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Recoil Tritium Reactions: Methyl Chloride¹

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Recoil tritium reactions with CH_3Cl give three important hot products HT, CH_2TCl , and CH_3T , in the approximate ratios 2.7:1.0:0.8 at 1 atmosphere pressure. When I_2 is used as the radical scavenger, CH_2TI is observed in yields comparable to that of CH_2TCl . Variation of the gas pressure during irradiation shows that the yields of CH_2TCl and CH_2TI are pressure dependent in a manner consistent with the reaction $\text{CH}_2\text{TCl}^* \rightarrow \text{CH}_2\text{T} + \text{Cl}$. Measurements in the liquid phase indicate that approximately half of the original molecules formed by substitution of T for H decompose at 1 atm. gas pressure before de-excitation can occur. The relative ease of replacement of H by T per C-H bond is about 0.78 to 1 for CH_3Cl vs. cyclo- C_6H_6 . The pressure-dependent reactions demonstrate the presence of a long-lived excited molecule and indicate that most of the observed CH_2T radicals are formed through a two-step mechanism. Steric inhibition of hot substitution reactions by Cl substituents is a small effect at most.

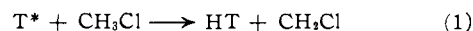
Introduction

The mechanisms of the chemical reactions occurring with high energy tritium atoms have been investigated in detail with various hydrocarbons, and plausible theories supporting these mechanisms have been developed.²⁻⁷ The introduction of a halogen atom into the molecular target for the tritium atom immediately offers both new possibilities in such reactions and sufficient variation in the molecule itself to test the general understanding of these high energy reactions. An over-all survey of recoil tritium reactions with various halogenated molecules has already led to the postulation of additional hypotheses for the mechanisms of these energetic reactions.⁸⁻¹⁴ The present paper is concerned with a detailed study of the reactions occurring with methyl chloride.

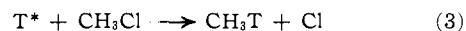
The recoil tritium atoms formed in nuclear reactions are created at very high energies (10^5 – 10^6 e.v.) in the ionic state, but do not form permanent chemical bonds until almost all of this energy has been dissipated.^{2,3} The chemical reactions which are subsequently observed include a large fraction which are initiated by neutral, ground-state tritium atoms with excess kinetic energies, as shown for example, by the observations of reactions unknown for thermal H or D atoms, by insensitivity of reaction yields to the presence of free-radical scavengers, and by observation of high excitation energies in product molecules.^{2,3} The stable labeled "hot" products obtained by reactions of energetic tritium with hydrocarbons are effectively isolated through the use of free radical scavengers from any thermal reactions also occurring in the system.

The two reactions which usually give the highest yields in hydrocarbon systems are written for methyl

chloride as eq. 1 and 2



Recoil tritium reactions carried out with chlorine-substituted molecules,^{8,10,13} and with CH_3Cl itself, have demonstrated the substitution of T for Cl, as in eq. 3. The abstraction of chlorine by an energetic tritium atom (eq. 4) must also be considered as a possible hot reaction.



The series of recoil tritium hydrocarbon experiments in our laboratories that have shown the yields of some labeled products to be pressure dependent, indicative of high excitation for the product molecule,^{3,4} have prompted a careful search for such effects in the methyl chloride system.

Experimental

Chemicals.—The recoil tritium atoms were obtained through neutron irradiation of appropriate mixtures containing He^3 for the gas phase, and LiF for the liquid phase experiments, respectively. Lithium fluoride of natural isotopic abundance was obtained from Riedel-DeHaen A.G., Seelze-Hannover, Germany. He^3 was obtained from Mound Laboratory, Monsanto Research Corp., and was purified from tritiated contaminants prior to use.

Methyl chloride was obtained from the Matheson Co. with a stated purity of greater than 99.5% and was used without further purification. The composition was confirmed by a gas chromatographic purity check.

Cyclobutane was obtained from Merck Sharp and Dohme of Canada, and was purified from its chief contaminant, *n*-butane, by distillation. The material used here contained less than 1% *n*-butane.

Oxygen (Linde Co.), I_2 , and Br_2 (both from Baker Chemical Co.) were used without purification.

Sample Preparation.—The gaseous samples were sealed *in vacuo* in 2.0-cm. i.d. Pyrex 1720 bulbs, following the techniques established previously.^{2,3} The typical bulb volume was 12 ± 1 ml. I_2 was introduced into gaseous samples in break-tip capillaries to avoid I_2 vapor contamination in the vacuum line. These inner break-tips were then broken by shaking prior to irradiation.

The liquid samples were sealed in capillary tubes, also of Pyrex 1720 glass, filled loosely with LiF. The scavenger I_2 or Br_2 was introduced onto the powdered LiF and kept there with liquid N_2 during evacuation. The CH_3Cl was added last using vacuum techniques.

Irradiations.—All gaseous samples were irradiated for 1 hr. in the rotary rack of the Omaha VA Hospital TRIGA reactor, in a nominal flux of 1.0×10^{11} n./cm.²/sec. The actual flux within the bulbs was reduced to about 5×10^{10} n./cm.²/sec. because of neutron absorption in the boron of the Pyrex 1720 glass.

(1) This research was supported by A.E.C. Contract No. At-(11-1)-407, and by fellowship support from the Pan American Petroleum Foundation (E. K. C. L.). Part of this work was presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(2) M. Henschman, D. Urch, and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961, p. 83.

(3) F. S. Rowland, J. K. Lee, B. Musgrave, and R. M. White, *ibid.*, Vol. 2, p. 67.

