular interest is the very high degree of internal excitation deposited in products following substitution reactions by hot F atoms with molecules containing at least two heavy atoms or groups. Using the $F + CH_2F_2$ system, it is shown that some substitution events occur in which more than 9.4 eV is deposited in the product molecule.

The reactions of translationally excited atoms have been extensively studied in recent years.[1] The results of these investigations have indicated the existence of chemical processes which are not normally observed in systems close to thermal equilibrium. With the recent development of energetic atomic beams [2] the time is approaching when the cross sections for many such reactions will be measurable over a wide range of energy, leading ultimately to a quantitative understanding of elementary processes in the finest detail. At present, knowledge of the detailed mechanisms of most energetic reactions is limited; probably the only well understood system is

$$H + H_2 \rightarrow H_2 + H \tag{1}$$

and its isotopic analogues, some of which were studied theoretically by Karplus *et al.*[3]

Several attempts have been made to study the theoretical aspects of more complex systems, such as the energetic tritium atom + methane system:

$$T + CH_4 \rightarrow HT + CH_3 \cdot \tag{2a}$$

$$T + CH_4 \rightarrow CH_3T + H \cdot \tag{2b}$$

The two principal reactions are abstraction (2a) and substitution (2b) of a hydrogen atom. Polanyi *et al.*[4] performed trajectory studies on T + RH, (where R was a structureless species of mass 12 a.m.u.) using a modified L.E.P.S. potential hypersurface. Bunker and Pattengill [5] performed restricted six atom trajectory calculations on $T + CH_4$, and, more recently, Valencich and Bunker [6] have reported results from a full six atom study.

Much cruder calculations, based on hard sphere models, have also been performed for the reactions (1) and (2). The kinematic model proposed by Suplinskas [7] was highly successful for reaction (1), in that it predicted energy dependences for the reaction cross sections very similar to those obtained by Karplus *et al.* Application of the kinematic model to the T + RH system was less successful, in that no significant substitution reaction (2b) was observed. However another hard sphere model [8] has been used on T + RH and its isotopic analogues,[9] and the results were useful in furthering our understanding of these reactions. The success of this latter model

prompted the present work in which a six body hard sphere model is developed and used to study some reactions of hot tritium and fluorine atoms with methane and the fluoromethanes.

THE SIX BODY MODEL

Essentially, the six body model is a straightforward extension of the three body model described previously.[8]   However, the representation of the five body reactant molecule by a tetrahedral arrangement of hard spheres in contact does increase the number of collision events which must be simulated in order to obtain cross sections with small statistical uncertainties, and does make the choice of reaction product somewhat more cumbersome than in the three body case.
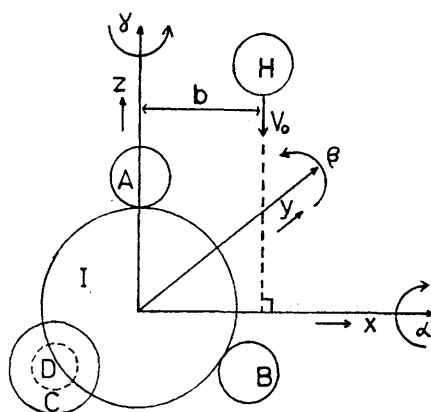

FIG. 1.—Coordinate system used in simulation of atom+tetrahedral molecule collisions.   The hot atom approaches the molecule with a velocity vector parallel to the z-axis and contained in the x-z plane.   The tetrahedral molecule is rotated about the x, y and z-axes through angles of α, β and γ respectively.

