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Reactions of Radioactive Recoil Atoms with (Halo)methanes

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Contents

G. A. Brinkman, born in 1933, is a senior researcher within the Chemistry Department of the National Institute of Nuclear Physics and High-Energy Physics, NIKHEF, section K, in Amsterdam. He joined the department as a student in 1955 and received his Ph.D. degree in 1961 with a thesis on the absolute standardization of radioisotopes with liquid scintillators. He later investigated the reactions of energetic radioactive recoil atoms—Mu, T, ^{11}C, ^{18}F, $^{34m,38}Cl$, ^{38}S, and $^{76,77}Br$—with arenes, chloroethylenes, and halomethanes. His interest is now focused on research at the Low Energy Chemistry Facility (LECH) of the 500 MeV electron accelerator MEA in Amsterdam (hot atom chemistry with ^{11}C, ^{18}F, and $^{34m,38,39}Cl$, radiation chemistry, isotope production, and dosimetry) and at the π–μ facility (μ^-, π^- capture in chemical compounds and muonium chemistry).

I. Introduction

This article is mainly dealing with the reactions of monovalent (T, Mu, halogen) recoil atoms with halomethanes. The most important reactions of atoms that possess an excess of kinetic energy (hot atoms) with methanes are the abstraction and the substitution of atoms. The kinetic energy of the hot atom is often great enough to displace more than one atom. Recoil ^{18}F atoms are able to displace all the four F atoms in gaseous CF_4. The formation of $C_2Cl_3{}^{34m}Cl$ from ^{34m}Cl recoiling in liquid CCl_4 requires the displacement of five Cl atoms in two CCl_4 molecules. Recoil T, F, and Cl particles react chemically as neutral atoms. The recoil chemistry of Br and I is far more complex, as reactions of atoms and ions, both in ground state and in electronically excited states, are often involved. Investigations with T and F are in general performed in gaseous systems, whereas more liquid-phase experiments are reported for Cl, Br, and I, as most of these halomethanes are liquids. The formation of labeled products in the liquid phase is quite often explained as being the result of reactions in an excited solvent cage, created by the recoil particle at the end of its track. Reactions between the recoil particle and radicals or excited molecules can take place before diffusion from the cage occurs. Many experiments have been performed with the aim of gaining more information about this type of reaction. Despite all that research, the theory of cage reactions suffers at the moment from a lack of substantiation of the mechanisms involved. In the main, the reactions of Mu are also studied with liquids. This is due to the fact that μ^+ particles are created with very high kinetic energies (~40 MeV). The stopping range of these ions in organic liquids is in the order of 2 cm

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fwhm, and this means that bulky samples (25 mL) are required. To investigate gaseous samples, the use of very large targets—that must also fit between the poles of a magnet—is desirable. The recent development of "surface" beams of μ^+ with kinetic energies of 4 MeV has resulted in the first gas-phase experiments with chloromethanes.

High-energy accelerators are essential for the production of several polyvalent recoil atoms (^{11}C, ^{13}N, ^{15}O). This is one of the reasons that the study of the reactions of these isotopes with halomethanes has received so little attention. Furthermore, the reactions of these atoms are far more complicated than those of hydrogen and halogen atoms, viz:

(1) The polyvalent atoms can react as ground-state atoms, but also as atoms in the first electronically excited state.

(2) H abstraction can result in the formation of reactive radicals, such as ^{11}CH, $^{11}CH_2$, and $^{11}CH_3$ in the case of recoil ^{11}C atoms. (Halogen abstraction is another possible reaction channel.)

(3) Insertion of bare atoms into C–H bonds quite often leads to very highly excited products that may easily decompose.

In order to attempt to bridge the gap between recoil chemistry and other branches of chemical research involving the reactions of bare atoms, information regarding nonradioactive atoms (in general the measurements of rate constants for abstraction of H and halogen atoms) is also included in this article. In the chapter dealing with tritium the reactions of energetic H and T atoms produced by photolysis will also be discussed.

Several reviews have been published on hot-atom chemistry,[1-4] while others have dealt with the reactions of radioactive recoil atoms with arenes and (halo)ethylenes,[5,6] respectively.

II. Tritium

Some 20 publications have dealt with the measurements of rate constants for the reactions of H atoms with CH_4. It is generally agreed that the mechanism of this reaction is the abstraction of an H atom.[7] From all the data collected in ref 7 and 8, the averaged values of A and ΔE from the Arrhenius equation can be calculated as $\log A$ (L mol^{-1} s^{-1}) = 10.2 ± 0.3 and ΔE = (41.6 ± 2.5) kJ mol^{-1}. From a critical review of available data, Sepherad et al.[9] calculated in 1979: $\log A = 10.88 \pm 0.06$ and $\Delta E = 49.9 \pm 0.8$. Most of the data were measured at temperatures between 400 and 700 K. An extrapolation to room temperature results in a rate constant of $k_{298} = 1.3 \times 10^3$ L mol^{-1} s^{-1}. Other data for the abstraction of H or halogen atoms from halomethanes are given in Table I.

For several halomethanes, Clark and Tedder[11] measured relative rates for the abstraction of Cl atoms by H atoms, that were generated in a Woods tube: $CDCl_2$–Cl, 1.0; $CFCl_2$–Cl, 2.0; CCl_3–Cl, 1.3; $CBrCl_2$–Cl, 1.0. They also measured relative rates for the abstraction of H, D, F, Cl, and Br atoms from a same molecule: $CHCl_2Br$, H/Cl = 3.4; $CDCl_3$, D/Cl = 3.3; $CFCl_3$, F/Cl = 0.21; $CHCl_2Br$, Br/Cl = 1.6; CCl_3Br, Br/Cl = 1.5.

TABLE I.[8] **Arrhenius Parameters for the Reactions of H Atoms with Halocarbons**

compd	A, 10^{10} L mol^{-1} s^{-1}	ΔE, kJ mol^{-1}	temp, K
H abstraction			
CH_2F_2	1.3	39.3	875–953
CHF_3	0.50	20.9	1105–1284
	0.32	46.9	350–600
F abstraction			
CH_3F	6.3	34.3	858–1088
	1.8	39.3	605–871
	6.3	21.8	298–652[a]
CF_4	70.8	182.8	1323–1523
	110	186.6	1173–1573
Cl abstraction			
CH_3Cl	9.5	31.9	870–1088
	3.7	38.9	510–998
	6.2	19.2	298–652[a]
CH_2Cl_2	1.1	25.5	298–460
$CFCl_3$	1.7	36.8	538–676
Br abstraction			
CH_3Br	5.4	18.0	297–480
	11.0	19.4	297–1088
	2.8	22.2	298–996
	1.3	15.5	298–650[a]
CF_3Br	436	73.0	1005–1284
I abstraction			
CH_3I	39	0	667–838

$k_{293} = 0.24 \times 10^{10}$ L mol^{-1} s^{-1}
$k_{293} = 0.59 \times 10^{10}$ L mol^{-1} s^{-1}

[a] Reference 10.

Martin and Willard[12] investigated reactions of hot (3 eV) H and D atoms that were produced by the photolysis of HBr and DBr: 6.2% of such H atoms react as hot atoms with CD_4 and 17% of the D atoms with CH_4. The latter value is not in conflict with a hot fraction of 5.7%, measured in CH_4 for the reactions of a mixture of 1.8- and 0.9-eV D atoms that were produced by the photolysis of DI.[13] Oldershaw et al.[14] studied the reactions of 1.1-eV H atoms—produced by the photolysis of HI—with CH_3Cl and CH_3Br. The ratio (X abstraction + X substitution)/(H + X abstraction + H + X substitution) was found to be 0.056 for CH_3Cl and 0.27 for CH_3Br. By varying the photolysis wavelength, Gould et al.[15] determined the threshold energy for Cl abstraction from CH_3Cl as (47 ± 14) kJ mol^{-1}.[15] This value is in close accord with activation energies of 38.9[16] and 31.9 kJ mol^{-1},[17] but not with a value of 19.2 kJ mol^{-1} (Table I).

Chou and Rowland[18-21] observed the reactions of hot (2.8 eV) T atoms—produced by the photolysis of TBr—with isotopic methanes, CH_4D_{4-n}. Experiments with Br_2 scavenged CH_4 showed a HT/CH_3T ratio of about 3.8. This value is much higher than that measured for more energetic T atoms, and agrees with a higher threshold energy for H substitution than for H abstraction.[20] Isotope effects were observed for the abstraction of an H or D atom in CH_4/CD_4 mixtures, as the ratio H/D abstraction is (1.7 ± 0.1).[21] The replacement of D atoms in CD_4 by F atoms has also an effect on the yield of D abstraction: the relative DT yields per C–D bond are 1.0:2.7:1.7 for CD_4:CD_3F:CDF_3. This sequence is in agreement with the theory that the lower the C–D bond energies, the lower the threshold energies for abstraction, and conversely, the higher the yields.[22] The relative ratio of H vs. D abstraction in CH_4, CH_3D, CH_2D_2, and CD_4—as measured with 2.8 eV T atoms—is (7.2 ± 0.2), (5.6 ± 0.3), (3.1 ± 0.3), and (1.0), respectively, or an average of (1.6 ± 0.2) per bond. This value contradicts the earlier tenet of hard-sphere atom–atom collisions (billiard-ball theory),[21] as in that case a value lower than 1 would be expected. The T-for-H vs. D-substitution ratio per bond is (1.06 ± 0.1) in CH_2D_2 and (1.2 ± 0.3) in CHD_3. These values, together with the above-mentioned results, are consistent with a primary isotope effect of (1.6 ± 0.2), favoring the substitution of H over D:

$$T^* + (CHX_3 \text{ or } CDX_3) \rightarrow CTX_3 + (H \text{ or } D)$$

and also with a secondary isotope effect of (1.6 ± 0.2), favoring substitution within a methyl group that contains more H atoms:

$$T^* + (CHX_3 \text{ or } CDX_3) \rightarrow CHTX_2 \text{ or } CDTX_2$$

By changing the wavelength for the photolysis of TBr, the energy of the T atoms could be varied between 1.1 and 6.0 eV. This type of experiment permits the determination of threshold energies, of which the following were measured for substitution reactions:[19,23,24] T-for-H in CH_3F, 1.8 eV, in CHF_3, (1.9 ± 0.2) eV; T-for-F in CH_3F, 1.3 eV, in CHF_3, (1.9 ± 0.3) eV; T-for-D in CD_4, 1.5 eV.

The lower threshold for F than for H substitution in CH_3F, and the T-for-H/T-for-F substitution ratio of about 0.2 (per bond) agrees with Walden inversion in the case of T-for-F substitution. This inversion is facilitated by the mobility of the three light H atoms.[23] In the case of CHF_3, the threshold energies for H and for F substitution are the same, and the T-for-H/T-for-F substitution ratio of about 20 (per bond) is much higher than for CH_3F.[24] These results indicate the absence of an inversion mechanism during F substitution in CHF_3, which is understandable in terms of adjusting two heavy F atoms to change their configuration.

A special type of reaction of tritium is the self-induced exchange of T_2 gas with CH_4.[25,26] The decay of T ($T \rightarrow {}^3He^+ + \beta^- + \bar{\nu}$) in $T_2 + CH_4$ mixtures gives rise to two effects:

(1) Primary formation of HeT^+. Although this molecule ion has a short lifetime, it will react with CH_4, yielding excited CH_4T^+:

$$HeT^+ + CH_4 \rightarrow [CH_4T^+]^\ddagger + He \quad (\Delta E = -326 \text{ kJ mol}^{-1})$$

Subsequent reactions of this ion with CH_4 can lead to the formation of CH_3T, C_2H_5T, and higher alkanes.

(2) The β^- radiation causes ionization of CH_4. The CH_4 ions can react with T_2 yielding CH_4T^+. Proton transfer can than produce CH_3T:

$$CH_4T^+ + CH_4 \rightarrow CH_3T + CH_5^+$$

A. Reactions with Methane

Reactions of recoil T atoms were reviewed in 1978 by Tang.[27] Thermal T atoms can only abstract an H atom from CH_4, but energetic atoms can substitute one or more atoms. In Br_2 scavenged gaseous CH_4, relative yields of HT, CH_3T, and CH_2TBr are 79:100:20.[27]

The first study on the reactions of recoil T atoms with CH_4 were performed by Wolfgang, Eigner, and Rowland[28] in 1956 with solid CH_4 and a slurry of a Li salt. The separation of labeled products was carried out by distillation techniques. The main products were HT and CH_3T, with minor amounts of higher alkanes. The first gas-phase experiments—using ^3He as the source of tritons—were performed by Gordus et al. in 1957.[29] The same products as mentioned above for the solid phase were found. It was suggested[28,30] that the higher hydrocarbons were formed through reactions of T^+ ions. The kinetic energy that the recoil tritons receive after the nuclear reaction is so high, that at the beginning of the decelerating process, the tritons are in the form of T^+ ions. At an energy of about 75 keV, the electron capture cross section of T^+ equals the ionization cross section of T, and at lower energies most or all of the tritons will be in a neutral state.[31,32] That they react as T atoms to form CH_3T is also proven by the observation that this yield is not affected by the presence of I_2 as an ion scavenger.[33] Furthermore, the CH_3T yield in moderated systems is found to decrease for the series Xe, Ar, Ne, He. The opposite effect would be expected for ionic reactions.[33] However, if He is used as a moderator, part of the recoil tritons may reach the chemical reactive zone as ions.[34] Experiments with H_2 and CH_4 moderated with He and Ar[35] and those with Br_2/C_2H_6 mixtures moderated with He,[36] prove that no T^+ ions are involved in the final product formation.

When CH_4 was irradiated at a neutron flux of 2×10^9 n cm^{-2} s^{-1} rather than of 5×10^{12}, the yield of HT was increased from 51% to 62%, and that of higher hydrocarbons dropped from 18 to 8%.[31,32,37] No appreciable changes in the product spectrum occurred when—at equal total dose—the dose rate was varied by a factor of 10, but similar effects as mentioned above were found as the amount of ^3He was diminished.[38] No explanation was given for these results.