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(5) J. W. Root and F. S. Rowland, *ibid.*, **85**, 1021 (1963).

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(14) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 2907 (1963).

The capillaries containing liquid CH_3Cl were irradiated for 3 hr. and were exposed to a flux only slightly diminished by absorption in the glass.

Analysis.—The gaseous labeled products were separated and measured by radio gas chromatography using helium as the eluent gas.^{15,16} The gas chromatographic separations were carried out on two or more of the following columns for each sample. The products observed from each are listed in the order of elution. (a) PCA column: 50-ft. column of propylene carbonate packed on 30–50 mesh activated alumina, 0°, flow rate 29 ml./min.; products: HT, CH_3T , $\text{C}_2\text{H}_5\text{T}$, CH_2TCl . (b) TTP column: 50-ft. column of tri-*o*-tolyl phosphate, packed on 30–40 mesh Chromosorb P, 50°, flow rate 30 ml./min.; products: (HT + CH_3T), CH_2TCl , CH_2TBr , $\text{C}_2\text{H}_5\text{TCl}$, *i*-Pr-Cl-*t*, *n*-Pr-Cl-*t*, CH_2TI , CH_2Cl_2 , butyl chlorides. (c) DMS column: 50-ft. column of dimethyl sulfolane, packed on 30–60 mesh firebrick, 24°, flow rate 25 ml./min.; products: (HT + CH_3T), $\text{C}_2\text{H}_5\text{T}$, CH_2TCl . (d) ACTN column: 80-ft. column of acetonyl acetone, packed on 30–40 mesh Chromosorb P, 0°, flow rate 30 ml./min.; products: (HT + CH_3T), $\text{C}_2\text{H}_5\text{T}$, cyclo- $\text{C}_4\text{H}_7\text{T}$, CH_2TCl . (e) DEHS column: 50-ft. column of di-2-ethylhexyl sebacate, packed on 40–60 mesh Chromosorb W-R, 105°, flow rate 28 ml./min.; products (HT + CH_3T), CH_2TCl , CH_2TI , CH_2TOH .

The PCA column was protected for the Br_2 -containing sample with a very short (few inches) column of TTP.

Mass peaks were measured through thermal conductivity response. The radioactivity was assayed by proportional counting of the gas mixture obtained after the addition of propane gas to the helium stream. Most measurements were made with a silver-walled glass counter of 85-ml. active volume¹⁶; a 20-ml. counter was sometimes used to separate closely neighboring peaks.

Many alkyl halides partially quench the internal proportional counting action within the counter by electron capture. However, no reduction in counting efficiency for an external Na^{22} source was observed during the passage of 10 ml. (STP) of CH_3Cl , so quenching corrections were unnecessary for the parent peaks.

Methyl iodide is a very bad quencher, and 10 ml. (STP) of CH_3I will normally reduce the counting efficiency to zero. The CH_2TI peaks were accompanied by small radiation damage CH_3I peaks and were hence checked for quenching. Mass peaks of CH_3I equal to the largest radiation damage peaks showed a small amount of quenching under our conditions for the determination of CH_2TI (about 2% decrease in efficiency at the peak maximum for 0.003 ml. (STP) of CH_2TI). This loss is within the error of the measurements, and no correction factor has been applied. Methyl bromide is also a quenching component, but its effect is not as marked as that of CH_3I , and no corrections were necessary for the mass peaks of CH_3Br accompanying CH_2TBr .

Previous experimenters have observed that CH_2TI in trace amounts from recoil tritium reactions of CH_3Cl must be carefully protected against adventitious loss in laboratory handling (e.g., photolysis).¹⁰ Our sample bulbs were dark brown after irradiation and were stored in the dark between irradiation and analysis. The entire sampling system was kept covered between withdrawal of successive aliquots.

The sample injection device for the radio-gas chromatography was equipped with Apiezon(N)-greased stopcocks, with the consequent possibility of loss of gaseous components in the grease. Such losses were minimized by very short contact times (usually 3 min.) between the breaking of the irradiation bulb and injection of the first aliquot into the chromatographic system. This aliquot was always used for measurement of the higher-boiling components; HT and CH_3T were separated in a later aliquot. The experimental consistency indicates no significant grease loss— CH_2TI is the most susceptible among the important products.

A slight tendency toward counter contamination has been observed with alkyl halides, and with CH_2TI peaks especially, in these experiments. One consequence is a greater uncertainty in the appropriate background count rate to use for CH_2TI peaks. The cumulative effect of slight uncertainties in counter quenching, counter contamination, photolytic decomposition, and possible loss in stopcock grease makes the CH_2TI peak measurements much less accurate than customary with hydrocarbon peaks. This error is reflected in the considerably larger limits placed on CH_2TI yields in the subsequent data tables.

Compounds containing tritium in labile positions (bonded to O, Cl, I, etc.) are not measurable with this chromatographic arrangement because of isotopic hydrogen exchange with substrates, etc. These activities were therefore routinely removed on a cotton plug in the sample system between the break-tip bulb and the chromatographic sample injection loop.

The only other nuclear reaction forming appreciable amounts of radioactivity with a half-life longer than a few hours is the reaction $\text{Cl}^{35}(\text{n,p})\text{S}^{35}$. The only S^{35} -labeled molecule observed in these reactions was OCS^{35} , which forms very readily in the presence of small amounts of CO .¹⁷ The yield of OCS^{35} was small, variable, and can be satisfactorily measured on either the TTP or DMS columns.¹⁸ Other gaseous S^{35} molecules were not observed.

