

[CONTRIBUTION 1708, STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

## Moderating and Reactive Collisions of Hot Hydrogen Atoms: A Study on Isotope Effects in Methyl Fluoride

BY H. CLEMENT JURGELEIT<sup>1</sup> AND RICHARD WOLFGANG

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Measurements on the isotope effect on the reaction of hot hydrogen atoms with protonated and deuterated methyl fluoride have been made. Recoil tritium from the  $\text{He}^3(n,p)\text{H}^3$  reaction was used as the source of hot hydrogen. The yield of total hot reaction products incorporating the tritium atom (with the exception of TF which was not measured) was 18% lower in  $\text{CD}_2\text{F}$  than in  $\text{CH}_2\text{F}$ . Smaller variations were found in the relative yields of the various products. These results can be accounted for by either several types of isotope effects on the reactive collision, or, more simply, by a greater moderating power of  $\text{CD}_2\text{F}$  compared to  $\text{CH}_2\text{F}$ . The implications of the latter hypothesis are quantitatively examined using idealized models of the moderation process. It appears that in the energy range where hot combination reactions occur, moderating as well as reactive collisions effectively involve only a small portion of the mass of the molecule struck, although that portion is probably larger than would correspond to a single atom.

Conclusions of this work regarding reactive collisions of the hot hydrogen atom are: (1) The mean energies at which the various hot reactions take place are: H abstraction < H displacement < F displacement < 2 atom displacement. (2) The billiard ball mechanism of hot reaction is inapplicable. (3) A possible secondary isotope effect on fluorine displacement has a magnitude less than experimental error. (4) No effect on hot reaction of the difference in bond strength between C-H and C-D was observed. If any such "bond energy effect" exists it is probably less than 5% per kilocalorie.

### Introduction

Isotope effects on the reactions of hot hydrogen atoms with methyl fluoride and deuteriomethyl fluoride have been measured. Recoil tritium from the  $\text{He}^3(n,p)\text{H}^3$  reaction was used as the source of hot hydrogen. This study was suggested by the finding, discussed in the preceding paper,<sup>2,3</sup> that hot hydrogen substitution for a heavy atom in a halocarbon was inhibited if other heavy groups were attached to the carbon atom at which attack occurred. The original purpose of the measurements reported was largely to establish whether such an effect might be detectable upon substituting deuterium for protium in methyl fluoride.

The inertial effect due to isotopic substitution was found to be no larger than the uncertainty in interpreting the data. However, since at most only a small difference between the protonated and deuterated species was expected, the experiments were performed at an unusually high level of precision. As a result the data obtained have proved useful in shedding light on the "moderating" process, *i.e.*, on the question of the energy loss suffered by a recoil tritium atom in the "chemical" energy region (<20 e.v.) on collision with a polyatomic molecule. Furthermore, information has been obtained on several aspects of the hot reactions in which the hydrogen atom combines; in particular on the effect of variation of bond strengths.

### Experimental

**General Method.**—The general technique previously described<sup>2,4</sup> was used: Small amounts of  $\text{He}^3$  and a scavenger (iodine, bromine or oxygen) were mixed with methyl fluoride in a quartz ampoule. The tritium was produced by the  $\text{He}^3(n,p)\text{H}^3$  reaction by reactor neutron irradiation. Tritiated products were separated by gas chromatography and assayed by flow counting. Only "hot" products were observed; tritium reaching thermal energies was captured by the scavenger to give species (TI, TBr,  $\text{TO}_2$ ) which were not analyzed. Furthermore, TF produced by hot reaction was not sought.

Most experimental details follow those of the preceding paper,<sup>2</sup> although much greater care was taken to reduce errors.

**Reagents and Filling.**—Methyl fluoride was prepared by a Schotten-Baumann esterification of  $\text{CH}_3\text{OH}$  or  $\text{CD}_3\text{OH}$  (Merck, Sharp and Dohme of Canada, Ltd.) with *p*-toluenesulfonyl chloride, followed by reaction of the ester with anhydrous KF. Mass spectrometric analysis showed that no isotopic exchange occurred during this preparation; the isotopic purity of the  $\text{CD}_3$  group was better than 98%. Chemical purity was checked gas

chromatographically; the only impurity found was a few tenths per cent of methyl chloride.

The quartz ampoules used were of the usual type, equipped with a break-off seal, an internal diameter of about 2.0 cm. and volumes of about 30 ml. which were individually calibrated. Filling was performed on a calibrated vacuum line, first condensing into the liquid nitrogen-chilled ampoules known amounts of the scavenger and the methyl fluoride, and then adding  $\text{He}^3$  before sealing off at a constriction. In certain runs equal pressures of  $\text{He}^3$  were added to three ampoules at once, one containing  $\text{CH}_2\text{F}$ , the second  $\text{CD}_2\text{F}$  and the third a monitor (see below). In this way error in estimating total activity due to any imprecision in measuring the pressure of  $\text{He}^3$  was eliminated.