Hot reactions are insensitive to changes in temperature and to the presence of scavengers, but the yields are dependent upon the amounts of inert additives (moderators).

(1) In unscavenged CH_4, the HT/CH_3T ratio was expected to increase at higher temperatures, as the thermal H abstraction reaction has a large temperature coefficient. However, such an effect was not found by raising the temperature from 295 to 473 K.[31,32]

(2) Addition of Br_2 and I_2 decreases the HT/CH_3T ratio from about 1.5 to 0.8.[29,31,32,37,39] ICl and IBr have the same effect as Br_2 and I_2.[40] Addition of C_2H_4 also decreases the HT/CH_3T ratio, but large amounts of C_3H_7T and C_4H_9T are generated. The butane is formed from the reactions between C_2H_4T radicals and C_2H_4.[38]

(3) The yields of HT and of CH_3T become negligible in Br_2 scavenged and highly moderated (99 mol % ^4He) CH_4.[31,32] The effect of moderators on the yield of hot reactions is more systematically studied by the addition of several noble gases.[33] The moderator efficiency is in the sequence of He > Ne > Ar > Xe, as was expected, since the extent of transfer of kinetic energy in a single collision decreases in this order.

The mechanisms of abstraction and substitution reactions have been discussed for several years. To answer the questions raised, many experiments with varied types of hydrogenated and deuterated hydrocarbons are conducted. Several reviews have been published[3,27,41] and only some remarks pertaining to experiments with CH_4 will be discussed here.

H Abstraction. In scavenged CH_4, the HT/CH_3T ratio is 0.79. The HT/RT ratio increases for larger molecules: viz., 2.4 for n-C_5H_{12}. Originally, it was thought that this effect was due to a decrease in the RT yield, and was attributed by Wolfgang et al. to the application of the "steric model".[39,43] In this model, abstraction was thought to proceed within a narrow cone along the C–H axis, and therefore, the HT yield per C–H bond would not be affected by the steric hindrance of larger atoms or groups. However, experiments in excess of C_2D_4, c-C_4F_6, and 1,3-C_4F_6—providing equal T energy distribution, and preventing both thermal H abstraction from the substrate and HT production from these additives—proved that the HT yield increases upon decreasing the C–H bond energies.[44-47] (The HT yield measured for $CH_3CD{=}CD_2$ was not in accordance with this correlation and it led to the conclusion that H abstraction by recoil T atoms takes place within 2–5 × 10^{-14} s.[48]) The observed relation between the HT yields and the C–H bond energies was explained by the "energy cut-off model",[46,47] in which it was assumed that (1) the threshold energy for abstraction decreases at decreasing bond energy, and (2) at a given energy, the cross section for abstraction is higher for lower bond energies.

This correlation between HT yields and bond energy was confirmed by classical trajectory calculations with a series of hydrocarbons.[49,50] By changing the bond dissociation energy, bond length, and mass, only the bond dissociation energy has a significant effect on the abstraction efficiency. Altering the barrier height for the abstraction reaction has a pronounced effect on the cross section, whereas changing the exoergicity has barely any influence. Even at higher energies of the T atoms, there may be a preference for H abstraction at lower C–H bond energies. The "stripping model" of Wolfgang[51-53] assumes that only a small fraction of the energy of the fast moving T atom is available to strip an H atom from the molecule.

H Substitution. Most of the comprehension of the mechanisms and energetics of T-for-H substitution reactions has been obtained by experiments with halomethanes: this subject will be discussed in more detail in the chapters on photolysis, halomethanes, and isotope effects. The threshold energy for the substitution reaction is about 1.5 eV.[55] Between 10 and 300 kPa of CH_4 pressure, there is almost no variation in the HT/CH_3T ratio, indicating that there is a broad spectrum—up to 5 eV—of excitation energies in the CH_3T^* molecules.[56] The double (CH_2TBr)/single (CH_3T) displacement ratio in Br_2 scavenged CH_4 hardly varies in the 10–300 kPa pressure range. However, this observation does not demonstrate if double H displacement is a single-step reaction or if it proceeds through H elimination from an excited CH_3T^* molecule.

Theory and Calculations. The distribution of labeled products originating from hot reactions has been described by the Estrup–Wolfgang theory.[57,58] For a mixture consisting of a single reactant (CH_4) and an inert moderator (rare gas), the total probability of reaction is given by

$$P = 1 - e^{-fI/\alpha}$$

in which

$$f = \frac{X_{\text{react}}S_{\text{react}}}{X_{\text{react}}S_{\text{react}} + X_{\text{mod}}S_{\text{mod}}}$$

where X and S refer to mole fractions and collision cross sections, respectively. α is the weighted sum of the average logarithmic energy loss on collision (=–ln (E(after collision)/E(before collision)) with reactant and moderator:

$$\alpha = f\alpha_{\text{react}} + (1 - f)\alpha_{\text{mod}}$$

and I is the reaction integral (the area under the excitation curve) plotted on a logarithmic energy scale:

$$I = \int_{E_1}^{E_2} \frac{p(E)}{E}\,\mathrm{d}E$$

From a combination of the above equations, a convenient relation can be derived:

$$-\frac{1}{\ln(1-P)} = \frac{\alpha_{\text{react}}}{I} + \frac{\alpha_{\text{mod}}}{I}\,\frac{1-f}{f}$$

From the straight line that can be obtained from a plot of $1/\ln(1-P)$ vs. $(1-f)/f$, α_{react} and I can be derived in units of α_{mod}. Partial reaction integrals—I_i—can be determined through the relationship

$$P_i = \frac{f}{\alpha} - \frac{f^2}{\alpha^2}K_i\ldots\ldots$$

(K_i and higher terms correct I_i by taking into account the probability that the hot atom has already reacted above energy E). A plot of $(\alpha/f)P_i$ vs. f/α gives the individual I_i values. Expressed in units of α_{He}, the derived values for the T + CH_4 system are

$$\alpha_{CH_4} = 2.8 \quad I = 1.74$$

$$I_{HT} = 0.83 \quad I_{CH_3T} = 0.62 \quad I_{CH_2T} = 0.16$$

The Estrup–Wolfgang theory has been discussed in detail.[41,59-62] Deviations observed in the application of this theory could be accounted for if α—and the $\alpha_{\text{react}}/\alpha_{\text{mod}}$ ratio—are not constants, but vary with energy.[63,64] A serious failure of the theory is that it does not consider the possibility of the decomposition of excited products. For CH_3T^*, this process will, in the main, result in the formation of CH_2T, which is detected as CH_2TBr or C_2HTI in scavenged systems. Decomposition of excited HT* is more difficult to detect experimentally. Computer simulations of the reactions of energetic T atoms with hydrocarbons predict the presence of large amounts of translationally excited HT molecules.[65-67] In collisions with rare-gas atoms, this translational energy is converted into vibrational energy, most effectively by Xe and least effectively by He. The collisional deexcitation of DT (formed from CD_4) is expected to be somewhat less effective than that of HT (from CH_4). Using He as a moderator in CH_4/CD_4 mixtures, no change in the HT/DT ratio at higher He concentrations is observed. However, with Ne as a moderator, this ratio increases from 1.05 to 1.25 in the range of 0–100 mol % of Ne.[68] The energetics of the collision processes are not fully understood, particularly as the energy of the recoil atom decreases toward chemical bond energies. If energy loss on collision is described as a simple elastic collision with a single outer atom of a molecule or with the entire molecule, then D_2 would be a more effective moderator for recoil T atoms than CH_4, but the reverse effect was found.[69] This means that in a collision with a CH_4 molecule much more energy must be transferred than can be expected on the basis of an elastic collision only.

As was shown by trajectory calculations, T-for-H substitution in CH_4 may proceed by the Walden inversion.[70] A three-atom model for the T–CH_4 reactions led to the following conclusions:[71]

(1) Abstraction and substitution are direct and concerted (as opposed to complex and sequential) reactions.

(2) Substitution is favored at intermediate energies (4–6 eV).

(3) Abstraction is favored at higher energies (>7 eV), due to stripping.

(4) Double displacement competes with abstraction above 7 eV.

(5) Translational energy in the products accounts for the largest proportion of the collision energy.

A six-particle classical trajectory study basically agrees with the above conclusions, and yields additional information:[72–75]

(6) Substitution involves strong interactions between at least 4 atoms.

(7) No inertial isotope effects were found when CH_4 was replaced by CD_4.

The calculated abstraction/substitution ratios for CH_4 agree very well with experimental (photolytical and recoil) data.[76]

B. Reactions with Halomethanes

The first investigation of the reactions of recoil T atoms with halomethanes (CH_4X_{4-n}) were performed by Odum and Wolfgang.[77,78] Apart from abstraction and substitution of H atoms, the substitution of an X atom and of two atoms (HX, X_2) were also found to be important reaction channels. H abstraction from fluoro-, chloro- and bromomethanes accounts, on the average, for about 8% per C–H bond. In a 14-fold excess of c-C_4F_6, Tachikawa et al.[79] found a decrease in the yield of HT (per C–H bond) if more Cl or Br atoms were present in the target molecule. This effect was explained by progressive weakening of the C–H bonds with additional X substituents. In the case of multiple F substitution, the C–H bonds are strengthened by polar effects and the HT yields per C–H bond are greatest for CH_2F_2.

In the case of H substitution, the yield per C–H bond decreases as the number of X substituents is increased. This effect was ascribed to steric obstruction by the halogen atoms. A very sharp drop observed in the yield of T-for-X substitution, when the number of X substituents was increased, was explained by Odum and Wolfgang[77,78] by inertial effects. They postulated that substitution reactions by hot H atoms, requiring the motion of heavy atoms or groups bound to the C atom, tend to be inhibited. However, after applications of corrections for secondary decomposition of excited products, the initial T-for-H and T-for-X reaction yields become much higher. From these corrected results, Rowland et al. concluded that T-for-H substitution in CH_3X decreases smoothly with increasing electronegativity of X[80–83] (Figure 1). There also seemed to be a trend that the T-for-H substitution yields increase linearly with an increase in the energy of the weakest bond in the molecule.[84] This correlation was ascribed to the decomposition of molecules containing weak C–X bonds. The corrected yields for the T-for-X substitution reactions increase from X = Cl to X = I, which was also related to a decrease in the C–X bond energy.[83]

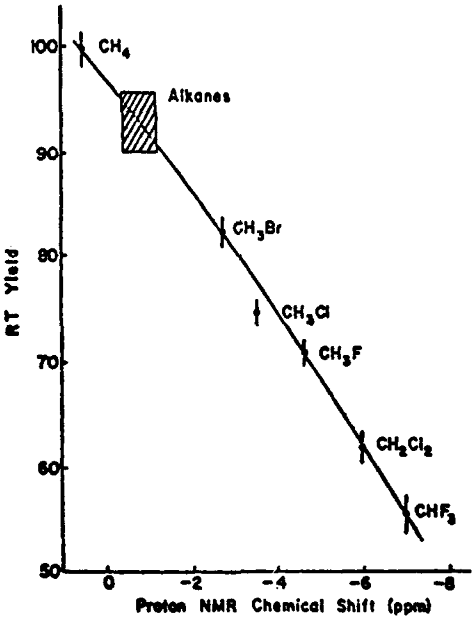

Figure 1. Correlation between the yields of T-for-H substitution products and the proton NMR chemical shift. Reproduced with permission from ref 27. Copyright 1978 Elsevier North Holland.

The above-mentioned corrections, due to decomposition, are a consequence of "double" and "triple" substitution reactions. Odum and Wolfgang had already noted that in I_2 and Br_2 scavenged gas-phase experiments, labeled iodinated and brominated products were formed. The highest double displacement yield was found in the formation of 8.1% CH_2TI in CH_3Cl/I_2. A major question was if such displacement reactions were proceeding in a fast one-step reaction, involving the simultaneous substitution of 2 atoms:

$$T + CH_3Cl \rightarrow CH_2T + H + Cl$$

or by a two-step mechanism involving a single substitution reaction:

$$T + CH_3Cl \rightarrow [CH_2TCl]^* + H$$

$$[CH_2TCl]^* \rightarrow CH_2T + Cl$$

When the pressure was varied and the decomposition/stabilization ratio of $[CH_2TCl]^*$ was measured, the lifetime of the excited intermediate molecule could be established as 10^{-8}–10^{-9} s, which was convincing evidence that a two-step reaction is the most important channel. (A one-step reaction proceeds in about 10^{-14} s.[79]) When C_2H_4 was used as a scavenger in gas-phase experiments with CH_2Cl_2, a considerable yield of c-C_3H_4TCl was formed, due to the addition of chlorocarbene to C_2H_4.[80,81] This "triple" substitution reaction proceeds also via a two-step mechanism:

$$T + CH_2Cl_2 \rightarrow [CHTCl_2]^* + H$$

$$[CHTCl_2]^* \rightarrow CTCl + HCl$$

c-C_3H_4TCl was also found in experiments with CH_2FCl, indicating the elimination of HF from excited CHTFCl.[80] Similarly, CTF was observed from the reactions of T with CHF_3, CH_2F, and CH_2FCl.[87–89] In the presence of C_2H_4 and O_2, the yields of c-C_3H_4TF—relative to the yield of the excited precursors (100)—are

$$CHF_3 \rightarrow [CHTF_2]^* \rightarrow CTF + HF \quad 98 \pm 8$$

$$CH_2F_2 \rightarrow [CHTF_2]^* \rightarrow CTF + HF \quad 48 \pm 2$$

$$CH_2FCl \rightarrow [CHTFCl]^* \rightarrow CTF + HF \quad 35 \pm 2$$

TABLE II. Relative Yields for Substitution Reactions of Recoil T Atoms (HT = 100)

compd	phase	scavenger	ref	H	Cl	2H	H + Cl	2Cl
CH_3Cl	gas	I_2	78[a]	37	32	2.2	36	
	gas	Br_2, I_2	80	37	31		35	
	gas	NO	85	48	33			
	liq	Br_2, I_2	80	55	32		10	
CH_2Cl_2	gas	Br_2	78[b]	15	9	<3	9	15
	gas	Br_2, I_2	82	16	8	1	*c*	15
	liq[d]	Br_2	82	29	22		11	3

[a] Absolute HT yield: (22.3 ± 1.0)%. [b] Absolute HT yield: (19.1 ± 1.8)%. [c] 16% with Br_2, 6% with I_2. [d] Liquid-phase results of ref. 86 are not reported as an unknown amount of ^{35}S was present.

