Unimolecular Reactions Subsequent to Recoil Tritium Reactions with Dichloromethane. Formation of Monochlorocarbene[1]

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Abstract: The reactions of recoil tritium atoms with dichloromethane produce $CHTCl_2{}^*$ and CH_2TCl^* by substitution of T for H and T for Cl, respectively. Unimolecular decomposition of $CHTCl_2{}^*$ proceeds largely through elimination of hydrogen chloride, with the formation of monochlorocarbene in the singlet state. The latter was detected through its addition to ethylene to form cyclopropyl-*t* chloride in both the presence and absence of O_2 as scavenger. The excited CH_2TCl^* molecules decompose by C–Cl bond breakage with no evidence for carbene formation as a competitive process. The relative yields of the primary hot reactions with CH_2Cl_2 are in the ratio $HT:CHTCl_2:CH_2TCl = 100:51 \pm 5:25 \pm 2$. These values were determined in scavenged liquid-phase experiments and are very different from previously measured values because of extensive unimolecular decomposition of the substitution products in the gas phase.

Energetic tritium atoms from nuclear recoil are able to react with most organic compounds to form various radioactively labeled compounds, many of which possess considerable excitation energy.[3,4] Study of the replacement of H by T in cyclobutane, as in reaction 1, has indicated that the median excitation en-

$$T^* + RH \longrightarrow RT^* + H \qquad (1)$$

ergy of the resulting c-C_4H_7T molecule is about 5 ev and is therefore large enough to produce secondary reaction by paths characteristic of unimolecular decompositions through thermal excitation.[5] Investigation of the decomposition induced by such primary reactions has disclosed several kinds of secondary reaction: cyclobutane decomposes to two molecules of ethylene;[5] methyl chloride splits the C–Cl bond to give CH_2T and Cl;[6] and ethyl chloride undergoes the molecular elimination of HCl.[7] These earlier studies have encouraged the use of recoil tritium substitution reactions as a means for investigating the unimolecular decompositions of other molecules,[8] and these techniques have been applied here to the labeled species formed in hot tritium reactions with dichloromethane.

The four hot tritium reactions expected with dichloromethane from earlier studies of the alkyl halides[9,10] are the abstraction of, and substitution for, atoms of either hydrogen or chlorine, as given in eq 2–5. The species of prime interest in this system for a study

$$T^* + CH_2Cl_2 \longrightarrow HT + CHCl_2 \qquad (2)$$

$$T^* + CH_2Cl_2 \longrightarrow CHTCl_2 + H \qquad (3)$$

$$T^* + CH_2Cl_2 \longrightarrow TCl + CH_2Cl \qquad (4)$$

$$T^* + CH_2Cl_2 \longrightarrow CH_2TCl^* + Cl \qquad (5)$$

of unimolecular reaction mechanisms are the two molecules formed by the substitution reactions, $CHTCl_2{}^*$ and CH_2TCl^*. The latter has previously been formed in the methyl chloride system, and a comparison of the decompositions of the same molecule formed in two different systems is therefore possible. Additional information was also expected from the study of excited dichloromethane-*t*, whose unimolecular reactions were not completely understood. The specific possibility that $CHTCl_2{}^*$ might decompose by the elimination of HCl,[11] as in reaction 6, was considered because of the earlier suggestion of this reaction in pyrolytic decomposition,[12] and the well-known liquid-phase formation of dichloromethyllithium from dichloromethane reactions with organolithium compounds.[13–15] Confirmation that this reaction indeed occurs has been published in a brief communication.[16]

$$CHTCl_2{}^* \longrightarrow CTCl + HCl \qquad (6)$$

The study of recoil tritium reactions with dichloromethane is also of considerable interest for the understanding of the primary reactions of the energetic tritium atoms themselves. The series of experiments carried out in the gas phase for a variety of halocarbons had previously shown that the ease of replacement of halogen atoms, as measured by the appearance of the T-for-X product, varied substantially with the nature of the other substituents adjacent to the original C–X bond.[9,10] Previous studies from our laboratory of reactions with methyl[6] and ethyl chloride[7] have indicated that a complete study of the pressure and phase dependence of product yields is usually nec-

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[3] F. Schmidt-Bleek and F. S. Rowland, *Angew. Chem. Intern. Ed. Engl.*, **3**, 769 (1964).

[4] R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

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

[6] Y.-N. Tang, E. K. C. Lee, and F. S. Rowland, *ibid.*, **86**, 1280 (1964).

[7] Y.-N. Tang and F. S. Rowland, *ibid.*, **87**, 3304 (1965).

[8] F. S. Rowland, E. K. C. Lee, F. Schmidt-Bleek, and Y.-N. Tang, "Symposium on the Kinetics of Pyrolytic Reactions," Ottawa, Canada, 1964, pp Q-1–Q-8.

[9] R. Odum and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 4668 (1961).

[10] R. Odum and R. Wolfgang, *ibid.*, **85**, 1050 (1963).

[11] The alternate isotopic reaction of elimination to TCl would also be expected, but the TCl so formed would be indistinguishable experimentally from that formed in reaction 4.

[12] A. E. Shilov and R. D. Sabirova, *Dokl. Akad. Nauk SSSR*, **114**, 1058 (1957).

[13] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

[14] G. L. Closs and G. M. Schwartz, *ibid.*, **82**, 5729 (1960).

[15] G. L. Closs, *ibid.*, **84**, 809 (1962).

[16] Y.-N. Tang and F. S. Rowland, *ibid.*, **87**, 1625 (1965).

essary in order to make a reasonable estimate of the original primary yield prior to decomposition of some of the excited molecules. The current experiments with CH_2Cl_2 furnish the primary yield data needed for comparison with the earlier alkyl halide data.

Experimental Section

General Procedure. These experiments were carried out by the usual techniques employed in studying the chemical reactions of tritium atoms produced by neutron irradiation of He^3 in the gas phase and Li^6 in heterogeneous liquid–solid systems.[3,6,7] Gas samples containing CH_2Cl_2 up to its room-temperature vapor pressure (about 0.5 atm), He^3, and other additives were sealed in Pyrex 1720 bulbs of about 12-ml volume. Liquid samples were condensed onto lithium fluoride at the bottom of capillary tubes. The neutron irradiations were carried out either at the TRIGA reactor of the Omaha Veterans Administration Hospital, or at the University of Kansas reactor, each with a nominal neutral flux of 10^{11} neutrons/(cm^2 sec). The gas samples were usually irradiated for 1 hr, while the liquid samples were irradiated for 3 hr.