Irradiations were performed in the "Instrument Tunnel" at the Brookhaven National Laboratory Reactor for 1-3 days at a flux of about  $3 \times 10^9$  n./cm.<sup>2</sup>-sec. and a temperature of about 20-25°. A tritium monitor was irradiated in close physical proximity to each pair of  $\text{CH}_2\text{F}$  and  $\text{CD}_2\text{F}$  samples. This monitor contained  $\text{He}^3$  and *n*-butane only. Tritium reacting with *n*-butane while hot yields tritiated hydrocarbons and HT; thermal tritium yields HT. Determination of the total volatile activity in the sample thus provides an accurate measure, for the given irradiation, of the total tritium produced per unit amount of  $\text{He}^3$ .

Gas chromatographic separation of the products was carried out using the columns described in the preceding paper on reaction of tritium with halocarbons.<sup>2</sup>

### Results

Results from the individual runs are presented in Tables I and II. The yield for each product is given in two ways: (1) relative to the yield of T for H substitution (*i.e.*, to the labeled "parent" molecule  $\text{CH}_2\text{TF}$  or  $\text{CD}_2\text{TF}$ ); (2) as a percentage of the total tritium being stopped in the gas phase and thus available for reaction. The total tritium was calculated from the total activity present in the butane monitor, making due allowance for the relative amounts of  $\text{He}^3$  in the monitor and the samples. A correction for recoil loss of tritium to the walls of the ampoule was also made.<sup>5</sup> It was estimated that only 96% of tritium stopped in butane would be stopped in methyl fluoride.<sup>6</sup> In runs in which no monitor was available only the yield relative to the parent is given.

Tables I and II do not include the results of several initial runs using  $\text{O}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  scavengers. These experiments gave results consistent with later data, but were of lower precision. Tables I and II do, however, give the results of the entire final series of fifteen runs in which only  $\text{I}_2$  was used as scavenger.

No products other than those listed were observed. Iodinated products are assumed, as in previous work,

(5) P. J. Estrup and R. Wolfgang, *ibid.*, **83**, 2661 (1960).

(6) This small correction (about 4%) is in itself somewhat uncertain because of the absence of data for the stopping of recoil particles in methyl fluoride. However, any error thus introduced will be similar for  $\text{CH}_2\text{F}$  and  $\text{CD}_2\text{F}$  and thus does not affect any of the conclusions.

(1) Work performed in partial fulfillment of requirements for the Bachelor of Arts degree at Yale University.

(2) R. A. Odum and R. Wolfgang, *J. Am. Chem. Soc.*, **85**, 1050 (1963). This paper contains most of the references relevant to this work.

(3) R. A. Odum and R. Wolfgang, *ibid.*, **83**, 4668 (1961).

(4) D. Urch and R. Wolfgang, *ibid.*, **83**, 2982 (1961).

TABLE I  
 PRODUCTS FROM THE REACTION OF HOT TRITIUM ATOMS WITH CH<sub>3</sub>F

Yields expressed as: A, relative to CH<sub>2</sub>TF = 100; B, as percentage of total T

Product	Run 25B		26C		27B		28B		29A		30		31	
	A	B, %	A	B, %	A	B, %	A	B, %	A	B, %	A	B, %	A	B, %
HT	196	25.3	196	22.8	197	24.8	195	—	200	—	195	—	200	—
CH <sub>2</sub> TF	100	12.9	100	11.7	100	12.6	100	—	100	—	100	—	100	—
CH <sub>3</sub> T	33.8	4.35	33.6	3.92	34.4	4.35	33.4	—	33.8	—	33.5	—	33.2	—
CH <sub>2</sub> TI	24.1	3.11	23.2	2.71	23.4	2.95	20.6	—	23.4	—	24.0	—	23.6	—
CHTFI	11.0	1.43	9.9	1.16	10.9	1.37	9.4	—	10.9	—	11.1	—	10.4	—
Total		47.1		42.3		46.0								

 TABLE II  
 PRODUCTS FROM THE REACTION OF HOT TRITIUM ATOMS WITH CD<sub>3</sub>F

Yields expressed as: A, relative to CD<sub>2</sub>TF = 100; B, as percentage of total T

Product	Run 22B		23C		24A		25C		26A		27A		28A		29B	
	A	B, %	A	B, %	A	B, %	A	B, %	A	B, %	A	B, %	A	B, %	A	B, %
DT	203	21.3	204	20.4	212	21.7	210	20.6	204	19.5	204	20.4	205	—	207	—
CD <sub>2</sub> TF	100	10.5	100	10.3	100	10.2	100	9.9	100	9.5	100	10.0	100	—	100	—
CD <sub>3</sub> T	31.8	3.34	31.6	3.24	32.8	3.35	32.4	3.20	32.0	3.15	31.8	3.19	33.0	—	33.4	—
CD <sub>2</sub> TI	19.6	2.06	26.4	2.71	19.9	2.04	20.0	1.94	17.8	1.70	20.9	2.09	18.8	—	19.8	—
CDTFI	6.8	0.72	13.7	1.41	8.6	0.84	11.5	1.11	7.3	0.70	7.2	0.72	4.9	—	8.4	—
Total		38.0		38.5		38.2		36.8		34.5		36.5				