The coordinate system used for these calculations is shown in fig. 1.   The origin is taken at the centre of the four coordinate atom, I.   The coordinates of the four ligand atoms, A, B, C and D, are initially taken to be:

$$x_A = 0.0 \qquad\qquad y_A = 0.0 \qquad\qquad z_A = r_{AI}$$

$$x_B = r_{BI} \sin a \qquad\qquad y_B = 0.0 \qquad\qquad z_B = -r_{BI} \cos a$$

$$x_C = -r_{CI}' \sin a \cos b \qquad y_C = r_{CI} \sin a \sin b \qquad z_C = -r_{CI} \cos a$$

$$x_D = -r_{DI} \sin a \cos b \qquad y_D = -r_{DI} \sin a \sin b \qquad z_D = -r_{DI} \cos a$$

where r_{ij} is the sum of the radii of atoms i and j,

$$a = 70°32' \quad \text{and} \quad b = 60°.$$

The cross sections were determined by examining the results of $\sim 150\,000$ approaches of the hot atom, H, along the z-axis after the tetrahedral molecule had been rotated about the x, y and z-axes by angles α, β and γ respectively.   Each rotation was performed in increments of $\pi/20$ between 0 and 2π.   The initial velocity of H was V_0, and the impact parameter, b, was varied from 0 to b_{max} (where b_{max} was such that no collision resulted) in steps of 0.01 nm.   The initial coordinates of H were $x_H = b$, $y_H = 0$.   The z-coordinate for H was determined by calculating the point at which the hot atom first came into contact with one of the hard spheres of the reactant molecule.

At the point of contact, hard sphere energy and momentum transfer take place between the hot atom and the struck atom, and then between the struck atom and any other atom with which it collides. Thus, whether the struck atom is the central atom of the molecule or one of the ligand atoms, energy may be transferred into some or all of the bonds of the original molecule as relative kinetic energy of motion of the respective hard spheres. The motion of the hot atom is then followed to see whether any other atoms are struck—in which case hard sphere energy and momentum transfer again take place. After these collision processes the vector velocity of each hard sphere is known and the relative kinetic energy of each pair of adjacent atoms may be evaluated using

$$E_{ij} = \tfrac{1}{2}\mu_{ij}(\overline{V}_i - \overline{V}_j)^2.$$

PRODUCT FORMATION

Just as in the case of the three body hard sphere model,[8] so here the probability of formation of the various possible reaction products is calculated by the application of a few simple rules as described below. There are two different reaction types which may be distinguished:

ABSTRACTION

$$\text{e.g.,} \quad \text{H} + \text{IABCD} \rightarrow \text{HA} + \text{IBCD} \tag{3}$$

We assume first that this process may occur only after H collides with A, or, if H collides with more than one atom, when the final collision is with A. Secondly, the line-of-centres relative kinetic energy of H and A prior to the collision must exceed the activation energy for that abstraction process. (If this condition is not met then H is considered to be scattered without reaction.) If these conditions are satisfied then the energy of the hot atom is reduced by an amount equal to the activation energy.[8] The probability of reaction (3) occurring is then taken to be proportional to the stability that the H—A bond would have if reaction (3) did occur. Similarly, the probability of the occurrence of reaction (4) is obtained from the stability of the I—A bond.

$$\text{H} + \text{IABCD} \rightarrow \text{H} + \text{IABCD} \tag{4}$$

As before,[8] the term stability, S_{ij}, is used in the energetic sense, and represents the energy required to dissociate the i—j bond in excess of that already present as relative motion of the i and j atoms. In common with the three body model, it has been assumed that the potential energy released in passing from the transition state to the products,[8] $E_{act} + \Delta E$ (where ΔE is the exothermicity of the reaction and has been taken as the difference in energy between the broken and newly formed bonds), has an equal probability of appearing as relative motion of the i—j pair and as translational motion of the separating products. In the three body model a uniform random number sequence was used to distribute this energy, but for the sake of simplicity in these calculations $\tfrac{1}{2}(E_{act} + \Delta E)$ was added to the relative energy of the i—j pair.

