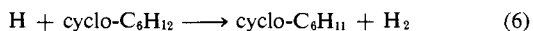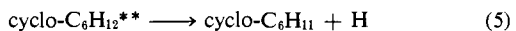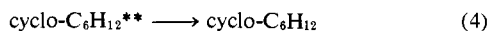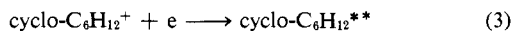would contribute to the matrix e.s.r. signal. This must be ruled out since the matrix signal remains constant during bleaching. Charge neutralization during bleaching would either produce a neutral molecule which would then decrease the e.s.r. matrix signal or result in bond rupture producing a cyclohexyl radical which would give an e.s.r. signal different from that of the postulated positive ion. The above reactions are shown in steps 3–6, where C_6H_{12}** is a cyclohexane molecule plus the energy of recombination.

$$cyclo\text{-}C_6H_{12}^+ + e \longrightarrow cyclo\text{-}C_6H_{12}** \qquad (3)$$

$$cyclo\text{-}C_6H_{12}** \longrightarrow cyclo\text{-}C_6H_{12} \qquad (4)$$

$$cyclo\text{-}C_6H_{12}** \longrightarrow cyclo\text{-}C_6H_{11} + H \qquad (5)$$

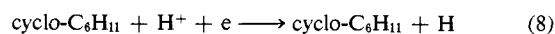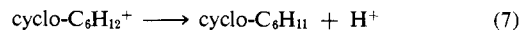$$H + cyclo\text{-}C_6H_{12} \longrightarrow cyclo\text{-}C_6H_{11} + H_2 \qquad (6)$$

The data are, therefore, consistent with the interpretation of the positive ion at 77°K. being a protonated free radical,[16] the cyclohexyl radical, and a proton. Such a configuration should given an e.s.r. signal of only the cyclohexyl radical. When the electron is returned to the radical ion, the proton is neutralized forming a hydrogen atom, which, because of its ability to diffuse at this temperature,[17] is ordinarily not detected by e.s.r. measurements at 77°K.,[18] thus leaving the cyclohexyl radical signal unchanged during charge neutralization (reactions 7 and 8).

(16) W. Busler, D. Martin, and F. Williams, *Discussions Faraday Soc.*, **36**, 102 (1963).
(17) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths Scientific Publications, London, 1958, pp. 223, 224.
(18) J. Willard, *Discussions Faraday Soc.*, **36**, 291 (1963).

$$cyclo\text{-}C_6H_{12}^+ \longrightarrow cyclo\text{-}C_6H_{11} + H^+ \qquad (7)$$

$$cyclo\text{-}C_6H_{11} + H^+ + e \longrightarrow cyclo\text{-}C_6H_{11} + H \qquad (8)$$

However, reaction 7 is highly endothermic and, therefore, ruled out. Alternatively, the results may be explained by an ion–molecule reaction involving proton transfer from a cyclohexane ion to a cyclohexane molecule (reaction 9).

$$cyclo\text{-}C_6H_{12}^+ + cyclo\text{-}C_6H_{12} \longrightarrow cyclo\text{-}C_6H_{13}^+ + \\ cyclo\text{-}C_6H_{11} \quad (9)$$
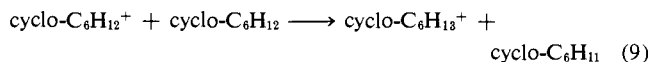
The e.s.r. matrix signal would be that of the cyclohexyl radical, and neutralization would occur with the protonated cyclohexane giving cyclohexane and a hydrogen atom (reaction 10).

$$cyclo\text{-}C_6H_{13}^+ + e \longrightarrow cyclo\text{-}C_6H_{12} + H \qquad (10)$$
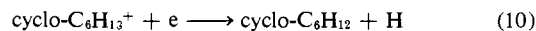
Reaction 9 is energetically favorable if the cyclohexane has a proton affinity of approximately 70 kcal./mole. Lampe and Field[19] have calculated the proton affinity for *n*-hexane as 103 kcal./mole. It must be further postulated that hydrogen formation by hydrogen atom abstraction from the matrix does not occur at liquid nitrogen temperature in this system because of an activation energy of about 8 kcal./mole[20] for this reaction. Therefore, the hydrogen atom must exist as a mobile entity, only undergoing reaction on an increase in temperature, or combining with other radicals or hydrogen atoms[21] as it diffuses through the matrix.

(19) F. Lampe and F. Field, *Tetrahedron*, **7**, 189 (1959).
(20) H. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).
(21) V. Voevodskii and Y. Molin, *Radiation Res.*, **17**, 366 (1962).

Moderator Effects on Recoil Tritium Reactions with Methyl and Methyl-d_3 Fluorides[1]

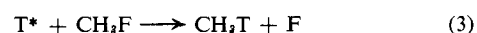E. K. C. Lee, George Miller, and F. S. Rowland

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas. Received March 28, 1964

The isotopic variations between CH_3F and CD_3F in recoil tritium reactions have been investigated for the O_2-scavenged compounds, and for O_2- and I_2-scavenged mixtures with a large excess of He^4. The relative yields of $HT:CH_2TF:CH_3T$ from CH_3F are 185:100:33, and of $DT:CD_2TF:CD_3T$ from CD_3F 187:100:31, but the absolute yields of all products from CH_3F are higher than from CD_3F. The ratios of CH_2TF/CH_3T and CD_2TF/CD_3T are only slightly affected by the presence of He^4 moderator, indicating that the reactions forming the compounds occur at about the same average kinetic energy for the tritium. The isotope effect in substitution for H or D favors H replacement by 1.27 ± 0.04 in a large excess of He^4. This fact implies that the primary source of the isotopic variation must lie in probability integral isotope effects, i.e., a larger probability for reaction per collision with CH_3F than for CD_3F and/or a larger range of tritium energy within which

reaction is possible. The average energy losses in nonbonding collisions are greater for tritium atoms in CH_3F than in CD_3F ($\alpha_{CH_3F}/\alpha_{CD_3F}$ = 1.23 ± 0.08).

Introduction

Recoil tritium atoms react with methyl fluoride (or CD_3F) by the three important hot reactions of abstraction of H, substitution of T for H, and substitution of T for F, as in eq. 1–3. Each of these reactions is initiated

$$T^* + CH_3F \longrightarrow HT + CH_2F \qquad (1)$$

$$T^* + CH_3F \longrightarrow CH_2TF + H \qquad (2)$$

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

by tritium atoms possessing excess kinetic energy remaining from the initial nuclear recoil and is of considerable interest in the understanding of the kinetics and mechanisms of such high energy reactions. An additional hot reaction, the abstraction of F to form

TF, as in eq. 4, is also possible but is much more difficult to measure because of isotopic hydrogen exchange

$$T^* + CH_3F \longrightarrow TF + CH_2 \qquad (4)$$
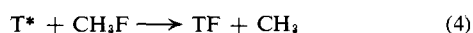
of TF with species formed by thermal reactions. Previous studies have concerned themselves with the absolute and relative yields of the first three reactions in the gas phase[2-6] and have shown that these yields are essentially independent of gas pressure in the range 0.2–1.0 atm.[6]

The bond-forming hot reactions observed in high mole fractions of methyl fluoride are initiated by tritium atoms with a wide spectrum of energies, largely in the 1–10-e.v. range.[7-9] Dilution of the methyl fluoride with helium as a nonreactive moderator presents an opportunity to alter this spectrum toward lower energies, and thereby obtain information about the distributions of tritium energies at which each reaction occurs. Furthermore, if the dilution is carried far enough that the total hot yield becomes quite small, considerable information can be obtained about the magnitude of the energy ranges and reaction probabilities for each of these reactions.[10-15]

The present series of experiments has involved dilution separately of both methyl fluoride and methyl-d_3 fluoride with helium in an effort to obtain such information.

