trinitrobenzene alone within experimental accuracy. The single dispersion region found for the trinitro-benzene–triethylamine complex indicates that the triethylamine molecule is involved in a stable polar complex with trinitrobenzene.

No evidence of a molecular complex between trinitrobenzene and triphenylamine was observed. Just as the dielectric constant, ϵ, of a dilute solution of a polar solute in a nonpolar solvent may be expressed[5] as

$$\epsilon = \epsilon_1 + a_i N_i \qquad (16)$$

where ϵ_1 is the dielectric constant of the solvent, N_1 the mole fraction of solute i, and a_1 a constant characteristic of the total polarization of the solute molecule, the dielectric constant of a tertiary solution in which there is no interaction between solute molecules may be written

$$\epsilon = \epsilon_1 + a_i N_i + a_j N_j \qquad (17)$$

For the 1:1 mole ratios of trinitrobenzene and tertiary amines used, this equation should represent the dielectric constants of dilute solutions if no complex is formed. As indicated in Table IV, the sum of the individual binary slopes agrees with that of the tertiary solution for the trinitrobenzene–triphenylamine system. The differences between the binary sum and the tertiary slope in the other two systems is an indication of a new polar species being formed. Further evidence for the lack of complexing between trinitrobenzene and triphenylamine is the agreement of the losses at 1.25 and 3.22 cm. for the tertiary solutions with those of triphenylamine itself.

Table IV

Slopes of the Static Dielectric Constant in p-Dioxane at 35°

Solute	Solute + dioxane	$C_6H_3(NO)_3$ slope + amine slope	$C_6H_3(NO_2)_3$ + amine + dioxane
1,3,5-Trinitrobenzene	1.28	. .	. .
Triethylamine	0.34	1.62	2.32
Tributylamine	0.33	1.61	2.19
Triphenylamine	1.93	3.21	3.16

On the basis of electron spin resonance measurements, Turkevich and Stamires[17] have concluded that the iodine–triphenylamine system exists largely as $[(Ph)_3N\ldots N(Ph)_3]^+$ and I_2^- radicals. Such radicals in the

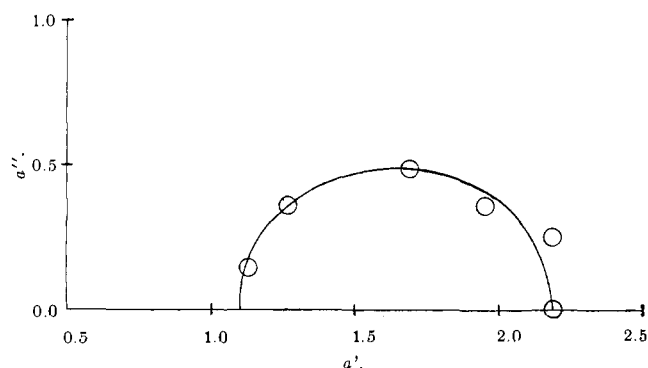(17) J. Turkevich and D. N. Stamires, *J. Am. Chem. Soc.*, **85**, 2557 (1963).

Fig. 2.—Calculated complex plane plot and experimental points for the tributylamine–trinitrobenzene system in dioxane at 35°.

trinitrobenzene–triphenylamine system would be consistent with the dielectric data, since neither of these radical species is dipolar. The observed additivity of the binary slopes would then be expected.

The trinitrobenzene–tributylamine system seems to be intermediate between the other two. The experimental data indicate a loss maximum at about 10 cm., but do not fit a Cole–Cole frequency distribution. A separation of the dispersion region in terms of two relaxation times was effected,[18] using the experimental relaxation time 30×10^{-12} sec. of tributylamine as one parameter. A reasonable fit to the experimental data was obtained with $c_1 = c_2 = 0.5$, $a_\infty = 1.10$, and $\tau_c = 75 \times 10^{-12}$ sec.; τ_c is the apparent relaxation time of the trinitrobenzene–tributylamine complex, a_∞ is the infinite frequency intercept, and c_1 and c_2 are relative weighting parameters. The experimental points are shown in Fig. 2 together with the curve calculated from the above parameters. The separation in terms of two relaxation times indicates that there is a considerable amount of uncomplexed tributylamine in the system. In view of the spectroscopic data[6] for the iodine complexes with triethylamine and tributylamine, this is not overly surprising. These latter measurements indicate that the iodine–tributylamine complex has an association constant about one-fourth that of the iodine–triethylamine. The greater bulk of the tributylamine molecule, which hinders close approach to an acceptor molecule, is probably responsible for this.

(18) K. Bergmann, D. M. Roberti, and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).

[Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas]

Isotope Effects in Recoil Tritium Reactions with Methyl Fluoride[1]

By Edward K. C. Lee and F. S. Rowland

The relative yields of radioactive products have been determined in mixtures of CH_3F and CD_3F with cyclobutane. The probability, per hydrogen atom in the target molecules, for forming CH_2TF from CH_3F is 0.61 ± 0.01 relative to the formation of cyclo-$C_4H_7T + C_2H_3T$ from cyclobutane. The corresponding figure for CD_2TF from CD_3F is 0.46 ± 0.01, indicating a probability integral isotope effect of 1.33 ± 0.04 for recoil tritium reactions with C–H bonds vs. C–D bonds. The yields of both CH_2TF from CH_3F and CD_2TF from CD_3F are independent of pressure within the accuracy of the measurements. A secondary isotope effect of 1.40 ± 0.05 is estimated for the replacement of F by T in CH_3F vs. CD_3F. The moderating ability of CH_3F and CD_3F for energetic tritium atoms is approximately equal. The isotope effect favoring replacement of H vs. D can arise from the formation of a short-lived transition complex, which breaks up by loss of H (or D) in competition with the T atom. The loss of the T atom corresponds to a highly inelastic "cushioning" collision.
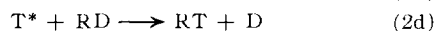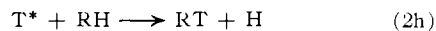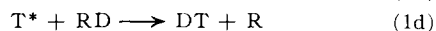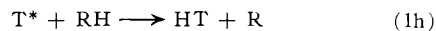
Introduction

The energetics and mechanisms of reactions involving high energy tritium atoms have been the subject of a

number of recent investigations.[2-11] One of the most promising general areas of study involved in the study

(2) F. S. Rowland, J. K. Lee, B. Musgrave, and R. M. White, "Chemical Effects of Nuclear Transformations," International Atomic Energy Agency, Vienna, 1961, Vol. 2, p. 67.

(3) M. Henchman, D. Urch, and R. Wolfgang, *ibid.*, Vol. 2, p. 83.

$$T^* + RH \longrightarrow HT + R \qquad (1h)$$

$$T^* + RD \longrightarrow DT + R \qquad (1d)$$

$$T^* + RH \longrightarrow RT + H \qquad (2h)$$

$$T^* + RD \longrightarrow RT + D \qquad (2d)$$

of such reactions is concerned with variations in behavior in these reactions with isotopic molecules, in particular those involving comparison of the behavior of protonated and deuterated molecules in reactions 1 and 2.[4-11]

While many of the experiments have been conducted with alkanes,[5-9] a careful quantitative study has recently been made of the reactions observed with CH_3F and CD_3F.[10,11] Since the preferred explanation[11] of the results obtained with the methyl fluorides appeared to be in direct contradiction to results obtained previously with the isotopic methanes,[6] either errors in the latter measurements or a marked difference in reaction behavior between methane and methyl fluoride was required for consistency. The methane results have recently been confirmed as correct, and an alternate explanation has been favored for the methyl fluoride results.[8]

The present series of experiments has been carried out with CH_3F and CD_3F in competition with cyclobutane to determine whether any marked difference in behavior for isotopic reactions exists for methyl fluoride and methane, and thereby to determine the origin of the observed isotopic variations in the methyl fluoride system.

The investigations with isotopic methyl fluorides furnish simultaneously an opportunity to investigate any isotopic variations arising in reaction 3

$$T^* + CH_3F \longrightarrow CH_3T + F \qquad (3h)$$

$$T^* + CD_3F \longrightarrow CD_3T + F \qquad (3d)$$
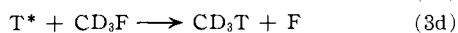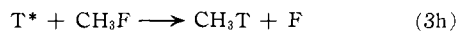
Experimental

General Procedure.—These studies have been carried out following our usual techniques for gas phase recoil tritium studies.[2,12,13] Samples containing about 1 cm. of He^3, 1–2 cm. of O_2, and a mixture of methyl fluoride and cyclobutane were irradiated in Pyrex 1720 bulbs (about 15 ml.) for 1 hr. in a nominal neutron flux of 1.0×10^{11} n./cm.^{2}/sec. The actual flux within the bulbs was approximately 5×10^{10} n./cm.^{2}/sec. Two aliquots from each sample were separated on different gas chromatographic columns, and analyzed by radio-gas chromatography. Mass peaks were also measured for each aliquot with a thermal conductivity detector.

Chromatographic Analysis.—The two columns used in this work were (packed in 0.25 in. o.d. copper tubing): 80 ft. ACTN, 16% by weight acetonylacetone on 30–40 mesh acid-washed firebrick, operated at 0°, with helium pressure 12 lb., flow rate, 0.50 ml./sec.; total flow rate, He + C_3H_8, 1.43 ml./sec.; 50 ft. PCA, 9.6% by weight propylene carbonate on 30–50 mesh activated alumina (F-1), operated at 0°, with helium pressure 10 lb.; flow rate, 0.47 ml./sec.; total flow rate, He + C_3H_8, 1.33 ml./sec.

The most important tritium-labeled products observed for recoil tritium reactions with cyclobutane alone are given here for a typical run (relative yields at 57.7 cm. pressure in parentheses)[14,15]: HT (150 ± 2); C_2H_3T (43.1 ± 0.6); and cyclo-C_4H_7T (56.9 ± 0.7). Minor yields are also present,[15] both from the cyclo-C_4H_8 and from the n-C_4H_{10} (0.76%) present in it as an

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(5) J. K. Lee, B. Musgrave, and F. S. Rowland, *J. Chem. Phys.*, **32**, 1266 (1960).