Thus

$$S_{ij} = D_{ij} - E_{ij} + \tfrac{1}{2}(E_{act} + \Delta E) \tag{5}$$

where D_{ij} is the dissociation energy of the i—j bond, E_{ij} is the relative kinetic energy of i and j after collision involving the hot atom at $(E - E_{act})$, and E_{act} is the activation energy for this abstraction reaction. Following the collision of H with A, S_{HA} and S_{AI} may be evaluated. If S_{AI} is zero or negative, then clearly reaction (3) must occur with

unit probability. Similarly reaction (4) must occur if $S_{HA} \leqslant 0$. If both $S_{HA} \leqslant 0$ and $S_{AI} \leqslant 0$ then the dissociation process (6) must occur.

$$H + IABCD \rightarrow H + A + IBCD \tag{6}$$

When S_{AI} and S_{HA} are both positive, the absolute probabilities, p_i, for reaction (3) and (4) to occur are obtained from

$$p_3 = S_{HA}/(S_{HA} + S_{AI})$$

and

$$p_4 = S_{AI}/(S_{HA} + S_{AI}).$$

SUBSTITUTIONS

$$H + IABCD \rightarrow IHBCD + A \tag{7}$$

$$\rightarrow IHCD\cdot + B + A \tag{8}$$

Reaction (7) is the simple substitution of A by H. This reaction was allowed to occur only when H collided with the central atom, I, and did so with a line-of-centres relative energy greater than the activation energy for the substitution process. Again, the relative kinetic energy of the collision was reduced by an amount equal to the activation energy. And, as before, the relative stability of each bond was calculated using eqn (5), and the S_{Ij} ignored in subsequent calculation if $E - E_{act} \leqslant 0$. If any one $S_{Ij} \leqslant 0$ then the substitution reaction which breaks that bond occurs with unit probability. If any two $S_{Ij} \leqslant 0$ then the simultaneous breaking of two bonds (reaction (8)) occurs with unit probability—a process known as *double knock*. The extension to other multiknock processes is obvious, although no such cases were observed in the systems studied in this work. (The same products are of course to be expected from sufficiently excited molecules by the consecutive ejection of two or more ligands. However, such unimolecular decay processes were not examined in this work.) If no $S_{Ij} \leqslant 0$ then the absolute probability for the breaking of the I—j bond was taken to be

$$p_{Ij} = (1 - S_{Ij})/4\sum_{k}S_{Ik}.$$

For any collision the absolute probability of occurrence of all possible reactions may be determined and an amount, $p_x \, bdbd\gamma$, added to the appropriate cross section counter. Thus the various cross sections may be determined as functions of α and β. Integration of the results over all angles gives the reaction cross sections reported below.

INTERNAL ENERGY OF PRODUCTS

Once the reaction probability for each possible abstraction or substitution has been evaluated, the internal energies of the products may be determined. For the abstraction product, Hj, this merely requires the evaluation of

$$\tfrac{1}{2}\mu_{Hj}(\overline{V}_H - \overline{V}_j)^2$$

(where μ_{Hj} is the reduced mass of H and j, and $\overline{V}_i$ is the vector velocity of atom i.)

For the substitution product, the total internal energy was taken to be the difference between the sum of the kinetic energies of the individual atoms in the product molecule and the kinetic energy of the centre of mass of the product. Internal energies were averaged over all collision parameters and the resulting distributions given in the form of ten block histograms.

RESULTS AND DISCUSSION

The hard sphere reaction cross section for all primary processes following the collision of energetic T and F atoms with CH_4 and CF_4 were determined.   The results are shown in fig. 2 to 5, where the excitation functions up to 30 eV for abstraction, substitution and dissociation are given.   The functions exhibit a number of significant features, and these will be discussed in relation to the available experimental data.

$$T+CH_4$$
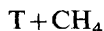
The principal reactions observed in the experimental recoil tritium-methane system [10] are abstraction (9) and substitution (10) of a hydrogen atom, two processes which occur with a comparable high efficiency.