Experimental

Experimental Factors Affecting the Final Calculations. The values of interest in moderator experiments are the fractions of total *stopped* tritium atoms found in each observable tritium-labeled species, measured as a function of the mole fraction composition of the original irradiated mixtures.[10-15] These fractional yields are obtained from the experimental observations through the following sequence of calculations:

(1) The total production of tritium is calculated from (a) the volume of the irradiation bulb, (b) the length of irradiation, (c) the neutron flux, and (d) the pressure of He[3] in the bulb.

(2) The fraction of the tritium which leaves the gas phase and enters the wall while still energetic is calculated from the known recoil energy of the tritons, the known dimensions of the irradiation bulb, and (e) the stopping powers of the various gaseous components within the bulb.

(3) After gas chromatographic separation into its components, the observed yield of tritium in each species is calculated from (f) the number of counts

measured in a particular radioactivity peak, (g) the fraction of the total sample passed through the counter for that peak, (h) the volume and efficiency of the counter, and (i) the flow rate of the gases passing through the counter.

The over-all accuracy of the experimental values of fraction yields is dependent primarily upon satisfactory measurement and control of the nine factors lettered above. The alternate approach of measuring all of the stopped tritium activity has not been applied because of the difficulties involved in making accurate determinations of both labile tritium (TF, HTO, etc.) and nongaseous wall activity concurrent with the radiogas chromatography of nonlabile gaseous species.

Considerable simplification can be obtained in these measurements if a standard monitor reaction is available for which the fractional tritium yield in a particular gaseous activity is accurately known. This procedure has been followed here, using unscavenged ethylene as the reacting monitor for the tritium production. In this way (c) the neutron flux and (h) the volume and counter efficiency are the same for monitor and methyl fluoride, and neither is actually evaluated.

Monitor Reaction with Ethylene. Two samples of C_2H_4 were irradiated simultaneously with the methyl fluoride samples and were analyzed in an identical manner. The yields of all gaseous components through n-$C_5H_{11}T$ (3 hr. on the ACTN column) were measured, and then the gas flow through the column was reversed. A large, fairly broad peak was back-flushed through the counter in this manner, emerging after a back flow equivalent to the original forward flow. We have assumed that all tritium atoms stopped in the gas phase in the ethylene monitors appeared in either the forward or backward runs, *i.e.*, that no appreciable nongaseous radioactivity (polymers, etc.) was formed. Of the gaseous tritium actually observed, 59% appeared in the C_2H_3T peak, 14% was found in the back-flush peak, and the remaining 27% was observed among a variety of other hydrocarbons. The ultimate basis for our measurement is therefore that the yield of C_2H_3T from unscavenged C_2H_4 is 59% of the total tritium stopped.

Gas Composition of Samples. Analysis for He[3]. The sample bulbs were filled by the usual techniques used in this laboratory for previous measurements of recoil tritium reactions.[6,8,9] The components were introduced in this order (not all were used in each sample): I_2, He[3], O_2, CH_3F or CD_3F, and He[4]. The normal procedure for all gaseous components after the first has been the filling of a capillary line above the bulb with the next component, followed by quick equilibration of the line with the bulb by the momentary opening of the stopcock. Ordinarily, the equilibration is repeated several times and the final pressure in the bulb is the same as that registered by the manometer on the capillary line.

This procedure is perfectly satisfactory when the final measurements involve only relative radioactivity yields, and the amounts of the various gaseous components need not be known too accurately. The chief source of error in this filling method is the counter-diffusion of gases already in the bulb against the turbulent flow entering from the capillary line. This hazard becomes much greater as the number of gaseous components

(2) R. Odum and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 4668 (1961).
(3) R. Wolfgang, *ibid.*, **84**, 4586 (1962).
(4) R. Odum and R. Wolfgang, *ibid.*, **85**, 1050 (1963).
(5) H. C. Jurgeleit and R. Wolfgang, *ibid.*, **85**, 1057 (1963).
(6) E. K. C. Lee and F. S. Rowland, *ibid.*, **85**, 2907 (1963).
(7) M. Henchman, D. Urch, and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961, p. 83.
(8) F. S. Rowland, J. K. Lee, B. Musgrave, and R. M. White, ref. 7, p. 67.
(9) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963).
(10) M. El-Sayed, P. Estrup, and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).
(11) P. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2661 (1960).
(12) P. Estrup and R. Wolfgang, *ibid.*, **82**, 2665 (1960).
(13) R. J. Cross, Jr., and R. Wolfgang, *J. Chem. Phys.*, **35**, 2002 (1961).
(14) R. Wolfgang, *ibid.*, **39**, 2983 (1963).
(15) F. S. Rowland and P. Coulter, *Radiochim. Acta*, **2**, 163 (1964).

Table I. Tritium-Labeled Products from Recoil Tritium Reactions with Methyl and Methyl-d_3 Fluorides

| Sample no. | Gas pressures, cm. | | | | Relative tritium product[b] | Recoil loss, % | Obsd. radioactivity of CH$_2$TF[c] | Radioactivity ratio[d] | |
	CH$_3$F	He^3	Scavenger O$_2$	Total[a]				CH$_3$T/CH$_2$TF	HT/CH$_2$TF
371	74.1	1.13	1.2	76.4	1.20	16	24,900 ± 200	0.328 ± 0.005	1.86 ± 0.02
372	74.1	1.08	1.2	76.4	1.21	16	26,200 ± 200	0.331 ± 0.005	1.84 ± 0.02
373	3.54	0.95	0.6	76.8	0.99	67	1,410 ± 40	0.34 ± 0.03	4.1 ± 0.2
374	3.51	0.95	0.6	76.8	1.06	67	1,620 ± 40	0.37 ± 0.03	4.2 ± 0.2
367	3.85	1.00		76.2	1.06	68	1,610 ± 40	0.37 ± 0.03	4.9 ± 0.2
368	3.77	0.96	I$_2$[e]	76.2	1.04	68	1,520 ± 40	0.39 ± 0.03	4.5 ± 0.2
369	1.97	0.97		76.2	1.10	74	630 ± 50	0.41 ± 0.07	7.0 ± 0.6
370	1.92	1.00		76.2	1.09	74	560 ± 40	0.35 ± 0.07	6.8 ± 0.6
	CD$_3$F						CD$_2$TF	CD$_3$T/CD$_2$TF	DT/CD$_2$TF
359	72.6	0.98	1.0	74.6	1.05	16	19,300 ± 200	0.311 ± 0.005	1.87 ± 0.02
360	72.6	0.97	1.0	74.6	1.06	16	19,900 ± 200	0.315 ± 0.005	1.87 ± 0.02
361	3.02	0.85	0.8	60.4	0.89	79	710 ± 40	0.22 ± 0.05	3.6 ± 0.3
362	3.10	0.84	0.8	60.4	0.88	79	710 ± 40	0.32 ± 0.06	4.0 ± 0.3
363	3.64	0.63		74.2	0.68	70	820 ± 40	0.31 ± 0.05	3.6 ± 0.3
364	3.68	0.73	I$_2$[e]	74.2	0.74	70	820 ± 40	0.34 ± 0.05	3.8 ± 0.3
365	1.41	0.71		74.2	0.78	78	240 ± 30	0.32 ± 0.16	8.3 ± 1.7