The analysis of the samples after irradiation was performed by radio gas chromatography.[17,18] These techniques, except for the particular separation columns employed, have been previously described for methyl chloride[6] and for many other systems. Accurate measurement of the labile tritium (including TCl, and atoms bonded to O, I, Br, etc.) was not possible with these chromatographic techniques, since isotopic exchange would have occurred in handling or on the columns. Accordingly, this tritium was removed from the gas sample by isotopic exchange on a cotton plug in the flow system during transfer of the sample for gas chromatography. The gas chromatographic columns employed in the analysis, with the order of separation observed on each, are described elsewhere.[19]

Cyclopropyl-*t* chloride and $CHTClCH{=}CH_2$ are not separated on the 50-ft tri-*o*-tolyl phosphate column ordinarily used, but were readily separated with the addition, in series with the TTP column, of a 20-ft $AgNO_3$–ethylene glycol column.

Quenching of Proportional Counter Action by Halocarbons. Dichloromethane, like many other alkyl halides, has an electron affinity sufficiently high to initiate quenching action within the proportional counter. Comparison of the macroscopic CH_2Cl_2 content of each aliquot with a calibration curve for its quenching action under our operating conditions showed an over-all correction for $CHTCl_2$ yield less than the statistical error of counting.[19]

Chemicals. Spectroquality dichloromethane was obtained from Matheson Coleman and Bell, checked by gas chromatography for purity, and used without further processing. Ethylene was obtained from the Matheson Co., with an impurity level less than 0.5%. Other chemicals such as cyclobutane, He^3, LiF, O_2, I_2, and Br_2 came from the same sources as described earlier.[5–7]

Results

Variation of Product Yields with Pressure. Absolute Yields. Several different methods have been employed in earlier studies for the comparison of results at different pressures, including (a) absolute measurement of the total radioactivity among the various products of reaction with cyclobutane; (b) comparison of relative yields in binary mixtures with cyclobutane or with methane; and (c) intramolecular comparison *vs.* the yield of a product for which the pressure dependence is known or can be reasonably assumed.[5–7]

Any one of these methods would be potentially satisfactory for establishing the dependence of product yields upon pressure in a system under investigation. However, the heterogeneous nature of the samples used in liquid-phase irradiations makes impossible the accurate measurement of absolute yields in such experiments. The experimental conditions for neutron irradiation limit the gas-phase measurements to roughly the pressure range from 10 to 35 cm for CH_2Cl_2, corresponding to a change of only about 10% in the yield of $CHTCl_2$, as established in measurements described below. Moreover, accurate absolute measurements in the gas phase require accurate knowledge of the stopping powers of the components in order to correct for recoil loss to the walls at the lower pressures;[20] the uncertainty involved is easily of the same order of magnitude as the expected change in yield with pressure. For these reasons, we have not used method a to establish the dependence of product yields on pressure in the CH_2Cl_2 system.

Absolute measurements of yield were performed with Br_2-scavenged gaseous samples of CH_2Cl_2 at approximately 0.5 atm pressure, using pure propane samples as monitors for the neutron flux. The absolute yields measured in these experiments were (in per cent of total tritium formed): HT, 18.7 ± 1.8; CH_2TCl, 1.6 ± 0.2; $CHTCl_2$, 2.8 ± 0.4; CH_2TBr, 2.9 ± 0.4. These results are in excellent agreement with the published results of previous experiments by Odum and Wolfgang.[10]

Competition Reactions with Cyclobutane. The yields from recoil tritium reactions with CH_2Cl_2 and cyclobutane in direct competition with one another are shown in Table I. Comparison with the sum of the yields of *c*-C_4H_7T and C_2H_3T (shown to be pressure independent in experiments with cyclobutane alone) indicates that the yield of $CHTCl_2$ is higher in the liquid phase than in the gas phase by more than a factor of 2.[21] The variation of yield with pressure anticipated for the small available range of gas pressures was not very great and falls within the relatively large limits of error for such binary mixture experiments.[21]

Pressure Dependence Studies. Halogen-Scavenged Samples. In earlier studies, the yield of HT from recoil tritium reactions was shown to be virtually independent of pressure for cyclobutane, methyl chloride, and ethyl chloride, and was therefore a logical choice as an intramolecular standard for experiments with CH_2Cl_2. The results from a series of gas- and liquid-phase experiments with Br_2 as the scavenger molecule are shown in Table II. The mole fraction of Br_2 is approximately the same in all samples, and variations in reactivity with mole fraction should be unimportant. Table III contains the data for a comparable series of I_2-scavenged gas-phase experiments, and includes the earlier data of Odum and Wolfgang for comparison.[10] All data in both Tables II and III have been expressed with the yield of HT = 100 as the relative base. The agreement between the two sets of data is quite satisfactory, except for the yields of CHTClX. We believe that the combined process of scavenging of the original radical, and preservation of the molecule through the analytical procedure, is more efficient for CHTClBr than for CHTClI, and we have based our later quantitative estimates on the Br_2-scavenged data of Table II.

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

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

(19) Y.-N. Tang, Ph.D. Thesis, University of Kansas, 1964.

(20) See, for example, J. W. Root, Ph.D. Thesis, University of Kansas, 1964.

(21) These experiments were not conducted at constant mole fraction, or over a range of mole fractions of the cyclobutane–dichloromethane mixtures. However, numerous experiments in other systems imply that variations in relative specific yields with mole fraction for these two species would be much smaller than the differences observed between gas and liquid phases: J. W. Root and F. S. Rowland, *J. Chem. Phys.*, **38**, 2030 (1963); see also ref 20.

Table I. Product Yields from Recoil Tritium Reactions with Gaseous and Liquid Mixtures of CH_2Cl_2 and Cyclobutane

Sample composition (CH_2Cl_2 + c-C_4H_8)	5.9 cm	27.6 cm	Liquid	Liquid
Scavenger	0.9 O_2	1.9 O_2	Br_2	I_2
Tritium source	1.5 cm He^3	1.5 cm He^3	LiF	LiF
Mole ratio[a]				
CH_2Cl_2/c-C_4H_8	2.96 ± 0.20	0.71 ± 0.04	1.35 ± 0.07	0.62 ± 0.03
Rel activities				
$CHTCl_2$	1435 ± 50	1790 ± 50	6210 ± 90	11,700 ± 120
c-C_4H_7T	2815 ± 60	17,540 ± 150	22,500 ± 160	86,400 ± 300
c-C_4H_7T[b]/(c-C_4H_7T + C_2H_3T)	0.47	0.54	0.82	0.82
Substitution[c] probability per C–H bond	0.33 ± 0.03	0.33 ± 0.02	0.68 ± 0.04	0.72 ± 0.03

[a] Measured by thermal conductivity. [b] Ratios in pure cyclobutane at same total pressure, from ref 5. [c] ($CHTCl_2$)/2(CH_2Cl_2) ÷ (c-C_4H_7T + C_2H_3T)/8(c-C_4H_8).