Results

Preliminary experiments were carried out with methyl chloride at 1 atmosphere pressure, both in unscavenged runs and with one of a variety of scavengers present. The relative yields of HT, CH_3T , and CH_2TCl from several such experiments are summarized in Table I and show reasonably good agreement with one another. Additional products were observed, especially CH_2TOH and CH_2TI in O_2 and I_2 scavenged samples, respectively. These experiments were analyzed with various combinations of chromatographic columns and showed no particular difficulties in analysis except for the presence of variable amounts of S^{35} radioactivity in the form of OCS^{35} . The general agreement among the various scavenger systems indicates that the removal of thermalized radioactive species can be performed rather consistently, and therefore that hot and thermal products can be readily distinguished.

TABLE I
NONLABILE RADIOACTIVE PRODUCTS FROM RECOIL TRITIUM REACTIONS WITH GASEOUS METHYL CHLORIDE AT 1 ATMOSPHERE PRESSURE

Composition, cm.—			$\frac{\text{CH}_3\text{T}}{\text{HT}}$	$\frac{\text{CH}_2\text{TCl}}{\text{HT} + \text{CH}_3\text{T}}$
CH_3Cl	He ³	Scavenger		
73.7	1.7	None	0.267 ± 0.012	0.260 ± 0.006
74.7	1.7	None	.269 ± .010	.252 ± .005
75.1	1.6	1.3 NO	.285 ± .013	.249 ± .006
72.8	1.5	3 3 O ₂	.269 ± .012	.271 ± .005
76.0	2.0	I ₂	.295 ± .004	.247 ± .006

The quoted errors of Table I include only the errors arising from the statistical errors of counting the random emission of radioactivity. While some of the ratios of Table I are apparently different from one another, these effects are approximately at the limits of error. Since these samples included variations in the source of CH_3Cl , conditions of irradiation, and columns for analysis, we do not regard any of the differences of Table I as statistically significant in the absence of further comparison data.

The unscavenged samples do not differ appreciably in product yields from those observed in the presence of the various scavengers, unlike the effects recorded for most hydrocarbon molecules.^{2,3} The most probable explanation for this absence of large product alteration without scavenger present is that CH_3Cl is effectively self-scavenging through the chlorine atom abstraction reaction of eq. 4. This chlorine-abstraction reaction could possibly be initiated either by hot or by thermal tritium atoms to form the same product, TCl , which would then be further obscured by exchange into

(17) E. K. C. Lee, Y. N. Tang, and F. S. Rowland, *J. Phys. Chem.*, **68**, 318 (1964).

(18) The initial S^{35} decay rate is about 0.16 times the decay rate of the tritium from $\text{He}^3(\text{n,p})\text{T}$, for 1 atm. CH_3Cl and 1 cm. He³.

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

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TABLE II

RADIOACTIVE PRODUCTS OF RECOIL TRITIUM REACTIONS WITH METHYL CHLORIDE-CYCLOBUTANE MIXTURES (CYCLO-C₄H₇T = 100)

Sample no.	XIV-303	XIV-302	XIV-301
Gas press., cm.			
CH ₃ Cl	3.0	6.6	14.0
Cyclo-C ₄ H ₈	8.7	25.1	59.1
He ³	1.1	1.1	1.1
O ₂	0.4	0.8	1.4
Total pressure	13.2	33.6	75.6
Mole ratio $\frac{\text{CH}_3\text{Cl}}{\text{cyclo-C}_4\text{H}_8}$ ^a	0.334	0.264	0.244
CH ₂ TCl activity ^e	1336 ± 50	1357 ± 50	1575 ± 50
Relative activity ^d			
HT	338 ± 2	300 ± 2	282 ± 2
CH ₃ T	8.6 ± 0.4	6.9 ± 0.3	6.0 ± 0.3
CH ₂ TCl	9.1 ± 0.4	7.1 ± 0.3	6.4 ± 0.2
C ₂ H ₅ T	101 ± 1	86 ± 1	74 ± 1
Cyclo-C ₄ H ₇ T	100	100	100
Corrected CH ₃ T ^b	7.6 ± 0.5	5.9 ± 0.4	5.1 ± 0.3
Specific activity ratio per bond ^c			
T for H	0.362 ± 0.014	0.384 ± 0.013	0.403 ± 0.013
T for Cl	0.90 ± 0.06	0.97 ± 0.06	0.97 ± 0.06

^a This mole ratio is calculated from measured mass peaks. None of the mass peak ratios are more than 3% different from the ratios of the measured pressures. ^b The contribution of CH₃T yield from cyclo-C₄H₈ is about 0.5% of the sum of cyclo-C₄H₇T and C₂H₅T, and the observed CH₃T yield was corrected for this contribution to compute the CH₃T yields from the chlorinated methanes. This correction factor is obtained from numerous runs on pure cyclobutane. ^c The specific activity per bond for T for H is given by

$$\frac{8}{3} \times \frac{\text{CH}_2\text{TCl}}{\text{C}_2\text{H}_5\text{T} + \text{cyclo-C}_4\text{H}_7\text{T}} \times \left(\frac{P_{\text{C}_4\text{H}_8}}{P_{\text{CH}_3\text{Cl}}} \right)$$

The specific activity per bond for T for Cl in CH₃Cl is given by

$$8 \times \frac{\text{CH}_3\text{T}}{\text{C}_2\text{H}_5\text{T} + \text{cyclo-C}_4\text{H}_7\text{T}} \times \left(\frac{P_{\text{C}_4\text{H}_8}}{P_{\text{CH}_3\text{Cl}}} \right)$$

^d These samples were analyzed with the acetonylacetone (ACTN) and propylene carbonate on alumina columns (PCA). ^e Counts observed from ACTN aliquot.

the general pool of labile hydrogen atoms in the system. The relative contributions of hot and of thermal processes to the cumulative yield of labile tritium have not been directly evaluated.