[a] Remainder, He^4. [b] Irradiation time × measured He^3 content, based on 1.0 = 1.0 cm. of He^3 in a 13-ml. bulb for 60 min. [c] Number of counts observed in PCA aliquot (average of PCA and of ACTN normalized to 39% aliquot). [d] Ratio of observed radioactivities in PCA aliquot. [e] At vapor pressure.

increases, and as components need to be added at pressures not too much in excess of the accumulated bulb pressure. The hazard was clearly too great in samples containing He^3, O$_2$, CH$_3$F or CD$_3$F, and He^4, and a procedure for determination of actual He^3 content in the irradiated samples was established.

The mass tracing from a sample containing He^3, CH$_3$F, He^4, and O$_2$ is shown in Figure 1, following separation on the 50-ft. PCA column. The retention volume of He^3 is significantly less than that of O$_2$ and gives an easily measurable negative thermal conductivity signal. The presence of He^4 in the sample does not interfere, since it also is used as the carrier gas. As shown in Figure 1, peak area measurements are slightly uncertain because of the rapid transition from the negative signal of He^3 to the positive signal of O$_2$. Since the retention volumes and the peak shapes were consistent for all measurements, the He^3 content of each sample was measured directly from the negative peak height obtained from the mass trace of the PCA aliquot. The numbers recorded in Table I as pressure of He^3 are obtained from the measured total He^3 content and the measured bulb volumes. The manometer pressures for He^3 originally placed in the bulbs were as much as 50% higher in the four-component systems as the values calculated from He^3 peak heights, indicating the importance of this counter-diffusion loss.

Gas Composition of Samples. Analysis for CH$_3$F and CD$_3$F. The loss of other components is not as serious as that of He^3, but is not negligible. The areas of the mass peaks observed with CH$_3$F and CD$_3$F were also measured for each sample, and the listed pressures for these gases are also back-calculated from the known bulb volumes. The specific thermal conductivity responses for both methyl fluorides were measured with the pure compounds (for equal volumes of gas, the peak area for CH$_3$F was approximately 2% greater than for CD$_3$F).

The CH$_3$F was obtained from Columbia Organic Chemical Co., Inc., but was too impure for direct use. After vacuum distillation, no impurities were observed

above the 1 p.p.t. level. Deuteriomethyl fluoride was obtained from Merck Sharp and Dohme of Canada, Ltd., and was used directly. Its impurity level was also in the 1 p.p.t. range. The quoted isotopic purity of the CD$_3$F is 99 atom % D.

He^4 was obtained from the Puritan Co. and was purified by distillation from molecular sieve material at −196°. Oxygen was used directly from the tank.

The mass tracings after irradiation showed CO$_2$ and ethylene at the part per thousand level. There was no indication of any appreciable radiation damage and no corrections have been necessary for such damage.

Recoil Loss. The tritons formed in the He^3(n,p)H^3 nuclear reactions with 192,000 e.v. of recoil energy require approximately 0.3 mg./cm.^{2} to degrade their energy to the thermal range. With bulbs of the size used in these experiments, an appreciable fraction (0.1–0.8) of the total amount of tritium formed in the system will not reach thermal energies in the gas phase, but will recoil into the glass walls of the irradiation bulb.[11] Pyrex 1720 glass is used in these experiments because those energetic tritium ions or atoms which have recoiled into the walls remain there and do not back-diffuse into the irradiation volume to undergo possible thermal reactions leading to gaseous products.[16]

The magnitude of this recoil loss can be calculated from the known dimensions of the bulb and the stopping powers of the individual gaseous components.[17] The stopping power of CH$_3$F has not been measured for protons or tritons of the appropriate energy and has therefore been calculated from a recent semi-empirical theory of molecular stopping powers.[18] The stopping powers used in these calculations are (expressed as the range of 192 kev. tritons at 20° and 76 cm. pressure): He^4 (and He^3), 1.60; CH$_3$F

(16) J. K. Lee, B. Musgrave, and F. S. Rowland, J. Am. Chem. Soc., 82, 3545 (1960).

(17) W. J. Argersinger, Jr., J. Phys. Chem., 67, 976 (1963). These calculations assume a uniform, isotropic neutron flux and right circular cylindrical bulbs. The experimental situation was close enough to these ideal conditions to permit the use of these tables with negligible error.

(18) J. W. Root, Ph.D. Thesis, University of Kansas, 1964; J. W. Root and F. S. Rowland, publication in preparation.

(and CD_3F), 0.248; O_2, 0.287; C_2H_4, 0.181 cm.

Corrections for recoil loss are made by multiplication of the observed radioactivity by the reciprocal of the fraction of atoms stopped in the gas phase. Small errors in the calculations of stopping power are greatly multiplied, then, if the recoil loss is high. For typical samples containing 1 cm. of He^3, 1 cm. of O_2, and either 74 cm. of CH_3F or 4 cm. of CH_3F and 70 cm. of He^4, the calculated recoil loss for a 10% greater and 10% lesser triton range in the *major* constituent would be 18 and 15% for the CH_3F sample and 70 and 63% for the helium-moderated sample.

Neutron Irradiations. All samples were sealed in Pyrex 1720 bulbs of 1.89 ± 0.02 cm. i.d. and approximately 13-ml. total volume, equipped with break-off seals. All bulbs were made from the same section of glass to minimize any variations in the wall thickness and the resultant neutron flux diminution from the boron in the glass.

The samples were irradiated simultaneously in the rotary specimen rack of the TRIGA reactor of the Omaha VA Hospital, for which the neutron flux varies by only ±5% around the circumference of the rack. Since the samples are rotated through this entire circumference during the irradiation period and are essentially identical in size and in effect on an external flux, the internal neutron flux is estimated to be accurate to ±1%. The insertion and removal of the samples into the rotary rack were controlled such that irradiation times are known with an accuracy of ±0.1 min. in irradiations lasting about 60 min. The volume of the irradiation bulbs was measured (after assay of the gaseous tritium content) through the weight of water contained; the volume of the break-off itself was lost but introduced an error of less than 0.3% in the measured volume.

Radiogas Chromatography. Each irradiated sample was broken in the vacuum line, and an aliquot was drawn off into a chromatographic sample loop large enough (62.0 ml.) to contain 43% of the sample when equilibrated with the volume containing the broken sample bulb. This first aliquot was analyzed on an 80-ft. ACTN column (16% by weight of acetonylacetone on 30–40 mesh acid-washed Chromosorb P, operated at 0°). A second aliquot, containing 39% of the original sample, was then drawn off with the aid of a mercury Toepler pump. This aliquot was analyzed on a 50-ft. PCA column (9.6% by weight of propylene carbonate on 30–50 mesh activated alumina, F-1, operated at 0°). The connections for the vacuum line were greased with Apiezon N stopcock grease.