Table II. Variation of Product Yields with Total Pressure in Recoil Tritium Reactions with Bromine-Scavenged CH_2Cl_2

Gas pressure, cm							
CH_2Cl_2	7.4	11.5	21.6	29.7	32.5	(~14)	(~18)
He^3	1.9	1.9	1.9	1.9	2.0	LiF	LiF
Br_2	1.2	1.7	3.0	4.1	4.2	(~2)	(~2.5)
Total pressure, cm	11.5	15.1	26.5	35.7	38.7	Liquid	Liquid
Product							
HT	100	100	100	100	100	100	100
$CHTCl_2$	14.2 ± 0.4	15.3 ± 0.3	15.8 ± 0.3	15.5 ± 0.4	15.2 ± 0.4	30.3 ± 0.6	27.3 ± 0.6
CH_2TCl	6.7 ± 0.2	7.3 ± 0.2	7.7 ± 0.2	8.1 ± 0.2	8.7 ± 0.2	23.0 ± 0.4	21.5 ± 0.4
CH_2TBr	15.3 ± 0.4	16.3 ± 0.3	16.3 ± 0.3	15.9 ± 0.3	15.5 ± 0.3	3.4 ± 0.2	2.6 ± 0.2
CHTClBr	16.9 ± 0.6	16.8 ± 0.5	17.4 ± 0.5	16.2 ± 0.5	...[a]	11.0 ± 0.5	10.3 ± 0.5

[a] Lost in handling.

Table III. Variation of Product Yields with Total Pressure in Recoil Tritium Reactions with Iodine-Scavenged CH_2Cl_2

Gas pressure, cm						
CH_2Cl_2	8.1	14.8	33.6	29.7	Liquid	~35
He^3	1.5	1.5	1.5	2.6	LiF	Yes
I_2	Yes	Yes	Yes	Yes	No	Br_2, I_2
Total pressure, cm	9.6	16.3	35.1	32.3	Liquid	~35
Product[b]						
HT	100	100	100	100	100	100.0 ± 9.4
$CHTCl_2$	13.9 ± 0.4	14.3 ± 0.3	15.3 ± 0.3	16.5 ± 0.3	33.6 ± 1.2	15.2 ± 2.1
CH_2TCl	6.9 ± 0.2	7.5 ± 0.2	8.3 ± 0.2	8.0 ± 0.2	27.8 ± 0.6	8.9 ± 1.0
CH_2TI	15.3 ± 0.4	14.8 ± 0.3	13.9 ± 0.2	14.6 ± 0.2	...[a]	15.2 ± 2.1
CHTClI	6.4 ± 0.6	6.4 ± 0.4	5.8 ± 0.6	...[a]	...[a]	9.4 ± 1.0
CH_3T	<0.1	<0.1	<0.1	0.3 ± 0.2	11.4 ± 0.4	...[a]

[a] Not measured. [b] Relative yield (HT = 100). C_2H_4TCl was observed (~2) in liquid samples.

Both $CHTCl_2$ and CH_2TCl gradually increase in yield with increasing pressure in the gas phase and rise quite sharply in the liquid phase to values more than double the gas-phase values, in complete consistency with the cyclobutane competition experiments. The results conform to the general scheme that excited molecules are formed by the hot substitution reactions 3 and 5, followed by unimolecular decomposition of these primary products. The large amount of CH_2TX obtained in the halogen-scavenged systems identifies the presence of CH_2T radicals, for which reaction 7 is undoubtedly the chief, if not the only, source. Similarly, CHTClX indicates the presence of CHTCl, for which reaction 8 is one possible source.

$$CH_2TCl^* \longrightarrow CH_2T + Cl \qquad (7)$$

$$CHTCl_2^* \longrightarrow CHTCl + Cl \qquad (8)$$

Since the combined total yield for $CHTCl_2$ and CHTClX is considerably greater in the liquid phase than in the gas phase, a search for other possible gas-phase decomposition products was initiated.

Ethylene Scavenger Experiments. Formation of Carbenes. A convenient standard technique for demonstration and exploitation of the presence of carbenes has been through their addition to olefinic molecules to form the corresponding cyclopropyl compounds,[16,22,23] and this method has been applied to show the presence of CTCl through the formation of cyclopropyl-t chloride, as previously reported.[16] The pyrolysis of CH_2Cl_2 had been suggestive of possible carbene formation, although tremendously complicated by the instability and reactivity of some products at pyrolytic temperatures,[23,24] and the elimination of HCl from CH_2Cl_2 and $CHCl_3$ has been widely observed under basic hydrolysis conditions.[13–15,25–27]

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(22) See, for example, W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(23) Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 626 (1966).

(24) M. R. Hoare, R. G. W. Norrish, and G. Whittingham, *Proc. Roy. Soc.* (London), A250, 180 (1959).

(25) M. Vacherot, R. Mari, and M. Niclause, *Compt. Rend.*, **252**, 1945 (1961).

Table IV. Recoil Tritium Reactions with Ethylene-Scavenged CH_2Cl_2

Gas pressure, cm						
CH_2Cl_2	25.0	26.2	5.0	23.6	23.2	12.5
He^3	3.0	1.8	3.0	1.8	1.8	1.8
C_2H_4	9.5	33.3	28.1	9.1	29.8	22.1
O_2	None	None	None	4.2	2.8	3.2
Total pressure, cm	37.5	61.3	36.1	38.7	57.6	39.6
Product[b]						
$CHTCl_2$	100	100	100	100	100	100
CH_2TCl	63 ± 4	52 ± 4	74 ± 10	52 ± 1	55 ± 2	58 ± 2
C_2H_4TCl	39 ± 1	23 ± 1	72 ± 5	2 ± 1	6 ± 1	5 ± 1
n-C_3H_6TCl	205 ± 4	301 ± 6	1050 ± 50	0	0	0
c-C_3H_4TCl	30 ± 1	24 ± 1	32 ± 3	20 ± 1	28 ± 2	22 ± 2
$CHTClCH{=}CH_2$	0 ± 1	...[a]	0 ± 1	...[a]	...[a]	...[a]
c-C_3H_5T	0	14 ± 4	25 ± 7	0	2 ± 2	0

[a] Not measured. [b] Relative yield ($CHTCl_2$ = 100).

Table V. Recoil Tritium Reactions with Ethylene-Scavenged CH_3Cl

Gas pressure, cm				
C=C	76.2	42.2	40.9	71.3
CH_3Cl	None	24.9	19.5	None
He^3	1.0	2.0	2.0	2.1
O_2	None	None	2.6	6.9
Total pressure, cm	77.2	69.1	65.0	80.3
Product[b]				
C_2H_3T	100	(102.6)	(100)	100
C_2H_5T	2.6			<0.01
C_3H_5T	0.35 ± 0.04	0.46 ± 0.02	0.39 ± 0.03	0.26
c-C_3H_5T	0.40 ± 0.04	0.43 ± 0.03	0.16 ± 0.03	0.04
$CH_2{=}C{=}CHT$	0	0		0.07
CH_2TCl	0	54 ± 0.1	4.9	0
c-C_3H_4TCl	...[a]	0	0	...[a]

[a] Not measured. [b] Relative yield (C_2H_3T = 100).