Since both O₂- and I₂-scavenged samples showed large yields of products indicating the presence of CH₂T radicals, experiments were carried out to determine the possible pressure dependence of the yields of CH₂T radicals and likely precursor molecules. Molecular I₂ was used as the scavenger for labeled methyl radicals, because the reaction of CH₂T with I₂ to form CH₂TI is more direct than that with O₂ to form CH₂TOH. Indeed, a larger yield of CH₂TI had been observed than of CH₂TOH in the preliminary experiments, indicating the superiority of I₂ for CH₂T assay.

Detection of a pressure dependence in the relative yields of recoil tritium reactions with a particular molecule requires the choice of some suitable basis of comparison for which the pressure dependence is known. Such a standard can be chosen external to the molecule under consideration through the irradiation of a mixture containing another target molecule whose pressure dependence is known. The sum of the yields of cyclo-C₄H₇T and C₂H₅T from recoil tritium reactions with cyclo-C₄H₈ has been shown to be pressure independent within the accuracy of present measurements.⁴ The yields of the products observed in CH₃Cl-cyclo-C₄H₈ mixtures are summarized in Table II. The amount of CH₂TCl found increases steadily with increasing pressure as shown by the row of values for the specific activity ratios of T for H per bond. The observation of this increased yield indicates the existence of highly-excited CH₂TCl molecules as the result of the substitution reaction 2.

The yields of CH₃T from substitution of T for Cl cannot be measured as accurately in these experiments, partially because of the necessity for correction for CH₃T formation from cyclo-C₄H₈. The measurements of Table II do not show any pressure dependence for CH₃T with wide error limits. The competition experiments reported here do not discriminate between hot HT formed from CH₃Cl and from cyclo-C₄H₈ and hence do not furnish any information about the possible pressure dependence of the former.

Measurements made on the series of I₂-scavenged methyl chloride samples at various pressures are summarized in Table III. For comparison, we have included in this table the halogen-scavenged 1 atmosphere data of Odum and Wolfgang,¹⁰ which are in good agreement with the present measurements at that pressure. The relative amounts of CH₂TCl and CH₂TI show a strong pressure dependence, while the HT and CH₃T yields maintain a nearly constant ratio to one another. The sum of the yields of the three compounds CH₃T, CH₂TCl, and CH₂TI is approximately 100 for all of these I₂-scavenged experiments, if each individual ratio is measured *vs.* HT = 100 as an internal standard. The constant value for this sum permits the convenient expression of these data against this internal standard, as shown in Table III. All of the data of Tables II and III are summarized in Fig. 1, arbitrarily normalizing the pure CH₃Cl experiments and the CH₃Cl-cyclo-C₄H₈ experiments at 0.5 atm. pressure.

The experimental results for irradiations carried out in the liquid phase are given in Table IV. These data are also expressed relative to the yield of HT as 100. The sum of the yields of CH₃T, CH₂TCl, and CH₂TI is again approximately 100 on this basis and provides

TABLE III
 RADIOACTIVITY RATIOS FROM RECOIL TRITIUM REACTIONS WITH I₂-SCAVENGED GASEOUS METHYL CHLORIDE

Sample no.	336	335	200	Ref. 10	347	348
Pressure, ° cm.						
CH ₃ Cl	9.1	31.2	76.0	~1 atm.	~140 ^b	~210 ^b
He ³	2.1	2.1	2.0	1-2	>0.6	>0.6
Relative yields ^c						
HT	100	100	100	100	100	100
CH ₃ T ^c	27.8 ± 0.7	29.8 ± 0.5	29.5 ± 0.4	31.8 ± 0.9	31.2 ± 0.5	29.6 ± 0.5
CH ₂ TCl ^d	30.5 ± 0.6	32.6 ± 0.4	36.5 ± 1.7	37.2 ± 1.7	34.8 ± 1.2	37.4 ± 1.0
CH ₂ Tl ^d	41.2 ± 1.6	36.5 ± 1.3	33.6 ± 1.3	36.3 ± 1.0	33.8 ± 1.4	32.5 ± 1.6

^a All samples contained I₂ at its vapor pressure (~0.02 cm.). ^b Sample numbers 347 and 348 were filled by cooling the contents into the bulbs with liquid N₂. The pressure measurements are approximate only. ^c CH₃T vs. HT from PCA column. ^d CH₂TCl and CH₂Tl vs. (HT + CH₃T) from TTP column. ^e CHTClI was not measured in these experiments. It is reported as 0.5 ± 0.3% of the total tritium production in ref. 10. The HT yield is quoted as 22.0 ± 1.0% in this earlier work. Our percentages are in reasonable agreement with this value, but have not been as accurately measured.

 TABLE IV
 RADIOACTIVE PRODUCTS FROM RECOIL TRITIUM IRRADIATIONS WITH LIQUID METHYL CHLORIDE

Sample no.	242	243	464	465	463
Scavenger	None	None	I ₂	I ₂	Br ₂
Product yields (HT yield = 100)					
HT	100 ^a	100	100	^b	100
CH ₃ T	42.2 ± 0.5	43.0 ± 0.5	34.2 ± 0.4	^b	30.4 ± 0.6
CH ₂ TCl	63.9 ± 0.7	67.9 ± 0.7	55.6 ± 0.6	(55.6)	54.0 ± .6
CH ₂ TBr	15.4 ± .4
CH ₂ Tl	7.5 ± 0.2	9.5 ± 0.5	...
CHTCl ₂	1.4 ± 0.2	1.7 ± 0.2	0.6 ± .1	0.7 ± .2	^c
C ₂ H ₄ TCl	5.7 ± .2	5.6 ± .2	2.3 ± .1	2.1 ± .1	^c
C ₂ H ₆ T	5.2 ± .3	5.9 ± .2	0.7 ± .2	^b	0.5 ± 0.2

^a Minor yields: *i*-C₃H₆TCl, 0.2; *n*-C₃H₆TCl, 0.2; *sec*-C₄H₈TCl (?), 0.3. ^b Not cleanly separated; in approximate agreement with 464; OCS³⁸ ~0.05 × CH₂TCl. ^c Not measured.