The PCA column separates He^3, H_2, CH_4, and CH_3F (or the isotopic counterparts) from one another; the ACTN column separates CH_3F from H_2 and CH_4, and serves as a check on the over-all accuracy. The small amount of ethylene-*t* observed with a high mole fraction of methyl fluoride is measurable from the ACTN runs as a small peak on the tailing part of the HT–CH_3T combination peak. Methyl fluoride and ethylene emerge together from the PCA column.

The radioactive content of each separated component was assayed with a proportional counter in series after the thermal conductivity detector. Propane was added to the gas flow between detectors to make a satisfactory proportional counting gas mixture.[19] The flow rates of
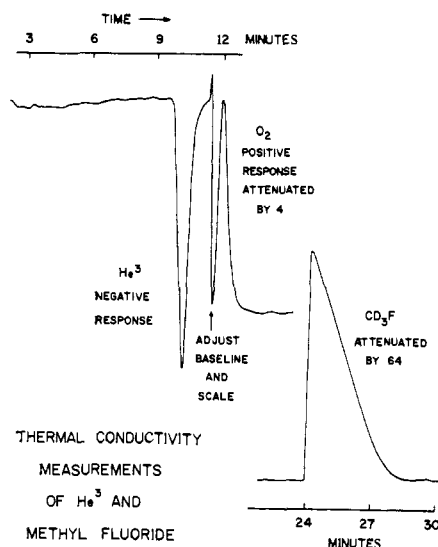

Figure 1. Thermal conductivity measurements of He^3 and methyl fluoride.

helium and propane were measured separately for each analysis and were maintained constant from run to run within ±1%. The ACTN and PCA columns were operated with 12 and 10 lb. of excess inlet pressure, respectively, and 1 atm. outlet pressure (the flow rates (ml./sec.) for the ACTN column: He, 0.49 and C_3H_8, 0.94; for the PCA column: He, 0.49 and C_3H_8, 0.85).

Separate experiments demonstrated that methyl fluoride in the amounts used here does not alter the counting efficiency of the proportional counter. Closely repetitive measurements showed no flow-rate change during the emergence of the methyl fluoride peaks.

Errors. One of the limiting sources of error in the measurement of samples containing appreciable He^4 was the random statistical error of counting. This error was especially significant for small CD_3T peaks immediately following much larger amounts of DT. Much longer irradiations could certainly increase the statistical accuracy of counting, but would carry concomitant risks of causing radiation damage severe enough to alter the observable distribution of radioactivity.

The absolute magnitude of per cent yields, etc., is somewhat sensitive to the exact stopping powers of CH_3F and CD_3F, through the recoil loss calculation. However, the major contributor to stopping power in the He^4-diluted samples comes from the He^4 and not the methyl fluoride, and the effect of errors in the contribution of the latter will be minor. In the methyl fluoride samples without He^4, the recoil loss itself is small, so errors in its estimation have again a minor over-all effect. Very little inaccuracy is introduced into the *ratios* of isotope effects, since the difference in stopping powers of the isotopic molecules will be small.

The knowledge of the actual pressure of a gaseous component is estimated as ±1% for He^3 and ±2% for the methyl fluorides. The oxygen scavenger concentrations are given as the difference between the pressure in the bulb measured during filling for He^3 + O_2 and the He^3 content measured during analysis.

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

Table II. Per Cent Yields of CH_2TF and CD_2TF from Recoil Tritium Reactions with CH_3F and CD_3F

Sample	Mole fraction (X_A) of CH_3F	% yield $(100P_{iA})$ of CH_2TF	$P_{iA}{}^A/X_A$	Sample	Mole fraction (X_A) of CD_3F	% yield $(100P_{iA})$ of CD_2TF	$P_{iA}{}^A/X_A$
371	0.97	14.0		359	0.97	12.4	
372	0.97	14.6	0.15	360	0.97	12.8	0.13
			$P_{iA}{}^{He}/X_A{}^{He}$				$P_{iA}{}^{He}/X_A{}^{He}$
373	0.046	2.44	0.53 ± 0.02	361	0.050	2.16	0.43 ± 0.02
374	0.046	2.61	0.57 ± 0.02	362	0.051	2.16	0.42 ± 0.02
367	0.051	2.67	0.53 ± 0.02	363	0.049	2.27	0.46 ± 0.02
368	0.050	2.61	0.53 ± 0.02	364	0.050	2.09	0.42 ± 0.02
369	0.026	1.22	0.47 ± 0.04	365	0.019	0.68	0.36 ± 0.05
370	0.025	1.13	0.45 ± 0.04				

Small amounts of O_2 may also have been lost by counter-diffusion during subsequent gas additions, and the accuracy of the O_2 concentrations is estimated as $\pm 10\%$.

Results

The data obtained from these experiments with CH_3F and CD_3F are summarized in Table I. After the gas pressure data, we have listed the correction for fluctuations in He^3 pressure, bulb volume, and length of irradiation, all gathered in the single factor of relative tritium production. The correction factor for recoil loss is listed separately in the next column. The actual observed radioactivity is given for the methyl-t fluoride peaks as an indication of the magnitudes involved. The last two columns express the yields of CH_3T and HT (or CD_3T and DT) relative to the CH_2TF (or CD_2TF) yields. The errors quoted on these relative yields are those arising solely from the random counting statistics.

The only other radioactive compound observed in any of these runs was about 0.2% ethylene-t from both CH_3F and CD_3F in the experiments carried out without He^4. No measurable quantity of ethylene-t was distinguishable above background in the He^4 dilution experiments (yield $< 0.2\%$).

The measurements of observed radioactivity provide accurate intramolecular evaluation of the relative probabilities for different hot reactions. However, inter-sample comparisons are more difficult to evaluate quantitatively because of the large number of additional variables to be controlled. The data for CH_2TF and CD_2TF in Table I have been converted to per cent yields of total tritium and are recorded in Table II. The largest applied correction is that for recoil loss listed in the first column. The next most important source of error arises from the monitor reaction and possible uncertainties in the hot yield of C_2H_3T from unscavenged C_2H_4. It is difficult to see how this monitor yield can greatly exceed 59%, since this number is obtained from experiments in which the remaining 41% was actually observed in other chemical forms. If, however, some tritium became incorporated in nongaseous forms, the actual hot yield of C_2H_3T would then be less than 59%. The amount of tritium actually observed was consistent with that observed from some unscavenged alkane samples irradiated simultaneously with the present series, so we have assumed that negligible radioactivity would be found as $>C_8$ compounds in the monitor runs. The calculations leading to the data of Table II ac-

tually involve only the ratio of the activities observed in two particular peaks (CH_2TF and C_2H_3T), corrected by the observed ratio of He^3 contents, by the calculated recoil losses (16 and 11%), and by minor variations in times of irradiation and chromatographic flow rates, and expressed relative to the C_2H_3T standard. The estimated errors quoted do *not* include any error in this standard.