The excited recoil tritium species which might eliminate HCl in the dichloromethane system include both $CHTCl_2$* and CH_2TCl*, from which CTCl and CHT would be anticipated, respectively. Excited CH_2TCl* could also conceivably eliminate H_2, with the formation of CTCl, in analogy with the H_2 elimination reactions observed from recoil tritium activated hydrocarbons.[28,29] In all cases, isotopically alternate reactions would also be expected, involving the elimination of TCl or HT in roughly comparable yields. The presence of much larger quantities of TCl and HT from the direct abstraction reactions 2 and 4 precludes any observation of the carbene-forming reactions except through detection of labeled carbenes themselves.

Ethylene scavenger experiments have been carried out with both CH_2Cl_2 and CH_3Cl as the original reactant molecule. In the latter case, the formation of CH_2TCl* by T-for-H reaction has been assumed to be a reasonable approximation of the species CH_2TCl* formed by T-for-Cl reaction with CH_2Cl_2. The experiments were conducted both with and without O_2 as additional scavenger to observe the contribution of radical–radical combination reactions. The data are summarized for CH_2Cl_2 in Table IV and for CH_3Cl in Table V. For background comparisons, the results found with C_2H_4 alone, in the presence and absence of O_2, are included. The data of Table IV are normalized relative to the yield of $CHTCl_2$ as 100. The different samples of Table V are normalized to one another by expressing the yield of C_2H_3T as 100 in all cases. This intercomparison assumes that very little C_2H_3T is formed by processes sensitive to the presence or absence of O_2 scavenger.

Experiments with Molecular Oxygen as Scavenger. The results obtained from a series of experiments with O_2-scavenged CH_2Cl_2 are listed in Table VI. The observed distribution of radioactivity was judged as unusual in some of the early runs, suggesting incomplete scavenging by the amounts of O_2 ordinarily used, and the full set of experiments confirms this observation. One I_2-scavenged experiment from Table III is included for comparison.

The data listed for the sample containing equal amounts of CH_2Cl_2 and O_2 show as the only important radioactive species (other than labile T) the three products anticipated from eq 2, 3, and 5.[30] In each of the other systems, covering the usual range of O_2 scavenger concentrations, CH_3T was also present, and the yield ratio of HT/$CHTCl_2$ was not constant. Since the total pressure in the systems did not vary greatly (except for one sample), the fractional decomposition of $CHTCl_2$* has been assumed to be essentially

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(26) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(27) H. E. Winberg, *J. Org. Chem.*, **24**, 264 (1959).

(28) E. K. C. Lee, J. W. Root, and F. S. Rowland, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna, 1965, p 55.

(29) E. K. C. Lee, Y.-N. Tang, and F. S. Rowland, *J. Am. Chem. Soc.*, **86**, 5038 (1964).

(30) The sample containing 34.1 cm of O_2 obviously contains more than a "scavenger" concentration of O_2, and other effects on the hot atom reactions (*e.g.*, hot reaction with O_2, or moderator effects) could be anticipated. Experiments with other molecules, chiefly hydrocarbons, indicate that these other effects in such systems usually involve gradual quantitative changes and not the qualitative changes shown in Table VI.

Table VI. Variation of Yields with O_2 Concentration in Recoil Tritium Reactions with CH_2Cl_2

Gas pressure, cm							
CH_2Cl_2	34.8	36.0	34.1	32.4	31.4	36.2	29.7
He^3	2.3	1.9	1.5	1.5	1.5	1.9	2.6
O_2	0	Trace	0.4	2.0	3.6	34.1	I_2
Rel yield							
$CHTCl_2$	100	100	100	100	100	100	100
CH_2TCl	55 ± 1	51 ± 1	45 ± 1	39 ± 1	41 ± 1	43 ± 1	49 ± 1
HT	1040 ± 60	964 ± 11	741 ± 10	543 ± 7	511 ± 7	557 ± 6	608 ± 8
CH_3T	107 ± 6	98 ± 2	45 ± 1	2 ± 1	1 ± 1	0	2 ± 1
CH_2TOH	0	0	11 ± 1	19 ± 1	13 ± 1	6 ± 1	...
C_2H_4TCl	9 ± 1	2 ± 1	0	0	0	0	0

constant, and the variations in the $HT/CHTCl_2$ yield ratio have been attributed primarily to changes in the HT yield with scavenger concentration and identity. The increases in yield of CH_3T and HT with decreasing O_2 concentration therefore indicate incomplete scavenging of CH_2T radicals and T atoms, respectively. The source of CH_2T radicals is undoubtedly the unimolecular decomposition of CH_2TCl^* formed by the primary T-for-Cl reaction, as in eq 7. Since the bond dissociation energy of C–H bonds in CH_2Cl_2 is substantially less than in alkanes,[31,32] the further reaction of these radicals by abstraction of H from the parent molecule, as shown in eq 9, is certainly plausible.

$$CH_2T + CH_2Cl_2 \longrightarrow CH_3T + CHCl_2 \qquad (9)$$

In contrast to the high O_2 concentrations required to suppress the CH_3T and extra HT yields, the yield of C_2H_4TCl is quickly eliminated by small amounts of oxygen and fluctuates with the trace concentrations of O_2 in experiments carried out without the deliberate addition of O_2 in per cent quantities. The formation of C_2H_4TCl presumably involves the combination of two radicals, while both CH_3T and the surplus HT are formed by the attack of one radical upon the parent molecule.

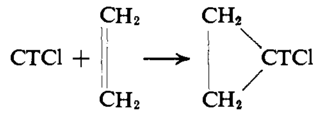
The formation of CH_2TOH is an indirect result of CH_2T reactions with the O_2 scavenger. The yields of CH_2TOH decrease to zero in the same scavenger range for which the CH_3T yields are increasing, supporting the postulate that each is formed by competing reactions of CH_2T.

Validity of HT Yield as an Intramolecular Standard in CH_2Cl_2 Reactions. Comparison of the HT yield observed from I_2- and O_2-scavenged samples in Table VI for approximately equal pressures of CH_2Cl_2 indicates that the agreement on $HT/CHTCl_2$ ratios is not quantitatively perfect. Consequently, the validity of the use of the HT yield as an intramolecular standard is open to question. The Br_2- and I_2-scavenged experiments of Tables II and III, however, are internally consistent, and we conclude that the additional yield of HT over that obtained with O_2-scavenged samples represents about the same fractional increase in all halogen samples.