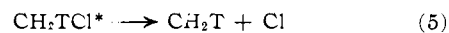
good support for the choice of the HT yield as a good internal standard for comparison. The implication is strong that the mechanisms of the initial energetic reactions are quite similar in the gaseous and liquid phases. A previous detailed comparison of gaseous and liquid phase recoil tritium reactions with *trans*-hexene-2 has shown that the same initial energetic reactions mechanisms are operative in both phases.¹⁹ The liquid phase data are also shown in Fig. 1.

Discussion

Pressure-Dependent Yield of CH₂TCl.—The purpose of the present experiments has been to discover the reaction mechanisms and energetics of recoil tritium reactions with methyl chloride, and the factors which control or influence these reactions. Many of the deductions about such hot tritium reactions have been based in the past upon gas phase measurement of the relative yields of two competing reactions with the same molecule, and upon variations in these relative yields from one molecule to another.^{2,3} However, the experimental observation of secondary decomposition (or isomerization) of labeled product molecules immediately calls into question the general validity of this whole procedure.^{3,4} The original hot yield of one product, and therefore its yield ratio to that of a second product, can be grossly underestimated if appreciable isomerization or decomposition of the former occurs at the pressures used in the experiment. Prior to any discussion of the significance of relative yields, an appropriate procedure for the evaluation of these relative yields must first be established.

The data of Tables II and III furnish clear evidence for an increase in the yield of CH₂TCl with an increase

in pressure and a complementary decrease in the yield of CH₂Tl in the I₂-scavenged system. These trends are precisely those expected from the formation of excited molecules of CH₂TCl in reaction 2, and their subsequent decomposition by the mechanism of reaction 5



Since the CH₂T radicals formed in reaction 5 will ordinarily be scavenged by I₂ or Br₂ to form CH₂Tl or CH₂TBr, a complementary relationship between CH₂TCl and the scavenged CH₂T yield is expected.

Comparison of the liquid phase data with those obtained in the gas phase demonstrates that the yield of HT is essentially insensitive to the presence of scavengers or to the difference between gas and liquid phases. Accepting this, it is clear that a substantially higher percentage of CH₂TCl molecules survive in the liquid phase than in the gas phase at any pressure used in our experiments. The most plausible explanation for this yield increase in the liquid phase is that many CH₂TCl molecules are formed in reaction 2 with sufficiently large excitation energies that liquid-phase collision frequencies are necessary for de-excitation to be competitive with the decomposition reaction 5.

Substitution-Decomposition Reactions.—The existence of labeled radicals as products of energetic tritium reactions with alkanes^{2,20} and alkyl halides¹⁰ has already been demonstrated. Since the formal stoichiometry of these reactions is the addition to a reacting molecule of one tritium atom and the accompanying loss of two atoms or groups, the over-all processes have been described as "double substitution reactions."¹⁰ Two mechanisms have been suggested as possibilities, without any clear choice possible on the then available evi-

(19) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **84**, 3085 (1962).

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

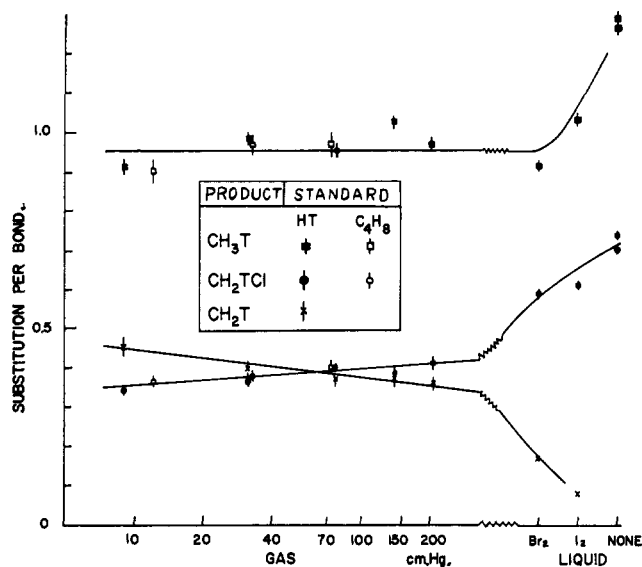


Fig. 1.—Products of recoil T reactions with CH₃Cl.

dence¹⁰: (a) a two-step mechanism of single substitution, followed by decomposition, as in reactions 2 and 5; (b) a one-step reaction involving the replacement or ejection, essentially simultaneously, of two groups in the initial energetic collision.

One of the most readily detectable differences experimentally between (a) and (b) is the time scale of the processes involved. The original experiments on CH₃Cl and other halocarbons, each carried out at a fixed gas pressure, provided no information about this time scale. A one-step reaction model involves very short reaction times, as, for example, the 10⁻¹⁴ sec. estimated for the model using a combination of steric and inertial factors.¹⁰

The reaction time involved in a two-step model is entirely dependent on the amount of excitation deposited, but might well fall into the range 10⁻¹¹ to 10⁻⁷ sec. or longer. With still higher excitation energies, the two-step model presumably could blend into the single-step model, as the deposited excitation energy no longer had sufficient time for equilibration throughout the molecule.