 TABLE III  
 SUMMARY OF ISOTOPE EFFECT ON REACTION PROBABILITY

Reaction	Product <sup>a</sup>	Absolute yield, % of total T			Yield relative to CH <sub>2</sub> TF = 100		
		CH <sub>3</sub> F	CD <sub>3</sub> F	H system D system	CH <sub>3</sub> F	CD <sub>3</sub> F	H system D system
H Abstraction	HT <sup>a</sup>	24.3 ± 0.6	20.7 ± 0.3	1.17 ± 0.03	197 ± 0.8	206 ± 1.1	0.957 ± 0.007
H Substitution	CH <sub>2</sub> TF <sup>a</sup>	12.4 ± .3	10.1 ± .1	1.23 ± .02	100	100	1
F Substitution	CH <sub>3</sub> T <sup>a</sup>	4.21 ± .12	3.24 ± .03	1.30 ± .02	33.7 ± .2	32.4 ± .2	1.040 ± .007
H, F Substitution	CH <sub>2</sub> TI <sup>a</sup>	2.92 ± .09	2.09 ± .15	1.4 ± .06	23.2 ± .4	20.4 ± .8	1.14 ± .04
2H Substitution	CHTFI <sup>a</sup>	1.32 ± .06	0.93 ± .11	1.4 ± .09	10.6 ± .2	8.6 ± .9	1.23 ± .09
All measured <sup>b</sup>	Total	45.1 ± 1.2	37.1 ± 1.1	1.22 ± .03			

<sup>a</sup> Or corresponding deuterated product. <sup>b</sup> Excludes F abstraction to form TF.

to result from combination of the corresponding radical formed by hot reaction with scavenger iodine. When bromine instead of iodine scavenger was used a similar yield of the corresponding bromide appeared.

Table III summarizes the results for each type of reaction (abstraction, displacement, etc.) and the corresponding products. Errors indicated are standard deviations of the mean as calculated from the scatter in Tables I and II. (For the absolute yields from CH<sub>3</sub>F this is only a rough approximation as there are only 3 replicate values.) These uncertainties are of the magnitude which would be expected from an assessment of the various sources of experimental error. The absolute yields show a relatively larger uncertainty than do those calculated normalized to CH<sub>2</sub>TF or CD<sub>2</sub>TF. This is of course to be expected since the absolute numbers include errors in measurement of the monitor and in normalizing it to the sample.

The salient feature of the results as summarized in Table III is that the probability for all of the reactions observed is lower in deuterated than in protonated methyl fluoride. The magnitude of the isotope effects on all five processes is surprisingly similar. However, the differences that are observed are clearly significant.

### Discussion

**Isotope Effects on Hot Atom Processes.**—In thermal reactions, isotope effects are principally due to such factors as small changes in bond energy and effective molecular volume, resulting from isotopic differences in vibrational and rotational molecular motion. These factors may still have some importance in hot processes, but several new types of isotope effects having quite different origins must be considered. The experimental results obtained here provide a basis for a discussion of the relative importance of these various possible

isotope effects. However, the conclusions we will reach must be regarded as preliminary and requiring much further work.

There are two distinct classes of isotope effects which must be considered in hot atom processes. One of these comprises all isotope effects on the reactive collision itself. It includes, but is not restricted to, all the familiar isotopic phenomena encountered in thermal reactions. The other class comprises an isotope effect on the moderation process, in which the hot species collides to lose energy but without entering chemical combination. Thus, the average energy loss upon collision may be significantly different in CH<sub>3</sub>F and CD<sub>3</sub>F. The number of collisions and hence the total reaction yield would then be different in the two systems.

We shall examine possible reactive isotope effects first. A case can be made for such effects for each of the reactions studied: (1) A bond energy effect may be responsible for the reduction of yield of hydrogen abstraction and/or substitution reactions at the C-H (C-D) bond. A finding that H abstraction was favored over D abstraction in CH<sub>2</sub>D<sub>2</sub> and mixed CH<sub>4</sub>-CD<sub>4</sub><sup>7</sup> may be interpreted<sup>8</sup> on the basis there is a sensitive bond energy effect on the ratio of hydrogen abstraction

(7) J. K. Lee, B. M. Musgrave and F. S. Rowland (*J. Phys. Chem.*, **64**, 1959 (1960)) found a large isotope effect favoring formation of HT over DT in reaction with CH<sub>2</sub>D<sub>2</sub> and mixtures of CH<sub>4</sub> and CD<sub>4</sub>. In these systems there can of course be no isotope effect due to moderator since both reactions occur in a single environment. In the absence of data on the yields of CHD<sub>2</sub>T and CH<sub>2</sub>DT from CH<sub>2</sub>D<sub>2</sub> and CH<sub>3</sub>T and CD<sub>3</sub>T from CH<sub>4</sub>-CD<sub>4</sub> mixtures the authors suggested that their results were due to a sensitive dependence of the ratio of abstraction to displacement reactions on the C-H (resp. C-D) bond strength (see also ref. 8). However, as pointed out in this paper, this ratio changes only slightly (and in the wrong direction) in going from C-H to C-D. The results of Lee, *et al.*, therefore present an anomaly which at this time lacks a consistent explanation.

(8) J. W. Root and F. S. Rowland, *J. Am. Chem. Soc.*, **84**, 3027 (1962).

to substitution. As has already been pointed out,<sup>9</sup> this now seems somewhat questionable since in the present work, the predicted decrease in this ratio in going from  $\text{CH}_3\text{F}$  to  $\text{CD}_3\text{F}$  is completely absent. Furthermore, on an *a priori* basis, it seems unlikely that hot atom reactions should be as sensitively dependent on bond energies as are thermal reactions (see ref. 9, footnote 4).