Multiplication of the observed $CHTCl_2$/cyclobutane-*t* specific activity ratio in Table I by the $HT/CHTCl_2$ ratio found in pure CH_2Cl_2 at the same pressure (from Table II or III) provides a crude estimate of HT yield *vs.* the cyclobutane standard as about 2.0 ± 0.2; *i.e.*, per C–H bond in each, abstraction of H from CH_2Cl_2 is twice as probable as substitution for H in cyclobutane. The constancy of this value indicates that the abstraction of H from CH_2Cl_2 does not vary much with pressure or phase for equivalent scavenger concentrations (on a mole fraction basis).

Discussion

A. Decomposition Reactions and Carbene Formation. Identification of Monochlorocarbene-*t* from Decomposition of $CHTCl_2$. Radioactive cyclopropyl-*t* chloride, formed in reaction 10, was observed in every ethylene-scavenged CH_2Cl_2 sample in Table IV, in amounts corresponding to 20–30% of the parent yield in the same system. The identification of this product has been used as proof of the formation of CTCl by HCl elimination from CH_2Cl_2, as in reaction 6.[16] Since these yields are presumably accompanied by a comparable, but undetected, decomposition to CHCl and TCl, the elimination of hydrogen chloride is a major pathway for the unimolecular decomposition of excited $CHTCl_2^*$. The close analogies observed in other systems between the decomposition of recoil tritium activated molecules and the pyrolytic mechanisms of reaction[5–8] strongly indicate that the pyrolysis of CH_2Cl_2 also involves HCl elimination as a major mechanistic pathway.



(10)

The application of the spin conservation rule to reaction 6 suggests that CTCl should be formed initially in the singlet electronic state.[22] The observation that the yield of *c*-C_3H_4TCl is not very much affected by the O_2 concentration indicates that the addition reaction to ethylene involves just such a singlet reactant CTCl, since any triplet CTCl present should be sensitive to the O_2 concentration, either as the triplet CTCl itself, or in the diradical CTCl–CH_2–CH_2, expected after reaction with ethylene.[22,33]

The data of Table IV also indicate that the ratio of *c*-C_3H_4TCl to $CHTCl_2$ activity is not very sensitive to the composition of the CH_2Cl_2–C_2H_4 binary mixture. This observation implies that reaction 10 is quite effective relative to other possible reactions, including both abstraction and insertion reactions with the C–H bonds of CH_2Cl_2.[34] Since such yield data alone do not

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[31] P. Goldfinger and G. Martens, *Trans. Faraday Soc.*, 57, 2220 (1961).

[32] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, N. J., 1958.

[33] H. M. Frey, *J. Am. Chem. Soc.*, 82, 5947 (1960).

[34] Only the abstraction of H or Cl has been reported for CH_2 reacting with CH_2Cl_2; see D. W. Setser, R. Littrell, and J. C. Hassler, *ibid.*, 87, 2062 (1965).

furnish accurate estimates concerning low yields of such reactions, a direct search was carried out for insertion reactions with C_2H_4.

Unimolecular Decomposition of CH_2TCl^*. Absence of Carbenes. The decomposition of excited CH_2TCl^* by C–Cl bond breakage is already well established[6] and can account reasonably well for all of such molecules which do decompose under our particular conditions, as shown by the near-constant sum of yields for CH_2TCl and CH_2TBr in Table II. However, the competing reaction of elimination of HCl from the excited CH_2TCl^* is also energetically feasible; the heat of this reaction can be estimated as about 80 kcal/mole by using $\Delta H_f°$ for methylene as 86 ± 2 kcal/mole.[35] Nevertheless, the recoil tritium experiments in Table IV with CH_3Cl–C_2H_4 mixtures show essentially the same cyclopropane-*t* and propylene-*t* yields observed for C_2H_4 alone, and therefore give no indication of additional carbene formation in the decomposition of CH_2TCl^*. These negative results indicate that the molecular elimination mode of decomposition of excited CH_2TCl^* is of negligible importance in recoil tritium excitation, and presumable also in thermal pyrolysis.

Insertion of Monochlorocarbene into C–H Bonds. The insertion of singlet CTCl into the C–H bond of C_2H_4 would give $CHTClCH{=}CH_2$ as the final product. Previous investigators have reported the failure to observe C–H insertion products following the α elimination of HCl from CH_2Cl_2 by organolithium compounds, and attribute this to the intermediacy of dichloromethyllithium rather than the free monochlorocarbene in this reaction.[13,36] However, in experiments involving the liquid-phase photolytic or pyrolytic decomposition of chlorodiazomethane, Closs, *et al.*, have obtained comparable amounts of insertion into the C–H bonds of *n*-pentane and addition to the double bond of *cis*-butene-2 when the former was in 100-fold excess.[36] When calculated on a per bond basis, the relative reactivites are 12,000/20/1 for addition to the double bond/insertion into secondary C–H bonds/insertion into primary C–H bonds.

In the present recoil tritium experiments, the yields of $CHTClCH{=}CH_2$ are negligible, *i.e.*, less than 2% as large as the observed c-C_3H_4TCl yield. This reactivity ratio *per bond* of >200 favoring addition to the double bond *vs.* insertion indicates a qualitative similarity to the reactivity of monochlorocarbene from chlorodiazomethane decomposition, while the experimental accuracy is not sufficient for more quantitative comparisons of reactivity.

Stability of Cyclopropyl-*t* Chloride. The absence of $CHTClCH{=}CH_2$ as a product in the experiments with ethylene-scavenged CH_2Cl_2 not only furnishes information about the possibility of insertion reactions, but also indicates that the cyclopropyl-*t* chloride formed in these experiments does not readily isomerize to monochloropropylenes. Cyclopropane formed at comparable pressures by the addition of CH_2 to ethylene would isomerize to propylene at a rate competitive with deexcitation by collision, and an appreciable yield of such propylene would be found. For cyclopropane, the heat of reaction of the addition process (plus some vibrational energy in the usual photolytic methylene experiments) is sufficiently larger than the 65-kcal/mole activation energy to account for the high rate of isomerization. Since the activation energy for isomerization of cyclopropyl chloride is probably not very different from that of cyclopropane,[37] the conclusion readily follows that the sum of the heat of reaction and of the vibrational energy of CTCl in these experiments is less than about 85–90 kcal/mole. Cyclopropyl-*t* fluoride, formed by CTF addition to ethylene, is also stable toward isomerization.[23]

An alternative decomposition by elimination of HCl might also be postulated, leading to the formation of cyclopropene-*t*, with an activation energy in the range of 50 kcal/mole.[38] While cyclopropene-*t* itself would probably not have been detected in any of the radio gas chromatographic procedures because of its reactivity, no logical isomerization or decomposition products of cyclopropene-*t* were measured either.