$$T+CH_4 \rightarrow HT+CH_3 \cdot \qquad (9)$$

$$T+CH_4 \rightarrow CH_3T+H \cdot \qquad (10)$$

The present model predicts hard sphere excitation functions which are qualitatively in agreement with this experimental result.   Averaged over all substitution events, the model predicts a mean internal product energy of ~ 5 eV, again in satisfactory agreement with the results obtained from pressure dependence studies with hydrocarbons other than methane.[11, 12]   No double substitution [13] events were observed, a finding consistent with recent pressure dependence results from ethane.[14]
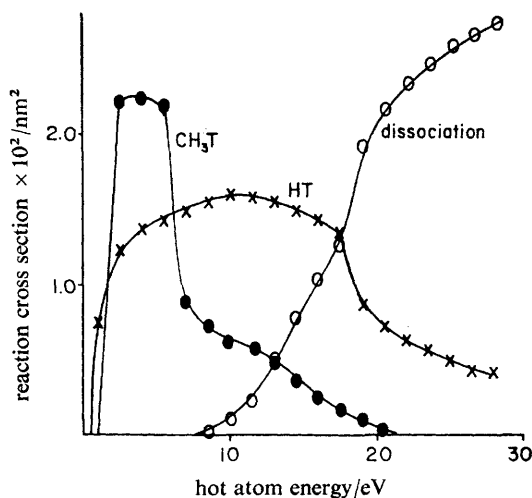

FIG. 2.—Excitation functions for all primary results of $T+CH_4$ collisions.   Points at which the cross sections are identically zero have been omitted.   The lines joining the points are purely schematic in this and subsequent figures.   The total hard sphere cross section was 0.058 nm² at all energies.

Apart from the relative magnitudes of the abstraction and substitution excitation functions, the functions of fig. 2 are qualitatively similar to the functions obtained earlier [9] using the three body hard sphere model for $T+RH$ (where R was treated as a structureless sphere of mass 12 amu).   In both cases the abstraction function was found to extend over a wider energy range and to exhibit a maximum at a higher energy than the substitution function.   In this case the abstraction function peaks at a T atom energy of ~ 10 eV, a value which compares favourably with the value of $\sim 8\frac{1}{2}$ eV (laboratory coordinates) obtained by Valencich and Bunker.[6]   However,

the substitution function obtained here, while possessing a high energy tail, peaks at significantly lower energies, resembling the result obtained by Polanyi et al.,[4] and quite unlike that recently reported by Valencich and Bunker.[6]

The principal features of the angular dependences of the abstraction function were found to be quite similar to those reported for the three body calculation.[19] The translational and internal energy distribution of the abstraction product were also comparable to the earlier findings, so that the possibility of dissociation of translationally excited abstraction product on subsequent collision [15] must be considered when comparing the results of the hard sphere calculations with experiment.[16] About 25 % of the initial T atom translational energy appears as internal energy of the abstraction products, in good agreement with the recent results of Valencich and Bunker.
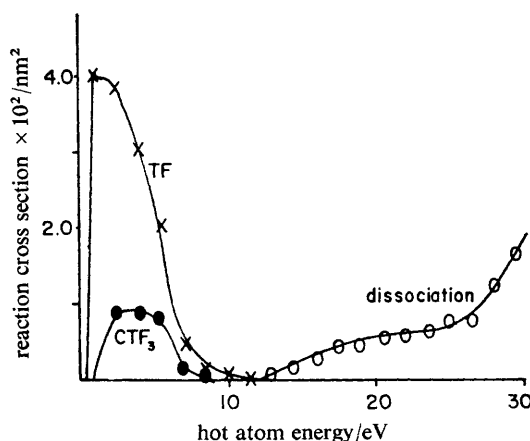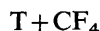

FIG. 3.—Excitation functions for all primary results of $T+CF_4$ collisions. The total hard sphere cross section was 0.099 nm^2.

$$T+CF_4$$

Of the hot tritium reactions with CF_4, only substitution (11) has been experimentally observed,[17] although it has long been recognised that significant abstraction (12) must also occur.

$$T+CF_4 \rightarrow CF_3T+F\cdot \tag{11}$$

$$T+CF_4 \rightarrow TF+CF_3\cdot \tag{12}$$

The predicted excitation functions shown in fig. 3 indicate that the substitution reaction in CF_4 is likely to occur with a much lower collision efficiency than the analogous process in CH_4. The predicted ratio of reactivity integrals,

$$I_i = \int_0^\infty \frac{p_i(E)}{E} \, dE,$$

from fig. 2 and 3 is

$$I_{CF_3T}/I_{CH_3T} \sim 0.18$$

which compares favourably with the experimental ratio of the substitution yields in unmoderated reactants [10, 17] of

$$P_{CF_3T}/P_{CH_3T} \sim 0.15$$

since the moderating efficiencies of CH_4 and CF_4 are known to be comparable.[10, 18]

The magnitude of the TF yield from CF_4 is unknown, although the present results indicate that a yield of about five times the substitution product yield would be anticipated in a recoil tritium experiment. In view of the masses involved, the absence of a high energy abstraction mode in this system is not surprising. About 60 % of the initial tritium atom energy appears as internal energy of the abstraction product, this factor varying only at energies above 8 eV, where the cross section has become small.