In Table II relative product yields are given for gaseous and liquid CH_3Cl and CH_2Cl_2, these being the most investigated compounds. In the liquid phase, the secondary reactions are greatly reduced due to rapid deexcitation of the primary products, but they do proceed to some extent.[82] Three possible explanations—or a combination of these—were given:[27]

(1) A very long tail of the excitation distribution spectrum extends into the very high energy range.

(2) The RRKM assumption of energy randomization fails when the excitation is localized and high.

(3) A single-step double displacement occurs.

C. Isotope Effects

Several types of isotope effects have been considered for the reactions of recoil T atoms with protonated and deuterated compounds.[27]

A. **Reactive isotope effects,** due to the difference in reaction probability per collision at a given energy for the two isotopically labeled molecules. These reactive effects can be further divided into

(1) **Primary isotope effects,** that refer to the variation in product yields caused by differences in the identity of the isotope being abstracted or replaced.

(2) **Secondary isotope effects,** that refer to the variation in product yields when replacing the same isotopic atom in a molecule which is differently labeled at the other nonradioactive positions.

An example of A.1 is H/D abstraction and substitution in CHF_3/CDF_3. Pure examples of A.2 are T-for-F substitution in CH_3F/CD_3F and in CHF_3/CDF_3.

B. **Moderator isotope effects** can be operative if the energy losses of the recoil T atom in nonreactive collisions are not the same for the two differently labeled molecules. Moderator isotope effects are absent in some cases: partially deuterated molecules such as CH_2D_2; mixture of two isotopically labeled molecules as CH_4/CD_4; an addition of an excess of a third molecule.

CH_4/CD_4. Rowland and co-workers[90-92] observed in 1960 the preference of recoil T atoms for the abstraction of an H atom from CH_2D_2 and from CH_4/CD_4 mixtures, rather than the abstraction of a D atom. The HT/DT ratio in both experiments was 1.3–1.4. At high concentrations of O_2, the HT/DT ratio in both systems drops toward unity, which can be explained by assuming a higher average energy of the reacting T atoms.

From experiments in mixtures of CH_4, CD_4 with C_4H_{10}, and C_4D_{10}, Root and Rowland[92] also found an isotope effect for the substitution reaction: $CH_3T/CD_3T = 1.26 \pm 0.05$. This ratio differs somewhat from the integrated cross section for the substitution reactions, as measured by Cross and Wolfgang:[93] $I(CH_4) = I(CD_4) = 0.29 \pm 0.04$. However, this equality means that the billiard model, developed by Libby[94] in 1947, was impractical for explaining these results, as this model predicts a $I(CD_4)/I(CH_4)$ ratio of 3.06. It was concluded that the reactions occur at energies less than 10–20 eV, by a mechanism that involves strong bond coupling, which means that momentum is not only transferred to the atom that is struck by the incoming T atom, but also to the neighboring atoms.[95] Baker and Wolfgang,[53] performing experiments with mixtures of CH_4/C_2D_6 and CD_4/C_2H_6, concluded from moderator experiments with Ne, that the abstraction reactions occur, on the average, at higher energies than the substitution reactions. Root and Rowland[96,97] irradiated mixtures of D_2/CH_4 and H_2/CD_4 and found that the ratio of DT/CH_3T—corrected for the mole ratio of the D_2/CH_4 mixture—was almost constant over the D_2/CH_4 concentration range of 0.12–16. This shows that both products are formed at the same energy. The HT/CD_3T ratio in H_2/CD_4 mixtures varies from 7.3 at a H_2/CD_4 ratio of 0.12, to 5.5 at a ratio of 16. This indicates that the threshold energy for HT formation is lower than that for CD_3T formation.

CH_xF_{4-x}/CD_xF_{4-x}. Apart from the study of isotope effects for the reactions of recoil T atoms with deuterated methanes, Wolfgang et al. and Rowland et al.[43,98,99] have also investigated the reactions with deuterated fluoromethanes. The isotope effects for hydrogen abstraction and for hydrogen and fluorine substitution are summarized in Table III. For all types of reactions, there is an H/D isotope effect of about 1.3. Jurgeleit and Wolfgang[43,98] concluded that the mean energies at which the various reactions in CH_3F and CD_3F take place are in the order H abstraction < H substitution < F substitution < 2-atom substitution. Lee et al.[99] found that the H/D substitution isotope effect in highly moderated CH_3F/CD_3F (95% ^4He) is, within experimental error, the same as for the unmoderated system. Furthermore, the HT/CH_2TF and

TABLE III: H/D Isotope Effects for the Reactions of Recoil T Atoms with CH_3F/CD_3F and CHF_3/CDF_3

system	scavenger	abstraction H	substitution H	substitution H	substitution 2H	substitution H + F	ref
CH_3F/CD_3F, gas	I_2	1.37 ± 0.03	1.23 ± 0.02	1.30 ± 0.02	1.4 ± 0.1	1.4 ± 0.1	43, 98
CH_3F/CD_3F, gas[a]	O_2	1.26 ± 0.05	1.33 ± 0.04	1.40 ± 0.05			99
CH_3F/CD_3F, gas[b]	I_2, O_2		1.27 ± 0.04				99
CHF_3/CDF_3, gas[c]	Br_2		1.32 ± 0.05	1.40 ± 0.06			100
CHF_3/CDF_3, liq[c]	Br_2		1.43 ± 0.08	1.48 ± 0.09			100

[a] Competition experiments with fourfold excess c-C_4H_8. [b] 95 mol % ^4He as moderator. [c] Binary mixtures with CH_3Cl.

DT/CD_2TF ratios have almost the same value and both ratios are insensitive to dilution with He. This should then mean that CH_3T, CD_3T, CH_2TF, and CD_2TF are all formed at the same average energy. The isotope effect for abstraction and substitution of H and D atoms are primary effects, whereas the F substitution isotope effect must be a secondary effect, as the moderator isotope effect is either 1.0 (in highly He moderated experiments) or slightly less (excess c-C_4H_8).[99] The isotope effect for H vs. D substitution in mono- and trifluoromethanes was explained by assuming the formation of a short-lived transient complex which breaks up with the loss of an H, D, or T atom. The lightest atom is more likely to be eliminated as it has a readier response to the changing potential during the interaction with the fluoromethanes and can move away more rapidly from the transient complex.[99,100] The secondary isotope effect found by T-for-F substitution in CHF_3/CDF_3 cannot be explained by inertial effects, as the moments of inertia of CHF_2 and CDF_2—30 and 32 $\times 10^{-40}$ g cm^2, respectively—are not very different. The magnitude of this effect is consistent with the individual relaxation of H and D, as the more rapid response of H atoms to the changing orbital electron distribution—caused by the interaction of the incoming T atom with fluoroform—results in a higher F substitution yield in CHF_3 than in CDF_3.[100] The yield of CTF_3 is about 1.7 times higher in the liquid than in the gas phase, for both CHF_3 and CDF_3, indicating extensive decomposition in the latter phase. This process is even more pronounced in the gas-phase substitution of F atoms, as the liquid/gas ratio is about 2.3 for both compounds.[100]

III. Muonium

Muonium (Mu) is the lightest hydrogen atom that is available for chemical research ($m_{Mu} \simeq {}^1/_9 m_H$), as it has a positive muon (μ^+) as the nucleus. The short half-life of μ^+ (1.5 μs) does not exclude chemical research. The experimental spin resonance techniques (μ^+Sr or MuSR) are based on the detection of the angular distribution rate of high energy positive decay electrons ($\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$), that are preferentially emitted in the direction of the spin of the muon, that is rotating in a magnetic field.[101-105] At the moment three types of muonic species can be detected: (1) free muonium (yield P_{Mu}), (2) free μ^+ or Mu bound in a diamagnetic compound (yield P_D), and (3) Mu bound in a paramagnetic compound (yield P_R). The absolute yields in liquid systems are determined relative to $P_D = 1$ in liquid CCl_4, but in general $P_{Mu} + P_D + P_R < 1$. The use of CCl_4 as a standard is justified by the fact that it has the same assymmetry coefficient as is found in copper and alumina, but it is not yet ascertained if this signal is due to bare muon or to bound muonium.

It is assumed that high energetic positive muons gather an electron to form muonium at kinetic energies of about 200 eV. As a consequence of the fact that Mu atoms are formed with high kinetic energies, hot reactions can take place. In fact, within an earlier concept of hot and thermal reactions of Mu atoms, the total diamagnetic yield was ascribed to the occurrence of hot reactions.[101] This indicates that in liquid CCl_4 all the Mu atoms react by hot abstraction:

$$Mu^* + CCl_4 \rightarrow MuCl + \cdot CCl_3$$

or by hot substitution:

$$Mu^* + CCl_4 \rightarrow CMuCl_3 + \cdot Cl$$

The observation that hot T atoms recoiling in liquid CCl_4 produce less than 1% $CTCl_3$ does not support the theory of hot substitution reactions of Mu atoms.[86] The consequence of this assumption is that the diamagnetic yield in liquid CCl_4 ($P_D = 1$) must be due to free μ^+ and/or to MuCl.[86] For the comparable T/CCl_4 system the main fraction (>93%) of the T activity could be extracted with water, which means that most of the activity was inorganic in nature, either as T^+ or as TCl. If it is supposed that all the recoiling T particles become neutralized before they can react chemically (<25 eV), this high inorganic yield could be due to hot Cl abstraction. However, the observation that the inorganic yield in liquid $CHCl_3$ and CH_2Cl_2 was only 1–2% led to the conclusion that hot abstraction was not the main reaction channel for recoil T atoms.[86] The high inorganic yield in CCl_4 is formed by reactions of thermal T atoms with Cl_2 that is produced through radiolytical reactions as a result of the high radiation doses received by the sample during the production of the recoil T atom in a nuclear reactor, as was discussed in the preceding section. The main conclusion was that almost all T atoms recoiling in liquid CCl_4 become thermalized rather than undergoing hot reactions. However, as the radiation doses that are received by the samples during the irradiations with muons are very low, reactions of thermal Mu atoms with Cl_2 can be precluded.

Hill et al.[106] noticed a correlation between the value of P_D and the donor number defined as the magnitude of the calorimetrically measured thermal effect of the reaction

$$D(soln) + SbCl_5(30/n) \rightleftarrows D\cdot SbCl_5(soln)$$

in liquid CH_2Cl_2.[107] This correlation seemed to hold for 13 compounds, among which were benzene, methyl methacrylate, acetone, and water, but only CCl_4 proved to be an absolute exception. However, such a correlation ignores the possibilities of the occurrence of hot atom reactions or that Mu formation may be inhibited in materials that are efficient electron scavengers, such as $CHCl_3$ and CCl_4.

Hill et al.[106] considered four alternatives with regard to the magnitude of the diamagnetic fraction:

(1) Loss of polarization due to spin exchange (i.e., with e^-_{aq} in aqueous solutions) and slow (>10^{-11} s) chemical reaction of Mu, in which case the correlation between the initial phases of the muons and the phases at the moment of reaction is lost.

(2) Rapid scavenging of e^-, which may prevent neutralization of μ^+, as can occur in CCl_4:

$$e^- + CCl_4 \rightarrow \cdot CCl_3 + Cl^-$$

An intraspur reaction between μ^+ and Cl^- was proposed,[103] but this theory was later rejected on the basis of results obtained in mixtures of CCl_4 with c-C_6H_{12} and C_6H_6.[108,109]

(3) Strong bonding between μ^+ and basic molecules or ions. (4) Rapid reaction of Mu (hot or thermal) to form diamagnetic products (or with unsaturated compounds to provide paramagnetic products).

