Recoil Tritium Reactions with Ethyl Chloride[1]

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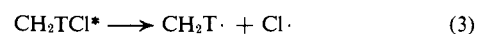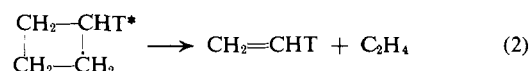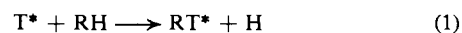
The substitution of energetic tritium atoms for H atoms in ethyl chloride leads to excited $C_2H_4TCl^*$ molecules, which exhibit pressure and phase dependence of yields, consistent with unimolecular decomposition of the primary product. The most important unimolecular reaction for $C_2H_4TCl^*$ is the elimination of HCl with the formation of C_2H_3T, while $15 \pm 5\%$ of the decomposing molecules react by C–Cl bond break. The substitutions of energetic tritium atoms for Cl to form $C_2H_5T^*$, for CH_3 to form CH_2TCl^*, and for CH_2Cl to form CH_3T^* are observed, and each of these products also undergoes unimolecular decomposition reactions. The primary yields of hot tritium reactions with ethyl chloride are estimated in the ratios: HT, 100; C_2H_4TCl, 56; C_2H_5T, 10; CH_3T, 7; CH_2TCl, 3. The replacement of Cl in ethyl chloride is 0.7 times as likely as the replacement of Cl in methyl chloride, confirming that C–T bond formation is more difficult with C_2H_5 than with CH_3.

Introduction

The high energy chemical reactions of recoil tritium atoms have been extensively investigated with hydrocarbons and halocarbons in the gas phase, and most of the theoretical interpretations and hypotheses about hot reactions have been based on these measurements.[3–18] The experimentally measured product yields from many of these molecules have been determined only at a single gas pressure with the tacit assumption that the values were essentially pressure independent.[3,4] Such pressure independence was indeed observed in the methane system.[3] However, recent experiments in our laboratories have demon-

strated that recoil tritium reactions in cyclobutane,[5] other alkanes,[17] and methyl chloride[18] all exhibit a marked dependence of product yields upon the gas pressure during irradiation. Furthermore, the mechanisms of the kinetically hot chemical reactions are quite similar in the gas and liquid phases, with most differences ascribable to the decomposition (or isomerization) of excited labeled molecules formed in the initial reactions.[19] Variations in the observed yields of products with the density of the system (i.e., with the collision frequency for de-excitation) now appear to be quite usual, at least for small molecules.

The previously observed pressure-dependent yields have been consistent with the known modes of thermal decomposition of the parent molecules, as in eq. 1–3 for cyclobutane and methyl chloride. The

$$T^* + RH \longrightarrow RT^* + H \tag{1}$$

$$\begin{array}{c} CH_2\text{—}CHT^* \\ | \qquad | \\ CH_2\text{—}CH_2 \end{array} \longrightarrow CH_2\text{=}CHT + C_2H_4 \tag{2}$$

$$CH_2TCl^* \longrightarrow CH_2T\cdot + Cl\cdot \tag{3}$$

coincidence of the reaction modes for molecules excited in thermal collisions with those formed in hot substitution reactions provides a tentative link between the two processes of excitation and offers the possibility for a better understanding of the energetic reaction mechanisms.[5,18]

The present experiments have been carried out with ethyl chloride as the target molecule, permitting further examination of the reaction types studied with methyl chloride. In addition to the substitution reactions involving the replacement by tritium of H and Cl, those involving CH_3 or CH_2Cl groups can also be observed with the two-carbon molecule. Thermally excited ethyl chloride does not decompose by a mechanism analogous to reaction 3, but has been thought rather to follow the course of reaction 4.[20–22] However,

$$C_2H_5Cl^* \longrightarrow C_2H_4 + HCl \tag{4}$$
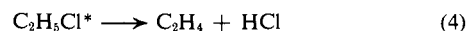
the kinetics of the pyrolysis of C_2H_5Cl can be accounted for through a chain mechanism starting with a C–Cl bond break, and reservations have still been expressed about the evidence for reaction 4.[23,24]

These additional complexities of reaction provide advantageous opportunities for determining the basic principles underlying recoil tritium reactions and for further study of the analogies between pyrolytic and recoil tritium decomposition mechanisms.

(1) This research was supported by A.E.C. Contract No. AT-(11-1)-407, and formed part of the work submitted by Y.-N. Tang in partial fulfillment of the Ph.D. requirements of the University of Kansas, Sept. 1964.

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Experimental

Sample Preparation, Irradiations, and Other Radioactivities. The preparation, neutron irradiation, and subsequent handling of ethyl chloride samples followed almost identically the procedures used in the methyl chloride experiments, and have already been described in considerable detail.[18] The gaseous labeled products were separated and measured by radio gas chromatography.[18,25,26] All samples were stored after irradiation until the short-lived halogen activities had decayed (>10 half-lives). The only radioactivity observed, other than H^3, was S^{35} in the form of OCS^{35}, which forms readily in the presence of traces of CO.[18,27] As discussed earlier,[18] the handling of halides is subject to special difficulties not encountered with low boiling hydrocarbons (*e.g.*, slight counter contamination, photolysis, possible loss into stopcock grease). These difficulties are somewhat worse for iodides, leading to slightly larger estimates of error for them in the data tables.

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, C=C, C—C, C≡C, C—C=C, CH_2TCl and C_3H_7T, C_2H_2TCl, CH_2TBr, C_2H_4TCl. The PCA column was protected for the Br_2-containing sample with a very short (few inches) column of TTP.

(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, and C_2 hydrocarbons, OCS^{35}, CH_2TCl and C_2H_2TCl, CH_2TBr and C_2H_4TCl, CH_2TI, $CHTCl_2$, C_2H_4TI.