If the elimination of hydrogen chloride from cyclopropyl-*t* chloride involved two atoms bonded to the same carbon atom (as in $CHTCl_2^*$ decomposition), TCl would always be eliminated and the companion cyclopropane would be unlabeled and undetected. Such a reaction has been reported for CHF addition to olefinic molecules such as $CH_2{=}CHF$.[39] However, our own experiments with CTF formed by recoil tritium reactions with CH_2F_2 indicate the formation of cyclopropyl-*t* fluoride in close analogy to these CH_2Cl_2 experiments[23] and suggest that a different intermediate is involved in the experiments of Gunning, *et al.*[39]

Formation of Monoradical Products. *n*-Propyl-*t* Chloride. The yield of n-C_3H_6TCl observed in CH_2Cl_2–C_2H_4 mixtures is substantial in the absence of oxygen as additional scavenger, but is almost completely suppressed by small amounts of added oxygen, indicating formation by a radical–radical combination reaction. The most likely tritiated precursor radicals are CHTCl and C_2H_4T, the latter from the addition of thermalized tritium atoms to ethylene; the required complementary radicals, C_2H_5 and CH_2Cl, are also likely radicals to be found in the system. The yields of *n*-propyl-*t* chloride shown in Table IV are quite insensitive to the amount of CH_2Cl_2 present in the system, and presumably include substantial contributions from C_2H_4T as the labeled precursor. Without intramolecular identification of the tritium activity, nothing of significance concerning CHTCl radicals can be obtained from the *n*-propyl-*t* chloride yields.

Collision Efficiencies for CH_2T Reactions. All of the lines of evidence suggest that the abstraction of H from dichloromethane by R radicals occurs quite rapidly, competitive with scavenging by O_2 or by ethylene and faster than radical–radical combination reactions. The abstraction of H by $\dot{C}H_2T$ is, however, suppressed by I_2 at its room-temperature vapor pressure (0.02 cm). If the reaction with I_2 is assigned a col-

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[35] H. M. Frey, *Progr. Reaction Kinetics*, **2**, 131 (1964).

[36] G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962); **87**, 4270 (1965).

[37] The activation energy for the isomerization of cyclopropyl fluoride is 61.0 ± 0.7 *vs.* 65.0 kcal/mole for the isomerization of cyclopropane; see F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3655 (1964).

[38] For example, the activation energy for the elimination of HCl from isopropyl chloride is 50.5 kcal/mole: S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 254–258.

[39] H. Gunning, *et al.*, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

lision efficiency of unity, then the collision efficiency of the abstraction reaction with CH_2Cl_2 is not larger than 5×10^{-4}. For comparable efficiency in prevention of the abstraction reaction, the pressure of O_2 must be approximately 10^2 higher, implying a collision efficiency for the removal of CH_2T radicals by reaction with O_2 of about 10^{-2} less than the collision efficiency of I_2. This value is in reasonable agreement with the measurement of the rate constant for removal of methyl radicals in reaction with O_2, which shows a third-order rate dependence in this pressure range.[40]

Comparison with Pyrolysis Experiments. The close analogies between the decomposition mechanisms for recoil tritium excited products and the pyrolytic decompositions of the corresponding nontritiated molecule have been pointed out for several other molecules.[5-8] However, in many cases, the mechanism of pyrolysis is sufficiently unclear that it is possible neither to confirm nor to deny mechanistic similarities between the two processes. The actual pyrolysis of a molecule of dichloromethane is rapidly followed by subsequent reactions of the branching chain variety, which account for most of the total decomposition in the system. Our radiochemical method of approach follows only the T atom formed in the original nuclear reaction. and a decomposition reaction is traced only through the fragment containing the radioactive atom. Under these conditions, the existence of a chain type of decomposition is immaterial once the chain has passed to a molecule which does not carry the radioactive atom, and the investigation will normally furnish information only about the first step of the decomposition process. The recoil tritium experiments have the further advantage that essentially all molecules except those actually activated by tritium substitution are still at room temperature, and hence quite unreactive compared to the molecules involved in high-temperature pyrolyses. One other advantageous consequence of this selectivity in excitation is that radioactive products can be detected readily, even though their activation energies for further reactions are lower than those of the recoil tritium excited species; in pyrolytic experiments, all products with lower activation energy for reaction quickly undergo these secondary reactions and are found in negligible over-all yields.

The identification of cyclopropyl-*t* chloride convincingly demonstrates that one important pathway for the decomposition of $CHTCl_2^*$ is through the formation of singlet CTCl, with the elimination of HCl. This unimolecular decomposition reaction is compatible with the pyrolytic experiments, since the bulk of all of the material decomposed in the latter could certainly still arise through a chain-reaction mechanism. The problem of possible alternate decomposition pathways is raised by the identification of CHTCl radicals in the system. While these could come from C–Cl bond breakage, they may also be the result of hydrogen-atom abstraction by CTCl, and no conclusive separation of the two possibilities seems available in our experiments.

Isotope Effects in the Elimination of HCl or TCl from $CHTCl_2^*$. If the relative yields for Br_2-scavenged experiments are compared through the data of Table II, the $CHTCl_2$ yield is observed to increase from gas to liquid phase from 15.4 to 28.8, an increase of 13.4 units while the CHTClBr yield falls from 16.2 to 10.7, a decrease of only 5.5 units. The discrepancy of 7.9 units between the parent increase and the product decrease is consistent with the stabilization in the condensed phase of excited $CHTCl_2^*$ molecules which would otherwise eliminate the unmeasured product of TCl, as in eq 11. The relative values for the elimination

$$CHTCl_2^* \longrightarrow CHCl + TCl \qquad (11)$$

of TCl (7.9) and of HCl (5.5) are comparable, while the errors involved in such an estimate are large enough that the apparent isotopic preference for elimination of TCl over HCl is probably not statistically significant. The data do not, however, suggest that the C–Cl bond breakage pathway is very important among the possible modes of decomposition of excited $CHTCl_2^*$.

B. Primary Reactions of Recoil Tritium Atoms. Pressure–Density and Phase Effects in Recoil Tritium Systems. The original gas-phase measurements on the CH_2Cl_2 system were carried out in connection with a general survey of the reactions of recoil tritium with a series of halocarbons, and showed yields of HT:$CHTCl_2$:CH_2TCl in the ratio 100:15 ± 2:9 ± 1. These measurements for the chlorocarbons are summarized in Table VII, expressed in absolute percentage yields.[10] The decreasing yields of the T-for-Cl and T-for-H reactions with increasing numbers of Cl substituents (together with similar observations of fluoromethanes) were the experimental basis for the "rotational inertia" hypothesis, which accounted for the lowered yields through a much reduced ability of radicals with heavy substituents, *e.g.*, F or Cl, to rotate rapidly enough to form a new bond in a hot tritium replacement reaction, *i.e.*, through rotational inertial restrictions on the substitution reactions.