(2) There may well be a primary inertial effect as a result of which the probability of hydrogen atom substitution or abstraction by hot tritium is directly affected by the mass of the bound hydrogen atom. One model which would quantitatively predict such an effect is the so-called billiard ball or weak-coupling model<sup>10</sup> of hot reactions. However, this model has been shown inapplicable and would predict a greater efficiency of deuterium relative to protium displacement. The origin of any such effect is therefore rather obscure.

(3) There may be a secondary inertial hydrogen-deuterium isotope effect on F substitution by T in methyl fluoride. This is discussed in the Introduction and the preceding paper.<sup>2</sup>

(4) Given the above possibilities of isotope effects on single atom substitution it is easy to rationalize almost any finding on two atom displacements.

It is thus evident that in the present state of our ignorance, we could rationalize our data on the basis of reactive isotope effects of a poorly understood nature. However, it seems unlikely, though not impossible, that these reactive isotope effects of rather different physical origin should have the coincidental similarity of magnitudes observed for the five reactions studied. On the other hand, as shown below, the hypothesis of a single isotope effect on the moderation process provides a far more natural and complete explanation of the data.

As a preliminary working hypothesis we therefore tend to discount reactive isotope effects as being *primarily* responsible for our results.

**Isotope Effect on Hot-Atom Moderation.**—If the observed isotopic differences are primarily due to an isotope effect on the moderation process, this must mean that  $\text{CD}_3\text{F}$  is a better moderator for tritium atoms than  $\text{CH}_3\text{F}$ , *i.e.*, the average energy loss per collision is greater in  $\text{CD}_3\text{F}$  than in  $\text{CH}_3\text{F}$ . If this is so, the hot tritium atom will make fewer collisions in passing through the energy range where it can enter combination. Hence the probability of reaction to give any product will be lower in  $\text{CD}_3\text{F}$  than in  $\text{CH}_3\text{F}$ . (The extent of the decrease for a given product depends in some measure on whether it is formed near the top or the bottom of the reactive energy range; this point is discussed later.)

A number of models of the moderation process can be assumed. One assumes elastic collision involving the mass of the whole molecule; we shall call this molecular elastic (M.E.) collision. At the other extreme there are a large number of possible models for inelastic collision with the molecule. One that provides a plausible mechanism for energy transfer is based on assuming collision with single atoms in the molecule. For purposes of calculating the energy transfer using momentum conservation, the mass of the struck atom is used, essentially assuming it to be very weakly coupled to the rest of the molecule. The kinetic energy received by this atom will then appear as vibrational energy of the bond, center of mass translational energy of the molecule, and, if the bond breaks, a translational kinetic energy of the

struck atom. We denote this as a quasi-elastic atomic (Q.E.A.) collision. The Q.E.A. model shares with the M.E. model the advantage that its consequences are easily calculable. (Despite this and its intrinsic plausibility one should not, however, forget the fact that it is only one of a large number of possible models for inelastic moderating collisions.)

The molecular elastic (M.E.) model would be expected to have its greatest validity at energies low compared to the bond strength, while quasi-elastic atomic (Q.E.A.) collisions would be dominant at much higher energies. The region in between is less clear and it is (naturally) also the region of interest, where hot chemical combination takes place.

The present data provide an opportunity to evaluate approximately the relative importance of the molecular elastic and inelastic contributions to the moderating process in the energy range where hot reaction occurs. It is easy to see qualitatively that since  $\text{CH}_3\text{F}$  is closer in mass to tritium than is  $\text{CD}_3\text{F}$ , the M.E. model would predict that it is a slightly better moderator. On the other hand, the fact that D is closer in mass to T than is H would lead to the expectation that Q.E.A. collisions would make  $\text{CD}_3\text{F}$  the better moderator. As the latter prediction is the one that is qualitatively borne out we can immediately conclude that the pure M.E. model is inapplicable.

These considerations are elaborated quantitatively in Appendix I. The experimental results are used to calculate a ratio of the effective stopping powers of  $\text{CH}_3\text{F}$  and  $\text{CD}_3\text{F}$ . This is then compared with the predictions of the molecular elastic and quasi-elastic atomic moderation models. Not surprisingly it is found that the moderating collisions are not purely elastic. Instead they are sufficiently inelastic that the energy loss per collision approaches that calculated from the quasi-elastic atomic model. However, the pure Q.E.A. model is probably not applicable either and the actual situation falls somewhere between the two models.