The data obtained in the unmoderated experiments with CH_3F and CD_3F are shown in Table III, in comparison with the previously published data from an extensive series of I_2-scavenged samples.[5] The ratios of CH_3T/CH_2TF and CD_3T/CD_2TF are in excellent agreement for the two series of data, and the ratio of CH_2TF/CD_2TF yields is in fairly good agreement. Our present O_2-scavenged experiments show consistently lower relative yields of HT or DT, and higher per cent yields than do the I_2-scavenged runs.

The discrepancy in per cent yields is traceable in large part to the difference in estimates of recoil loss correction. Our estimate of 16% loss is greater than that estimated by Jurgeleit and Wolfgang by about 10%, reflecting the much lower atomic stopping power attributed to the fluorine atom by Root and Rowland.[18] If nonvolatile activity is formed in the C_2H_4 monitor system, correction for it would tend to bring the per cent yields of the two data sets toward each other.[20]

The minor differences existing in HT and DT yields from the two sets of data are comparable to those observed for I_2- and O_2-scavenged hydrocarbons and probably represent a similar effect.[21] All of the data confirm the striking similarity in the product ratios from CH_3F and CD_3F and therefore in the magnitude of the isotope effects of the three hot reactions by which they are formed.

Discussion

Kinetic Theory of Energetic Reactions. The observed yield of each radioactive product from recoil tritium reactions can be expressed in a quantitative manner through the terminology of the kinetics of hot reaction.[11,12,14,22] The most important parameters in this terminology are α_A, the average logarithmic energy loss in collisions with molecule A, and I_{iA}, the reac-

(20) The experiments of ref. 5 utilized unscavenged *n*-butane as a monitor reaction. It is difficult to see how this could lead to a low estimate of per cent yields unless a systematic error existed involving the loss of some He^3 from the methyl fluoride bulbs.

(21) J. W. Root and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 1021 (1963).

(22) J. M. Miller and R. W. Dodson, *J. Chem. Phys.*, **18**, 865 (1950).

Table III. Comparison of Recoil Tritium Data for CH_3F and CD_3F without Moderator

| | CH₃Fᵃ | | | CD₃Fᵃ | |
	O_2ᵇ	I_2ᶜ		O_2ᵈ	I_2ᶜ
HT	185 ± 1	197 ± 0.8	DT	187 ± 1	206 ± 1.1
CH₂TF	100	100	CD₂TF	100	100
CH₃T	32.9 ± 0.3	33.7 ± 0.2	CD₃T	31.3 ± 0.4	32.4 ± 0.2
CH₂TF, % yield	14.3 ± 0.3	12.4 ± 0.3	CD₂TF, % yield	12.6 ± 0.2	10.1 ± 0.1
Ratio of % yields,	CH₂TF/CD₂TF	1.14 ± 0.03ᵉ		1.23 ± 0.02ᵉ	

ᵃ With O_2 and I_2 as scavengers. ᵇ Values from this work with ratios relative to CH₂TF = 100. ᶜ From ref. 3 and 5. ᵈ From this work with ratios relative to CD₂TF = 100. ᵉ This work.

tivity integral. The latter is a measure of the probability for formation of product i in hot reaction with

$$I_{iA} = \int_{E_{min}}^{E_{max}} \frac{P_{iA}(E)}{E} \, dE \qquad (5)$$

molecule A and is defined by eq. 5. The total reactivity integral, I_A, is simply the sum of the individual values of I_{iA} over all i products.

A large fraction of recoil tritium atoms react in methyl fluoride while still quite energetic, with a consequent progressive diminution in the fraction surviving to lower and lower energies. If He⁴ serves only as a nonreactive sink for the kinetic energy of recoil, as is assumed, the fraction of tritium atoms surviving unbonded after collision at any given energy (below the maximum at which bonding can occur) will increase monotonically with increasing mole fraction of He⁴. The preference for the usage of a logarithmic energy scale in the definition of reactivity integral ultimately rests on the assumption that the fractional energy loss in collisions with inert gases is reasonably independent of energy, i.e., α_{He} can be assumed to be an energy-independent constant. Under these conditions, the flux of tritium atoms in a large excess of He⁴ is inversely proportional to energy, the flux per unit (ln E) is constant, and, since the total hot reaction is low, equal areas of the reactivity integral will contribute equal reaction yields. The product yields for two species from the same molecule will then be found in the ratio $P_{iA}^{He}/P_{jA}^{He} = I_{iA}/I_{jA}$.

Reactive Moderators in Kinetic Theory. Recoil tritium atoms colliding with a reactive species A can also be described through the corresponding term, α_A, representing the moderating ability of the reactive species itself. For reasonable assumptions, the total hot yields in pure A, P_A^A, and the molecule A in excess He⁴, are expressed by eq. 6 and 7,[11,12,14,15] in which f_A^{He} represents the fraction of total tritium collisions that occur with molecule A in a binary mixture with He⁴. If suitable values can be determined from other

$$\frac{f_A^{He} I_A}{\alpha_{He^4}} \cong -\ln (1 - P_A^{He}) \qquad (6)$$

$$\frac{I_A}{\alpha_A} = -\ln (1 - P_A^A) \qquad (7)$$

experiments for f_A and α_{He^4}, then eq. 6 can be used to estimate I_A, and this value can be used in turn in eq. 7 to estimate α_A.[23] Again, the assumption is implicit that

the average energy loss in nonbonding collisions with A is essentially energy independent. If this average energy loss varies appreciably with energy, then the α_A of eq. 7 will have a complicated relationship with the actual energy losses. No data exist with which this assumption can be tested at the present time.

While the tritium flux is controlled in part by the moderating ability of the reactive molecule as expressed in α_A, the flux in pure A will be depleted at lower energies by the removal of some atoms in hot reactions at higher energies. In this situation, the lower energy areas of reactivity integrals are exposed to a reduced tritium flux and hence contribute less to the total hot reaction than equal areas at higher energies. Thus, if I_{iA} is generally at a higher average energy than I_{jA}, then $P_{iA}/P_{jA} > I_{iA}/I_{jA}$. Experiments of this kind with hydrocarbon molecules, RH, have shown that

$$P_{RT/RH}^{RH}/P_{HT/RH}^{RH} > P_{RT/RH}^{He}/P_{HT/RH}^{He}$$

$$(= I_{RT/RH}/I_{HT/RH})$$

and therefore indicate that the substitution reaction leading to RT from RH occurs at a higher average energy than the abstraction reaction leading to HT.[24]

Intermolecular Comparisons in Kinetic Theory of Hot Reactions. Comparison of the average energy of different hot reactions is not limited to use of the same molecule as reactant *and* reactive moderator, as with RH above, but can be conducted with an entirely different molecule, Q, as the bulk reactive constituent. The comparison can then be made of P_{iA}^Q/P_{jA}^Q vs. I_{iA}/I_{jA}, with different values again indicative of variations in the average energy of reaction for the processes leading to products i and j. The use of different reactive molecules as bulk constituents offers the possibility of obtaining different sets of P_{iA}/P_{jA} values, as the tritium flux is altered to that characteristic of each bulk molecule. The greatest utility in such comparisons will be obtained with reactive moderators whose bond-forming hot reactions have appreciable probabilities through the energy ranges in which i and j are formed.