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(9) J. W. Root and F. S. Rowland, *J. Chem. Phys.*, **38**, 2030 (1963).

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

(11) H. C. Jurgeleit and R. Wolfgang, *ibid.*, **85**, 1057 (1963); see also ref. 14–17, 25, and 26.

(12) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

(13) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *ibid.*, **34**, 741 (1962).

(14) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963).

(15) E. K. C. Lee, Ph.D. Thesis, University of Kansas, 1963.

impurity: C_4H_7T-1 (1.8 ± 0.2); 1,3-butadiene-t (0.7 ± 0.2); propylene-t (0.4 ± 0.1); CH_3T (0.5 ± 0.2); $HC\equiv CT$ (1.0 ± 0.2); C_2H_5T (0.3 ± 0.1); C_3H_7T (0.2 ± 0.1); and n-C_4H_9T (0.7 ± 0.1). The products from CH_3F (or CD_3F) observed in the present runs included HT, CH_2TF, and CH_3T. No search was made for the oxygenated products in these experiments.

Propylene-t emerges from the ACTN column with the CH_2TF peak, and must be subtracted from the observed yield prior to calculation. The magnitude of this propylene-t correction (4.0 × 10^{-3} × the sum of C_2H_3T and cyclo-C_4H_7T) was calculated from pure cyclobutane runs.[14,15] Methane-t and HT were separated on the PCA column, as were C_2H_5T and C_2H_3T.

Radioactive Assay.—Many fluorocarbons, including some fluoroalkanes, interfere with the operation of the proportional counter, presumably through electron capture and the consequent quenching effect. Measurements with CH_3F indicate an effect of $\leq 1\%$ under our conditions of operation for 1.5 cm.^{3} S.T.P. of CH_3F (approximately the amount present in the first aliquot of the highest pressure sample) and a lesser effect for lesser quantities. Under our operating conditions,[13] cyclobutane does not affect the counter operation during its passage through the active counter volume. Glass, silver-walled counters with 85-ml. active volume were used throughout.

Mass Assay.—The relative molar ratios of the mass peaks (calculated from relative thermal response) obtained after irradiation with a typical aliquot (No. 351) from CH_3F were: cyclo-C_4H_8 (100), CH_3F (38.8), n-C_4H_{10} (0.20), C_2H_4 (0.14). The corresponding values for a CD_3F sample (No. 309) were: cyclo-C_4H_8 (100), CD_3F (18.5), n-C_4H_{10} (0.68), C_2H_4 (0.13).

Chemicals.—Cyclobutane was obtained from Merck, Sharp, and Dohme of Canada, Ltd., and contained n-butane as an impurity. The n-butane concentration was reduced through vacuum distillation to less than 1%, varying somewhat from batch to batch.

Methyl fluoride was obtained from Columbia Organic Chemical Co., Inc., but was too impure to use directly. After vacuum distillation, no impurities were observed above the 1 part per 10^3 level.

Deuteriomethyl fluoride was obtained from Merck, Sharp, and Dohme of Canada Ltd. and was used directly. No impurities were observed above the 1 part per 10^3 level. No correction has been made in the CD_3F samples for the presence of CD_2HF. The quoted isotopic purity (atom % D in hydrogen) is 99%.

Results

These experiments have been run with mixtures of cyclobutane and the appropriate methyl fluoride and analyzed for the radioactive products from recoil tritium reactions with each of these target molecules. Oxygen has always been present in order to suppress thermal reactions that might otherwise lead to some of the products observed in the hot reactions.

Such competitive experiments have been performed because the simultaneous exposure in the same reaction vessel ensures that both molecules are exposed to the identical (but not necessarily known) tritium flux at all energies.[8,9,16,17] The observed results can then be calculated as integrated probabilities of each hot reaction and can be expressed relative to any of the reactions as standard. The use of a common competitor, cyclobutane, permits intercomparison of two relative integrated probabilities *vs.* a common standard. The mole fraction of cyclobutane was deliberately kept high in order to make it the dominant molecule in each system as far as energy loss is concerned, thus keeping any differential effect caused by CH_3F or CD_3F quite small.

Cyclobutane has been chosen as the standard for comparison because it has been very thoroughly studied in our laboratory[14,15] and because measurements of methyl fluoride-t can be performed without undue interference from the cyclobutane products. The two chief labeled hydrocarbons from recoil tritium reactions with cyclobutane, C_2H_3T and cyclo-C_4H_7T, are both pressure dependent, indicating the unimolecular decomposition of part of the latter to the former in this pressure range.[14] However, the sum of these two

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(17) J. W. Root and F. S. Rowland, *ibid.*, **84**, 3027 (1962).