A re-examination of earlier data<sup>5,10,11</sup> on the isotope effect on reaction of hot hydrogen with  $\text{CH}_4$  and  $\text{CD}_4$  leads to similar conclusions. Again the yields of all products from the deuterated species are lower than those from the protonated species. Although these methane results are of lower precision than the present work, the analysis given in Appendix I shows that the energy loss in moderating collisions is intermediate between that calculated from the M.E. and Q.E.A. models. However, it should be noted that this model of moderator isotope effects does not provide an explanation of certain results of Lee, Musgrave and Rowland on hydrogen abstraction from  $\text{CH}_2\text{D}_2$  and mixed  $\text{CH}_4$  and  $\text{CD}_4$ .<sup>7</sup>

The conclusions that we have thus reached on the nature of moderating collisions in the energy range for hot reaction ( $\sim 2\text{--}20$  e.v.)<sup>10</sup> parallel conclusions on the nature of the reactive collisions. In earlier work it was found that in reaction of hot hydrogen atoms the interaction was localized and involved only one or two bonds,<sup>2,4</sup> not the whole molecule. Yet the billiard ball model of reaction in which the hot atom underwent a quasi-elastic atomic (Q.E.A.) collision with a single atom loosely coupled to the rest of the molecule was also found to be inapplicable.<sup>10</sup>

Clearly any collision, reactive or moderating, in the hot reaction range can be considered neither as occurring with the whole molecule (in the sense that the entire molecule acts as a single body in absorbing momentum) nor with only individual atoms loosely coupled to the rest of the molecule. The situation

(9) R. Wolfgang, *J. Am. Chem. Soc.*, **84**, 4586 (1962).

(10) J. Cross and R. Wolfgang, *J. Chem. Phys.*, **35**, 2002 (1961).

(11) P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2665 (1960).

lies somewhere between. Such a conclusion can hardly be surprising in view of the fact that the energies involved are of the order of bond energies, and the collision times of the order of the vibrational period. The collision can thus not be considered as being either completely adiabatic (which would lead to collision effectively with the whole molecule) or completely non-adiabatic (which would lead to collision with single uncoupled atoms).

In earlier work using the kinetic theory of hot atom reactions molecular elastic (M.E.) moderation processes were implicitly assumed.<sup>11</sup> This was the simplest assumption to make in the complete absence of data relating to any model of moderation. In Appendix II the effects on the kinetic theory of different moderation mechanisms are examined. It is found that the earlier conclusions are unaffected, but that certain precautions must be taken in any future kinetic analysis of hot reaction with more complex molecules.

**Isotope Effects on Hot Atom Reactions.**—If moderator rather than reactive isotope effects are thus tentatively accepted as dominant in this system, further analysis of the data in Table III leads to a number of conclusions regarding the hot reactions themselves.

**Relative Mean Energies for Hot Product Formation.**—In a better moderator, the fraction of hot atoms which reach the lower part of the hot reaction region is larger. Since there are fewer collisions in a given energy range, the chance of reaction at the top of the range is reduced and more atoms pass through to lower energies. A familiar example of this is the nuclear chain reactor where efficient moderators are used to increase the number of neutrons reaching thermal energy. For hot atoms the existence of such an effect can readily be put on a quantitative basis using the kinetic theory.

Since  $CD_3F$  is a better moderator than  $CH_3F$  those products formed at relatively low mean energies should be enhanced. A study of the isotopic ratios listed in the last column of Table III then shows that the various hot reactions take place in the following order of increasing mean energy: H abstraction < H displacement < F displacement < 2 atom displacement. With the possible exception of 2 atom displacement this order is very unlikely to be a chance result of the experimental uncertainty.

This ordering of relative formation energies is in the direction to be expected. H Abstraction has the lowest threshold as it is the only reaction that can proceed even at thermal energies.<sup>5</sup> F Displacement is more endoergic than H displacement by about one electron volt.<sup>12</sup>

**Billiard Ball Displacement.**—The billiard ball reaction model has been extensively discussed in a recent paper<sup>10</sup> dealing with isotope effects in noble gas moderated  $CH_4$  and  $CD_4$ . This mechanism would predict much more efficient substitution of atoms similar in mass to that of the incident tritium. Thus in the present system hydrogen displacement should be enhanced in  $CD_3F$  while abstraction and fluorine displacement should remain unaffected. However, no trend whatsoever of this nature can be detected in the ratios (H displacement:H abstraction) and (H displacement:F displacement) in going from  $CH_3F$  to  $CD_3F$ .

This accords with the previous conclusion that the billiard ball model is of no importance in the reactions of gas phase hot hydrogen atoms.

**Secondary Inertial Effect on F Atom Displacement.**—In the preceding paper<sup>2</sup> it was shown that T-for-F substitution per C-F bond was 80% smaller in  $CH_2F_2$  than in  $CH_3F$ . This effect was ascribed to the higher

rotational inertia of  $CH_2F$  compared to  $CH_3$ . The present work was initially undertaken largely to determine whether replacement of the methyl hydrogens by deuterium might yield a detectable isotope effect of similar origin.

Table III indicates that substitution of fluorine is indeed reduced in  $CD_3F$ . However, as shown in the preceding discussion, this is probably primarily due to other causes. The effect due to increase in rotational inertia is probably less than about 4%.

The difference between the moments of inertia of  $CD_3$  and  $CH_3$  is about one-tenth of that between  $CH_2F$  and  $CH_3$ . Since an 80% reduction in F substitution/C-F bond was noted from  $CH_3F$  to  $CH_2F_2$ , an 8% reduction from  $CH_3F$  to  $CD_3F$  might have been expected had this inertial effect been linear with the moment of inertia. That it is not linear should not have been surprising. What is involved here is probably more of a threshold phenomenon. When the moment of inertia of the group attached to the F atom exceeds a certain value it can no longer rotate rapidly enough to capture the attacking tritium atom. The  $CD_3$  group appears to be below this threshold while  $CH_2F$  is above it.