(c) TTP column: 10-ft. column as in b; 100°, flow rate 25 ml./min. Products, as in b: HT through OCS^{35}, CH_2TCl and C_2H_2TCl, CH_2TBr and C_2H_4-TCl), CH_2TI, $CHTCl_2$, C_2H_4TI, CHTClI.

(d) DMS column: 50-ft. column of dimethylsulfolane, packed on 30–60 mesh firebrick; 24°, flow rate 25 ml./min. Products: HT + CH_3T, C—C and C=C, C_3H_7T, C—C=C, OCS^{35}, n-C_4H_9T, C_2HT, butene-1, c-C_4H_7T, butadiene, CH_2TCl, C_2H_2TCl, C_2H_4TCl.

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.

Quenching of Counter Action by Halides. Many alkyl halides partially quench the internal proportional counting action within the counter by electron capture.[26,28] However, no reduction in counting efficiency for an external Na^{22} source was observed during the passage of 10 ml. (STP) of C_2H_5Cl, so quenching corrections were unnecessary for the parent peaks.

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Almost all iodides are very bad quenchers, and 10 ml. (STP) of any of the lower alkyl iodides will normally reduce the counting efficiency to zero. The CH_2TI, CHTClI, and C_2H_4TI peaks were accompanied by small unlabeled radiation damage peaks and were hence checked for possible quenching action. Mass peaks of CH_3I or CH_2ClI equal to the largest corresponding radiation damage peaks showed negligible quenching (less than 1%) under our conditions for the determination of CH_2TI and CHTClI. This loss is within the error of the measurements, and no correction factor has been applied. The mass peaks of C_2H_5I are larger, with a maximum quenching effect of about 3% decrease in counting efficiency during the passage of the peak. Since this effect is small compared to the statistical error, no correction has been applied. Methyl and ethyl bromides also are quenching components, but the effects are not so large as with the iodides, and no corrections were necessary for the bromide mass peaks.

Chemicals. Ethyl chloride, obtained from the Matheson Co., was used without further purification, after gas chromatographic confirmation that the impurity level was below 0.1%. Methane of Phillips research grade (quoted purity greater than 99.9%) was used. Diphenylpicrylhydrazyl (DPPH) was obtained from the Eastman Kodak Co. The cyclobutane, He^3, LiF, O_2, I_2, and Br_2 came from the same sources described earlier.[18]

Mass Peak Measurements. All samples were regularly monitored by thermal conductivity measurements to determine the macroscopic composition of the irradiated materials. The per cent composition of the samples containing two parent molecules was determined from these recorder traces (and not from the less accurate listed filling pressures), after correction for thermal conductivity response.[28]

Results

Gas Phase Experiments. Intramolecular Standard. The earlier search for possible pressure-dependent yields for recoil tritium reactions with cyclobutane[5] and methyl chloride[18] has clearly shown the necessity for establishment of a suitable standard for comparison. In both of these systems, the gas phase hot abstraction reaction to form HT by eq. 5 has been shown to be

$$T^* + RH \longrightarrow HT + R \qquad (5)$$
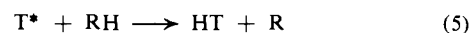
essentially pressure independent when carried out in the presence of O_2 as a scavenger. Table I contains the data obtained with O_2-scavenged ethyl chloride, expressed relative to HT = 100, on the hypothesis that the "hot" HT yield is also approximately pressure independent in reactions with ethyl chloride.

The observed tritium-containing molecules of Table I can be classified by the magnitude of the yields into three major components (HT, C_2H_4TCl, and C_2H_3T), two minor components (C_2H_5T and CH_3T), and three trace components (C_2HT, CH_2TCl, and C_2H_2TCl). These same compounds can also be classified by the qualitative changes in yield with decreasing gas pressure during irradiation: increasing yields—C_2H_3T, C_2HT; essentially pressure independent—$CH_3T(?)$, C_2H_2TCl, HT (assumed); decreasing yields—C_2H_4TCl, C_2H_5T, CH_2TCl.

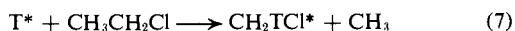**Table I.** Radioactive Products from Recoil Tritium Reactions with O_2-Scavenged Gaseous Ethyl Chloride

Sample no.	439	408	438	407	406	437	405
Gas pressure, cm.							
C_2H_5Cl	4.1	5.5	12.6	12.9	30.3	74.8	80.3
He^3	1.8	1.7	1.8	1.7	1.7	1.8	1.7
O_2	0.9	1.3	1.1	1.7	2.5	1.5	3.6
Relative activity							
HT	100	100	100	100	100	100	100
C_2H_4TCl	23.6 ± 0.7	22.8 ± 0.6	27.1 ± 0.3	26.2 ± 0.3	31.0 ± 0.3	31.8 ± 0.3	35.5 ± 0.3
C_2H_3T	22.7 ± 0.5	21.1 ± 0.7	21.8 ± 0.2	20.6 ± 0.2	20.7 ± 0.2	18.7 ± 0.2	19.3 ± 0.2
C_2H_5T	5.8 ± 0.3	5.2 ± 0.4	5.8 ± 0.1	5.7 ± 0.1	6.5 ± 0.1	6.2 ± 0.1	7.2 ± 0.1
CH_3T	3.4 ± 0.2	3.8 ± 0.4	3.9 ± 0.1	3.7 ± 0.1	4.2 ± 0.1	3.8 ± 0.1	4.2 ± 0.1
CH_2TCl	0.6 ± 0.2	NM^a	0.6 ± 0.1	0.5 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.9 ± 0.1
C_2H_2TCl	0.9 ± 0.2	NM	0.7 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.9 ± 0.1	0.9 ± 0.1
C_2HT	0.9 ± 0.2	NM	0.9 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.6 ± 0.1

[a] Not measured.