The internal energy distribution of the substitution product was similar to that found following H-substitution in CH_4, and averaged to about 5.5 eV. Again no double substitution was observed at any energy.

$$F + CH_4$$

Hot fluorine atom reactions have been extensively studied by Rowland et al.[19] and Root et al.[20, 21] The two principal features of hot fluorine reactions with hydrocarbons are : (1) a very high yield of the H-abstraction product,[20] and (2) a substantial
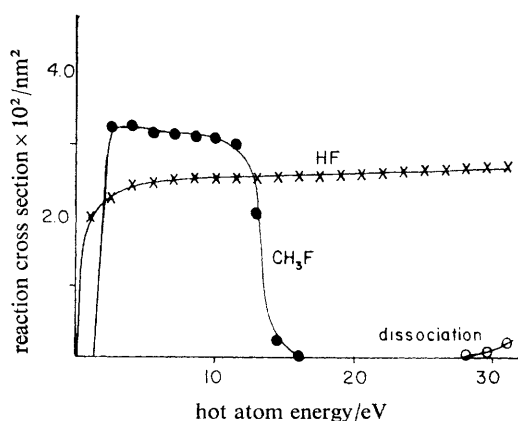

FIG. 4.—Excitation functions for all primary results of $F + CH_4$ collisions. The total hard sphere cross section was 0.087 nm^2.

fraction of the F for H substitution product containing high internal energies.[21] The excitation functions for the H-abstraction (13) and substitution (14) reactions are shown in fig. 4.

$$F + CH_4 \rightarrow HF + CH_3 \cdot \tag{13}$$

$$F + CH_4 \rightarrow CH_3F + H \cdot \tag{14}$$

The abstraction function is likely to be characteristic of H-abstraction from other molecules containing C—H bonds, thus the present result suggests that HF formation should be a very efficient reaction. This finding is in good agreement with the report by Root et al.[20] that > 50 % of ^{18}F activity induced in CH_3CF_3 appears in the form of HF. The excitation function for HF, shown up to 30 eV (lab. energy) in fig. 4, continues to rise slowly up to ca. 40 eV, and thereafter slowly declines, falling to approximately 1/5 of its peak value at 100 eV. Not surprisingly most of the hot atom energy remains in the product in the form of translational motion, ~10 % of the energy appearing in vibration over the entire energy range studied.

The substitution reaction (14) resulted in a product which invariably contained about 50 % of the initial hot atom energy in the form of internal energy. In view of the similarity between the reactant masses, and the low mass of the particle ejected on

substitution, this is not at all surprising. As will be seen below, the high internal energies of substitution products reported by Root et al.[21] and Rowland et al.[22] were found only from reactants containing at least two heavy atoms or groups (e.g., CH_3F).
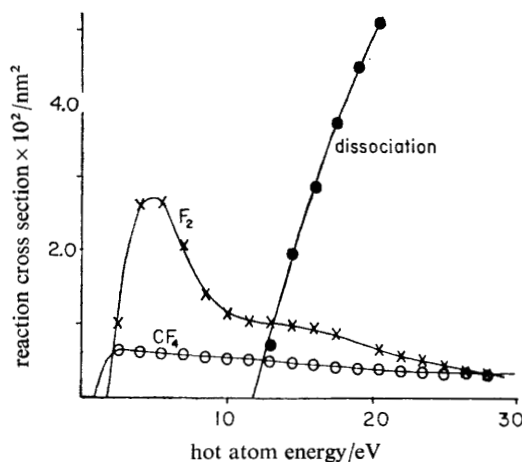