**Effect of Bond Energy on Hot Atom Reactions.**—In  $CD_3F$  the C-D bond is about 0.9 kcal. stronger than the C-H bond in  $CH_3F$ ,<sup>13</sup> while the strength of the C-F bond is virtually the same in both molecules. Yet the ratio (hydrogen displacement:fluorine displacement) and the ratio (hydrogen abstraction:fluorine displacement) are both slightly larger in  $CD_3F$  than in  $CH_3F$ . This effect is of course in the "wrong" direction to be caused by the variation in carbon-hydrogen bond energy. In any case, as pointed out previously, it appears to be a consequence of the moderation process.

Rowland has recently suggested that a decrease in C-H bond energy may lead to an increase in the ratio of hot abstraction to displacement. This was proposed as an alternative to the steric explanation<sup>4</sup> of the variation of this ratio in various hydrocarbons. The effect postulated was quite large: a change from a primary to a secondary C-H bond (about 4 kcal.) had to correspond to an increase in abstraction by a factor of the order of two. In this work we find a ratio of abstraction to displacement of  $1.97 \pm 0.01$  for a C-H bond and  $2.06 \pm 0.01$  for the stronger C-D bond. Again this is in the "wrong" direction for the bond strength hypothesis.

From these studies it would appear that an effect of bond energy on hot hydrogen reaction at C-H bonds is not larger than about 5% per kcal. This finding was expected. If the hot atom has excess energy available its reactions should to a first approximation be independent not only of temperature but of changes in bond energy. (These considerations apply only to primary or direct hot displacement and abstraction reactions. If an intermediate with a lifetime longer than a vibrational period is formed, as happens in hot addition reactions, the decomposition of this intermediate is governed by the usual factors controlling unimolecular decay. The final products will therefore be quite dependent on bond energies, as has been observed by Urch and Wolfgang.<sup>14</sup>)

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(13) S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 666.

(14) D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **81**, 2025 (1959).

(12) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, N. J., 1958.

TABLE IV  
AVERAGE LOGARITHMIC ENERGY LOSS PER COLLISION:  $\alpha$

Model	CH <sub>3</sub> F	CD <sub>3</sub> F	CH <sub>3</sub> F/CD <sub>3</sub> F	CH <sub>4</sub> /CD <sub>4</sub>
Molecular elastic, $\alpha^{ME}$	0.170	0.150	1.13	1.22
Quasi-elastic atomic, $\alpha^{QEA}$	0.435	0.600	0.725	0.66
Experimental, $\alpha$	$\begin{pmatrix} 0.36 & -0.10 \\ & +0.08 \end{pmatrix}$	$\begin{pmatrix} 0.48 & -0.18 \\ & +0.12 \end{pmatrix}$	$0.76 \pm 0.10^a$	$0.79 \pm 0.07^b$

<sup>a</sup> Maximum estimated error. The standard deviation could not be calculated since TF yields had to be estimated; it is probably much smaller. <sup>b</sup> Standard deviation.

### Appendix I

**Calculation of  $\alpha$ , Average Logarithmic Energy Loss per Collision.**—The average logarithmic energy loss per collision is given by<sup>11</sup>

$$\alpha = \ln \frac{E(\text{after collision})}{E(\text{before collision})} = 1 - \frac{(M-m)^2}{2Mm} \ln \left| \frac{M+m}{M-m} \right|$$

where  $m$  is the mass of the incident atom (tritium) and  $M$  is the mass of the body struck. For molecular elastic collisions  $M$  is the mass of the molecule. This gives  $\alpha^{ME}$ . For quasi-elastic atomic collisions  $\alpha$ 's are first calculated for each of the various atoms involved ( $\alpha^{\text{atom}}$ ). To get  $\alpha^{QEA}$  the  $\alpha$ 's for each atom multiplied by the relative probability for striking that atom ( $f^{\text{atom}}$ ) are summed

$$\alpha^{QEA} = \sum_{\text{all atoms}} f^{\text{atom}} \alpha^{\text{atom}} \quad \sum_{\text{all atoms}} f^{\text{atom}} = 1$$

For CH<sub>3</sub>F and CD<sub>3</sub>F the probability of collision with H, D and C is taken as equal and that with F is taken as twice as large ( $f^{H,C,D} = 0.167$ ,  $f^F = 0.333$ ). The value of  $\alpha^{QEA}$  thus computed is not very sensitive to the exact validity of this assumption.

The  $\alpha$ 's for CH<sub>3</sub>F and CD<sub>3</sub>F, together with their ratios, are given for the two models of the moderation process in the first two rows of Table IV.