Furthermore, such average energy experiments are not limited to intramolecular comparisons of two hot reactions from the same reactive species, but can be extended to intermolecular comparisons through the measurements of yields for two hot reactions occurring with different molecules in excess He⁴, and again in an excess of a reactive moderator Q. In this case, the procedure now involves comparison of the ratio ($P_{iA}^Q/$

(23) The procedure for verification of the applicability of these equations through measurements carried out over the entire mole fraction range has been outlined and applied in ref. 12, 14, and 24. We have

assumed that the methyl fluorides will behave similarly and have made measurements only at the two mole fraction extremes for which eq. 6 and 7 have been shown to be quite satisfactory in ref. 15.

(24) A. Rosenberg and R. Wolfgang, *J. Chem. Phys.*, 41, 2159 (1964).

$f_A{}^Q)/(P_{kB}{}^Q/f_B{}^Q)$ vs. I_{iA}/I_{kB}. If the former is larger than the latter, the conclusion would then follow that the average energy of reaction for forming i from A is higher than that for forming k from B.

The intermolecular ratio comparison given above seems to imply that the cross sections for collisions with tritium of molecules A, B, Q, and He[4] must be accurately known. However, while these data are desirable, they are not necessary for the comparison above, since it can be rewritten (in the limit of large excess of Q, and He[4], respectively) as $(P_{iA}/X_A)/(P_{kB}{}^Q/X_B{}^Q)$ vs. $(P_{iA}{}^{He}/X_A{}^{He})/(P_{kB}{}^{He}/X_B{}^{He})$ (in which $X_A{}^Q$ represents the mole fraction of A in a binary mixture with Q) and the collision cross sections have cancelled out. In practical experimental situations, the cancellation can be sufficiently good to present no hindrance to interpretation. (In the present paper involving comparison of isotopic molecules, the cancellation is effective to an even higher order since the relationship between f_A and X_A will be nearly unaffected by isotopic substitution.)

In principle, measurements of the yields from a whole series of hot reactions in large excess of He[4], and then again in large excess of reactive moderator Q, permits the intercomparison of the average energies at which each of the reactions occurs. Potentially, at least, each of the hot tritium reactions with every molecule could be ordered into a series of steadily decreasing average energies at reaction.

Isotopic Intermolecular Comparisons. In the present set of experiments, the general principles of both intramolecular and intermolecular comparisons have been applied to the specific problem of isotope effects in hot reactions. The measurement of CH_3T and CH_2TF yields from CH_3F in excess He[4], together with the already measured ratios in pure CH_3F, permits estimation of the relative energies of formation of these two species. The energies of formation of CD_3T and CD_2TF from CD_3F can be evaluated in a similar manner. Finally, the intermolecular comparison of the ratio of $(P_{CH_2TF/CH_3F}{}^{He}/X_{CH_3F}{}^{He})/(P_{CD_2TF/CD_3F}{}^{He}/X_{CD_3F}{}^{He})$, *i.e.*, $I_{CH_2TF/CH_3F}/I_{CD_2TF/CD_3F}$, with the previously measured ratio of $(P_{CH_2TF/CH_3F}{}^{C_4H_8}/X_{CH_3F}{}^{C_4H_8})/(P_{CD_2TF/CD_3F}{}^{C_4H_8}/X_{CD_3F}{}^{C_4H_8})$ permits evaluation of the relative energies of formation of CH_2TF and CD_2TF.

Sources of Isotopic Variations. The experiments described here, together with those reported earlier,[3,5,6] have been concerned with differences between CH_3F and CD_3F in reactions with hot tritium atoms. Only a few systems have been examined for such isotopic variations, but the basic sources of these variations may be deduced from the investigations on the basis of current general knowledge of energetic reactions. Four conceivable sources of variation are illustrated in Figure 2. The shapes of the curves for the various reactivity integrals are purely conjectural.

The processes by which kinetic energy in the 5–20-e.v. region is lost in nonbonding collisions are not accurately understood, and it is possible that the average energy loss in such interactions is different for two isotopic molecules. This situation is illustrated by the upper diagram in Figure 2, in which the average energy loss in collisions with A is less than with B. A higher hot yield is expected from reactions with A, than with B, if the reaction probabilities per collision are comparable (as illustrated), since more collisions occur in the reac-

tive range in the former case. An isotopic variation of this type is designated as a "moderator isotope effect."

If there are no such moderator differences, then isotopic variations may still be expected if the reactivity integrals are not identical. We shall use the general term "reactive isotope effects" to cover all of the cases in which the reactivity integrals are not identical for isotopic molecules. The middle pair of diagrams in Figure 2 illustrates two types of inequality in the reactivity integrals. In the upper, the probability of reaction per collision is higher for A than B; in the lower, the energy range over which reactions occur is larger for A than B. Both these effects would be expected to give a higher hot yield from A than from B. It has not yet been found possible to separate these two types experimentally, and they can be grouped as "probability integral isotope effects."[6]

A fourth source of isotopic variation is illustrated in the bottom diagram, for which the flux of tritium atoms surviving to low energies has been noticeably diminished by some higher energy reaction. Then fewer hot reactions will be observed with B than with A even if the areas under the reaction probability curves are of equal magnitude. Such an effect may be designated as a "average energy isotope effect," indicating that there is a difference in the average energy of the tritium atoms initiating the hot reactions.

Experimental Evidence for Types of Isotopic Variation. The first experiments with the CH_3F–CD_3F system[3,5] demonstrated that the per cent yields of the three major products from CH_3F samples were consistently higher than the corresponding yields from CD_3F samples (Table III). These data, alone, are consistent with either "moderator" and/or "probability integral" isotope effects as described above and illustrated in Figure 2, with CH_3F being the A molecule.

The second experimental approach[6] involved comparison of the results obtained with methyl fluoride–cyclobutane mixtures with those found in methyl-d_3 fluoride–cyclobutane mixtures. Since excess cyclobutane was present in each case, the nonbonding collisions should be similar in the two kinds of mixtures, and hence the tritium atom flux should not be appreciably affected by the choice of the isotopic fluoride molecule. Thus, the possibility of a moderator effect was effectively eliminated. In addition, the recoil tritium reactions with cyclobutane could be used as a useful internal standard for comparison purposes. An isotopic preference for the formation of CH_2TF from CH_3F vs. CD_2TF from CD_3F of 1.33 ± 0.04 was found. The result was explained as a probability integral effect,[6] but an alternative explanation could have been suggested, involving an average energy isotope effect. If, on the lowest diagram of Figure 2, A and B represent the substitution reactions in CH_3F and CD_3F, and if the cyclobutane reactions occurred in roughly the same energy range as shown for A, an isotopic variation would have been expected as long as the hot reaction with C_4H_8 led to serious flux depletion in the energy range available to B. (A combination of a moderator difference and this effect could then have accounted for the separate observations in CH_3F and in CD_3F.)

In combination with the methyl fluoride–cyclobutane competitive experiments, the current measurements in He^4–CH_3F mixtures can distinguish between prob-

ability integral and average energy isotope effects.[25] Variations caused by differences in the magnitude of the reaction probabilities will persist in mixtures with a high mole fraction of helium. However, isotopic variations in the average energy of reaction will not directly cause any differences in yield in excess of He^4, since the tritium flux will not be depleted in these nonreactive collisions. The actual yields for each will be determined by the collision densities through the two energy ranges involved. These densities will be slowly dependent upon changes in the average fractional energy loss in $T-He^4$ collisions as a function of T energy, but should be energy independent to a good approximation.