The observation of pressure dependence in the gas phase yield of CH₂TCl indicates excited molecules decomposing with lifetimes in the 10⁻⁸ to 10⁻⁹ sec. range and provides convincing evidence that the two-step substitution-decomposition reaction does occur with methyl chloride. Furthermore, the differences in CH₂TCl yield between gaseous and liquid phases strongly suggest the existence of additional excited molecular lifetimes in the 10⁻⁹ to 10⁻¹¹ sec. range and that the substitution-decomposition process is the predominant "double substitution" reaction with methyl chloride.

The pressure-dependent reactions of recoil tritium with cyclobutane have been interpreted as showing an average excitation energy of 5 e.v. (with a broad spectrum) for the cyclo-C₄H₇T molecules formed in that system.⁴ This energy is consistent within rather wide limits of error for the data presented here. Although reaction 5 describes the decomposition of pyrolytically excited CH₂TCl,²¹ the necessary kinetic constants are not sufficiently well known to permit a calculation comparable to that carried out with cyclobutane.

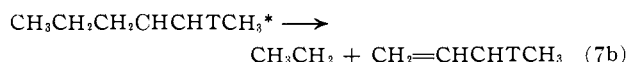
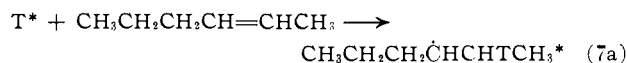
(21) A. E. Shilov, *Doklady Akad. Nauk SSSR*, **98**, 601 (1954).

Recoil Tritium Reactions in the Liquid Phase.—While the yields of various labeled products are different for Br₂- and I₂-scavenged liquid phase systems, the heterogeneous nature of the irradiated LiF-CH₃Cl-molecular halogen mixture in liquid phase capillary experiments has prevented accurate measurement of the scavenger concentrations. Qualitatively, however, the I₂ concentration was certainly lower than that of Br₂ in the liquid phase experiments. The observed product distributions are consistent with incomplete scavenging of CH₂T radicals by molecular iodine in the liquid phase. Such unscavenged radicals can consequently react by the isotopic exchange reaction 6 and add to the observed yield of labeled parent molecule.



Accordingly, we conclude that the best estimate of the *minimum* amount of original CH₂TCl is obtained from its yield in the Br₂-scavenged liquid phase experiments.

An ambiguity remains in the interpretation of the liquid phase yields of CH₂T and, consequently, in the question of the possible yield contributions of a one-step double substitution reaction for CH₃Cl. Relatively little is known about the relative rates of decomposition and de-excitation for highly excited molecules in the liquid phase. Molecules with low energies of excitation will seldom decompose, but experimental information is not readily available for more excited molecules. Some related experiments have been performed involving the highly excited radicals created by the addition of an energetic tritium atom to *trans*-hexene-2. The radical decomposition reaction shown in eq. 7a and 7b is reduced in yield in the liquid phase from that observed in the gas, but is definitely not eliminated—the specific product butene-1-*t* can still be readily identified in the liquid phase.²²



The occurrence of liquid-phase radical decompositions for these large radicals indicates that the CH₂T yield measured as CH₂TBr in Br₂-scavenged solution can plausibly arise entirely from rapid decomposition of excited CH₂TCl molecules. The *maximum* estimate of the total original CH₂TCl yield would then be given by the sum of the CH₂TCl and CH₂TX yields in either of the halogen-scavenged liquid systems. This maximum estimate must include as a corollary the assumption that one-step double substitution reactions provide a negligible contribution to the total yield.

Some further circumstantial evidence can be adduced about liquid phase experiments through a comparison of cyclobutane⁴ and methyl chloride (see Fig. 1) as shown in Table V. The yields of RT and decomposition products are broken down into pressure increments, and show a rough similarity in percentage behavior for these increments. The C₂H₃T yield does not correspond to any feasible one-step double substitution reaction from cyclo-C₄H₈, but is the only probable decomposition product from highly excited molecules.

The present evidence demonstrates the existence of the substitution-decomposition mechanism and shows

(22) E. K. C. Lee and F. S. Rowland, *J. Chem. Phys.*, **36**, 554 (1962).

TABLE V

COMPARISON OF RADIOACTIVE PRODUCT YIELDS FROM RECOIL TRITIUM REACTIONS WITH CYCLOBUTANE AND METHYL CHLORIDE (TOTAL IN CYCLO-C₄H₈ = 100)

Target molecule, RH cyclo-C ₄ H ₈	CH ₃ Cl	
RT yields (total)	100	78
9 cm.	50	36
Increase between 9 and 80 cm.	10	5
Increase between 80 cm. and liquid	22	22
Obsd. in liquid only as decompn. prod. (C ₂ H ₅ T or CH ₂ TBr)	18	15

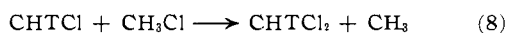
that it is the more abundant "double substitution" reaction with methyl chloride. There is no conclusive evidence for the existence of any appreciable amount of one-step reaction, and the maximum contribution cannot be higher than the CH₂T radical contribution in the liquid phase. The probable situation appears to be that most or all of the CH₂T radicals found in the liquid phase originate with decomposing CH₂TCl molecules.