**Table II.** Radioactive Products from Recoil Tritium Reactions with Methane–Ethyl Chloride Gas Mixtures

Sample no.	451	449	446
Gas pressure, cm.			
C_2H_5Cl	3.2	16.8	40.1
CH_4	1.9	13.8	38.6
He^3	1.8	1.8	1.8
O_2	0.7	0.7	1.7
Mole ratio $C_2H_5Cl/CH_4{}^a$	1:68	1:22	1.04
Relative activity			
HT	550 ± 13	483 ± 4	412 ± 4
CH_3T	135 ± 4	159 ± 2	157 ± 2
C_2H_5T	22.9 ± 1.2	20.6 ± 0.4	19.1 ± 0.4
C_2H_3T	100 ± 3	69 ± 1	56 ± 1
C_2H_4TCl	100	100	100
Corrected relative activity			
CH_3T	120 ± 6	146 ± 3	145 ± 3
C_2H_5T	22.5 ± 1.8	20.2 ± 0.6	18.7 ± 0.6
Specific activity ratio per bond for C_2H_5Cl vs. CH_4			
T for H	0.396 ± 0.020	0.450 ± 0.012	0.531 ± 0.012
T for Cl	0.445 ± 0.040	0.454 ± 0.015	0.496 ± 0.015
Specific activity ratio C_2H_3T vs. CH_3T	0.49 ± 0.02	0.39 ± 0.01	0.37 ± 0.01

[a] Measured from chromatographic trace of mass peaks.

These observations fit readily into the general pattern of high energy recoil tritium substitution reactions, followed by secondary decomposition of some excited molecules. The initial hot reactions anticipated in this system (and previously reported for $C_2H_5Cl^{11}$) from general observations of recoil tritium reactions include the two predominant reactions: replacement of hydrogen by tritium (eq. 1), and abstraction of hydrogen by tritium (eq. 5), as well as substitution of tritium for other atoms or groups, such as Cl, CH_3, and CH_2Cl (reactions 6–8). If the product molecules formed in

$$T^* + C_2H_5Cl \longrightarrow C_2H_5T^* + Cl \qquad (6)$$

$$T^* + CH_3CH_2Cl \longrightarrow CH_2TCl^* + CH_3 \qquad (7)$$

$$T^* + CH_3CH_2Cl \longrightarrow CH_3T^* + CH_2Cl \qquad (8)$$

these reactions were excited and were to decompose by the normal decomposition modes observed for the corresponding thermally excited molecules, the subsequent reactions of CH_2TCl^*, CH_3T^*, and $C_2H_5T^*$ would be given by eq. 3,[29,30] 9,[31] and 10,[32] respectively.

(29) A. E. Shilov and R. D. Sabirova, *Russ. J. Phys. Chem.*, **33**, 1365 (1959).

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(31) M. Boudart, *Ann. Rev. Phys. Chem.*, **13**, 241 (1962) (some molecules would decompose by C–T bond rupture to form CH_3 + T).

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$$CH_3T^* \longrightarrow CH_2T + H \qquad (9)$$

$$C_2H_5T^* \longrightarrow CH_3 + CH_2T \qquad (10)$$
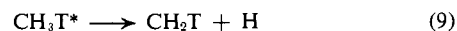
The over-all mechanism embodied in these reactions can account for lowered yields at lower pressures for C_2H_4TCl, C_2H_5T, CH_2TCl, and CH_3T, and a rising yield at lower pressures for C_2H_3T and CH_2T, the latter unmeasured in O_2-scavenged systems. None of the results of Table I are inconsistent with these expectations, with the qualification that the observed pressure variations are small in some cases, and the choice of HT as a pressure-independent standard certainly needs confirmation.

Gas Phase Experiments. Intermolecular Standards. A simple approach to the problem of a suitable standard is the use of a second, known parent molecule in binary competition. The CH_3T^* formed by the hot substitution of T for H does not vary appreciably in yield in the 0.1–1.0-atm. range, partially in consequence of the very high activation energy (102 kcal./mole) for reaction 9. The reaction of recoil tritium with CH_4 to form CH_3T can thus serve as a satisfactory internal standard when reactions are carried out with mixtures of CH_4 and C_2H_5Cl. The trace amounts of CH_3T formed from tritium reactions with C_2H_5Cl are small compared to its yield from CH_4 and require only a

Table III. Radioactive Products from Recoil Tritium Reactions with Cyclobutane–Ethyl Chloride Gas Mixtures

Sample no.	445	443	442	441	440
Gas pressure cm.					
C_2H_5Cl	4.2	8.8	10.5	22.0	38.0
c-C_4H_8	3.6	7.5	10.7	19.7	33.4
He^3	1.8	1.8	1.8	1.8	1.8
O_2	0.5	0.9	0.9	1.3	1.9
Mole ratio C_2H_5Cl/ c-C_4H_8[a]	1.14	1.24	1.01	1.19	1.15
Relative activity					
HT	977 ± 15	999 ± 12	. . .	813 ± 8	. . .
C_2H_5T	26.6 ± 0.8	28.3 ± 0.7	. . .	23.3 ± 0.5	. . .
C_2H_7T	293 ± 5	290 ± 4	. . .	213 ± 2	. . .
c-C_4H_7T	169 ± 3	169 ± 2	202 ± 3	174 ± 2	~152
C_2H_4TCl	100	100	100	100	100
Corrected relative activity of C_2H_5T	25.8 ± 1.3	27.6 ± 1.0	. . .	22.6 ± 0.9	. . .
Specific activity ratio for C_2H_4TCl vs. c-C_4H_7T	0.507 ± 0.020	0.505± 0.018	0.504 ± 0.018	0.514 ± 0.015	~0.58
Specific activity ratio per bond for C_2H_5Cl vs. c-C_4H_8					
T for H	0.396 ± 0.016	0.416 ± 0.015	0.462 ± 0.015	0.462 ± 0.012	~0.549
T for Cl	0.51 ± 0.04	0.57 ± 0.03	. . .	0.52 ± 0.02	. . .