In this context a fifth possibility can be considered: the occurrence of cage reactions. In the case of reactions

TABLE IV. Muon Polarization (P) and Relative Fraction (f) in Percent for Gases (G) and Liquids (L)[103,111-114]

compd	phase	P_D	P_M	f_D	f_M
CH_4	G (120 kPa)	3.2 ± 0.2	25 ± 1	13 ± 4	87 ± 4
	G (300 kPa)	5.3 ± 0.2	34 ± 1	13 ± 4	87 ± 4
CH_2Cl_2	G (33 kPa)	13 ± 1	59 ± 2	17 ± 2	83 ± 2
	G (67 kPa)	15 ± 2	70 ± 3	18 ± 2	82 ± 2
	L	74 ± 4[a]			
$CHCl_3$	G (19 kPa)	14 ± 2	38 ± 2	26 ± 3	74 ± 3
	G (41 kPa)	18 ± 2	55 ± 3	25 ± 3	75 ± 3
	L	80 ± 6[a]	19 ± 3	49 ± 4	51 ± 4
CCl_4	G (16 kPa)	18 ± 2	27 ± 3	53 ± 3	47 ± 3
	G (33 kPa)	30 ± 1			
	L	100			
$CHBr_3$	L	94 ± 6			
CH_2I_2	L	66 ± 4			

[a] Reference 103: CH_2Cl_2, 70; $CHCl_3$, 85.

of recoil Cl atoms with liquid CCl_4, it was discussed that the major proportions of labeled CCl_4 was not formed by a direct hot substitution reaction, but rather by recombination of the radioactive atom and CCl_3 radicals formed at the end of the track of the recoil atom.[110] Such cage reactions were not considered to be important for T atoms recoiling in liquid CCl_4, because due to their small radius, T atoms can easily escape from such a reactive cage before radical recombination takes place.[68] Accordingly, cage reactions will also not be an important reaction channel in liquid Mu chemistry. Fleming et al.,[111,112] using μ^+ beams of rather low kinetic energy (range 140 mg cm^{-2})[113] performed experiments with gaseous (chloro)methanes. The results are given in Table IV, together with earlier liquid-phase results. As can be seen, the total ($P_M + P_D$) gas-phase yields are much lower than 1.0. Appreciable loss of polarization occurs when the time between collisions is in the order of $1/\nu_0 = 0.22$ ns, where ν_0 is the mixing frequency between the eigenstates of the $\mu^+ - e^-$ interaction. There is no missing fraction if corrections are applied for this loss of polarization and for the wall effect (at low pressures some muons may scatter into the walls of the target). A missing fraction of about 20% is found for most of the liquid-phase experiments and this probably indicates that muonic radicals lost spin polarization during encounter with paramagnetic species in the spur.[115] It is therefore more convenient to express gas-phase results in relative fractions, e.g., $f_D = P_D/(P_D + P_M)$ and $f_M = P_M/(P_D + P_M)$ (Table IV). In the gas phase neither spur or cage reactions nor reactions with radiolytically produced Cl_2 are of any importance: the main reaction channel leading to the diamagnetic fraction is a hot atom reaction.[111-113]

In order to gain more information about (1) relative reaction rates of Mu, (2) occurrence of hot Mu reactions, and (3) the high diamagnetic yield in CCl_4 ($f_D = 1$), several experiments have been performed in liquid mixtures. In several mixtures no preferential interaction with one of the two components was observed. The linear increase of f_D as a function of additive concentration between 0 and 100 mol % (from 0.56 to 0.85 in CH_3OH/CH_3Cl, from 0.16 to 0.56 in C_6H_6/CH_3OH,[103] and from 0.16 to 0.61 in C_6H_2/c-C_6H_{12}[108,109]) was taken as evidence for hot Mu reactions. In a mixture of C_6H_6 and CH_3I the values of f_D and f_R deviate significantly from the proposed linearity for hot reactions.[116] The results indicate that both compounds compete in reaction with thermal Mu; CH_3I being the more efficient.

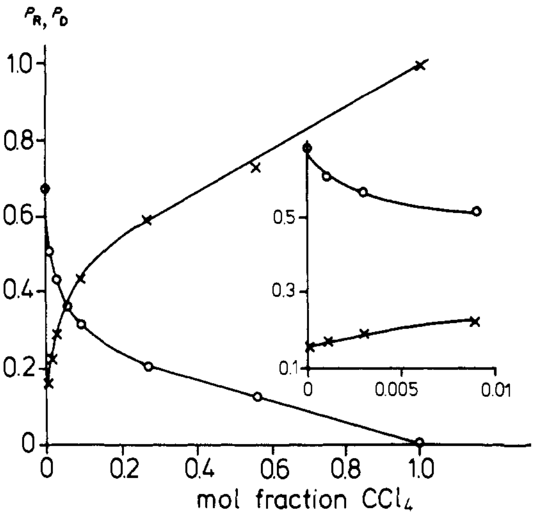

Figure 2. P_R (o) and P_D (*) in C_6H_6/CCl_4 mixtures. Reprinted with permission from ref 117. Copyright 1984, North Holland.

More information was obtained by investigations of Roduner[117] on binary mixtures of C_6H_6 with c-C_6H_{12}, DMBD (2,3-dimethyl-1,3-butadiene), and CCl_4.

(1) From experiments with C_6H_6/c-C_6H_{12}, the rate constant for addition of Mu to C_6H_6 was found to be $(8.9 \pm 0.6) \times 10^9$ M^{-1} s^{-1}, which is considerably below the diffusion-controlled limit proving that Mu is not hot when it adds.

(2) From experiments with C_6H_6/DMBD, the rate constant for addition of Mu to DMBD was deduced as 4×10^{10} M^{-1} s^{-1}, which is close to the diffusion-controlled limit. The selectivity for addition to DMBD over that to C_6H_6 (by a factor of 4.5) is much lower than for thermal H atoms. This effect was attributed to tunneling, rather than to reactions of hot Mu.

(3) In former experiments with C_6H_6/CCl_4 mixtures only P_D values were measured.[108,109] Roduner[117] has also measured P_R values, in particular at low CCl_4 concentrations (Figure 2). As it was proven that Mu atoms are the direct radical precursors for addition to C_6H_6, it was concluded that CCl_4—an excellent electron scavenger—inhibits Mu formation by scavenging spur electrons before their combination with μ^+. This means that thermal Mu is formed in an end-of-track process: $\mu^+ \rightarrow e^- \rightarrow$ Mu. The rate constant of 2.7×10^{12} M^{-1} s^{-1} for the reaction of CCl_4 with electrons reveals that Mu is formed within a picosecond after the creation of the last spur.

IV. Fluorine

The study of the reactions of F atoms with organic compounds was hampered in the past due to the lack of a convenient method for their production. Dissociation of F_2 has the disadvantage that an excess of highly reactive molecular fluorine is always present. Apart from the reactions of thermalized recoil ^{18}F atoms—to be discussed later—the production of ^{19}F atoms through the reaction of N atoms with NF_2 radicals

$$N + NF_2 \rightarrow 2F + N_2$$

has contributed considerably to the reliability of measured rate constants.[118]

The most important reaction of thermal F atoms with aliphatic compounds is H abstraction. Rate constants for such reactions with CH_4, CD_4, and halomethanes can

TABLE V. Rate Constants (10^{10} L mol^{-1} s^{-1}) for H Abstraction by ^{19}F Atoms at 298 K[a]

CH_3F	5.3 (130); 2.3 (131)
CH_2F_2	1.1 (131); <0.14 (131)
CHF_3	0.019 (130); ~0.014 (131); 0.009 (132); 0.011 (127); 0.018 (133)
CH_3Cl	0.58 (124); 0.55 (134); 0.21 (122); 0.21 (123); 2.88 (131); 1.44/1.56 (127)
CH_2Cl_2	0.33 (124); 0.32 (134); 0.58 (131)
$CHCl_3$	0.10 (124); 0.096 (134); 0.22 (131)
$CDCl_3$	0.043 (134)
CHF_2Cl	0.016 (125); 0.052 (134); 0.05 (135); 0.15 (130); 0.058 (136)
$CHFCl_2$	0.39 (125); 0.14 (134); 0.09 (135)

[a] (Reference number in parentheses.)

be found in some recent papers and tables in CRC.[118–121] Besides H abstraction, the abstraction of Br and I atoms from halomethanes has also been reported for ^{18}F and ^{19}F atoms, but the replacement of Cl, Br, and I atoms was only investigated with thermalized recoil ^{18}F atoms.

Methane. Six rate constants for the abstraction of an H atom from CH_4 have been reported. Three experiments were performed through dissociation of F_2, the constants being at 298 K: 1.62, 0.17, and 4.29 × 10^{10} L mol^{-1} s^{-1}.[122–124] The other three were determined as 4.37, 4.27, and 3.63 × 10^{10} L mol^{-1} s^{-1} through the N + NF_2 reaction, through flash photolysis of a WF_6HF laser, and through microwave discharge of CF_3, respectively.[125–127] The average value of these three results is $k_{298} = (4.1 \pm 0.2) \times 10^{10}$ L mol^{-1} s^{-1}. Recommended in ref 4: $k_{298} = 4.8 \times 10^{10}$ L mol^{-1} s^{-1}. H and D abstraction from CH_4 and CD_4 were measured by Foon et al.,[128] relative to H abstraction from C_2H_6, through F_2 dissociation. The ratio $k(CH_4)/k(CD_4)$ is $(1.0 \pm 0.3)[\exp(1.0 \pm 0.8)/RT]$. The ratio of H/D abstraction from CH_2D_2 (microwave discharge of SF_6) is reported as 1.29 ± 0.08.[129]

Fluoro- and Chloromethanes. A survey of rate constants for H abstraction from fluoro- and chloromethanes is given in Table V. In the case of fluoromethanes, the constants decrease by an order of magnitude going from CH_3F to CH_2F_2 to CHF_3, but the constants are quite steady for the chloromethanes. The relative abstraction rate for $CHCl_3/CDCl_3$ is $(0.81 \pm 0.25)[\exp(2.6 \pm 0.2)/RT]$.[129]

Perhalomethanes. The rate constants for Cl abstraction from CF_xCl_{4-x} are very low, due to the high activation energies of 55, 70, and 88 kJ mol^{-1} for x = 1, 2, and 3, respectively.[137,138] Zetsch[133] reports rate constants for these compounds of approximately 10^6 L mol^{-1} s^{-1} at room temperature, but those measured by Foon et al.[137,139] are much lower. In a fluorine/halocarbon flame (~1600 K) Cl replacement takes place:[140,141]

$$F + CF_xCl_{4-x} \rightarrow CF_{x+1}Cl_{3-x} + Cl$$

Contradictory results were reported for CCl_4. Abstraction (37 kJ mol^{-1} endothermic) is far more likely than replacement (150 kJ endothermic).[142] Clark and Tedder[143] reported a rate constant for Cl abstraction as 2 × 10^{10} L mol^{-1} s^{-1}, but data later obtained are considerably lower: ≤5 × 10^7,[133] 2.4 × 10^5,[144] and 6.9 × 10^2.[137] The very high values are probably due to heterogeneous catalyzed reactions.[137,145] F abstraction from CF_4 has been observed at high temperatures (1700–3000 K); the activation energy was determined as 358 kJ mol^{-1}.[146] Br abstraction was measured in CCl_3Br, with a rate constant of 5.6 × 10^{10} L mol^{-1} s^{-1}.[147] For the reaction with CF_3Br a rate constant of 4 × 10^6 L mol^{-1} s^{-1} was reported by Pollock and Jones,[130] but later Kaufman and co-workers[142,148,149] gave a value of 10^5–10^6. They could not detect Br atoms and hence argued that the displacement of Br by F was unlikely, due to a steric barrier, and postulated the primary formation of CF_3BrF. Jacox[150] has observed this product through microwave discharge of NF_3 in argon carrier gas leading it over CF_3Br in an argon matrix at 14 K. Similar products were found with CF_3Cl, CF_3I, and also CH_4. The rate constant for I abstraction from CF_3I is given as 7.2[147] and 10.2 × 10^{10} L mol^{-1} s^{-1}.[151,152] A rate constant of 12.0 × 10^{10} L mol^{-1} s^{-1} was measured for CH_3I, but it was impossible to distinguish if H, I, or H and I abstraction occurred: no CH_3F was observed, and so no displacement takes place. In general, some 50–60% of the energy released in H abstraction reactions is partitioned as vibrational energy between the ν = 1,2,3 levels of HF. For CH_4, the population of these three levels is in the ratio 20:65:15,[153,154] for monohalomethanes this ratio is generally 30:40:30.[154–159] Two deviations from these data have been reported:

(1) The proportion of energy that is converted into HF vibrational modes decreases with enhanced chlorination, viz. 50% for CH_3Cl, 23% for CH_2Cl_2, and 13% for $CHCl_3$.[159] The slow departure of the heavy CCl_3 radical from the reactive center may be the reason that the H atom oscillating in the HF molecule come again within the vicinity of the CCl_3 radical and transfer some additional energy.

(2) The population of the ν = 1,2,3 levels in HF originating from CH_2F_2 and CHF_3 is in the order of 70:30:1, a shift toward ν = 1.[158] Due to the rather low rate constants for H abstraction from both compounds, high concentrations were needed and there may have been some relaxation of vibrationally excited HF.

Recoil ^{18}F atoms used in the studies treated in this section were produced by several nuclear reactions:

(1) $^{19}F(\gamma,n)^{18}F$ ($t_{1/2}$ = 110 min, threshold, 10.4 MeV). Bremsstrahlung beams were produced by high energy electrons in a converter of high Z material. In general, the high energy tail of the bremsstrahlungsbeam is above the 18.7 MeV threshold of the $^{12}C(\gamma,n)^{11}C$ nuclear reaction, and a cooling time of several hours is necessary.

(2) $^{19}F(n,2n)^{18}F$ (threshold, 10.4 MeV). The fast neutrons can be produced in two ways: (a) With high energy protons or deuterons impinging upon a Be target. If the energy is low (i.e., 26 MeV deuterons), no ^{11}C will be produced by the $^{12}C(n,2n)^{11}C$ reaction. (b) With a D–T neutron generator—via the $d(T,\alpha)n$ reaction—yielding neutrons with an energy of some 14 MeV, which is above the threshold for ^{18}F production, but below that for the production of ^{11}C. A disadvantage is the low neutron flux, but this has enabled the study of reactions of thermalized recoil ^{18}F atoms with suitable compounds that are present in low concentrations (1–2 mol %) in inert perfluoro moderators (SF_6, CF_4, C_2F_6), that also serves as the source for the ^{18}F atoms.

(3) By charged particles, as $^{20}Ne(d,\alpha)^{18}F$, $^{19}F(p,pn)^{18}F$. In these cases, the samples are subjected to a high ra-

TABLE VI. Absolute Product Yields (Corrected for Statistical Loss of ^{18}F) for the Reactions of Recoil ^{18}F Atoms with CF_4 + Cl_2[169]

product	yield, %	energy range, eV
$CF_3{}^{18}F$	2.08 ± 0.06	1.7–5.7
$CF_2{}^{18}FCl$	2.40 ± 0.08	5.7–9.5
$CF^{18}FCl_2$	2.21 ± 0.09	9.5–14.8
$C^{18}FCl_3$	0.73 ± 0.12	14.8–20.4
total	7.41 ± 0.19	1.7–20.4

diation dose, with the consequence of considerable radiation damage. This can be of use for the in-beam production of special labeled compounds, but these nuclear reactions are not particularly suitable for the study of hot and thermal reactions of recoil ^{18}F atoms.[160]

The first investigations of the reactions of recoil ^{18}F atoms with halomethanes were performed by Wolfgang and co-workers.[161–165] In the case of CF_4, they found a yield of about 3% of $CF_3{}^{18}F$, almost an order of magnitude lower than the T-for-H substitution yield in CH_4. This behavior was ascribed to two factors:

(1) Due to the greater mass of the F atom, the collision time will be longer, the excess energy is better transmitted over the whole molecule, and therefore the probability of bond rupture and substitution at the point of attack is reduced.