TABLE I

OBSERVED RADIOACTIVITY IN TYPICAL METHYL FLUORIDE–CYCLOBUTANE RECOIL TRITIUM SAMPLES

Radioactivity given in observed counts

| | No. 351 | | No. 309 | |
Tritiated product	ACTN	PCA	ACTN	PCA
Hydrogen	} 82,400 ± 400	77,130 ± 300	} 70,040 ± 450	65,290 ± 300
Methane		1,470 ± 50		630 ± 60
Acetylene[a]	200 ± 40	} 200 ± 40	150 ± 40	} 180 ± 40
Ethane	} 20,870 ± 300		} 18,970 ± 240	
Ethylene		} 22,940 ± 150		} 18,680 ± 150
Methyl fluoride	} 4,350 ± 80		} 1,670 ± 60	
Propylene		(200 ± 20)[b]		(180 ± 20)[b]
Propane	200 ± 100	...	190 ± 60	...
n-Butane	210 ± 40	...	360 ± 40	...
Butene-1	980 ± 50	...	760 ± 50	...
Cyclobutane[c]	28,150 ± 200	...	24,300 ± 150	...
Butadiene	...	...	510 ± 60	...
"220 min."[c]	...	...	220 ± 50	...

... Peak did not emerge from column during run

[a] HC≡CT undergoes isotopic exchange on the PCA column. With larger samples, ~65% of the tritium radioactivity is removed in one pass. No exchange loss has been observed with the ACTN column. [b] Estimated from pure cyclobutane runs = 4.0 × 10⁻³ × (C_2H_3T + cyclo-C_4H_7T). [c] Cyclobutane emerges at 142 min. The 220-min. peak is in the range of methylcyclobutane or cyclobutene.

TABLE II

RADIOACTIVE PRODUCTS OF RECOIL TRITIUM REACTIONS WITH METHYL FLUORIDE–CYCLOBUTANE MIXTURES

			Number			
	353	352	351	310	309	308
Gas pressure, cm.[b]						
CH_3F	2.1	4.1	17.6	...	...	...
CD_3F	...	...	...	3.2	7.9	11.2
C_4H_8	7.0	16.5	45.5	16.6	40.7	58.1
O_2	1.5	1.6	1.3	1.0	1.3	1.6
He^3	1.6	1.6	1.6	1.0	1.0	1.0

Radioactivity yield (cyclo-C_4H_7T = 100)

Product[a]						
Cyclo-C_4H_7T	100	100	100	100	100	100
C_2H_3T	103 ± 1	90 ± 1	74 ± 1	94 ± 1	77 ± 1	72 ± 1
HT	329 ± 2	310 ± 2	287 ± 2	309 ± 2	285 ± 2	272 ± 2
CH_2TF + C_3H_5T	14.9 ± 0.4	12.1 ± 0.4	15.5 ± 0.4	7.2 ± 0.3	6.9 ± 0.3	6.3 ± 0.3
CH_2TF (corrected)[c]	14.1 ± 0.4	11.3 ± 0.4	14.8 ± 0.4	6.4 ± 0.3	6.2 ± 0.3	5.6 ± 0.3
Mole ratio, CH_3F/C_4H_8[b]	0.293	0.253	0.388	0.192	0.200	0.185
Specific activity[b,d] per C–H bond	0.63 ± 0.02	0.63 ± 0.02	0.58 ± 0.02	0.46 ± 0.02	0.46 ± 0.02	0.47 ± 0.02

[a] Or the corresponding deuterated compound. [b] The mass composition of the samples analyzed simultaneously with the radio-activity analysis. None of the mole ratios is outside the estimated accuracy of the pressure ratios. The observed mole ratios have been used in the calculation of specific activity ratios. [c] The corrected values for methyl fluoride-t are obtained by subtracting 4.0 × 10⁻³ × (the sum of the activities of C_2H_3T + cyclo-C_4H_7T). This correction factor is obtained from numerous runs on pure cyclo-butane. [d] The specific activity per hydrogen atom is given by $\frac{8}{3} \times \left(\frac{CH_2TF}{C_2H_3T + cyclo\text{-}C_4H_7T} \right) \times \left(\frac{P_{C_4H_8}}{P_{CH_3F}} \right)$.

products is not dependent upon pressure within the accuracy of present measurements (estimated 1–2%), and serves as a convenient pressure-independent standard for such competitive reactions.

Three samples of each methyl fluoride were run *vs.* cyclobutane over a broad range in pressures to determine whether the hot reactions with the methyl fluorides showed any pressure dependence.

The complete radioactivity assays of one sample each of the CH_3F and CD_3F competitive samples are shown in Table I, in order to indicate the over-all accuracy of the measurements. The magnitudes of the observed mass peaks for these same runs were given in the Experimental section.

The relative yields for the most important radioactive compounds are given in Table II for each of the six runs. The most significant measurement from each of these experiments is the ease of replacement of protium or deuterium in methyl fluoride relative to the reaction of tritium with cyclobutane. The final row in Table II expresses these relative measurements per C–H or C–D bond in the molecule.