The kinetic theory of hot atom reactions<sup>11</sup> gives for the total probability of hot reaction

$$P = 1 - e^{-f/I}$$

where  $f$  is the probability of collision with the reactant molecule (CH<sub>3</sub>F or CD<sub>3</sub>F) and  $I$  is the integral of the probability of reaction at energy  $E$ ,  $p(E)$  over the total reaction energy range  $E_2$  to  $E_1$ .

$$I = \int_{E_1}^{E_2} \frac{p(E)}{E} dE$$

In accordance with the discussion we ascribe the difference between  $P_{\text{CH}_3\text{F}}$  and  $P_{\text{CD}_3\text{F}}$  primarily to a difference between  $\alpha_{\text{CH}_3\text{F}}$  and  $\alpha_{\text{CD}_3\text{F}}$ . If  $I_{\text{CH}_3\text{F}}$  is therefore assumed equal to  $I_{\text{CD}_3\text{F}}$

$$\frac{\alpha_{\text{CH}_3\text{F}}}{\alpha_{\text{CD}_3\text{F}}} = \frac{\ln(1 - P_{\text{CD}_3\text{F}})}{\ln(1 - P_{\text{CH}_3\text{F}})}$$

(Since the mole fractions of He<sup>3</sup> and I<sub>2</sub> are similar for the CH<sub>3</sub>F and CD<sub>3</sub>F runs,  $f_{\text{CH}_3\text{F}} = f_{\text{CD}_3\text{F}}$ .)

The  $P$ 's represent the total hot reaction products. This includes the yields of TF, which were not measured. We estimate these to be equal to half the yield of HT (or DT). Then

$$P_{\text{CH}_3\text{F}} = 45.1 + 12.0 = 57.1\%$$

$$P_{\text{CD}_3\text{F}} = 37.1 + 10.3 = 47.4\%$$

Substituting into the preceding equation we obtain

$$\alpha_{\text{CH}_3\text{F}}/\alpha_{\text{CD}_3\text{F}} = 0.76 \pm 0.10$$

The uncertainty given is an estimate of the maximum error and includes due allowance for the fact that the yield of TF had to be assumed.

If the ratio of stopping power thus obtained from experimental data is interpreted in terms of a linear combination of contributions from ME and QEA moderation, we can write

$$\alpha_{\text{CH}_3\text{F}} = X\alpha_{\text{CH}_3\text{F}}^{ME} + (1-X)\alpha_{\text{CH}_3\text{F}}^{QEA}$$

$$\alpha_{\text{CD}_3\text{F}} = X\alpha_{\text{CD}_3\text{F}}^{ME} + (1-X)\alpha_{\text{CD}_3\text{F}}^{QEA}$$

This is shown graphically in Fig. 1 where  $\alpha_{\text{CH}_3\text{F}}$ ,  $\alpha_{\text{CD}_3\text{F}}$  and their ratio are plotted against  $X$ , the coefficient of the contribution from M.E. moderation (assumed to be similar for both CH<sub>3</sub>F and CD<sub>3</sub>F). The experimental ratio 0.76 is seen to correspond to about a 0.3 contribution from M.E. moderation and 0.7 contribution from Q.E.A. moderation. However, the error of 0.10 in the experimental ratio makes any  $X$  from 0.0 to 0.7 possible. A wide range of  $\alpha$ 's corresponding to this is possible, as shown in Table IV.

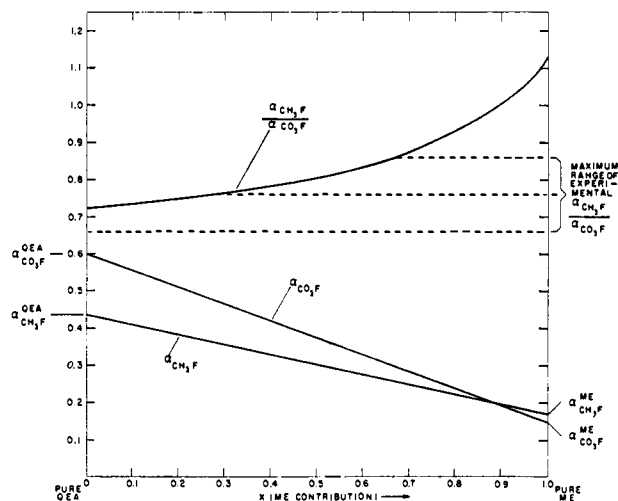


Fig. 1.—Plot of calculated average logarithmic energy loss  $\alpha$  in CH<sub>3</sub>F and CD<sub>3</sub>F vs. contribution,  $X$ , from molecular elastic (M.E.) collisions. The calculated ratio  $\alpha_{\text{CH}_3\text{F}}/\alpha_{\text{CD}_3\text{F}}$  vs.  $X$  is also shown; ( $\alpha_{\text{CH}_3\text{F}}/\alpha_{\text{CD}_3\text{F}}$ ) experimental represents the actual ratio, with estimated maximum error, as determined from the data.

This analysis serves to show that the experimental results are very insensitive to the actual values of  $\alpha$ . Although our data are quite accurate they can be fitted by moderation mechanisms ranging from pure Q.E.A. to 70% M.E. However, moderation in the reactive energy range by pure molecular elastic collision is definitely excluded.

A similar calculation can be carried out using earlier data<sup>10</sup> on hot tritium reaction with CH<sub>4</sub> and CD<sub>4</sub>. The experimental value of the ratio  $\alpha_{\text{CH}_4}/\alpha_{\text{CD}_4}$  and the values calculated from the M.E. and Q.E.A. models are given in the last column of Table IV. The error indicated is again the estimated maximum uncertainty. (Although the CH<sub>4</sub>-CD<sub>4</sub> experiments were less precise than those on CH<sub>3</sub>F-CD<sub>3</sub>F all products were measured leading to a similar net uncertainty.) Again the experimental moderation factor can be considered as a linear combination of contributions of similar magnitude from the M.E. and Q.E.A. models.