(2) Steric hindrance will be more marked in F approach to the C–F bond than in T approach to the C–H bond.

Apart from the substitution of a single atom, double displacement was also observed in the $^{18}F/CF_4$, $^{18}F/CH_4$, and T/CH_4 systems through the detection of $CF_2{}^{18}FI$, $CH_2{}^{18}FI$, and CH_2TI, respectively, if I_2 was present. The ratios of single/double displacement for the three systems are 1.24, 3.18, and 4.65, respectively, and they are in agreement with the concept of more efficient transfer of energy over the whole molecule for the reactions of recoil ^{18}F atoms. The observation that the substitution of an H atom in CH_4 by ^{18}F is some three times greater than the substitution of an F atom in CF_4 is in accord with the concept of steric hindrance.

Manning et al.[164] observed that the (Y_0/Y^0) values for ^{18}F-for-F processes exhibit a simple monotonic dependence upon the unimolecular critical decomposition energies (ϵ_e). Y_0 is the measured ^{18}F-for-F substitution yield at low pressure and Y^0 is the total primary hot yield, the latter including the decomposition of excited compounds. The data ranged between $Y_0/Y^0 = 0$ for c-C_3H_6 (ϵ_e = 1.7 eV) and 0.50 for CF_4 (ϵ_e = 5.5 eV).

Rowland and co-workers[165,166] found that, in the presence of olefins, reactions of recoil ^{18}F atoms with CH_2F_2, CHF_3, and CF_4 lead to the formation of ^{18}F labeled fluorocyclopropane. These products could only be formed by the addition of labeled carbenes to these olefins. In the case of $CH^{18}F$, the formed fluorocyclopropanes correspond with a stereospecific addition reaction, indicating the addition of singlet carbenes, whereas the amount of excitation energy appears to be insufficient for isomerization or decomposition. The carbenes were further used for the study of insertion reactions with hydrogen halides, demonstrating rapidly decreasing reactivity of $CF^{18}F$ in the order HI > HBr > HCl. Pauwels[167] found high yields of a water-soluble gas fraction by the irradiation of fluoromethanes: 28% for CF_4, 19% for CHF_3, 11% for CH_2F_2, and 8% for CH_3F. These fractions were ascribed to $CF^{18}FO$, formed by the reaction of $CF^{18}F$ with traces of oxygen. Whereas C_2H_4 + I_2 were present as scavengers, these fractions could very well have consisted of 1,2-$C_2H_4{}^{18}FI$, which is soluble in water.[168]

More recent work by Root and co-workers, who investigated the $^{18}F/CF_4$ system in the presence of Cl_2, has shown that the situation is even more complex, as apart from $CF_3{}^{18}F$, $CF_2{}^{18}FCl$, and $CF^{18}FCl_2$, $C^{18}FCl_3$ was also detected.[169] This means that up to three F atoms can be eliminated from an excited $CF_3{}^{18}F$ molecule. Assuming that the primary reaction is ^{18}F-for-F substitution yielding excited $CF_3{}^{18}F$, then when the yields are corrected for an equal probability of the elimination of an ^{18}F or ^{19}F atom from the excited molecule, the initial product distribution at 0.13 MPa being given in Table VI. The total yield increases monotonically from 7.4% at this pressure to 12.3% at 13 MPa. At the higher pressure, more energy is removed from the excited products through collision, and this indicates that at the low pressure limit at least 4.9% of the primary $CF_3{}^{18}F$ molecules dissociate completely into bare C atoms. This means that the total internal energy distribution extends to at least 25 eV. This investigation is one of the finest examples of pure "hot" atom chemistry. If a correction for unimolecular translational energy disposal is included, and if the four experimentally derived data are fitted by a polynomial regression

TABLE VII. Absolute Product Yields (%) for the Reactions of Recoil ^{18}F Atoms with Gaseous Halomethanes

	substitution of							
compd	1H	1F	1Cl	2H	2F	1H + 1F	1H + 1Cl	ref
CH_4	15.6							162, 163
	13.1							167
	15.8			4.6				170
CH_3F	1.9	2.2						171
	2.2	2.5						167
	3.4	4.7		0.4		2.1		170
CH_2F_2	1.1	2.0						167
	0.9	2.6		0.8	2.8	2.9		170
CHF_3	1.0	1.5						167
	1.3	1.4		1.0	3.3			170
CF_4		3.2			1.8			161, 162
		3.6						167
		2.8			2.5			170
		2.1			1.8			169
CH_3Cl	<0.5		7.9				7.3	170
CF_3Cl		1.4	0.2					168, 172
CF_2Cl_2		<3	~1					168, 172
		1.3	3.1					168, 172

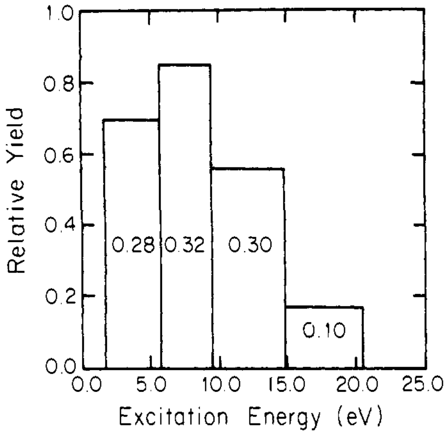

Figure 3. Approximate lower bound thermochemical excitation energy distribution for $CF_3{}^{18}F$ produced from hot F-for-F substitution in CF_4. Reproduced with permission from ref 169. Copyright 1981, Akad Verlagsgesellschaft (Wiesbaden).

TABLE VIII.[167] **Absolute Product Yields (%) for the Reactions of Recoil ^{18}F Atoms with Mixtures of CF_4 and Alkanes**[a]

additive (mol %)	$CF_3{}^{18}F$	$CHF_2{}^{18}F$	$CH_2F^{18}F$	$CH_3{}^{18}F$	$C_2H_3{}^{18}F$
	2.50				
0.1% CH_4	2.25	0.25	0.00	0.00	0.00
28% CH_4	0.82	0.00	0.12	1.37	0.19
0.1% C_2H_6	2.22	0.33	0.00	0.00	0.00
28% C_2H_6	0.87	0.00	0.08	1.15	0.41
0.1% C_3H_8	2.12	0.38	0.00	0.00	0.00
28% C_3H_8	0.48	0.00	0.12	0.62	1.27

[a] Total pressure 101 kPa.

analysis, an energy distribution in the $CF_3{}^{18}F$ molecule is obtained as given in Figure 3.

In Table VII a summary is given of published single and double substitution yields in halomethanes: most of the yields are on the order of 2–3%. Spicer and Swida measured the ^{18}F-for-F substitution yields in CH_3F and CD_3F in samples diluted with 50% to 98% CF_4.[173] The ratios of the yields indicate the existence of a reactive CH_4/CD_4 isotope effect of 1.3, whereas the moderating isotope effect is very small.

Relative ^{18}F-for-X substitution yields in SF_6/CH_3X mixtures (X = F, Cl, Br, I) increases by a factor of 8 when going from CH_3F to CH_3I.[174] This parallels the increase of the size of X and the decrease in the C–X bond energies. If the mole fraction of CH_3X is decreased to below 0.25, the relative yields for the substitution of Cl, Br, and I (but not of F) are increased, which indicates that the energetics of the reactions, and not the size of the halogen, is the more important factor.

Pauwels[167] has measured product yields in CF_4 diluted by up to 30% with CH_4, C_2H_6, and C_3H_8 (Table VIII). In this concentration range the yield of $CF_3{}^{18}F$ decreases monotonically, whereas the yields of $CH_2F^{18}F$, $CH_3{}^{18}F$, and $C_2H_3{}^{18}F$ increase monotonically. The yield of $CHF_2{}^{18}F$ peaks at low RH concentrations. A reaction mechanism—analogous with comparable T results with hydrocarbons—cannot fully explain these results:

$$^{18}F + R\text{-}CH_3 \rightarrow [R\text{-}CH_2{}^{18}F]^* \rightarrow CH_3{}^{18}F$$

$$^{18}F + R\text{-}CH_3 \rightarrow [R\text{-}CH_2{}^{18}F]^* \rightarrow C_2H_3{}^{18}F$$

TABLE IX. Absolute Product Yields (%) for the Reactions of Recoil ^{18}F Atoms with Condensed Fluoromethanes

compd	phase	substitution of 1H	1F	1Cl	ref
CH_3F	sol (77 K)	13	17		171
	sol (113 K)	16	23		167
CH_2F_2	sol (113 K)	24	39		167
CHF_3	sol (108 K)	20	45		167
CF_4	sol (88 K)		40		167
$CFCl_3$	liq (RT)		12	13	175

However, insertion of $CF^{18}F$ into C–H bonds can explain the increase in the yields of some of the products:

$$CF^{18}F + R\text{-}CH_3 \rightarrow [R\text{-}CH_2\text{-}CHF^{18}F] \rightarrow CH_2F^{18}$$
$$\rightarrow CH_3{}^{18}F$$
$$\rightarrow C_2H_3{}^{18}F$$

It has previously been mentioned that in the case of CF_4, the total hot yield increases monotonically when increasing the pressure from 0.13 MPa to 13 MPa. A similar effect was found by Richardson and Wolfgang in the case of CH_3F: the yields of $CH_2F^{18}F$ and of $CH_3{}^{18}F$ increase from 2% at low pressure to a plateau value of 5% above 5 MPa, characteristic of the behavior of collisional deexcitation of excited $CH_2F^{18}F$ molecules.

Very high substitution yields were measured in condensed fluoromethanes (Table IX). These high yields are ascribed to cage reactions between ^{18}F atoms and radicals produced at the end of the track,[167,171] e.g.

$$^{18}F + CH_3F \rightarrow CH_3 + F + {}^{18}F \rightarrow CH_3{}^{18}F$$

$$^{18}F + CH_3F \rightarrow CH_2F + H + {}^{18}F \rightarrow CH_2F^{18}F$$

In the gas phase the radicals and atoms will separate, but in the condensed phases these products remain in a cage and can recombine.

A special application of recoil ^{18}F atoms is the investigation of their thermal reactions with compounds present in low concentrations in inert gases such as SF_6, CF_4, and C_2F_6, that have a low probability for reactions with hot and thermal ^{18}F atoms. Thermal abstraction and substitution reactions have been measured in highly moderated systems (98%). The rate constant (at 300 K) for H abstraction from CH_4 was determined relative to the thermal addition rate to C_2H_2[176,177] and C_3F_6[119] as (3.8 ± 0.4) and (4.0 ± 0.2) × 10^{10} L mol^{-1} s^{-1}, respectively. This is in agreement with the above-mentioned average value of (4.1 ± 0.2) × 10^{10} L mol^{-1} s^{-1}, which proves the reliability of this type of kinetic data measurements. Rate constants measured by the same groups for D abstraction from CD_4 are (2.2 ± 0.4) and (1.94 ± 0.11) × 10^{10} L mol^{-1} s^{-1}. The isotopic ratios for CH_4/CD_4 are (1.7 ± 0.4) and (2.06 ± 0.16), respectively, in accord with the established value of 1.47 as discussed before. Manning et al.[178] measured rate constants—relative to H_2—for (fluoro)methanes: CH_4 (2.58 ± 0.06), CD_4 (1.66 ± 0.02), CH_3F (1.49 ± 0.03), CH_2F_2 (0.283 ± 0.013), and CHF_3 (0.026 ± 0.006). The CH_4/CD_4 ratio is (1.55 ± 0.04). Iyer and Rowland[179-181] measured rate constants—relative to the addition of C_2H_2—for several abstraction and substitution reactions:

$$^{18}F + CH_3Br \rightarrow H^{18}F + CH_2Br \quad (3.7 \pm 0.4) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

$$^{18}F + CH_3I \rightarrow H^{18}F + CH_2I \quad (10.5 \pm 0.9) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

$$^{18}F + CH_3I \rightarrow I^{18}F + CH_3 \quad (10.5 \pm 0.9) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

$$^{18}F + CF_3I \rightarrow I^{18}F + CF_3 \quad (9.8 \pm 1.0) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

$$^{18}F + CH_3F \rightarrow CH_3F + F \quad (0.7 \pm 0.2) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

$$^{18}F + CH_3Cl \rightarrow CH_3{}^{18}F + Cl \quad (2.2 \pm 0.8) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

$$^{18}F + CH_3Br \rightarrow CH_3{}^{18}F + Br \quad (1.0 \pm 0.2) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

$$^{18}F + CH_3I \rightarrow CH_3{}^{18}F + I \quad (4.8 \pm 1.8) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

Absolute ^{18}F-for-X substitution yields in CH_3X increase with decreasing bond energy: CH_3F (0.12 ± 0.02)%, CH_3Cl (0.27 ± 0.02)%, CH_3Br (0.62 ± 0.03)%, and CH_3I (0.93 ± 0.03)%.[176] No thermal substitution was observed for CF_3X (whereas the C–X bond energies for CH_3X and CF_3X are similar with respect to X = Br and I): CF_4, (0.12 ± 0.01)% or 0.03% per bond; CF_3Br, (0.03 ± 0.01)%; and CF_3I, (0.05 ± 0.03)%.[182] It was concluded that "... the thermal substitution reactions are facilitated by the small mass of the H atoms and their much more rapid response to changing force fields during the substitution process." The results of some experiments were reported for the reactions of recoil ^{18}F atoms with fluorochloromethanes. Sadek et al.[183] investigated CF_2Cl_2 and $CFCl_3$, but no absolute product yields were given. Palmer[184] produced ^{18}F via the $^{20}Ne(d,\alpha)^{18}F$ reaction: the samples received high radiation doses (4.6–23 eV per molecule). The systems were highly moderated as only 1–2% of halocarbons were present in the matrix. Nevertheless, high yields (10–30%) of ^{18}F-for-F and Cl-substitution products were found in CF_4, CF_3Cl, CF_2Cl_2, and $CFCl_3$. Palmer proposed that these high yields were the results of reactions with radiolytically produced radicals, and that wall reactions (the aluminum vessels were coated with fluorine from former experiments) may be highly relevant. Brinkman and Visser[172] produced ^{18}F by the $^{19}F(p,pn)^{18}F$ nuclear reaction. The product yields are given in Table VII. In the case of CF_3Cl, the total gas activity increased with integrated beam intensity from about 10% (at 12.5 nAh) to 76% (at 300 nAh), this being thought to be due to the formation of $SiF_3{}^{18}F$.