Discussion

Models for Isotope Effects in Hot Reactions.— The current hypotheses concerning recoil tritium reactions assert that those labeled molecules whose production is unaffected by free radical scavengers are formed in "hot" reactions occurring before the recoil atom has ever reached thermal equilibrium with its surroundings.[2,3] Models for these reactions in which the energetic tritium atom emerges with a stable chemical bond will ultimately involve some determination of the probability of bond-forming reaction per collision as a function of energy.[2,3,16] At low energies (below the activation energy), this probability is zero because the atom possesses too little energy for reaction to occur. At high energies, this reaction probability is also zero, for these interactions involve so much energy that the tritium atom breaks free from any temporary interactions occurring during collisions. Between these energies, the probability is nonzero, as evidenced by the observation of nonzero "hot" yields. Some hypothetical curves for such reaction probabilities are shown in Fig. 1.
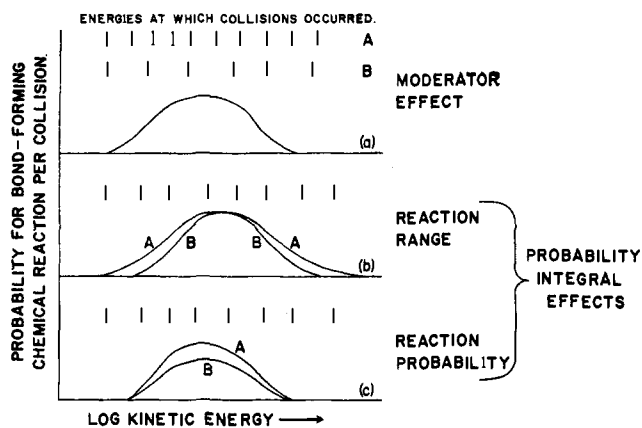
Figure 1.

Several possible sources have been suggested for variations in the yields measured for isotopic molecules in recoil tritium reactions[8,11] and are illustrated in Fig. 1. If the probability of reaction per collision were identical for two chemical species at all energies, isotopic variations could still be observed if the energy losses in nonreacting collisions are not the same for the two molecules. These differences are defined as *moderator isotope effects*. They would lead to a higher yield in A than in B of Fig. 1a because of the lower average energy loss and consequent larger number of possibly reactive collisions in species A.

If the energy loss mechanisms for nonreacting collisions are identical, isotopic yield variations could arise from a wider range of possible reaction energies (Fig. 1b) available for one species, or through a higher probability of successful reaction *per collision* for one species than for the other (Fig. 1c). The two latter possibilities have been jointly designated as *probability integral isotope effects*[8] and cannot easily be separated with most current chemical procedures.[18]

Any or all of these sources of isotopic variations might be present in comparisons of the recoil tritium reactions of a particular pure molecule with its deuterated counterpart. The measurements of the relative yields of radioactive products obtained in separate experiments with CH_3F and with CD_3F are shown in Table III.[10,11] The percentages for total tritium observed in the gas phase (*e.g.*, TF and TI were not observed) were obtained by comparison of the absolute yields measured from methyl fluoride with that separately measured for *n*-butane irradiated simultaneously, and the data for individual compounds have been expressed here on the same basis.[19]

Table III shows a larger total yield for *all* of the products measured from CH_3F than for the corresponding product from CD_3F.

The data of Table III, taken alone, could be explained by a moderator isotope effect in which the average energy loss in nonreactive collisions is sufficiently greater in CD_3F than in CH_3F (CD_3F = B, CH_3F = A in Fig. 1a) to cause about a 25% reduction in the yields of all reactions. This explanation has been preferred in reference 11. However, if differences in the moderating power of CH_3F and CD_3F were essentially responsible for the variations of Table III, then probability integral isotope effects would have to be correspondingly unimportant in the methyl fluoride system, since the isotopic variations observed with reactions 1,

(18) The term "reactive isotope effects" used in ref. 11 has essentially the same significance as our term probability integral isotope effects.

(19) The measurement of intra-sample relative yields is more precise than that obtained for the inter-sample comparisons of percentage yields, largely because several additional measurements were made for CH_3F.

TABLE III

RECOIL TRITIUM REACTIONS WITH METHYL FLUORIDE[a]
(I₂ Scavenged)[c]

		CH_3F	CD_3F	Ratio H/D
Tritium, %				
Observed, total		45.1 ± 1.2	37.1 ± 1.1	1.22 ± 0.03
		(42.3–47.1)	(34.5–38.5)	

		Yields of individual products, %		
	Product	CH_3F	CD_3F	Ratio H/D
H abstraction	HT[b]	24.0 ± 0.6	20.7 ± 0.3	1.17 ± 0.03
H substitution	CH_2TF	12.4 ± .3	10.1 ± .1	1.23 ± .02
F substitution	CH_3T	4.21 ± .12	3.24 ± .03	1.30 ± .02
T for H, F	CH_2TI	2.92 ± .09	2.09 ± .15	1.4 ± .06
T for H, H	CHTFI	1.32 ± .06	0.93 ± .11	1.4 ± .09

[a] Data of H. C. Jurgeleit and R. Wolfgang, *J. Am. Chem. Soc.*, 85, 1057 (1963). [b] Or deuterated product. [c] Vapor pressure, 25°, ~0.02 cm. of I₂.