Table VII[a]

	Reaction			Total yield of double substn products
	H abstn[b]	Substn for H[b]	Substn for Cl[b]	
Molecule				
CH_4	7.2	7.7	...	2.7
CH_3Cl	7.4	2.8	7.1	8.6
CH_2Cl_2	9.6	1.5	0.8	5.0
CCl_4	...	...	<0.05	...

[a] Reference 10. [b] % per C–H bond.

Any quantitative evaluation of the effects of various parameters upon the primary reactions of energetic tritium atoms must necessarily be based upon accurate estimates of the primary yields. Our experiments have been influenced in their design by our special interest in the unimolecular reactions of excited molecules formed in recoil tritium substitution reactions. Consequently, we have looked for evidence of such unimolecular decompositions in the yields of the products CH_2TCl and $CHTCl_2$, and have interpreted the small gas-phase variations and the larger gas-to-liquid changes in yields as pressure–density effects on the collisional stabilization of highly excited molecules. From this point of view, the present investigations clearly indicate that gas-phase measurements of the primary products

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(40) W. G. Sleppy and J. G. Calvert, *J. Am. Chem. Soc.*, **81**, 769 (1959).

alone lead to serious underestimates of the true primary yields for both the T-for-Cl and T-for-H reactions. Our best estimates of the primary yields are then sought from liquid-phase experiments, for which the secondary decomposition reactions have been greatly reduced by the more rapid deexcitation of excited primary products. However, since other experiments on the decomposition of molecules excited in recoil tritium reactions indicate that such secondary decompositions still proceed to some extent in condensed phases,[5-8] additional correction will usually still be necessary if the original primary yields are to be accurately estimated.

An alternate source of possible differences between recoil tritium reactions in gaseous and condensed phase systems has been suggested:[4] the possibility of a Franck–Rabinovitch cage effect, with condensed phase enhancement of the primary yield of a hot reaction. Such an effect could occur if the hot tritium atom, after undergoing a bond-rupturing collision with a molecule of the medium, were then held in the vicinity of a just-formed radical and subsequently reacted with it. Operationally, such a procedure is equivalent to the lengthening of the collision time and relaxation of any inertial restrictions upon reaction,[41] and the specific case of CH_2TCl from CH_2Cl_2 has even been suggested as a possible example of just such an effect.[4]

We have assumed that primary cage effects are of small or negligible importance in these recoil tritium systems for several experimental reasons. (a) One is the conclusive observation of the secondary decomposition reaction in several systems, in condensed phases, *e.g.*, $CH_3CHTCH{=}CH_2$ from T* + 2-hexene;[42] propylene-*t* through HCl elimination from CH_2TCHCl-CH_3*;[43,44] C_2H_3T from *c*-C_4H_7T*;[5] etc. We conclude that secondary decomposition in the liquid phase should be expected in many systems, and watched for in all. (b) Close comparison of the substitution of energetic T atoms for H in 2-hexene,[45] *n*-C_4H_{10},[46] etc., indicates very little change in yield between the gas-phase (1 atm) and liquid-phase experiments.

Estimates of Primary Yields. The uncertainties in the measurement of HT from CH_2Cl_2 are sufficiently great, tracing essentially to the weak C–H bond in the molecule, that a more appropriate standard of comparison for the hot yields is the T-for-H substitution reaction in cyclobutane. The two liquid-phase competition experiments indicate 0.70 ± 0.02 for the specific activity ratio, *per bond*, of T for H in the CH_2Cl_2 *vs.* this standard. The cyclobutane system is relatively straightforward, however, for the only major decomposition product of *c*-C_4H_7T* is C_2H_3T, and its yield in the liquid phase has been measured and included in the standard.[5] The corresponding decomposition of $CHTCl_2$* has been shown to lead frequently to CTCl and HCl, or, by inference, CHCl and TCl, and no measurement can be readily made of the latter path. If the CHTClBr yield in Br_2-scavenged liquid phase CH_2Cl_2 is assumed to arise chiefly from the decomposition of $CHTCl_2$, then the yield of 28.8 ± 1.5 listed in Table II for $CHTCl_2$* should be increased by at least 10.7. If the CHTCl radicals arise from C–Cl bond break, the value 10.7 would be an accurate correction; if CHTCl arises from abstraction reactions of CTCl, as seems quite likely, then the corresponding yield of CHCl + TCl would not be recorded through a measured radioactive product, and the 10.7 yield should be supplemented by an appropriate correction for this decomposition path, an additional 10.7 if a negligible isotope effect is assumed for the decomposition to hydrogen chloride and monohalocarbene.

Since our experiments do not provide the experimental information necessary to choose among these possibilities, our best estimate of the original primary yield of $CHTCl_2$ is an uncertain intermediate choice: $28.8 + 10.7 + 11 = 51 \pm 5$ relative to HT in Table II, or 0.94 ± 0.10 relative to the cyclobutane standard. An estimate of the yield of T for Cl can be obtained by adding the CH_2TBr yield (3.0 in Table II) to the observed CH_2TCl yield (22.3) to give a value of 25 ± 2 relative to HT, or 0.47 ± 0.04 relative to the cyclobutane standard.

These estimates of the primary yields of T-for-X and T-for-H reactions in CH_2Cl_2 are three and three and one-half times as large, respectively, as the previous estimates based on gas-phase experiments only.[10] The very sharp decline in the gas-phase yields of the T-for-X reaction from CH_3Cl to CH_2Cl_2 may thus be traced largely to the relative stability toward secondary decomposition of the CH_3T from the former to the CH_2TCl from the latter, rather than to variations in the probability of the primary substitution process itself.

The possible additional influence of factors such as rotational inertia upon the primary yields thus requires much more accurate measurements than anticipated on the basis of gas-phase comparisons. The relative value of 0.47 ± 0.04 for T for Cl in CH_2Cl_2 is definitely less than the corresponding value of 0.95 ± 0.04 per C–Cl bond for the same reaction in CH_3Cl,[6] and confirms that the primary substitution of energetic tritium for chlorine does occur more readily in the less halogenated molecule. Such an observation could be the result of the increased rotational inertia of CH_2Cl *vs.* CH_3, or of the electronegativity of the Cl atom, and cannot be distinguished on the basis of measurements on the two compounds alone.[19,47]

The measurement of the relativity probability of the T-for-H reaction in various molecules also shows very much less variation than originally postulated on the basis of gas-phase experiments alone. Measurements of the per bond yields from a number of molecules in solution in methyl chloride indicate that the probabilities of substitution vary at most by factors of approximately 2 over a wide variety of molecules, and differences of only 10–30% are common.[47] The large errors inherent in the measurement of the yields from T-for-H reactions in CH_2Cl_2, as reflected in the value of 0.94 ± 0.10, make detailed comparisons of lesser value for this particular molecule.