One experiment has been reported for the reactions of ^{18}F with liquid $CFCl_3$, but only relative product yields were measured: 41% $CF^{18}FCl_2$, 37% $C^{18}FCl_3$, 14% $C_2{}^{18}FCl_3$, and 9% 1,2-$C_2F^{18}FCl_4$ (the total organic yield was 33%).[175] The high yield of $C^{18}FCl_3$, compared with that of $CF^{18}FCl_2$ does not support the involvement of cage reactions—as was suggested for the reactions of ^{34m}Cl and ^{38}Cl with $CFCl_2$—because radiolysis of $CFCl_3$ should primarily lead to the formation of $CFCl_2$ radicals, and not to that of CCl_3 radicals.

TABLE X. **Kinetic Data for Abstraction Reactions by ($^2P_{3/2}$) Cl Atoms from (Halo) Carbons**[a]

compd	E, kJ mol^{-1}	log A, L mol^{-1} s^{-1}	log k_{298}, L mol^{-1} s^{-1}
		H Abstraction	
CH_4	11.5 ± 0.8	9.85 ± 0.15	7.85 ± 0.02
CD_4	24.8	10.73	6.47
CH_3F	6.3	9.46	8.35
CHF_3	35.2	9.23	3.06
CH_3Cl	12.9 ± 0.8	10.58 ± 0.12	8.33 ± 0.07
CH_2Cl_2	12.6 ± 0.3	10.51 ± 0.11	8.39 ± 0.09
$CHCl_3$	13.2 ± 0.8	10.31 ± 0.20	7.81 ± 0.19
$CDCl_3$	18.7 ± 1.5	10.00 ± 0.30	6.74 ± 0.04
		Cl Abstraction	
CH_3Cl	104.6	11.0[b]	
CH_2Cl_2	89.5	11.0[b]	
$CHCl_3$	87.5	11.0[b]	
CCl_4	82.3 ± 0.16	11.1 ± 0.1[c]	
$CFCl_3$	131.0	11.3	
		Br Abstraction	
$CBrCl_3$			8.14

[a] Average data from ref 120. [b] Estimated value. [c] Calculated from kinetic data for the reverse reaction.

TABLE XI.[185] **Absolute Rate Constants (10^{11} L mol^{-1} s^{-1}) for Collisional Removal of Electronically Excited Cl(3 $^2P_{1/2}$) Atoms**

CF_4	CF_3Cl	CF_2Cl_2	$CFCl_3$	CCl_4
0.90 ± 0.24	1.32 ± 0.24	1.26 ± 0.24	1.87 ± 0.36	1.26 ± 0.36

V. Chlorine

Cl atoms are in general produced through microwave discharge or photolysis of Cl_2. These atoms react with halomethanes by H, Cl, or Br abstraction, but the rate constants for these reactions are 2 orders of magnitude lower than for the comparable reactions of F atoms. Most of the available information regarding the reactions of thermal nonradioactive Cl atoms with halomethanes is compiled in ref 120. Average values for activation energies, *A* factors, and rate constants (at 298 K) are calculated from these data and given in Table X. Rate constants for the collisional removal of excited ($^2P_{1/2}$) Cl atoms—0.11 eV above the $^2P_{3/2}$ ground state—are given in Table XI.

Lee and Rowland[186] determined the rate constant for H abstraction from CH_4 by thermalized ^{38}Cl recoil atoms as $(1.9 \pm 0.4) \times 10^7$ L mol^{-1} s^{-1} at 243 K, which value is in good agreement with a value of 2.4×10^7, as can be calculated from the averaged data in Table X.

The radioactive recoil Cl atoms whose reactions are discussed in this section were produced by several methods:

(1) $^{35}Cl(n,2n)^{34m}Cl$ ($t_{1/2}$ = 32.4 min), with fast neutrons either from a D–T neutron generator (14 MeV) or from accelerated particles impinging upon a Be target.

(2) $^{35}Cl(p,pn)^{34m}Cl$, with energetic protons.

(3) $^{35}Cl(\gamma,n)^{34m}Cl$, with bremsstrahlung beams produced by energetic electrons in a convertor of high *Z* material.

(4) $^{37}Cl(n,\gamma)^{38}Cl$ ($t_{1/2}$ = 37.3 min), with thermal neutrons from a nuclear reactor or with moderated fast neutrons from a cyclotron.

(5) $^{37}Cl(d,p)^{38}Cl$, with energetic deuterons.

TABLE XII. Absolute Substitution Yields (%) for the Reactions of Recoil Cl Atoms with Gaseous Halomethanes

	substitution of						
compd	H	Cl	F	Br	2 atoms	scavenger	ref
CH_4	6.4				2H: 1.3	$C_2H_4 + I_2$	199, 200[a]
CH_3Cl	4.7	10.4					201
	1.2	2.4			H + Cl: 1.4	$C_2H_4 + I_2$	199[a]
	0.7	3.1				$C_2H_2Cl_2$	203[b]
	0.6	3.4			H + Cl: 21		202
CH_2Cl_2	<0.5	1.7			2Cl: 1.2	$C_2H_4 + I_2$	199[a]
$CHCl_3$	<0.2	0.6			2Cl: <0.2	$C_2H_4 + I_2$	199[a]
CCl_4		1.7					203[c]
		0.6				$C_2H_4 + I_2$	199[a]
		0.28				$C_2H_2Cl_2$	204
		1.91			2Cl: 0.7	$C_2H_2 + I_2$	205[d]
		1.0			2Cl: 9.3		206[e]
CH_3F	<0.5		3.5		H + F: 2.0	$C_2H_4 + I_2$	199[a]
CH_3Br	1.4			3.4	H + Br: 0.8	Br_2, I_2	207
CH_2ClBr		0.25		2.0	Cl + Br: 0.3	Br_2, I_2	208
CF_4			0.92			$C_2H_2Cl_2$	204
CF_3Cl		0.73	0.64			$C_2H_2Cl_2$	204
		1.0	0.6		F + Cl: 0.7		209[f]
		2.7	1.8		2F: 0.16	C_3F_8	210
CF_2Cl_2		1.0	0.43			C_2H_2Cl2	204
		0.55	0.10		2Cl: 1.8 F + Cl: 1.4		209[g]
$CFCl_3$		<4					210

[a] 60% Ar. [b] Yield ratio $CH_2Cl_2/CH_3Cl = 0.3$ for ^{34m}Cl, ^{38}Cl, and ^{39}Cl. [c] Scavenger unknown, data from ref 205. [d] These yields are at 2.4 mol % C_2H_4. With 0.2 mol % C_2H_4 the yields are 2.6% $CCl_3{}^{38}Cl$ and 2.4% $CCl_2{}^{38}ClI$. [e] Average value for 10 mol % n-C_6H_{14}, 1-C_6H_{12}, CHT, and $C_2H_4 + I_2$. [f] $C_2H_4 + I_2$, $C_3H_8 + I_2$, $C_2h_2Cl_2 + I_2$. [g] C_2H_4 or C_2H_2 with HI or H_2S.

(6) $^{40}Ar(\gamma,p)^{39}Cl$ ($t_{1/2} = 56$ min), with bremsstrahlung beams.

The research of recoil T and ^{18}F atoms with (halo)-methanes is mainly focused on gaseous systems, but in the case of recoil Cl atoms, the majority of publications have dealt with liquid-phase systems. This is quite understandable, as most of the production modes require a source containing Cl, and a vast proportion of the chloromethanes are liquids at room temperature. In general, experiments in the gaseous phase are more straightforward than in the liquid phase, where spur and cage reactions may be involved. In the spur of the slackened recoil particle, ions and radicals and excited products are formed that may still be in the close vicinity of the recoil atom, when it has slowed to an energy where chemical reactions can take place (<25 eV). At the end of its track, the recoiling atom can be trapped in a cage containing radicals and excited species. Libby[187] and Willard[188] proposed cage reactions in liquid recoil chemistry, and such reactions were further discussed in more detail by both Stöcklin[189] and Berei and Ache.[190] This type of reaction is often termed "Rabinowitch caging",[191-197] which was originally restricted to the presence of only radicals, and furthermore, with no excitation energy present. Many investigations dealing with the reactions of recoil Cl atoms with halomethanes were performed in mixtures, with the aim of gaining information about the role of cage reactions.

A. Gaseous Phase

Gordus and Willard[198] found a total organic yield of 20% in gaseous CH_4, when traces of HCl, CCl_4, or n-C_3H_7Cl were present as the source of ^{38}Cl. In Table XII a survey is given of the reported yields of recoil Cl atoms with halocarbons. The yields per atom are generally 1% or less, as are those for double displacement, when corrected for the possible loss of the radioactive label from an excited molecule. As a consequence of differences in pressure, scavenger, radiation dose, and the specific Cl isotope involved, the reported yields from a given compound sometimes differ considerably. It is therefore pointless to enter a detailed discussion. However, two series of measurements, each performed under similar conditions, warrant more attention:

(1) The work of Spicer and Wolfgang[199] with ^{39}Cl (60% Ar present) with the series $CH_4 \rightarrow CCl_4$. From the results it is apparent that (a) the total yield of substitution reactions decreases with increasing Cl substitution, a trend that corroborates the steric hindrance model, as discussed for the reactions of recoil ^{18}F atoms with fluoromethanes,[161-163] and (b) the Cl atom is preferentially displaced. After the energetic encounter, the resultant energy of the C–Cl bond becomes much greater than that of the C–H bond, which may result in the observed effect.

(2) The work of Lee and Hower[204] of ^{38}Cl with the series $CF_4 \rightarrow CCl_4$. Again substitution of the heavier atom is favored; however, the energy deposition in fluorochloromethanes may be higher than in the chloromethanes, and consequently more decomposition of the excited molecules may occur, and this can mask the observations of steric and inertial effects.

On the basis of the yields of single and double substitution products in the $^{38}Cl/CF_2Cl_2$ system, Lee and Rowland[209] calculated that the total original hot yields are 4.2% for Cl, and 2.2% for F substitution. However, these values may be underestimated, as even further decomposition of excited molecules may occur, just as was found in the $^{18}F/CF_4$ system.[169] Tang et al.[211] observed c-$C_3H_5{}^{38}Cl$ from the reactions of recoil ^{38}Cl atoms with CH_2Cl_2, scavenged with C_2H_4. This compound can only be formed by the addition of $CH^{38}Cl$ to C_2H_4, and indicates that the carbene is produced by the substitution of one H and two Cl atoms in CH_2Cl_2. Spicer[212] found an H/D isotope effect of 1.6 for the substitution of a single H or D atom in argon moderated (60–100%)

TABLE XIII. Average Logarithmic Energy Loss (α) and Reactivity Integrals (I) for Reaction of Recoil ^{38}Cl Atoms

compd	α	I	ref
CH_3Cl	$\alpha_{CH_3Cl}/\alpha_{He} = 7.40 \pm 0.41$	$I_{CH_3Cl/(CH_2Cl_2)}/\alpha_{He} = 0.296 \pm 0.021$	201
	$\alpha_{CH_3Cl}/\alpha_{Ne} = 3.03 \pm 0.13$	$I_{CH_3Cl(CH_2Cl_2)}/\alpha_{Ne} = 0.121 \pm 0.008$	
CH_3Cl^a	$\alpha_{CH_3Cl}/\alpha_{He} = 7.0$	$I_{CH_3Cl}/\alpha_{He} = 0.20 \pm 0.02$	
	$\alpha_{CH_3Cl}/\alpha_{Ar} = 2.3$	$I_{CH_2Cl_2}/\alpha_{He} = 0.035 \pm 0.003$	202
	$\alpha_{CH_3Cl}/\alpha_{Kr} = 2.2$	$I_{CH_2ClBr}/\alpha_{He} = 0.13 \pm 0.02$	
CCl_4	$\alpha_{CCl_4}/\alpha_{Ar} = 1.82$	$I_{CCl_4}/\alpha_{Ar} = 0.037$	205
		$I_{CCl_3}/\alpha_{Ar} = 0.017$	
		$I_{Cl_2}/\alpha_{Ar} = 0.016$	
CH_3Br	$\alpha_{CH_3Br}/\alpha_{He} = 5.6$	$I_{CH_3Cl}/\alpha_{He} = 0.14 \pm 0.1$	207
		$I_{CH_2ClBr}/\alpha_{He} = 0.10 \pm 0.10$	

[a] Br_2 scavenged.

CH_4/CD_4, and of 1.8 for double displacement.