[a] Measured from chromatographic trace of mass peaks.

Table IV. Radioactive Products from Recoil Tritium Reactions with Gaseous Ethyl Chloride

Sample no.	331	330	329	248	249	Ref. 11	334	28	25
Gas pressure, cm.									
C_2H_5Cl	3.1	11.0	36.4	73.3	76.8	~76	≤150	67.7	68.7
He^3	1.6	1.6	2.0	1.5	1.5	Yes	≥1.6	1.9	1.8
Scavenger	I_2	I_2	I_2	I_2	I_2	I_2, Br_2, O_2	I_2	5.4 (NO)	None
Abstraction HT product	100.0	100.0	100.0	100.0	100.0	100.0	100.0	116	120
Direct substitution products									
C_2H_4TCl	24.7 ± 1.4	28.2 ± 0.4	31.8 ± 0.4	31.3 ± 0.4	30.8 ± 0.3	32.8 ± 3.7	36.6 ± 0.4	(32)[b]	(32)[b]
C_2H_5T	4.2 ± 1.0	5.8 ± 0.2	6.2 ± 0.1	6.3 ± 0.1	5.6 ± 0.1	5.9 ± 0.7	6.5 ± 0.3	4	5
CH_2TCl	NM[a]	0.8 ± 0.2	0.6 ± 0.1	0.7 ± 0.1	NM	~0.7	0.7 ± 0.1	0.4	0.3
CH_3T	5.7 ± 0.8	4.9 ± 0.2	4.9 ± 0.1	4.2 ± 0.1	3.5 ± 0.1	4.1 ± 0.7	5.2 ± 0.1	4	3
Elimination decomposition products									
C_2H_3T	31.5 ± 1.2	24.5 ± 0.4	19.4 ± 0.2	18.4 ± 0.2	18.3 ± 0.2	8.5 ± 3.0	17.0 ± 0.2	1.6	18
C_2H_2TCl	NM	1.0 ± 0.2	1.3 ± 0.1	0.6 ± 0.1	NM	. . .	0.6 ± 0.1	. . .	. . .
C_2HT	0.8 ± 0.8	1.0 ± 0.2	0.7 ± 0.1	0.5 ± 0.1	NM	. . .	0.3 ± 0.1	. . .	. . .
Radical decomposition products									
C_2H_4TI	5.0 ± 0.8	3.9 ± 0.2	3.4 ± 0.1	2.5 ± 0.1	2.1 ± 0.1	4.1 ± 1.1	2.7 ± 0.1	. . .	. . .
CH_2TI	10.7 ± 0.8	10.7 ± 0.8	9.2 ± 0.2	7.8 ± 0.2	7.6 ± 0.1	9.2 ± 3.3	7.6 ± 0.2	. . .	. . .
$CHTClI$	NM	NM	1.4 ± 0.3	0.7 ± 0.1	NM	. . .	1.6 ± 0.3	. . .	. . .

[a] Not measured. [b] Arbitrary standard.

small correction. The experimental results from CH_4–C_2H_5Cl mixtures are given in Table II and confirm the yield vs. pressure relationships indicated by the data of Table I. The same data also confirm that the yield of hot HT from C_2H_5Cl is pressure independent within the errors of measurement.[33]

An alternate internal standard, cyclobutane, has been used in several previous measurements. The sequential reactions 1 and 2 provide both c-C_4H_7T and C_2H_3T as labeled products from recoil tritium reaction with the parent cyclobutane. While the individual yield of each is pressure dependent, the

(33) Experiments with hydrocarbons have shown that the HT yields are sensitive to the percentage of O_2 scavenger present, being lower in the presence of appreciable (10–30%) O_2 concentrations. Use of HT as the only standard thus requires careful evaluation at each pressure of the HT yield vs. O_2 concentration.

sum of these two yields is essentially pressure independent in the 0.1–1.0-atm. range.[5] In favorable circumstances, mixtures of cyclobutane and other molecules can therefore be irradiated, utilizing the sum of the yields of c-C_4H_7T and C_2H_3T from c-C_4H_8 as an internal standard.[5,17,18] However, the requisite sum of yields cannot be readily measured for ethyl chloride–cyclobutane mixtures, since both c-C_4H_7T and C_2H_4TCl give C_2H_3T as a decomposition product. Nevertheless, such competition experiments have been conducted, and the specific activity ratios (RT/RH) of the two parent molecules have been compared directly. The experimental results of these C_4H_8–C_2H_5Cl competition experiments are given in Table III, arbitrarily expressed with the yield of C_2H_4TCl as 100.

Table V. Radioactive Products from Recoil Tritium Reactions with Ethyl Chloride in the Liquid Phase

Sample no.	332	333	524	526	467	468	466
Scavengers	None	None	DPPH	DPPH	I_2	I_2	Br_2
Relative. activity							
HT	100	100	100	100	100	100	100
C_2H_4TCl	49.7 ± 0.7	49.9 ± 0.6	42.1 ± 0.3	48.0 ± 0.4	48.2 ± 0.8	48.8 ± 0.5	46.9 ± 0.6
C_2H_5T	22.1 ± 0.4	21.7 ± 0.3	11.5 ± 0.1	12.5 ± 0.2	9.9 ± 0.4	NM^a	9.6 ± 0.2
CH_2TCl	NM	2.6 ± 0.1	2.4 ± 0.1	2.3 ± 0.1	2.1 ± 0.1	NM	2.0 ± 0.2
CH_3T	7.3 ± 0.1	7.2 ± 0.1	6.7 ± 0.1	7.3 ± 0.1	6.5 ± 0.3	NM	7.0 ± 0.2
C_2H_3T	6.1 ± 0.1	6.7 ± 0.1	8.1 ± 0.1	8.2 ± 0.1	0.2 ± 0.2	NM	0.2 ± 0.1
C_2H_2TCl	NM	1.0 ± 0.1	1.3 ± 0.1	1.3 ± 0.1	0.9 ± 0.1	NM	0.0
C_2HT	NM	0.4 ± 0.1	0.6 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	NM	NM
C_2H_4TX	...	...	...	...	NM	3.8 ± 0.2	4.2 ± 0.2
CH_2TX	...	...	...	...	NM	2.6 ± 0.2	1.6 ± 0.2
$n\text{-}C_4H_9T$	NM	1.4 ± 0.1	NM	0.6 ± 0.1	0.4 ± 0.1	NM	NM

^{a} Not measured.