Unscavenged Liquid Phase Reactions.—The radioactive molecules found in minor amounts after tritium reaction with liquid CH₃Cl in the absence of scavenger molecules include the two carbon molecules C₂H₅T and C₂H₄TCl, higher alkyl chlorides, and CHTCl₂. Ethane, ethyl chloride, and methylene chloride are all observed as macroscopic components of the solution after irradiation, but in very small quantities. The specific activities of CHTCl₂, C₂H₅T, and C₂H₄TCl are all at least ten times the specific activity of CH₂TCl, indicating that these radioactive molecules are formed in specific reactions of the recoil tritium atoms, and not through general radiation damage to the parent CH₃Cl molecule.

The observation of CHTCl₂ strongly implies the existence in the solution of CHTCl radicals reacting according to eq. 8. Possible sources of the CHTCl radicals might be a subsidiary decomposition of CH₂TCl by breaking the stronger C-H bond, a true one-step decomposition reaction, or decomposition reaction proceeding through methylenic radicals to CHTCl by abstraction. These CHTCl radicals have already been detected (see footnote *e* to Table III) in I₂-scavenged gas phase systems,¹⁰ through the observation of CHTCl₂ in a yield roughly comparable to the CHTCl₂ measured here. No distinction among these mechanisms seems possible from the present data, but CHTCl₂ formation is very likely the result of hot reactions initiated by particularly energetic tritium atoms.

The increment in CH₃T yields between the scavenged and unscavenged liquid phase systems similarly identifies the abstraction reaction 9. This reaction apparently competes rather well with the abstraction of chlorine by reaction 6.

The two-carbon compounds can readily result from combination of CH₂T radicals with CH₃ or CH₂Cl radicals from radiolysis. The possibility that the abstraction reactions may involve "hot" radicals makes calculation of relative rate constants for CH₂T reactions of uncertain value.



Pressure Dependence of CH₃T.—The substitution of T for Cl in the CH₃Cl molecule can also conceivably

lead to CH₃T molecules sufficiently excited to undergo subsequent decomposition. The cyclobutane competition experiments do not show any pressure dependence of CH₃T yield, although they could be consistent with a slow fall with decreasing pressure because of the larger errors involved. However, little difference in relative yield of CH₃T exists between high pressure gas phase and liquid phase experiments, and the over-all evidence thus indicates that CH₃T is formed in states of excitation for which decomposition is unlikely. This comparative lack of decomposition for CH₃T probably is directly traceable to the lack of any reaction path with an activation energy less than 100 kcal./mole. The yields of CH₃T and CH₂TF from T-for-H substitutions in CH₄ and CH₃F, respectively, likewise fail to show any appreciable dependence upon gas pressure.^{3,4,14}

If the average energy of the reacting tritium atom is comparable prior to substituting for H and for Cl, the excitation energy deposited for each reaction will depend upon the heats of reaction and upon the kinetic energies of the respective ejected atoms. The replacement of Cl by T is exothermic by about 25 kcal./mole, but no information is available about the kinetic energies of any replaced atoms in these experiments. No analyses have yet been performed on the average excitation energies left after Cl atom replacement, but the pressure-dependent decomposition of CH₂TCl has been observed from CH₂Cl₂ reactions.²³ From the present data, we can conclude only that the average tritium energies appear to be comparable prior to hot replacement of H and of Cl.

Relative Probabilities of Substitution of T for H in Different Molecules.—Measurements made at 1 atmosphere pressure show percentage yields of labeled parent molecule of 30.8 ± 2, 12.1 ± 0.5, and 8.3 ± 0.1 for CH₄, CH₃F, and CH₃Cl, respectively.¹⁰ This decrease has been correlated with the increasing size of the F and Cl atoms and attributed to a reduction in the probability of substitution of T for H in an energetic collision through steric hindrance effects.¹⁰ This suggestion is in close analogy to the hypothesis for alkyl group interference in alkanes.^{2,20} However, the present observation of a pressure-dependent yield of CH₂TCl from CH₃Cl forces re-examination of conclusions drawn from experiments conducted entirely at 1 atmosphere gas pressure.

The relative probability of substituting T for H in CH₃Cl and in cyclobutane, per H atom in the molecule is given in the bottom row of Table III and in Fig. 1. These values (0.36 to 0.40) are measured relative to the sum of cyclo-C₄H₇T and C₂H₅T from cyclo-C₄H₈, and thus include the decomposition products for one molecule and not the other. A more meaningful comparison can be made through the numbers in Table V.

If all of the decomposition products of each are included in the measurement of RT, then the ratio of substitution per H atom of the target molecule is 0.78 to 1 for CH₃Cl/cyclo-C₄H₈. If the decomposition products are arbitrarily excluded for both, the ratio becomes 0.77. While neither of these procedures is necessarily entirely correct, it is unlikely that subsequent experiments will indicate a value very much dif-

(23) Y. N. Tang, E. K. C. Lee, and F. S. Rowland, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

ferent from 0.78. The comparison of relative probabilities of T for H substitution can be extended through other binary comparisons to CH₄, CH₃F, and *n*-C₄H₁₀, giving the ratios shown in Table VI.^{4,5,14}

TABLE VI

RELATIVE PROBABILITY OF T-FOR-H SUBSTITUTION REACTION PER C-H BOND IN THE MOLECULE

Target molecule, RH	Ratio for RT alone ^a vs. cyclo-C ₄ H ₇ T + C ₂ H ₅ T		—Decomposition product—			Relative probability of reacn.
	Ref.	Ref.	Identity	Yield	Ref.	
CH ₄	0.83	4	CH ₂ T	0.12 × RT	20	0.93
<i>n</i> -C ₄ H ₁₀	.82	4, 23	C ₂ H ₄ T(?)	≥ .82 ^b
CH ₃ F	.61	14	?	≥ .61 ^b
CH ₃ Cl	.41	Present work	CH ₂ T	This work		.78
Cyclo-C ₄ H ₈	.60	4	C ₂ H ₅ T	0.40	4	1.00

^a Measured at about 1 atmosphere. ^b Possible decomposition products not included in the absence of experiments in the liquid phase.