Abstraction of an H atom or an halogen atom is more difficult to establish, because compounds such as HCl, Cl_2, or FCl are barely detectable. Mudra[205] found a yield of some 0.8% $C_2H_4Cl^{38}Cl$ in CCl_4, scavenged with C_2H_4. This compound was purported to be formed through the addition of $Cl^{38}Cl$. Brinkman et al.[206] found 5.7% 1,2-$C_6H_{12}Cl_2$ in CCl_4 scavenged with 10% 1-C_6H_{12} (samples at 373 K, with high radiation doses involved). Lee and Rowland[209] placed an upper limit of 5% on hot halogen abstraction from CF_2Cl_2, but they feel that the real yield for abstraction is less than 1%. The yields of hot reactions can be expressed in the terms of the kinetic theory, as discussed in the chapter dealing with recoil T atoms. For some systems, average logarithmic energy losses (α) and reactivity integrals (I), both expressed in terms of α for noble gases, were reported (Table XIII). The energy losses in collisions with the halomethanes indicate a substantial lack of elasticity.

Experiments with charged particle beams have confirmed that high radiation doses can result in considerable radiation damage, probably through reactions in thermalized recoil Cl atoms with formed products and radicals. In the case of reactions of ^{34m}Cl—produced by the $^{35}Cl(p,pn)^{34m}Cl$ nuclear reaction—with gaseous CCl_4 (at 373 K), 13% $CCl_3{}^{34m}Cl$ is formed by the reactions of thermal ^{34m}Cl atoms with radiolytically produced CCl_3 radicals (in unscavenged CCl_4, the total yield of $CCl_3{}^{34m}Cl$ was found to be 19.4%, but dropped to about 1% in the presence of suitable scavengers.[206] Even more severe effects were found by the reactions of ^{38}Cl—produced by the $^{37}Cl(d,p)^{38}Cl$ nuclear reaction—with gaseous fluorochloromethanes. For instance, in unscavenged $CFCl_3$ the yield of $CFCl_3{}^{38}Cl$ was (54 ± 2)%, whereas the addition of C_3F_6 decreased this yield to less than 4%.[210] Such extreme radiation conditions may be useful for the production of high yields of labeled compounds, but they barely contribute to a better understanding of real hot atom reactions.

B. Condensed Phase

Table XIV contains most of the data that were derived from the substitution of H and Cl atoms, and from the total organic yields in CH_2Cl_2, $CHCl_3$, and CCl_4. (The data of Black and Morgan[217] are not included in this table, as their experiments were conducted at 408 K, and a considerable part of the contents of the ampoules may therefore have been in the gaseous phase.)

TABLE XIV. Main Absolute Product Yields (%) for the Reactions of Recoil Cl Atoms with Liquid Chloromethanes

				CH_2Cl_2				
	a	*b*	*c*	*d*	*e*	*f*		average
subst Cl	28	21	20	21	15	14		20
subst H					6	5		7
org yield	37	34	34	34	49	36		37
				$CHCl_3$				
	a	*b*	*c*	*d*	*e*	*f*		
subst Cl	28	18	15	17	16	14		18
subst H			13		6	5		8
org yield	40	34	28	33	40	31		34
				CCl_4				
	a	*b*	*c*	*d*	*g*	*h*	*i*	
subst Cl	37	29	23	23	38	35	34	31
org yield	41	39	33	28	44	45	40	39

[a] Reference 213, ^{38}Cl(reactor), no scavenger, 1 h at 10^6 n cm^{-2} s^{-1}. [b] Reference 213, ^{38}Cl(Po/Be source), no scavenger, 20 h at an integral flux rate of 10^7 n s^{-1}. [c] Reference 213, ^{38}Cl(reactor), 0.5 mol % I_2, as in *a*. [d] Reference 213, ^{38}Cl(Po/Be source), 0.5 mol % I_2, as in *b*. [e] Reference 214, ^{34m}Cl(cyclotron), no scavenger, 30 min at 10^{11} n cm^{-2} s^{-1}. [f] Reference 214, ^{34m}Cl(cyclotron), 1 mol % I_2, as in *e*. [g] Reference 215, ^{38}Cl(reactor), no scavenger, 1 min at 10^{12} n cm^{-2} s^{-1}. [h] Reference 215, ^{34m}Cl(cyclotron), no scavenger, 20 min at 10^{11} n cm^{-2} s^{-1}. [i] Reference 216, ^{38}Cl(reactor), 10^{-5} N Br_2, 3–4 s at 10^{13} n cm^{-2} s^{-1}.

Substitution yields are much greater in the liquid than in the gaseous phase. A rather interesting effect was observed by van Dulmen and Aten[215] using neutrons—produced by 26 MeV deuterons in a Be target—for experiments with liquid CCl_4. The fast neutrons were slowed in a block of paraffin, in which the sample was placed. However, the paraffin was not thick enough to moderate all of the neutrons completely. Apart from the reactions of thermal neutrons—$^{37}Cl(n,\gamma)^{38}Cl$, reactions of fast neutrons—$^{35}Cl(n,2n)^{34m}Cl$—were also detected. The fluxes of both thermal and fast neutrons were very low, and the induced activities did not permit the determination of individual product yields; only total organic yields could be determined: (44.9 ± 2.0)% for recoil ^{34m}Cl atoms and (35.5 ± 0.6)% for ^{38}Cl. These results are important because the reactions of both of the recoil atoms were proceeding under similar conditions of temperature and radiation dose. (Similar effects were found for C_2Cl_4: (59.0 ± 3.2)% for ^{34m}Cl and (37.3 ± 2.2)% for ^{38}Cl.) The cause of this effect was not discussed, but it may be as a consequence of differences in the recoil energies of the two atoms.[218]

Using ^{34m}Cl recoil atoms, Brinkman et al.[214] compared product yields for $CHCl_3$ and $CDCl_3$. Relative to the ^{34m}Cl-for-H substitution yields in both compounds, the $CCl_3{}^{34m}Cl$ yields were (37.5 ± 0.8)% for $CHCl_3$ and (47.4 ± 1.0)% for $CDCl_3$, and so thus an H/D isotope effect of (0.79 ± 0.03). A similar experiment performed by Wai[219] with recoil ^{38}Cl atoms resulted in relative yields

TABLE XV. **Absolute Product Yields (%) for the Reactions of Recoil Cl Atoms with Solid CCl_4**

isotope	temp (K)	CCl_4	C_2Cl_4	C_2Cl_6	org yield	ref
^{34m}Cl	233	63	3	12	80	215[a]
	233				63	215[b]
^{38}Cl	236				51	226
	193				75	226
	75	61	7	75		227
	233				63	215[b]

[a] Fast neutron facility at NIKHEF, 10^{11} n cm^{-2} s^{-1}. [b] Measured in one sample in the thermal neutron facility at NIKHEF, 10^8 n cm^{-2} s^{-1}.

of (29.1 ± 0.8)% and (23.2 ± 0.7)%, respectively, or an isotope effect of (1.25 ± 0.05). Also in contradiction with the ^{34m}Cl results, Spicer[220] found an inverse isotope effect for several product yields for the reactions of ^{38}Cl with $CHCl_3$ and $CDCl_3$. No viable explanation could be provided for these discrepancies.

Apart from the products formed by recoil Cl-for-H and Cl substitution, labeled ethylenes and ethanes were also detected: in the case of CCl_4, 2–3% labeled C_2Cl_4 and 3–6% C_2Cl_6. Both products were also observed in the radiolysis of CCl_4 (C_2Cl_4 only in the presence of scavengers for Cl atoms[221–223]). It was proposed that C_2Cl_4 was formed through reactions of CCl_2 biradicals:

$$CCl_2 + CCl_4 \rightarrow (C_2Cl_6)^*$$

$$(C_2Cl_6)^* \rightarrow C_2Cl_4 + Cl_2$$

In photolysis of gaseous CCl_4, C_2Cl_4 was observed at energies above 7 eV and it was suggested that C_2Cl_4 was formed through reactions of CCl radicals:[224]

$$CCl + CCl_4 \rightarrow (C_2Cl_5)^*$$

$$(C_2Cl_5)^* \rightarrow C_2Cl_4 + Cl$$

This means that three Cl atoms ($CCCl^*$) or even four Cl atoms (CCl^*) must be displaced for the production of labeled C_2Cl_4. Labeled C_2Cl_6 is thought to be formed by the recombination of a labeled CCl_3 radical with a caged CCl_3 radical. This agrees with a spur mechanism as proposed by Bibler[223] for the formation of C_2Cl_6 in the radiolysis of CCl_4, where the addition of small amounts of Br_2 did not influence the C_2Cl_6 yields. In the $^{34m}Cl/CHCl_3$ system, eight labeled methanes, ethylenes, and ethanes were observed. The same products were found in radiolysis experiments of $CHCl_3$.[214]

Some data have been published regarding the reactions of ^{34m}Cl and ^{38}Cl recoil atoms with liquid $CFCl_3$: the total organic yields were (38 ± 7) and (39 ± 1)%, respectively.[175] Only relative product yields were measured, but—if no high boiling products are formed—the yield of labeled $CFCl_3$ is 30% for both isotopes and 6% for labeled CCl_4. The yields were explained by caged recombination between recoil Cl atoms and $CFCl_2$.

Product yields were also measured for solid CCl_4 (Table XV). The yields of labeled CCl_4 and C_2Cl_6 are double those in the liquid phase, indicating an enhancement of cage recombination reactions. The results of Goldhaber et al.[226] point to a temperature effect, while those of van Dulmen et al.[215] indicate a dose effect. van Dulmen et al. found the same organic yield for recoil ^{34m}Cl as for ^{38}Cl atoms in the same sample, irradiated in the (former) IKO thermal neutron facility.

C. Liquid Mixtures

One of the techniques used to differentiate between hot and thermal reactions of recoil atoms, is to evaluate the effect of scavengers for thermal atoms on the absolute product yields. Br_2 and I_2 are efficient scavengers for thermal Cl atoms, and the addition of 1 mol % of Cl_2, Br_2, or I_2 to CCl_4 decreases the total organic yields by 4–16%, but the results were not particularly consistent (Table I in ref 228). The addition of more of these halogens resulted in still lower yields. These experiments did not permit the arrival of definite conclusions on hot and/or thermal reactions in liquid CCl_4.

In 1950 Miller and Dodson[229] observed that the total yield or organic bound recoil ^{38}Cl atoms in liquid CCl_4 (43%) decreased sharply to 20% upon the addition of 25 mol % of c-C_6H_{12}. At higher hexane concentrations this yield decreased monotonically to 14% for pure c-C_6H_{12}. A similar trend was observed by Vasáros et al.,[230] who added CH_3OH, C_2H_5OH, and C_3H_7OH to CCl_4. Product analysis by GLC proved that the decrease in the organic yield was mainly as a consequence of a decrease in the yield of $CCl_3{}^{38}Cl$ from about 35% for pure CCl_4 to about 10% upon the addition of 25 mol % of the alcohols. This effect was attributed to reactions of the recoil ^{38}Cl atoms with the alcohols. Stöcklin and Tornau[231] found a decrease in the $CCl_3{}^{38}Cl$ yield from 37% to 10% upon the addition of 25 mol % C_6H_6, and to 12% on adding $C_6H_5CH_3$. Apart from direct reactions of ^{38}Cl atoms with arenes:

$$^{38}Cl + ArH \rightarrow Ar^{38}Cl$$

they also proposed a reaction of excited $CCl_3{}^{38}Cl$ molecules with the arenes:

$$(CCl_3{}^{38}Cl)^* + ArH \rightarrow CHCl_2{}^{38}Cl + Ar^{38}Cl$$

Berei and Vasáros[227] published similar data for the CCl_4/C_6H_6 system, but for the CCl_4/C_6H_5Cl system the organic yield increased from 38% in pure CCl_4 to some 55% upon the addition of 25 mol % C_6H_5Cl, this effect being caused by the formation of about 25% $C_6H_5{}^{38}Cl$; at the same time, the $CCl_3{}^{38}Cl$ decreased to about 18%. The authors pondered as to whether cage reactions were of importance in liquid CCl_4 mixtures, but a kinetic investigation of the product yields obtained for CCl_4/1,1-$C_2H_4Cl_2$ mixtures seemed to contradict this theory of caging.[232] Kontis and Urch[233–235] found that the organic yield for recoil ^{38}Cl atoms with liquid CCl_4 decreased sharply upon the addition of 25 mol % of several hydrocarbons, alkyl chlorides, and alcohols, but they also found an increase on adding C_6H_5Cl. They explained these results by the existence of two types of reactions: in the aliphatic systems, the organic yield is achieved in a single hot zone, either through a true hot reaction or by reactions with a high concentration of radicals (cage model), which will reflect a certain aspect of radiation chemistry; in the case of C_6H_5Cl a second stage must be involved, in which thermal diffusive ^{38}Cl atoms react with C_6H_5Cl via an exchange reaction, probably via an σ-complex. For the analysis of their results, Kontis and Urch developed a theory that was based on the assumption of different cross sections (σ) for the reactions of recoil ^{38}Cl atoms with the two compounds (A and B). They calculated relative

TABLE XVI.[236-238] **Reactivity Parameters S (= σ_A/σ_B) and S' (= $\sigma_{A'}/\sigma_{B'}$) for the Reactions of Hot and Thermal Recoil ^{38}Cl Atoms with Mixtures of Chloromethanes**

	S		
A	B = CH_2Cl_2	$CHCl_3$	CCl_4
n-C_5H_{12}	5.7	12.5	11
n-C_8H_{12}	14.1	14.0	9.9
c-C_8H_{12}	13.5	18.0	12.0
n-C_4H_9Cl			5.4
n-$C_8H_{13}Cl$			9.6
CH_3OH	6.5	7.0	6.0
C_2H_5OH	7.4	7.0	8.7
C_3H_7OH	12.8	7.0	
C_4H_9OH	17.0	10.0	
$C_8H_{17}OH$			20
	A = aniline		
	B = CH_2Cl_2	$CHCl_3$	CCl_4
S	28.6	31.4	23.0
S'	10.0	12.8	18.6

TABLE XVII.[228] **Effects of Several Additives on the Absolute Product Yields (%) for the Reactions of Recoil ^{34m}Cl Atoms with Liquid CCl_4**

additive (mol fraction)	CCl_4	$CHCl_3$	C_2Cl_4	C_2Cl_6	high boiling	org yield
	30		2	5	10	47
1% I_2	24		2	4	7	37
25% c-C_8H_{12}[a]	3	4	1	1		35
25% C_8H_8[b]	16	3	2	2	39	70
5% 1-C_6H_{12}[c]	14	nm[e]	nm	nm	48	75
5% CHT[d]	3	2	1	nm	82	89
10% $C_6H_5NH_2$	8	1	2	1	14	26
sat. DPPH	33		3	1	45	82

[a] 5% c-$CH_{11}{}^{34m}Cl$. [b] 7% $C_6H_5{}^{34m}Cl$. [c] 11% 1,2 $C_8H_{12}Cl^{34m}Cl$. [d] Cycloheptatriene. [e] Not measured.