The fraction of C_4H_7T molecules surviving without decomposition rises from about 0.50 to 0.82 between 10 cm. of gas pressure and the liquid phase. Multiplication of these numbers by the specific activity ratios for C_2H_4TCl vs. $c\text{-}C_4H_7T$ demonstrates a variation in C_2H_4TCl survival of almost a factor of two over the corresponding range of conditions, in further agreement with Tables I and II.
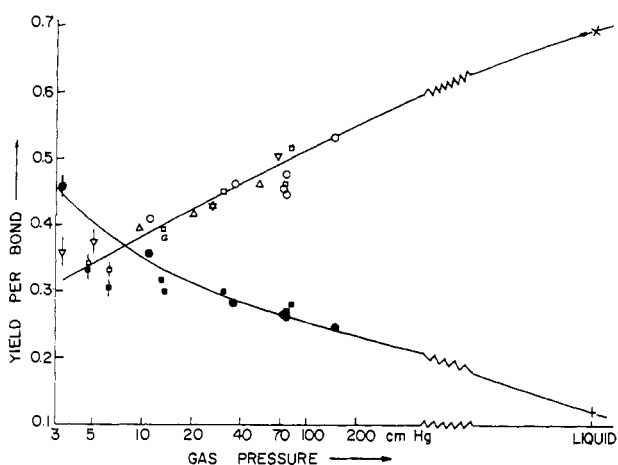

Figure 1. Pressure dependence of the yields of C_2H_4TCl and C_2H_3T from recoil tritium reactions with C_2H_5Cl. Yields of C_2H_4TCl: vs. $C\text{-}C_4H_8$, $\triangle$; vs. CH_4, $\triangledown$; I_2-scavenged, ϕ; O_2-scavenged, $\Box$; liquid, $\times$. Yields of C_2H_3T: I_2-scavenged, $\bullet$; O_2-scavenged, $\blacksquare$; liquid $+$.

A fourth set of gas phase measurements, carried out with I_2 as scavenger, is shown in Table IV, relative to HT = 100 as standard as in Table I. Two earlier ethyl chloride experiments, carried out with nitric oxide as scavenger and without scavenger, respectively, gave results quite consistent with these data, although the yield of HT in these two samples was greater than in the I_2-scavenged samples. The previously published data on recoil tritium reactions with ethyl chloride in the presence of O_2, Br_2, and I_2 are included here for comparison.[11] The agreement is quite satisfactory, except for the measurement of C_2H_3T yields, for which a very large error is quoted in the earlier results. Since the C_2H_3T yield is especially susceptible to subsequent reactions with some of the scavengers, no basic disagreement appears to exist among the various sets of data.

Liquid Phase Experiments. If the mechanism of reaction outlined for the gas phase experiments is directly carried over to the liquid phase, the primary changes to be anticipated in yields would be those attributable to the greatly increased frequency of molecular collisions. If the variation in collision frequency between 5 and 80 cm. of gas pressure permits observable effects, then the much greater change involved between 80 cm. and the liquid phase could readily demonstrate significant variations. Experiments have therefore been carried out here with liquid ethyl chloride in the presence of Br_2, I_2, or DPPH as scavengers, and with the unscavenged pure liquid. The results of these experiments are summarized in Table V. The differences between gaseous and liquid phases in Tables I–V are entirely consistent with mechanisms of reactions 1–10.
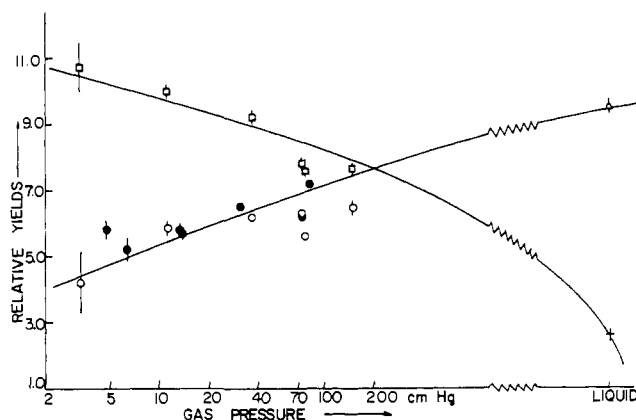

Figure 2. Pressure dependence of the yields of C_2H_5T and CH_2TI from recoil tritium reactions with C_2H_5Cl. Yields of C_2H_5T: I_2-scavenged, ϕ; O_2-scavenged, $\bullet$; liquid, $\triangle$. Yields of CH_2TI: I_2-scavenged, $\Box$; liquid, $+$.

Figures 1 and 2 summarize normalized data from Tables I–V, illustrating the complete over-all consistency of the results from various sets of experimental conditions and various choices of the standard reactions used as the basis of comparison.