The directly measured values for P_{iA}/X_A at about 95 mole % He^4 are 0.54 for CH_2TF from CH_3F and 0.43 for CD_2TF from CD_3F, indicating an isotope effect of 1.25 ± 0.03 favoring substitution of T for H vs. T for D. However, the measurement of the ratio of two values of P_{iA}/X_A should really be carried out under conditions of equal tritium flux, i.e., infinite dilution and $P_{iA} = 0$. Such is not quite the circumstance for experiments with 95% helium, and an approximate correction for flux depletion by hot reaction should be made by dividing each observed yield of CH_2TF (or CD_2TF) by the factor [1−0.5(total hot yield)]. To obtain the correction factor accurately, the hot TF from eq. 4 should be included. However, this yield has not been measured, and it would be difficult to separate from labile, tritiated species formed in thermal reactions and would anyway be expected to be small compared to the sum of the three products measured (Table I). Using this sum of the three observed products in the above approximate expression for a correction factor, the infinite dilution values for P_{iA}/X_A are estimated as 0.58 and 0.46. The ratio of these two values leads to an estimate of 1.27 ± 0.04 for the relative sizes of I_{CH_3F} and I_{CD_3F}.

Comparison of the value of 1.27 ± 0.04 for the isotope effect in an inert moderator with the 1.33 ± 0.04 observed in a reactive moderator leads to an estimate of the ratio of these two values as 1.05 ± 0.05. Within the accuracy of the measurement, then, the conclusion follows that the substitutions of T for H in CH_3F and T for D in CD_3F occur at the same average energy, i.e., that no average energy isotope effect has been observed in this system. (In contrast, the ratios of HT/RT from reactions 1 and 2 with alkanes can change by 50% or more as the alkane is diluted with He^4.) The difference given is in the direction of a lower average energy for the replacement of D than for H, but is statistically without significance.

The isotopic variation in He^4 mixtures has earlier been investigated for CH_4 and CD_4 as a test of the "billiard-ball" theory of substitution reactions, with the conclusion that the data showed no isotope effect greater than 20%.[13] Since the expected effect for billiard ball collisions was a factor of three favoring replacement of D over H, such a mechanism was ruled
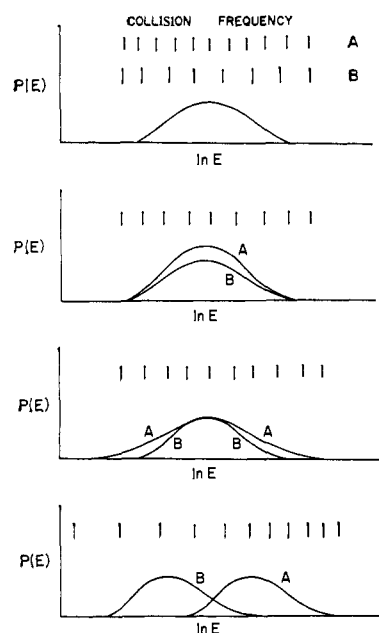

Figure 2. Possible sources of isotopic variation in recoil tritium experiments. Top: moderator isotope effect, $\alpha_A < \alpha_B$. Middle pair: probability integral isotope effects—greater reaction probability per collision for A vs. B (upper); greater range for reaction for A vs. B (lower). Bottom: average energy isotope effect, reaction with B occurs at lower energies, for which the tritium flux has been reduced by reaction at higher energies.

out. This conclusion is confirmed by the present data. We expect that more precise He^4 dilution experiments with CH_4 and CD_4 will demonstrate a probability integral effect similar to that obtained for methyl fluorides (of the order of 1.3), only slightly outside the estimated error of the earlier measurements.

The assumption has been implicitly made in these arguments that an appreciable fraction of the total hot reactions with cyclobutane occurs in the same energy region as those with CH_3F and/or CD_3F. This assumption could be verified by separate measurement of methyl fluoride vs. cyclobutane in helium and in some reactive moderators.

Ratios of Radioactive Products in Helium-Moderated Systems. Inspection of Table I shows that the yield ratios of CH_3T/CH_2TF and CD_3T/CD_2TF have virtually the same value, and both ratios are essentially insensitive to dilution with He^4. The insensitivity of these product ratios to He^4 addition indicates that CH_3T and CH_2TF are formed at the same energies, as are CD_3T and CD_2TF. Since the latter two of each pair have been indicated to occur at the same energy by the absence of an average energy isotope effect, the over-all conclusion results that all four of these tritiated species (CH_3T, CD_3T, CH_2TF, CD_2TF) are formed at approximately identical average energies.

The hydrogen abstraction/hydrogen substitution ratios, HT/CH_2TF and DT/CD_2TF, do show marked increases as the He^4 mole fraction increases. The values obtained with I_2 scavenger for these ratios are doubtful because of the possibility of thermal chemical reactions involving TI impurities formed during the irradiations.[21] The experiments conducted with O_2 scavenger are probably good measures of the real hot yield ratios. However, since the scavenging of thermal hydrogen or

(25) We make here the implicit and reasonable assumption that the hot reactions with CH_3F and CD_3F do not occur entirely within an energy region in which hot reactions with cyclobutane are absent. Reactivity integrals (e.g., "spike" distributions) can be drawn which could negate flux depletion effects, but these have been rejected here as physically inconsistent for comparisons of the T-for-H reaction in two molecules. Furthermore, experiments with cyclobutane suggest such a broad range of reaction energies that appreciable overlap of reactivity integrals seems inevitable.[9]

tritium atoms is much more difficult than the scavenging of radicals, extensive experiments with a variety of scavenger molecules may be required to demonstrate that the HT and DT observed did not partially originate in reactions not truly "hot." If the ratios given in Table I do represent only hot products, as seems likely, then the *average* energy of the tritium atoms prior to the abstraction reactions must be lower than for either of the substitution reactions for H (or D) or F.

Evaluation of α, f, and I. The formulation of the kinetic theory of hot reactions permits quantitative evaluation of the various I values if the parameters f_A and α can be calculated or measured. If only f_A values are available, a value of α_{He^4} can be assumed as the standard, and relative values of α_A and I_A can be obtained. The values of f_A and α_{He^4} can be estimated from thermal data and a rigid-sphere model, respectively, to give crude values for I_A and α_A. More accurate calculations can be made if satisfactory interaction potentials are available for each collision type, in this case, T–CH_3F, T–CD_3F, and T–He[4].