The data of Table VI include gas phase comparisons only for the molecules CH₃F and *n*-C₄H₁₀ and are consequently subject to possible increase if some of the originally produced labeled molecules have decomposed at this pressure. No gas pressure-dependent yields were observed with CH₄ or CH₃F, but labeled radicals have been caught with I₂ scavenger in each case.^{10,20} Liquid phase scavenger experiments have not yet been run because of the very high vapor pressures at ambient reactor temperature.^{4,14} The yield of *n*-C₄H₉T from *n*-C₄H₁₀ does show a gas phase pressure dependence,²⁴ but liquid phase studies indicate that decomposition in the 1-atmosphere gas phase work is not severe.²⁵

The relative figures in the final column of Table VI indicate that the variations in T-for-H substitution are much less than the factors of 3 suggested by the per-

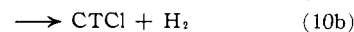
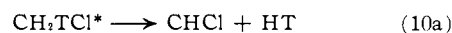
(24) E. K. C. Lee, Ph.D. Thesis, University of Kansas, 1963.

(25) R. Koob and F. S. Rowland, unpublished results.

centage yields of labeled parent molecule measured at 1 atmosphere gas pressure. We conclude that the average ease of substitution of T for H does not change greatly among these molecules, and, as a corollary conclusion, that steric interference with the substitution reaction is not very important for either chlorine atoms or alkyl radicals. If there is a variation in the last column of Table VI, it may be a decrease in the direction CH₄-CH₃Cl-CH₃F and indicates an influence not of atomic size of H, Cl, and F, but probably of increasing electronegativity. Experiments with liquid CH₃F seen necessary to determine whether any appreciable decomposition of CH₂TF has taken place if a more accurate estimate of these relative T for H substitution probabilities is described.

The Abstraction of H by Energetic T Atoms.—A large fraction of the recoil tritium atoms formed in the presence of CH₃Cl react by abstracting an H atom to form HT. Comparison of the results in scavenged and unscavenged samples indicates that essentially all of this HT yield is obtained from a hot reaction. The magnitude of this yield has been definitely correlated with the bond strength of the C-H bonds in the target molecule, and results with CH₃Cl are in reasonable agreement with those obtained for hydrocarbons.²⁶

If CH₂TCl molecules decomposed partially by dehydrohalogenation, a pressure-dependent yield of HT could arise from eq. 10a. The constancy of the HT yield relative to the total gaseous activity indicates no appreciable contribution from such methylenic decompositions.



Acknowledgment.—The cooperation of the operating personnel of the Omaha VA Hospital reactor is gratefully acknowledged.

(26) W. Breckenridge, J. W. Root, and F. S. Rowland, *J. Chem. Phys.*, **39**, 2374 (1963).

[CONTRIBUTION NO. 1173 FROM THE CHEMICAL LABORATORIES OF INDIANA UNIVERSITY, BLOOMINGTON, IND.]

Electron Diffraction Determination of the Molecular Structure of the Butyl Halides. V. The Structure and Conformational Analysis of Isobutyl Chloride

BY G. H. PAULI, F. A. MOMANY, AND R. A. BONHAM¹

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The structure and conformational analysis of gaseous isobutyl chloride has been carried out by the sector-microphotometer method of electron diffraction. The molecular parameters for the bonded distances were found to be: $r_{\mu}(\text{C-H})_{\text{av}} = 1.105 \text{ \AA.}$, $r_{\mu}(\text{C-C}) = 1.534 \text{ \AA.}$, and $r_{\mu}(\text{C-Cl}) = 1.804 \text{ \AA.}$; $l_m(\text{C-H}) = 0.074 \text{ \AA.}$, $l_m(\text{C-C}) = 0.053 \text{ \AA.}$, and $l_m(\text{C-Cl}) = 0.052 \text{ \AA.}$; and $\angle \text{C-C-C} = 111^\circ$, $\angle \text{C-C-Cl} = 112^\circ$, $\angle \text{C-C-H (methyl)} = 110^\circ$, and $\angle \text{C-C-H (tertiary hydrogen)} = 108^\circ$. About 80% of the molecules at room temperature were in the conformer where the chlorine is *gauche* to one methyl group and *trans* to the other. The *gauche* angle for this conformer was found to be 66° . A summary of the data on the available structural parameters for butyl halide molecules is given.

Previous work on the analysis of alkyl halide structures in the gas phase^{2,3} has shown that fluorine and chlorine groups stabilize *gauche* conformations if the opposite substituent is a methyl or methylene group.

(1) The authors wish to thank the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for their financial support of this work.

(2) (a) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958); (b) T. Ukaji and R. A. Bonham, *J. Am. Chem. Soc.*, **84**, 3631 (1962).

(3) E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962).

On the other hand, it appears that methyl and bromine substituents stabilize *trans* conformations^{4,5} when the opposite group is methyl or methylene. Isobutyl chloride is thus a very interesting case to investigate as the Cl atom can either be *trans* and *gauche* to methyl groups at the same time or else simultaneously *gauche*

(4) F. A. Momany, R. A. Bonham, and W. H. McCoy, *J. Am. Chem. Soc.*, **85**, 3077 (1963).

(5) R. A. Bonham and L. S. Bartell, *ibid.*, **81**, 3491 (1959).