Discussion

Secondary Reactions of Excited C_2H_4TCl. The earlier experiments with cyclobutane[5] and with methyl chloride[18] showed that two separate groups of reactions are involved in the creation of the radioactive product

spectrum observed in a recoil tritium sample. The first set of reactions consists of the initial interactions of the energetic tritium atom with the parent molecule; the second set includes the decomposition or isomerization reactions occurring because of the high excitation of the molecules formed in the first step. Potentially, recoil tritium reactions can provide information about either or both sets of reactions if the respective contributions can be separated and suitably identified. The secondary processes are of interest in themselves, if these processes have not previously been completely understood, while knowledge of the extent of secondary reaction is prerequisite to any quantitative estimate of the yields of the initial hot processes.
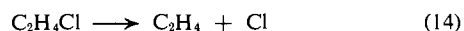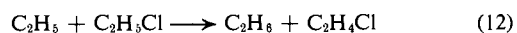
Some of the observed labeled molecules are formed in the true primary hot atom reactions, while others arise from the more complex sequence of primary plus secondary reaction. The possibility must always be considered, too, that some molecules may be formed by more than one reaction path. With this reservation in mind, the labeled products can be qualitatively separated into "primary" and "secondary" groups, whose chief distinguishing characteristics are that they respectively increase (or remain constant) and decrease with the increasing density of the irradiated sample.

These primary and secondary products can frequently be paired into complementary relationships through parallel pyrolysis experiments, by chemical reasonability, and by the quantitative magnitudes involved. The evidence is, however, only circumstantial since no direct observable link exists between particular primary and secondary products.

Examination of Figure 1 and the data tables shows conclusively that the largest yield changes involve $C_2H_4TCl^*$ as the primary product and C_2H_3T as the secondary product. This relationship is quite satisfactorily accounted for through reaction 4a.[34] The

$$C_2H_4TCl^* \longrightarrow C_2H_3T + HCl \qquad (4a)$$
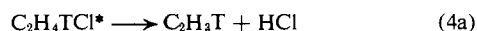
comparable nontritiated reaction (eq. 4) is presently the favored explanation for the kinetic behavior of pyrolyzed C_2H_5Cl, although a consistent chain mechanism can be written for which the first step is reaction 11, followed by (12–14) and the chain termination steps.[24]

$$C_2H_5Cl^* \longrightarrow C_2H_5 + Cl \qquad (11)$$

$$C_2H_5 + C_2H_5Cl \longrightarrow C_2H_6 + C_2H_4Cl \qquad (12)$$

$$Cl + C_2H_5Cl \longrightarrow C_2H_4Cl + HCl \qquad (13)$$

$$C_2H_4Cl \longrightarrow C_2H_4 + Cl \qquad (14)$$

While the excited molecules formed in recoil tritium and pyrolytic systems apparently behave in very similar manner, the subsequent reaction paths could be very different. In the pyrolytic systems, all of the molecules are at the same high temperature, and radical chain reactions are quite feasible for some molecules. In the recoil tritium systems, *only* the labeled molecule is excited, while the other molecules are still at the ambient temperature, usually about 20°. The consequences of the latter are twofold: (a) chain reactions will almost never occur or will be very short in the recoil system, and (b) the detection system observes only the molecular fate of the *original* radioactive species. If an excited $C_2H_4TCl^*$ molecule decomposed by C–Cl bond break, as in (11), our radio gas chromatographic measurements would follow the C_2H_4T radical, would observe it as C_2H_5T from reaction 12, and would be completely unaffected by any further chain reaction of unlabeled radical species. The experimentally observed C_2H_4TI in I_2-scavenged systems probably results from just such C–Cl bond break in $C_2H_4TCl^*$, in analogy with eq. 11. Quantitatively, the data indicate that about $15 \pm 5\%$ of decomposing $C_2H_4TCl^*$ molecules in this system follow the C–Cl bond rupture path. The radical C_2H_4T would not lead to C_2H_3T as a major observed product under any of the experimental conditions employed in this work.

A reasonable complementary relationship exists between the yields of C_2H_4TCl and C_2H_3T, especially since an exact balance should not be expected. Reaction 4b should be a minor contributor relative to

$$C_2H_4TCl^* \longrightarrow C_2H_4 + TCl \qquad (4b)$$
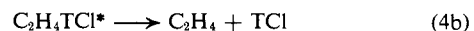
(4a), 20% or less dependent upon the hydrogen isotope effect, and the TCl yield from this reaction cannot readily be distinguished from much larger yields of the same molecule from other reactions such as Cl abstraction by hot T atoms.

We draw from these results the conclusion that the primary mode of decomposition of $C_2H_4TCl^*$ formed by recoil tritium reactions is the elimination of HCl to form C_2H_3T, as in (4a). By combining these observations with those on the cyclobutane and methyl chloride systems, we conclude further that a very close parallel exists in the molecular reaction patterns of molecules excited thermally with those excited by recoil tritium T-for-H substitution reactions and that reaction 4 is the predominant decomposition mode for thermally excited $C_2H_5Cl^*$ molecules.[35]

The yield of C_2H_2TCl is about $\leqslant 1$ relative to HT = 100 and is thus a rather minor product. This labeled species could be formed by the elimination of H_2 from excited $C_2H_4TCl^*$, but is no more than a minor side reaction ($<5\%$ of total decomposition) even if this is the only source for C_2H_2TCl.[36] The yield of C_2HT is also very low and could be accounted for through the elimination of HCl from a molecule of $C_2H_2TCl^*$ still excited from its own formation reaction. However, plausible alternate mechanistic pathways can be written for each of these products, and the mechanisms suggested above are merely speculative on the basis of the present data.

Comparison with Radiolysis. The radiolysis of ethyl chloride with 2.8-Mev. electrons also leads to the formation of ethylene, vinyl chloride, and acetylene, with G values of 2.06, 0.66, and 0.75, respectively.[37] Study of dose rate and scavenger effects leads to the conclusion that these molecules are formed primarily by molecular detachment processes from excited ethyl chloride molecules. The vinyl chloride and acetylene

(34) None of our experiments provides any information about the structure of the first C_2H_4 entity formed in reaction 4. If the product is ethylidene (CH_3–CH:), the rearrangement to ethylene is very rapid.