### Appendix II

**The Consequences of an Uncertainty in the Energy Loss Factor,  $\alpha$ , on Conclusions Drawn from the Kinetic Theory of Hot Atom Reactions.**—The kinetic theory of hot reactions<sup>11</sup> predicts that for a given product  $i$  of

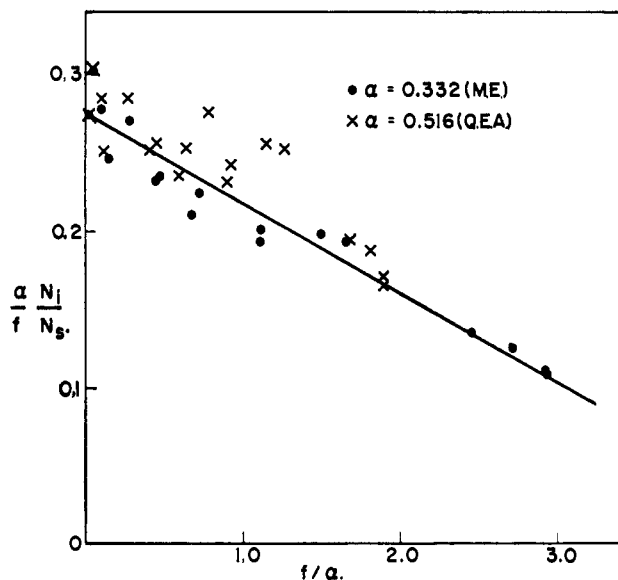


Fig. 2.—Kinetic theory plot according to methane data of Estrup and Wolfgang. One set of points was calculated using molecular elastic (M.E.) model of moderation, the other using quasi-elastic atomic collision (Q.E.A.) model. (For the latter model equal probability of collision of T with a carbon atom and any given hydrogen atom is assumed; the points are very insensitive to exact validity of this assumption.) The line is drawn through M.E. points.

a hot atom reaction

$$\frac{N_i}{N_s} = \frac{f}{\alpha} I_i - \frac{f^2}{\alpha^2} K_i + \frac{f^3}{\alpha^3} L_i$$

where  $N_s$  is the total number of hot atoms reacting,  $N_i$  is the number incorporated in product  $i$ ,  $f$  is the probability of collision with the reactive species (*i.e.*, not the inert moderator).

$$I_i = \int_{E_i}^{E_1} \frac{p_i(E)}{E} dE$$

where  $p_i(E)$  is the probability that a collision with the reactive molecule at energy  $E$  will yield product  $i$ ;  $K_i$ ,  $L_i$ , etc., are more complex definite integrals. Unless the

total probability of hot reaction is close to unity only the first two terms are important. A plot of  $\alpha N_i/fN_s$  vs.  $f/\alpha$  should therefore yield a straight line of slope  $K_i$  and intercept  $I_i$ .

In early work on methane<sup>11</sup> in the absence of any relevant data,  $\alpha$  was arbitrarily calculated assuming molecular elastic collisions (M.E.). This assumption has been questioned in the past<sup>15</sup> and the present work shows it is definitely incorrect. Fortunately, as has been pointed out previously, the treatment was not sensitive to this assumption. Figure 2 shows the methane data plotted using  $\alpha_{CH_4}$ 's calculated using both M.E. moderation and quasi-elastic atomic (Q.E.A.) moderation.<sup>16</sup> The lines drawn through the two sets of points have quite similar intercepts and slopes.

For  $CD_4$ , however, the  $\alpha_{CD_4}$ 's vary much more widely depending on the moderation model used. Even so, the intercept  $I$  is not sensitive to the value of  $\alpha_{CD_4}$  that is chosen. This is obvious since near the intercept, where  $f/\alpha \rightarrow 0$ , the system contains very little of the reactant gas; it is almost all inert gas moderator. There is of course no uncertainty about  $\alpha_{inert\ gas}$  (collisions in the "chemical" energy range will be completely elastic). Hence the over-all  $\alpha$  of the system near the intercept has little uncertainty.  $I$ -values obtained from the kinetic theory are thus almost independent of the  $\alpha$  of the reactant molecule which may be chosen. The conclusions of the previous work on billiard-ball reactions, as studied in moderated  $CH_4$  and  $CD_4$ , are thus unaffected.<sup>10</sup>

In future work with more complex molecules the ratio of the  $\alpha$ 's calculated from the M.E. and Q.E.A. models may be very large. In the absence of measurements of the actual  $\alpha$  by the techniques discussed in Appendix I, the Q.E.A.  $\alpha$ 's will probably provide the better approximation.

(15) See for example remarks of A. G. Maddock and R. Wolfgang, "Chemical Effects of Nuclear Transformation," International Atomic Energy Authority, Vol. II, 1961, p. 110.

(16) In Fig. 2 the quantity  $f$  has been calculated using a diameter for T of 1.1 Å. as was done in ref. 5. The actual effective diameter of T at the relevant energies is not well known; 1.1 Å. is on the low side while the van der Waals radius (2.4 Å.) is probably somewhat high (see L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1961, p. 257). The value of the intercept and of  $I$  are affected by this uncertainty, though in a rather insensitive manner. No other conclusions are affected.