2, and 3 are of very similar magnitude. In particular, the absence of an appreciable effect in reaction 1 would be in clear contrast with the measurements made on CH_2D_2, for which moderator isotope effects must be entirely absent, and which show a preference for H abstraction over D in the ratio 1.32.[6,8] Although such contrasting behavior for methane and methyl fluoride seemed unlikely,[8] the present experiments have been carried out with the isotopic methyl fluorides to test this possibility.

Competitive Reactions in Isotopic Recoil Tritium Systems.—Moderator and probability integral isotope effects cannot be readily distinguished in the comparison of experiments involving isotopic molecules taken separately. In principle, the obvious experiment to separate these two possibilities is the measurement of two reactions in the same system in direct competition with each other, *i.e.*, in the same recoil tritium flux and therefore in the absence of any possible moderator isotope effects. In practice, however, this measurement has only been satisfactorily achieved for reaction 1, involving as it does the separation and measurement of two labeled isotopic components, HT and DT.[5,6,8] The corresponding separations required here for direct comparisons in reactions 2 and 3, CH_2TF from CD_2TF and CH_3T from CD_3T, have not yet been attained in a manner suitable for accurate measurement of yield ratios. An indirect method must therefore be substituted, and the comparison of integrated reaction probabilities through cyclobutane competitions has been used.

The essential measurements of Table II can be summarized as: (a) The replacement of an H atom in CH_3F is 0.23 times as likely *per molecule* as is reaction with cyclobutane to give either C_2H_3T or cyclo-C_4H_7T; the relative probability of these reactions is 0.61 ± 0.01 when expressed per H atom in each molecule. (b) The replacement of a D atom in CD_3F is 0.17 times as likely *per molecule* as is reaction with cyclobutane to give either C_2H_3T or cyclo-C_4H_7T; the relative probability of these reactions is 0.46 ± 0.01 when expressed per D or H atom in each molecule. (c) A probability integral isotope effect occurs for reaction 2 favoring the reaction with CH_3F *vs.* CD_3F, of a magnitude 1.33 ± 0.04, when estimated through comparison to the standard of reaction with cyclobutane. (d) The yield of neither CH_2TF nor CD_2TF from reactions 2h and 2d is pressure dependent within the accuracy of the present measurements.

Conclusion (c) indicates that a probability integral isotope effect is present in the replacement of protium *vs.* deuterium of approximately the magnitude of the isotopic yield variations observed for this reaction in the separate experiments of Table III. Therefore, moderator isotope effects must be of secondary im-

portance in explanation of the data of Table III concerning the substitution of tritium for H or D.

Other Probability Integral Isotope Effects; Secondary Isotope Effect in Fluorine Replacement.—The earlier interpretation of the individual experiments with CH_3F and CD_3F led to the conclusion that no probability integral isotope effect greater than 4% existed for reaction 3h vs. 3d.[11] However, combination of the data of Table III with the ratio of 1.33 for k_{2h} vs. k_{2d} indicates a probability integral isotope effect for reaction 3 of $1.33 \pm 0.02 \times (1.30 \pm 0.02)/(1.23 \pm 0.02) \cong 1.40 \pm 0.05$. This reaction thus demonstrates a secondary isotope effect in a hot reaction, i.e., an influence of isotopically different substituents on a substitution reaction in which the isotopic species are not replaced.

Since CH_3T (or CD_3T) was also observed in each of the present experiments, a separate calculation of k_{3h} vs. k_{2h} can be made through indirect comparison vs. the cyclobutane standard. These calculations require a subtraction correction for the CH_3T observed in pure cyclobutane ($5.0 \times 10^{-3} \times$ the sum of C_2H_3T plus cyclo-C_4H_7T) that represents as much as 30% of the total methane-t formed, so that the ratio measured in this way is accurate only as 1.3 ± 0.1. Inasmuch as cyclobutane was the predominant molecule in all of these experiments, the yield of HT from CH_3F or DT from CD_3F was completely obscured by the abstraction reaction with cyclobutane, and no measurement of (1h) vs. (1d) was attempted. A value has again been estimated from the I_2-scavenged data of Table III. However, the most recent measurements with I_2-scavenged CH_2D_2 indicate that I_2 at its vapor pressure at 25° is not a completely efficient scavenger in preventing reaction 1h for low energy (thermal or near-thermal) tritium atoms.[8] In the absence of appropriate published data for O_2-scavenged methyl fluoride, a larger error is therefore quoted for the abstraction reaction in Table IV. Again, a probability integral isotope effect is observed favoring the abstraction of H over D; no inconsistency then exists with the measurements on CH_2D_2.