FIG. 5.—Excitation functions for primary results of $F + CF_4$ collisions. In addition to the functions shown, a very small number of double substitution events were observed. The cross section for this process was negligible compared with the reactions shown. The total hard sphere cross section was 0.135 nm^2.

$$F + CF_4$$

The abstraction reaction (15) gives a hard sphere excitation function (fig. 5) which peaks at a comparatively low F atom energy of ~ 5 eV.

$$F + CF_4 \rightarrow F_2 + CF_3 \cdot \qquad (15)$$

$$F + CF_4 \rightarrow CF_3F + F \cdot \qquad (16)$$

Comparison of the abstraction functions in fig. 4 and 5, quite apart from the expected variation in hot atom collision densities, suggests that F to F_2 abstraction would be a considerably less efficient process than F to HF abstraction, although still two or three times more efficient than F for F substitution in a fully fluorinated alkane. Root et al.[20] have reported an HF/F_2 ratio from the $F + CH_3CF_3$ system of about 10 to 1. Although the F to F_2 abstraction does exhibit a high energy tail, the low dissociation energy of the F—F bond and the fact that most of the F_2 formed in the high energy region is predicted to contain >2 eV of internal energy, suggests that collisional dissociation may result in the destruction of at least part of the F_2 formed in experimental systems. Consequently a rather low yield of F_2 would be expected, compared with the HF yield anticipated from the results of fig. 4.

The substitution reaction (15) occurred with a very low collision efficiency in these calculations, largely as a result of the small probability of a collision between the hot F atom and the central carbon atom of CF_4. This result alone is consistent with a primary yield of F for F substitution product of only $\sim 3.5 \%$ in CH_3CF_3. However, the high efficiency of energy transfer around this system, in which several of the atoms in contact are of similar mass, resulted in the substitution function extending to beyond 30 eV before the reaction efficiency had fallen to half its peak value. In addition much of the substitution product was formed with a high degree of internal excitation. For example, at 20 eV more than half of the product formed contained more than

16 eV of internal energy. The bulk of the available experimental data [20-22] has, indeed, suggested that residual vibrational energies in F for F substitution products are large (8-20 eV). The present result indicates that this fact can be interpreted largely in terms of the kinematics of the collision.

$$F + CH_2F_2$$

To investigate the deposition of energy in substitution products, a study was made of the reactions of F atoms with difluoromethane. The excitation functions obtained are shown in fig. 6. The principal features of the possible reactions (17)-(20) are
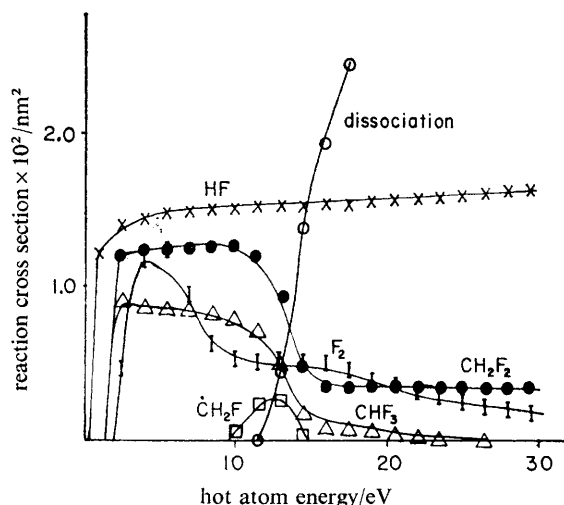
FIG. 6.—Excitation functions for all primary results of $F + CH_2F_2$ collisions. The function □ arose from double substitution events in which both F ligands were ejected. No double substitutions involving H atom ejection were observed. The total cross section for this sytem was 0.109 nm².

essentially the same as would have been inferred from the results in fig. 4 and 5, bearing in mind that the substitution cross sections are largely determined by the number of collisions between the hot atom and the central atom.

$$F + CH_2F_2 \rightarrow HF + CHF_2\cdot \qquad (17)$$
$$\rightarrow FF + CH_2F\cdot \qquad (18)$$
$$\rightarrow CH_2FF + F\cdot \qquad (19)$$
$$\rightarrow CHF_2F + H \qquad (20)$$

Again, a high energy tail is found for the F for F substitution process, arising primarily from the high efficiency with which translational energy of the struck carbon atom is transformed into vibrational energy of C—F bonds.