Estrup has recently shown that more realistic interaction potentials lead to much lower values for α_{He^4} and for various α_A values than do the rigid-sphere models.[26] However, interaction potentials have been measured and/or calculated only for collisions involving some of the simplest species.[27–30] Moreover, in the best-evaluated system, the potential for He–He collisions, a discrepancy of as much as a factor of two exists in the e.v. range between the calculated values and the experimental values used by Estrup.[29–31] While unequivocal calculations do not seem feasible at the present time, it is quite clear that the use of rigid sphere collision diameters will lead to estimates of α_{He^4} that are too large.[26] Since I_A is approximately given by

$$I_A \xrightarrow[X_A \to 0]{} \frac{\alpha_{He^4}}{R_{A/He}} \frac{P_A{}^{He}}{X_A} \tag{8}$$

eq. 8 in which $R_{A/He}$ is defined as the frequency ratio of energetic tritium atom collisions with A *vs.* He, it is also evident that an overestimate of α tends toward an overestimate of I_A. This error in the estimate of α_{He^4} from rigid sphere calculations can be as large as an order of magnitude, depending on the interaction potential chosen.[26,32]

Other competitive experiments have been conducted with He[4] as a moderator,[11–14,32] and detailed discussion of the magnitudes of α_A and I_A values will be deferred to a later publication. Certainly, however, conclusions based on quantitative estimates of these parameters obtained from rigid-sphere scattering potentials must be carefully re-examined.[11–14,26,32,33]

Relative Values of α_{CH_3F} and α_{CD_3F}. The calculation of α_A values from $P_A{}^A$ and $P_A{}^{He}$ is possible in principle,

but depends, in fact, completely on the evaluation of α_{He^4}. In addition, eq. 6 and 7 are actually applicable only to total hot yields, and not to individual hot yields. Equation 8 is applicable to individual yields if the values of $P_{iA}{}^{He}$ are used instead of $P_A{}^{He}$. However, since the value of α_{He^4} will be the same for CH_3F–He[4] mixtures, and since the relationship between f_A and X_A will vary little with isotopic substitution, the *ratio* of $\alpha_{CH_3F}/\alpha_{CD_3F}$ can be estimated. If the hot yield of TF is negligible from both CH_3F and CD_3F, the ratio $\alpha_{CH_3F}/\alpha_{CD_3F}$ is found to be 1.23 $\pm$ 0.08; a yield of hot TF equal to one-third that of hot HT in all samples leads to a change much less than the standard error. This ratio indicates a moderator isotope effect in the methyl fluorides, such that the average energy losses are greater and the collisions fewer for CH_3F than for CD_3F.

If we choose 2.0 as a reasonable value for $R_{CH_3F/He}$ in eq. 8, and assume that the HT and DT yields in O_2-scavenged samples are true hot yields, then crude estimates of I_{CH_3F} and I_{CD_3F} as $1.7\alpha_{He^4}$ and $1.2\alpha_{He^4}$, respectively, can be obtained from eq. 6. Substitution of these values into eq. 7 leads to approximate estimates that CH_3F is 2.8 and CD_3F is 2.3 times as efficient in moderating recoil tritium as He[4]. Even if α_{He^4} is of the order of 0.1, as suggested by Estrup,[26] these values represent energy losses greater than possible through elastic collisions.

Reaction Mechanisms Resulting in Isotopic Variations. The cumulative explanation for all of the data on recoil tritium reactions with CH_3F or CD_3F indicates the existence of both a moderator and a probability integral isotope effect. The existence of the latter in substitution for H or D, coupled with virtually identical product ratios from CH_3F and from CD_3F, indicates the simultaneous existence of comparable probability integral effects for each of reactions 1 to 3.

The abstraction reaction has been shown to be correlated with C–H bond dissociation energies, and the isotope effect observed here is very closely that expected from the differences in bond energy between C–H and C—D bonds.[21,34] The effect observed in the replacement of F must involve the isotopic differences between the CH_3 and CD_3 residues with which the recoil tritium atom combines and can be labeled as a "secondary" isotope effect. The isotope effect in the substitution of T for H or D could be either the result of the isotopic difference between the atoms replaced or between the CH_2F and CD_2F residues with which the T atom then combines.[35] By analogy with the F replacement reaction, the residue effect would seem to be sufficient to account for most of the isotopic difference. The slightly greater isotope effect in F replacement (32.9 *vs.* 31.3 in Table III) might then be expected as the consequence of three H (or D) atoms in the CH_3 residue *vs.* only two in CH_2F. In contrast to the abstraction reaction, the substitution of T for H is quite insensitive to bond-dissociation energies, while exhibiting almost

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(35) No experiments which would distinguish between these two effects have yet been reported. Comparison of the yields of $CHTD_2$ and CH_2DT from CH_2D_2 would furnish a critical test—the requisite chromatographic separation has not yet been achieved with sufficient accuracy. Comparison of the intramolecular distributions of tritium in $(CH_3)_3CH$ and $(CH_3)_3CD$ would also distinguish between these two effects.

identical isotope effects. The yield variations in the substitution reactions are consistent with a more rapid relaxation of H atoms into positions favorable for successful bonding of the T atom. However, more work is needed to clarify the nature of the reaction mechanisms in both of the recoil substitution reactions.

The moderator isotope effect measured here is in the opposite direction from that discussed earlier[5] and is not consistent with a quasi-elastic atomic collision process (T vs. H or D in the respective fluoride). Furthermore, the magnitude of the average energy loss is much too large for molecular elastic collisions and confirms the earlier measurements of substantial energy loss by inelastic collision mechanisms.[14,24,33] Detailed quantitative analysis of the process of moderation by polyatomic molecules is not feasible, however, until a suitable value of α_{He^4} or some other standard has been established.

The Polymerization of Cyclopentadiene by Free Ions. Determination of the Propagation Rate Constant[1,2]

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The technique of radiation-induced ionic polymerization at low temperature has been used to determine the propagation rate constant, $k_p = 5.8 \times 10^{8 \pm 1} M^{-1} sec.^{-1}$, for the polymerization of cyclopentadiene by free ions at $-78°$. In this method, ammonia has been employed as a terminating agent to obtain the ratio of rate constants, k_r/k_p, for termination to propagation, while the value of k_r has been calculated from the Smoluchowski-Debye theory for encounter-controlled reactions. The significance of high k_p values for polymerization by free ions is discussed with reference to conventional ionic polymerization.

Introduction

Evidence has accumulated which indicates that under certain conditions, the radiation-induced polymerization of several monomers including isobutylene,[3] α-methylstyrene,[4] β-pinene,[5] styrene,[6–9] isobutyl vinyl ether,[10] and butadiene[11,12] is caused by ionic intermediates. Despite the attention devoted to this topic, little progress has been made in the elucidation of rate constants. In particular, no information has been available to allow any discrimination between the possible participation of free ions and/or ion pairs in these polymerizations. Some theoretical views[13–15] have been advanced, but a lack of precise knowledge has hampered any further clarification of this subject.

The present contribution deals with certain aspects of the radiation-induced polymerization of cyclopentadiene at $-78°$. We have previously reported[2,16] on the use of ammonia as a suitable ion scavenger and retarder of ionic polymerization. In this paper, results are presented on the molecular weights of the polymer formed in the presence of ammonia, and the Mayo-Overberger relation[17,18] is applied to obtain the ratio of rate constants for propagation to retardation. By employing tritiated ammonia, it has been possible to measure the concentration of amino groups in samples of soluble polymer. In addition, we report on the effects of temperature, dose rate, and other additives on this radiation-induced polymerization.

Experimental

Materials. Cyclopentadiene monomer was prepared by the thermal decomposition of the dimer 3a,4,7,7a-tetrahydro-4,7-methanoindene (Matheson Coleman and Bell, practical, 95%) in an 8-ft. Vigreux column under an atmosphere of nitrogen. After condensation, the monomer was collected in a receiving flask held at $-78°$. By vapor phase chromatography, the purity of the

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