TABLE IV

PROBABILITY INTEGRAL ISOTOPE EFFECTS IN REACTIONS OF RECOIL TRITIUM ATOMS WITH ORGANIC MOLECULES

1. Primary isotope effects
(a) Abstraction of H vs. D

Compound	Comparison std.	HT/DT	Reference
CH_2D_2	Direct	1.32 ± 0.01	8
CH_3CD_3	Direct	$1.34 \pm .01$	20
CH_3F/CD_3F	Cyclobutane	$1.26 \pm .05$	11 + this work
CH_4/CD_4	Direct	$1.28 \pm .02$	6

(b) Substitution of H vs. D

Group	Comparison std.	T for H/T for D	Reference
CH_3 of isopropyl	Benzoate	1.41	4
CH_3F/CD_3F	Cyclobutane	1.33 ± 0.04	This work
CH_4/CD_4	n-C_4H_{10}	$1.31 \pm .05$	8
n-C_4H_{10}/n-C_4D_{10}	CH_4	$1.21 \pm .05$	8

2. Secondary isotope effects
(c) Substitution of T for F

Compounds	Comparison std.	H/D	Reference
CH_3F/CD_3F	Cyclobutane	1.40 ± 0.06	11 + this work

Origins of Probability Integral Isotope Effects. (a) Substitution for H or D: "Cushioning" Collisions.—The preference for replacement of protium vs. deuterium in the substitution reaction 2 was first observed in intramolecular comparisons of variously deuterated isopropyl benzoates.[4] While these original

(20) J. W. Root and F. S. Rowland, unpublished results.

data are not without objection,[21] the existence of such a probability integral isotope effect has now been amply confirmed by the intermolecular comparisons in alkanes[7] and by the present experiments with methyl fluoride. The phenomenon is presumably general in reactions at saturated carbon positions.

The key facts that need to be accounted for in explanation of this isotopic preference for replacement of H over D are: (a) The substitution reaction of T for H has been demonstrated to leave the resulting product RT with sufficient excitation to undergo unimolecular decomposition, estimated as an average of 5 e.v. for RH = cyclobutane,[14] and must therefore occur at kinetic energies averaging 5 e.v., or more if the exiting H atom is nonthermal. (b) The replacement reaction is sensitive to the difference between H and D and favors replacement of H.[22]

The most logical explanation for these observations seems to us as described below. The entire process constitutes a collision interaction which can be described by the term "cushioning collision."[9]

(a) The energetic tritium atom striking the atoms of a saturated carbon grouping transfers much of this kinetic energy into internal energy of the struck molecule, and is itself greatly reduced in velocity of motion.[23]

(b) This internal energy is not confined to the struck bond, but in part is transferred into adjacent vibrations, i.e., excitation of at least a section of the molecule.

(c) The tritium atom has become imbedded in the electron distribution of the struck molecule to such an extent that some bonding forces exist between it and the struck grouping—a "complex" exists at least momentarily.

(d) This "complex" involves too many groups for stable bonding and decomposes in a competitive manner. The lifetime of such a "complex" is rather uncertain, but must be long enough for reasonably normal isotope effects on decompositions to be in effect.[24]

(e) When C–T and C–H interactions exist in close proximity, the latter are more likely to break on the average, because of the lighter mass of H. A similar, but less pronounced, effect will exist for C–T vs. C–D.

(f) If the formation rate of complexes is assumed approximately equal for C–H and C–D, relatively more H will be replaced than D and relatively more C–T interactions will be ruptured in the deuterated molecule.

(g) The survival of the labeled molecule that remains will then depend on the amount of energy transferred inelastically to the rest of the molecule, the

(21) The experiments with isopropyl benzoate have two doubtful points. First, the radiochemical purification of liquid isopropyl benzoate by distillation is quite difficult, and the published data indicate that the parent compound was not radiochemically pure prior to degradation.[4] The effect of this on the measurements, and on the conclusions concerning isotope effects, could be negligible, and could be important to the extent of invalidating the experiment, depending upon the identity and amount of the unknown radioactive contaminant.
Second, the competitive experiments carried out much later involving aromatic rings indicate that they react very efficiently with relatively low energy tritium atoms, and can tend to "scavenge" all or most of the recoil atoms getting through the aliphatic reaction range without having formed a stable bond.[16] Thus, if fewer atoms reacted with a deuterated molecular grouping, more would survive to lower energies and might be available to the aromatic ring, thereby substantially enhancing the measured effect.

(22) The direct transfer of kinetic energy to a struck H or D atom in an elastic atom–atom collision (neglecting the coupling of the struck atom), designated as a billiard ball collision, favors larger energy transfer to D atoms, and leads to a prediction that D atoms should be replaced preferentially.[7] This type of mechanism has been shown not to be operative by the earlier isotopic experiments.[7,8]

(23) Efficient energy transfer between translational and vibrational energy does not usually occur in thermal reactions because the approach velocity is small relative to the vibrational "velocity." However, with high kinetic energy tritium atoms, these velocities are comparable, and energy transfer should occur efficiently.

(24) The authors of ref. 4 have previously suggested that their observations indicated an isotope effect in the decomposition of a complex.

rapidity with which it is removed by collision, and the stability of the molecule itself toward decomposition or isomerization.

(h) When the C–T "bond" is ruptured, the tritium atom will usually emerge very much degraded in energy.

(b) **Abstraction of Hydrogen.**—The preference for abstraction of protium over deuterium, resulting in an HT/DT ratio of 1.32 in recoil tritium reactions with CH_2D_2, and by a similar magnitude for CH_3F vs. CD_3F, has been pointed out as correlating well with the expected isotope effect attributable to the bond energy difference.[6,8,17] In other words, the observed HT/DT ratios are very close to the limits obtained by extrapolation of transition state theory to very high temperatures. In the absence of more detailed theoretical consideration of this problem, there is no inconsistency between the experimental observations and the high temperature extrapolated limit.