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(41) Another kind of cage effect might also arise if the products of the unimolecular decomposition of an already-formed primary species were held in close proximity to one another and re-formed the original species; *e.g.*, $CH_2TCl \rightleftharpoons CH_2T + Cl$. Molecules formed by such back-reactions would be quite properly counted as primary hot products in the experimental assay of the system.

(42) E. K. C. Lee and F. S. Rowland, *J. Chem. Phys.*, **36**, 1954 (1962).

(43) E. K. C. Lee, Y.-N. Tang, and F. S. Rowland, *J. Am. Chem. Soc.*, **86**, 5038 (1964).

(44) Y.-N. Tang and F. S. Rowland, *J. Phys. Chem.*, in press.

(45) E. K. C. Lee and F. S. Rowland, *ibid.*, **84**, 1085 (1962).

(46) R. Koob, J. Root, and F. S. Rowland, unpublished results.

(47) Y.-N. Tang and F. S. Rowland, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

Decomposition of CH_2TCl^* Formed in Dichloromethane. The excitation energy of labeled molecules formed by recoil tritium substitution reactions comes primarily from the difference in kinetic energy between the reacting tritium atom and the displaced atom (H or Cl from dichloromethane). Since the substitution of T for Cl is approximately 1 ev exothermic, this energy should appear as excitation energy of the product molecule, together with any kinetic energy difference between the reacting T atom and the Cl atom replaced by it. Experiments with methyl fluoride have indicated that the energies of tritium atoms prior to substitution for H and for F are approximately equal;[48] no evidence exists concerning the kinetic energy of the displaced atoms in any recoil tritium system, although the assumption is often tacitly made that these atoms are in the thermal-to-1-ev region. The percentage decomposition of CH_2TCl^* after T-for-Cl and T-for-H reactions seems to indicate additional excitation energy in the former, for which about two-thirds of the molecules decompose as compared to only one-half of the latter at the same pressure (0.5 atm).

[48] E. K. C. Lee, G. Miller, and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 190 (1965).

Vibrationally Excited 1,2-Dichloroethane Produced by the Mercury Photosensitization of Dichloromethane[1]

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Abstract: The mercury photosensitization of dichloromethane has been examined as a prototype method for generating chemically activated alkyl halide molecules. It is shown that if the chlorine atoms are removed from the reaction system by a suitable scavenger, then the measured nonequilibrium unimolecular rate constant for HCl elimination from the chemically activated 1,2-dichloroethane formed by association of chloromethyl radicals agrees well with previously determined values. Some discussion of the reactions between the various chlorine-substituted alkyl radicals that may occur in the propene-inhibited system is presented. The chemically activated 1,3-dichloro-2-methylpropane formed by association of chloromethyl and 1-chloroisopropyl radicals does not undergo unimolecular reaction down to pressures of 2 mm. Calculated estimates for the HCl elimination rate constant from 1,3-dichloro-2-methylpropane support this observation; similar calculations were also done for *n*-chloropropane.

The gas-phase kinetics of chemically activated chloroethanes produced by the combination reactions of methyl- and chlorine-substituted methyl radicals have recently been reported[3,4] from this laboratory. Such chemically activated molecules possess ~90 kcal $mole^{-1}$ of vibrational energy and lose HCl by unimolecular reaction unless the excess energy is removed by collisions.[5] For reasonably efficient deactivating bath gases, such as CH_3Cl, one-half of the vibrationally excited molecules were stabilized at the following pressures: C_2H_5Cl, 35 cm; 1,2-$C_2H_4Cl_2$, 1.8 cm; 1,1-$C_2H_4Cl_2$, 110 cm; and 1,1,2-$C_2H_3Cl_3$, 2.2 cm. The H and Cl abstraction reactions by CH_2 from CH_3Cl and CH_2Cl_2 were used to produce the methyl and chloromethyl radicals.[3] On the basis of the work just mentioned, chemically activated chloroethanes would be expected in systems containing the appropriate radical precursors, *i.e.*, methyl and chlorine-substituted methyl radicals.[6] Systems that certainly should show evidence of these hot molecules and their subsequent reactions are the mercury photosensitization of various chloromethanes, especially CH_2Cl_2. In this paper data are presented which demonstrate that the chemically activated 1,2-$C_2H_4Cl_2$ generated *via* the mercury photosensitization of CH_2Cl_2 has the same kinetic behavior as the chemically activated 1,2-$C_2H_4Cl_2$ from the CH_2 + CH_3Cl or CH_2Cl_2 reaction systems.[3,4]

The primary processes in the mercury photosensitization of CH_3Cl have recently been measured.[7]

$$CH_3Cl + Hg(^3P_1) \longrightarrow CH_3 + Hg + Cl = 71\% \qquad (1a)$$

$$\longrightarrow CH_3 + HgCl = 29\% \qquad (1b)$$

The quenching cross section[8] is large (22 Å^2), and the over-all quantum yield is unity. These processes are followed by secondary radical reactions; fast hydrogen abstraction from CH_3Cl by chlorine atoms which gives CH_2Cl radicals is of particular importance. Gunning and co-workers[7-9] were mainly interested in the quenching reactions and apparently made no real ef-

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[1] Part of this work was presented at the Midwestern Regional American Chemical Society Meeting, Lawrence, Kan., Oct 1966.

[2] Alfred P. Sloan Foundation Fellow

[3] D. W. Setser, R. Littrell, and J. C. Hassler, *J. Am. Chem. Soc.*, **87**, 2062 (1965).

[4] (a) J. C. Hassler, D. W. Setser, and R. L. Johnson, *J. Chem. Phys.*, **45**, 3231 (1966); (b) J. C. Hassler and D. W. Setser, *ibid.*, **45**, 3237 (1966); (c) *ibid.*, **45**, 3246 (1966).

[5] J. D. Hassler and D. W. Setser, *J. Phys. Chem.*, **71**, 1364 (1967).

[6] The importance of vibrationally excited molecules in the photolysis of CH_2Cl_2 (M. H. J. Wijnen, Sixth Informal Photochemistry Conference, University of California, Davis, Calif.; 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965) has been discussed; S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1967); see also ref 3.

[7] J. K. S. Wan, O. P. Strausz, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, **42**, 2056 (1964).

[8] H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 243 (1963).

[9] K. R. Osborn and H. E. Gunning, *Can. J. Chem.*, **37**, 1315 (1959).