(35) However, even assuming this parallel to be exact, these experiments do not "disprove" the chain mechanism in the pyrolysis studies, since a relatively small fractional decomposition by (11) could be multiplied into the major cause of C_2H_5Cl removal by long chains at pyrolytic temperatures.

(36) The HT formed by the alternate isotopic pathway would be negligibly small compared to HT from the direct abstraction reaction 5.

(37) R. N. Schindler, *Radiochim. Acta*, 2, 62 (1963).

yields relative to ethylene are clearly much higher from molecules excited through electron radiolysis than from molecules excited through hot T-for-H substitution.

Other Secondary Reactions. Other plausible complementary pairs of reactions can be suggested including the decompositions of (3) and (10). More definite establishment of these relationships is not feasible, since the yield changes are relatively small; *e.g.*, if an appreciable fraction of $C_2H_5T^*$ molecules were to react by eliminating H_2,[36] the resulting C_2H_3T would not be experimentally detectable in the presence of the much larger yield from $C_2H_4TCl^*$ decomposition.

The excited molecules $C_2H_5T^*$ and CH_2TCl^* have also been formed by the T-for-H substitution reaction with the respective unlabeled molecules. In each case, some pressure dependence is observed, indicative of considerable internal excitation. Comparison of the relative yields of secondary to primary products at the same pressure indicates *more* decomposition of $C_2H_5T^*$ after substitution of T for Cl in C_2H_5Cl than after T for H in C_2H_6.[38] Similarly, a larger fraction of molecules is observed to decompose after the substitution of T for CH_3 in C_2H_5Cl than for T for H in CH_3Cl.[18] These results can be consistently described if the average initial tritium energies are approximately the same prior to each reaction, since T for Cl and T for CH_3 are both about 20 kcal./mole exothermic while T for H is nearly thermoneutral. Direct searches for *differences* in the average energies of recoil tritium prior to reaction for T for X and T for H have so far failed.[39]

Initial Yields of Energetic Reactions. The variations in relative yields of different products shown in the previous tables and figures demonstrate conclusively that the phase or pressure conditions of irradiation can seriously alter the distribution of radioactivity observed in recoil tritium–ethyl chloride systems. If the variations are the result of excited molecular decompositions, then the primary hot yields are more closely approached when secondary reactions are kept to a minimum, *i.e.*, in the scavenged liquid phase samples. Since secondary decompositions persist even in the liquid phase,[40,41] corrections must still be made for losses from the initial primary yields.

The C_2H_3T found in irradiated liquid C_2H_5Cl can plausibly be assigned as a secondary product of the decomposition of $C_2H_4TCl^*$, and a reasonable estimate of the original primary yield of the T-for-H reaction is given in Table VI by the sum of the yields of C_2H_4TCl, C_2H_3T, and C_2H_4TI.[42] The "true" liquid phase yield of C_2H_3T is estimated from the results obtained with DPPH as the scavenger molecule. Ethylenic products were partially removed by preferential reaction of radiolytic species (presumably H atoms) in the unscavenged sample and were almost completely removed by chemical reaction with the scavenger in I_2- or Br_2-scavenged liquid samples.

(38) J. W. Root, Ph.D. Thesis, University of Kansas, 1964.
(39) E. K. C. Lee, G. Miller, and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 190 (1965).
(40) E. K. C. Lee and F. S. Rowland, *J. Chem. Phys.*, **36**, 554 (1962).
(41) E. K. C. Lee, Y. N. Tang, and F. S. Rowland, *J. Am. Chem. Soc.*, **86**, 5038 (1964).
(42) The correction for decomposed $C_2H_4TCl^*$ should be adjusted upward for the TCl yield from reaction 4b and downward for possible contributions to C_2H_3T yield from other sources, *e.g.*, $C_2H_5T^* \rightarrow C_2H_3T$ + H_2. Both corrections should be small and are omitted here.

Table VI. Relative Yields of Tritium-Labeled Products from Recoil Tritium Reactions with Methyl and Ethyl Chloride

Hot reaction	Labeled product	Parent molecule	
		CH_3Cl	CH_3CH_2Cl
		Relative yields (HT = 100)	
T for H	RCHTCl	69 ± 2	58 ± 3
T for Cl	RCH_2T	30 ± 1	10 ± 1
T for CH_3	CH_2TCl	...	3 ± 1
T for CH_2Cl	CH_3T	...	7 ± 1
Relative Yields Normalized per Atom in RCH_2Cl to T for H in c-C_4H_8 as 1.0 per H Atom			
T for H		0.78 ± 0.03	0.81 ± 0.03
T for Cl		1.02 ± 0.06	0.7 ± 0.1

The initial yields of C_2H_5T, CH_3T, and CH_2TCl have all been estimated in Table VI from the I_2- and Br_2-scavenged systems, but highly accurate values cannot be obtained because of the uncertainty in assignment of the yield observed for CH_2TX, and because of the existence of small yields of other products containing I or Br, respectively. Each of these three molecules exhibits a higher yield in the liquid phase than in the 1-atm. gas samples, indicating the deposition of sufficient energy for subsequent decomposition reactions in the substitution of T for Cl to form $C_2H_5T^*$, of T for CH_3 to form CH_2TCl^*, and T for CH_2Cl to form CH_3T^*. The higher yields of C_2H_5T in the unscavenged and DPPH-scavenged systems are tentatively attributed to abstraction reactions by C_2H_4T radicals. This assignment is sufficiently uncertain that the choice of the halogen-scavenged data for use in Table VI may result in slightly too low an estimate for C_2H_5T. The data for tritium recoil reactions with methyl chloride are included for comparison.