The internal energy of the substitution products obtained from hot F atoms at 8.5 and 14.5 eV are shown in fig. 7. Since the available energy is ∼70 % of the F atom laboratory energy, it is clear that virtually all of the relative energy in the system is converted to vibrational energy during the F for H substitution reaction. During F for F substitution the conversion is less efficient, although high excitation energies are produced by reaction below ∼15 eV, and more than half of the product formed in

the high energy tail region (which extends to > 100 eV) contains enough energy to break a C—F bond (~ 4.7 eV).

Experimentally, the yields of CH_2FF,[18] CHF_2F [18] and the corresponding radicals derived from a single bond rupture, sum to ~ 10 % of the available F.[18] Rowland et al.[22] have estimated that the true primary hot yield may be more than double this
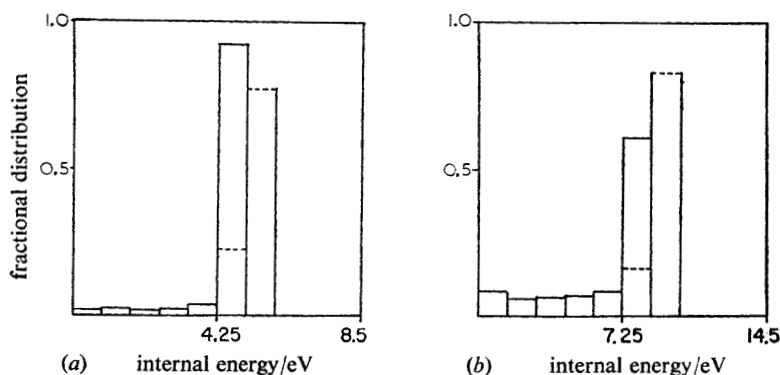

FIG. 7.—Internal energy distribution of products resulting from F for F (——) and F for H (– – –) substitution in CH_2F_2, with initial hot atom energies of (a) 8.5 and (b) 14.5 eV respectively.

TABLE 1.—PARAMETERS USED IN ATOM + TETRAHEDRAL MOLECULE CALCULATIONS

atom	mass/a.m.u.	hard sphere diam.[a]/ nm
H	1	0.075
T	3	0.075
C	12	0.150
F	19	0.130

bond	bond dissociation energy/eV
H—T	4.5
H—F	6.4
C—H	4.5
C—F	4.7
F—F	2.7

process	activation energy[b]/ eV
abstractions:	
T to HT	0.50
F to HF	0.20
T to TF	0.13
F to F_2	2.05
substitutions:	
T for H	1.5
T for F	1.0
F for H	1.5
F for F	1.5

[a] Based on bond lengths, see ref. (9); [b] activation energies for H to H_2 and F to HF abstractions are known.[23] Others are estimated values based on threshold measurements and discussion given in ref. (24).

figure, a result which would be consistent with the magnitudes of the excitation functions given in fig. 6. In view of the large amount of energy deposited in the primary substitution products it would not be surprising to find that $\gtrsim 50\%$ of the product decomposed via HF elimination (~ 2.8 eV endothermic) and F_2 or $2F$ elimination (> 7 eV endothermic).

In the $F + CH_2F_2$ system a small amount of double substitution was observed with the hard sphere model. The efficiency of the process was low and its occurrence was confined to a relatively narrow energy range (see fig. 6). Only the two F atoms were ejected by the *double-knock* events, although certainly the magnitude of the excitation function was such that it would be difficult to differentiate experimentally between this product and that arising from the unimolecular decomposition of an excited substitution product. The significance of this finding in the calculations is in the indication that more than 9.4 eV may be transferred to the reactant molecule, while at the same time the hot atom can become bound. This is a particularly interesting result in view of Root's [21] recent observation of products from hot F reactions with CH_3CF_3 which require excitation energies of primary products of more than 9.3 eV.

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