(c) **Substitution for Fluorine.**—The preference for replacement of fluorine bonded to CH_3 vs. that bonded to CD_3 is consistent with the previous observations that the probability for replacement of fluorine goes down as the mass of the reacting residue goes up (e.g., $CH_3 > CH_2F > CHF_2$). This effect has been attributed to "rotational inertia" in the substitution process in the latter case.[25,26]

Cushioning Collisions : Failure to Form C–T Bonds. —The cushioning collision hypothesis suggested above implies the frequent rupture of C–H vs. C–T or C–D vs. C–T interactions, in reasonably comparable numbers, with the release of very low energy H, D, or T atoms. The first two, of course, leave stable bonds for the entering tritium atom. In the latter case, the T atoms are still free to form a chemical bond in a further reaction, but may not have enough energy left to initiate additional "hot" reactions. The observed chemical consequence would then be that the energetic tritium atom had entered into one collision at high kinetic energy and had emerged from it unbonded but almost completely degraded in energy. Such highly efficient energy transfers in inelastic collisions would correlate very well with the recent observation that CH_4 is considerably superior to D_2 as a moderator for tritium reactions, despite the near-perfect mass match between that of the tritium atom and either the mass 2 or 4 of the deuterium atom or molecule.[9] Further, if these highly inelastic collisions degrade the recoil atom essentially to thermal energies, the noticeable effects would be higher thermal yields and lower hot yields for deuterated species, in agreement with the actual observations for alkanes.[7,20]

Unimolecular Decomposition of Tritiated Molecules.—The replacement of H by T is usually accompanied by the deposition of several e.v. of energy in the internal modes of the product molecule. If the labeled product is readily isomerized or decomposed, pressure dependent yields of the initial labeled species and its reaction products can be observed.[2,14] No such pressure dependence is exhibited in the substitution reactions of T for H in CH_3F or T for D in CD_3F, according to the data of Table II. In these cases, however, the activation energies for decomposition are very high and little decomposition would be expected at the pressures used.

The CH_3T and CD_3T measurements made in the present experiments are too inexact for tests of possible

pressure dependence, and the earlier more exact experiments were all carried out at constant pressure.[10,11] Therefore, no estimate can yet be made from methyl fluoride experiments of the amount of energy deposited in the hot replacement of F by T.

Relative Ease of Replacement of H.—Our concern in these experiments has primarily been with the comparison of CH_3F with CD_3F. Direct measurements, however, were carried out of the relative ease of replacement of H in CH_3F vs. cyclobutane. The value of 0.61 ± 0.01 for the specific activity of Table II corresponds to almost identical *surviving* specific activities per H position in the high pressure experiments, for cyclo-C_4H_7T constitutes about 60% and C_2H_3T 40% of the denominator in this ratio. In the absence of suitably scavenged liquid phase experiments with CH_3F, we conclude only that the individual H atoms of CH_3F can be replaced about 80 ± 20% as easily as those in cyclobutane.

Magnitude of Moderator Isotope Effects in CH_3F and CD_3F.—The possible existence of moderator isotope effects in comparisons of CH_3F vs. CD_3F is a subject of considerable interest, and several conclusions which have been previously drawn should now be briefly reconsidered. The variations in yield of CH_2TF from CH_3F and CD_2TF from CD_3F may now be regarded as arising from a combination of a probability integral isotope effect and a moderator isotope effect. By combining the estimate of 1.33 ± 0.04 for the former with the 1.23 ± 0.02 observed for the combined effect, an estimate of 0.92 ± 0.05 can be obtained for the relative number of collisions in the chemical reaction range for CH_3F compared to CD_3F.

This ratio is sufficiently close to 1.0 to justify a semi-quantitative statement that the energy loss processes in nonreacting collisions are quite similar in CH_3F and in CD_3F; the value is just enough less than 1.0 to suggest that energy losses are slightly greater in CH_3F than in CD_3F. However, firm conclusions about any measurable isotopic variation will require greater precision than in the present experiments. While the relative percentage yields obtained with the pure molecules alone could be improved (e.g., additional measurements with CH_3F), the indirect determination used here for probability integral effects should be replaced by a direct competition between the two methyl fluoride molecules.

Since the moderator isotope effect as calculated above is either 1.0 or slightly less, no conclusions are possible about the relative order of mean energies of reaction of the various hot reactions in the methyl fluoride systems. Similarly, the present data do not favor either the quasi-elastic atomic (QEA) or molecular elastic models (ME) for energy loss in nonreactive collision, as outlined earlier[11]; the experimental measurements obtained with mixtures of CH_4 and D_2 in fact indicate that neither the QEA nor the ME models are as satisfactory as the cushioning collision hypothesis.[9]

(25) R. Odum and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 4668 (1961).
(26) R. Odum and R. Wolfgang, *ibid.*, **85**, 1050 (1963).