The data in the upper part of Table VI are normalized relative to the hot yield of HT for each molecule as 100 and would be normalized relative to one another only if the abstraction of H from methyl and ethyl chlorides were equally likely, per H atom. The yields can be empirically normalized to one another through the competition of each with cyclobutane reactions in methyl chloride–cyclobutane and ethyl chloride–cyclobutane mixtures. The results from this normalization procedure are shown in the lower part of Table VI.

Mechanism of Hot Substitution Reactions. Two clear results emerge from the comparisons available in Table VI: (a) Cl is more easily replaced if the energetic tritium atom replacing it is combining with CH_3 than with CH_2CH_3, but the difference in yields is only 30% (1.02 *vs.* 0.7) and not factors of three or more; (b) during C–C bond break in ethyl chloride, the tritium atom is more likely to combine with CH_3 than with CH_2Cl (7 *vs.* 3). A third conclusion is that the probability for replacement of H in ethyl chloride, averaged over all five H atoms, is approximately equal to the average in methyl chloride, and both are about 20% less easily replaced than the C–H atoms in cyclobutane. The absence of data concerning the intramolecular distribution of tritium in C_2H_4TCl discourages any more extensive conclusions concerning the replacement of H atoms, other than the fact that the variations are by 20–30%, and not by factors of two or three.

The preference for combining with CH_3 rather than

a larger group after replacement of Cl or after C–C bond break is consistent with the trend postulated on the basis of gas phase data on halocarbons,[10,11] even though these gas phase data have been shown in the present experiments to underestimate very seriously the primary hot yields of these products. The results themselves are therefore also consistent with the explanation that the preference for reaction with CH_3 arises from a lower rotational inertia of this group, thereby facilitating changes in orientation leading to successful C–T bond formation. The data on methyl and ethyl chloride alone, however, are equally consistent with other postulates of the origin of the effects for R and Cl groups, e.g., electron-withdrawing power of substituents, and furnish no method for choosing among these postulates. Further experiments with other molecules, with careful evaluation of the magnitude of primary product decomposition, are required to establish the significance of these trends.

Nitric Oxide and Iodine Catalyzed Isomerization of Olefins. IV. Thermodynamic Data from Equilibrium Studies of the Geometrical Isomerization of 1,3-Pentadiene[1a]

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Contribution from the Stanford Research Institute, Menlo Park, California. Received January 16, 1965

The thermodynamics of the nitric oxide catalyzed, homogeneous, gas phase isomerization of cis-1,3-pentadiene $\overset{k_5}{\underset{k_6}{\rightleftarrows}}$ trans-1,3-pentadiene have been studied over a temperature range between 126 and 394°. The measured values for the equilibrium constant, $K_{5,6} = k_5/k_6$, ranging from 3.47 to 2.23, yield a straight line when plotted as log $K_{5,6}$ vs. $1/T(°K)$. The least-squares fit of our data to a quadratic equation using a regular computer regression program yields with standard error $\overline{\Delta C_p°}_{533}$ $= -0.13 + 0.75$ gibbs/mole. Our data can be fitted to both a linear and a quadratic equation equally well yielding $\Delta H°_{533} = -1.04 \pm 0.03$ kcal./mole and $\Delta S°_{533} = -0.14 \pm 0.05$ gibbs/mole. These values deviate significantly from the comparative estimates given by Kilpatrick, et al., and reported in the API tables, which necessarily have larger error limits attached to them. In contrast to our experimental values, these latter data would imply that throughout our temperature range cis-1,3-pentadiene is more stable than the trans isomer when the opposite is true. The value of $\Delta H°(25°)$ $= -1.66 \pm 0.27$ reported by Fraser, et al., from heats of combustion measurements also deviates significantly from the value of $\Delta H°_{300} = -1.01 \pm 0.18$ kcal./mole, calculated from this work. With either NO_2 or I_2 as a catalyst, equilibrium is established much faster than with NO, which is to be expected from the differences in the reaction mechanism in the two systems. Unlike nitric oxide, NO_2 and I_2 cause large amounts of side reactions and increased difficulties in product separation.

Introduction

The measurement of equilibrium constants of the iodine-catalyzed gas phase reactions of olefins and their parent hydrocarbons has been shown to be a very simple, direct, and valuable method to determine precise differences in the thermodynamic properties of the reactants.[2a]

Applied to the *cis–trans* isomerization of 1,3-pentadiene, the present paper reports an appreciable amount of side reactions and considerable difficulties in product separation. This result is in contrast to the clean-cut experiments on the isomerization of 2-butene, reported earlier.[2]

The only important two side reactions, the polymerization of 1,3-pentadiene and the formation of diiodide in the lower temperature range, are shown to be a consequence of the considerably more stable radical intermediate formed with 1,3-pentadiene compared to 2-butene. The consecutive-step mechanism for the *cis–trans* isomerization discussed earlier[2b] involves the addition of an iodine atom to the double bond and subsequent internal rotation in the adduct radical. The addition of an I atom at the 4-position of 1,3-pentadiene generates allylic resonance in the radical intermediate. The iodine adduct radical with 1,3-pentadiene is therefore stabilized by the allylic resonance energy of 12.6 kcal.[3] compared to the *sec*-butyl iodide radical. Using NO as a catalyst instead of iodine, the stabilizing effect of the allylic resonance on the radical intermediate, when compared to 2-butene is just about compensated by the difference in bond strength between the secondary C· · ·NO bond (37 kcal.)[2b] and the secondary C· · · ·I bond (53 kcal.).[2b]

The NO-catalyzed system, reported in the present paper, showed excellent reproducibility and no measureable side reactions. NO_2 gave rise to the same

(1) (a) This work has been supported in part by Grant PAU-5235 from the Public Health Service to Stanford Research Institute; (b) Postdoctorate Research Fellow.

(2) (a) D. M. Golden, K. W. Egger, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5416 (1964); (b) S. W. Benson, K. W. Egger, and D. M. Golden, *ibid.*, **87**, 468 (1965).

(3) K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, **86**, 5420 (1964).