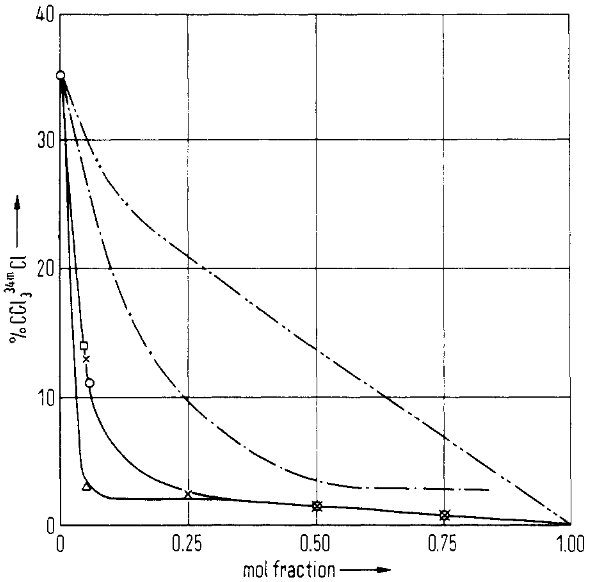

Figure 4. The yield of $CCl_3{}^{34m}Cl$ as a function of the mole fraction of n-C_6H_{14} (○), c-C_6H_{12} (×), 1-C_6H_{12} (□), CHT (△) in CCl_4, and C_2H_5OH (- - -, ref 230 for ^{38}Cl), 1,2-$C_2H_4Cl_2$ (-·-·-), ref 232 for ^{38}Cl). Reproduced with permission from ref 225. Copyright 1979, Akad Verlagsgesellschaft (Wiesbaden).

cross sections (S) for both the hot ($S = \sigma_A/\sigma_B$) and thermal ($S' = \sigma_{A'}/\sigma_{B'}$) reactions. This type of analysis was later applied by Bhave and Rao[236-238] on mixtures with CH_2Cl_2, $CHCl_3$, and CCl_4 (Table XVI). (The model was later extended to a two-stage process[239].) [No thermal substitution of a Cl atom in CCl_4 by thermalized recoil Cl atoms is to be expected, but even if such a reaction could take place, its rate constant would be several orders of magnitude lower than for (Table XVII) (1) reaction with Br_2 or I_2, (2) addition to unsaturated compounds, and (3) H abstraction from hydrocarbons.

Less than 1 mol % of I_2 prevents thermal Cl-for-Cl exchange in liquid C_6H_5Cl, but this amount of I_2 is insufficient to decrease the 35% yield of $CCl_3{}^{34m}Cl$ or $CCl_3{}^{38}Cl$ to about 5% (the real hot substitution yield).[228] The observation that relatively large amounts of saturated and unsaturated hydrocarbons (10–20%) are needed to decrease the initial 35% labeled CCl_4 yield to 5% was ascribed to the involvement of cage reactions.[225] High energy recoil ions will be decelerated in liquids by ionizing collisions, and ions, radicals, and excited molecules will be created in the track of the particle. In the keV range, the ion will be neutralized and lose its kinetic energy by elastic collisions. When the recoil particle reaches the eV range, where chemical reactions leading to stable products can take place, it will be surrounded by radicals and excited molecules. Depending upon the mass of the recoil atom and the concentration of radicals in the cage, it can react by a caged recombination process, or escape from the cage and then react as a thermal atom in a normal diffusion controlled reaction. This latter process seems to take place for T atoms recoiling in liquid CCl_4 (no $CTCl_3$ is formed[86]), but the heavier Cl atom cannot escape as readily from the cage, and so hence the high yield of labeled CCl_4. The major proportion of radicals in the cage are Cl and CCl_3, the Cl atoms more readily escaping than the heavier CCl_3 radicals. The reactions to be expected are

$$^{34m}Cl + CCl_3 \rightarrow CCl_3{}^{34m}Cl$$

and

$$^{34m}Cl + Cl \rightarrow Cl^{34m}Cl$$

probably followed by

$$Cl^{34m}Cl + CCl_3 \rightarrow CCl_3{}^{34m}Cl + Cl$$

In this model it is apparent that rather large amounts of additives are required to prevent these cage reactions, as some of these molecules must form part of the cage. The rivalry between several additives in reaction with these cage recoil ^{34m}Cl atoms is illustrated in Figure 4, from which it can be seen that the reaction rate is in the order of CHT → n-C_6H_{14} → C_6H_6. It is obvious from the changes in the total organic yield (Figure 5) that different reactions of the caged ^{34m}Cl atoms with the additives take place,[110,225] but these reactions are outside the scope of this article. Another illustration of cage reactions of Cl atoms recoiling in liquid CCl_4 is given in Figure 6. The pattern of the decrease in the $C_2Cl_5{}^{34m}Cl$ yield upon the addition of hydrocarbons is comparable with that observed for $CCl_3{}^{34m}Cl$, and is quantitatively similar to the increase in the $CHCl_2{}^{34m}Cl$ yield. This behavior was explained as a double displacement reaction yielding $CCl_2{}^{34m}Cl$ radicals, followed by a caged recombination reaction, or by H abstraction:

$$CCl_2{}^{34m}Cl + CCl_3 \rightarrow C_2Cl_5{}^{34m}Cl$$

$$CCl_2{}^{34m}Cl + RH \rightarrow CHCl_2{}^{34m}Cl + R$$

The initial slopes of the $CHCl_2{}^{34m}Cl/C_2Cl_5{}^{34m}Cl$ ratios when plotted as a function of the relative hydrocarbon concentrations $[RH]/[CCl_4]$ is a measure of the rate of

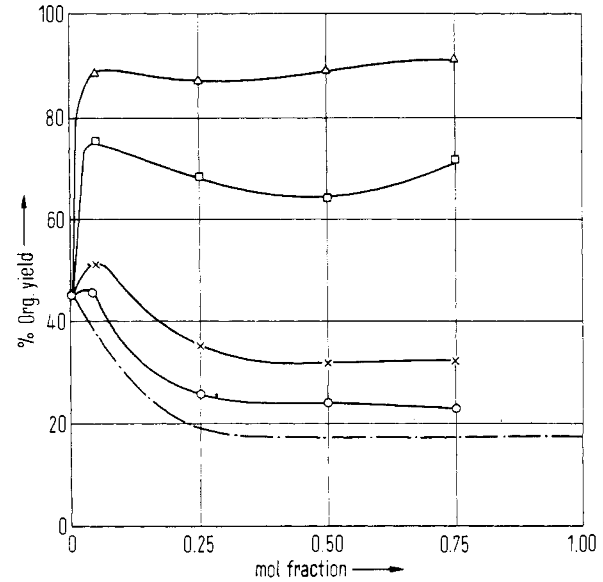

Figure 5. The total organic yield as a function of the mole fraction of n-C_6H_{14} (○), c-C_6H_{12} (×), 1-C_6H_{12} (□), CHT (△) in CCl_4 and C_2H_5OH (---, ref 230 for ^{38}Cl). Reproduced with permission from ref 225. Copyright 1979, Akad Verlagsgesellschaft (Wiesbaden).

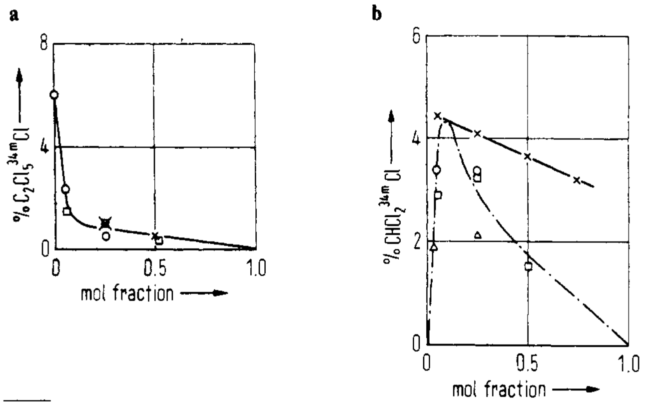

Figure 6. (a) The yield of $C_2Cl_5{}^{34m}Cl$ as a function of the mole fraction of n-C_6H_{14} (○), c-C_6H_{12} (×), and 1-C_6H_{12} (□) in CCl_4. (b) The yield of $CHCl_2{}^{34m}Cl$ as a function of the mole fraction of n-C_6H_{14} (○), c-C_6H_{12} (*), 1-C_6H_{12} (□), CHT (△), and C_2H_5OH (---, ref 230 for ^{38}Cl) in CCl_4. Reproduced with permission from ref 225. Copyright 1979 Akad. Verlagsgesellschaft (Wiesbaden).

H abstraction from the additives, and was determined for CHT:n-C_6H_{14}:1-C_6H_{12}:C_6H_6 as 1:3.7:2.4:0.3[240] (no H abstraction from $CHCl_3$ was observed in mixtures of CCl_4 and $CHCl_3$).

Apart from hot ^{34m}Cl-for-Cl substitution in CCl_4, hot abstraction reactions yielding $Cl^{34m}Cl$ may also take place. In this type of research it is virtually impossible to measure the $Cl^{34m}Cl$ yield quantitatively. However, in a mixture of CCl_4 with 5 mol % of 1-C_6H_{12}, a yield of 12% of 1,2-$C_6H_{12}{}^{34m}Cl$ was observed, which could be an indication of hot Cl abstraction reactions, if this compound is indeed formed by the addition of a $Cl^{34m}Cl$ molecule to 1-C_6H_{12}, and not through step-by-step reactions.

VI. Bromine

Arrhenius parameters for the reactions of ground-state ($^2P_{3/2}$) Br atoms with halomethanes are given in Table XVIII.[8] Only some rate constants for the collisional removal of excited ($^2P_{1/2}$) Br atoms—0.46 eV above the ground state—are reported: CH_4 (2.41×10 L mol^{-1} s^{-1}), CF_4 (1.20×10^8), and CF_3Br (3.01×10^7).[241]

TABLE XVIII. Arrhenius Parameters for the Reactions of Ground-State Br($^2P_{3/2}$) Atoms with (Halo)methanes[8]

compd	A (10^{10} L mol^{-1} s^{-1})	ΔE (kJ mol^{-1})	compd	A (10^{10} L mol^{-1} s^{-1})	ΔE (kJ mol^{-1})
H Abstraction			Br Abstraction		
CH_4	5.6	77.8	CH_3Br	5.0	95.8
CH_3F	4.2	65.7	CH_2Br_2	10.0	
CH_2F_2	1.9	67.8	CF_3Br	7.2	103.6
CHF_3	1.5	93.7	CCl_3Br	8.1	43.1
CH_3Cl	4.2	60.7			
CH_2Cl_2	1.0	46.5	I Abstraction		
$CHCl_3$	0.23	38.9	CF_3I	8.1	45.2
CH_2FCl	7.8	61.9			
$CHFCl_2$	1.0	55.7			
CH_3Br	7.1	67.8			
CH_2Br_2		57.3			
$CHBr_3$	1.0	45.2			

TABLE XIX. Production Modes of Radioactive Recoil Bromine Isotopes

$^{79}Br(n,\gamma) \rightarrow {}^{80m}Br$ (4.4 h)
$^{79}Br(n,\gamma) \rightarrow {}^{80}Br$ (17.6 min)
$^{81}Br(n,\gamma) \rightarrow {}^{82m}Br$ (6.1 min)
$^{81}Br(n,\gamma) \rightarrow {}^{82}Br$ (35.4 h)
^{80m}Br (4.4 h) $\xrightarrow{IT}$ ^{80}Br (1.76 min)
^{82m}Br (6.1 min) $\xrightarrow{IT}$ ^{82}Br (35.4 h)
^{235}U (n,fission) $^{84-89}Br$

A. Reactions with Methane

Various types of nuclear reactions can lead to the production of radioactive recoil Br atoms and ions (Table XIX):

(1) Thermal neutron activation of ^{79}Br and ^{81}Br resulting in energetic ground $^{80,82}Br$ and metastable $^{80m,82m}Br$ atoms.

(2) Isomeric transition of $^{80m,82m}Br$ to ground-state $^{80,82}Br$. As these transitions are highly converted, the ground state Br particles are multiply charged Br^{n+} ions. The metastable isotopes are in general incorporated in compounds such as HBr, Br_2, CH_3Br, and CF_3Br.

(3) Electron capture decay of ^{76}Kr also yield multiply charged $^{76}Br^{n+}$ ions. The β^+ decay of ^{77}Kr gives rise to 60% $^{77}Br^-$, 20% Br^0, and 20% Br^{n+} particles.

(4) Fission of ^{235}U results in the direct formation of $^{84-89}Br$ isotopes with high kinetic energies and to their indirect formation through β^- decay of the corresponding Se isotopes, resulting in Br^+ ions.

Due to the differences in recoil energies and charges, the recoil chemistry of bromine is a complicated matter. Urch[3,41] has published two review articles on these reactions.

Methane. The first article on the reactions of recoil Br particles was published by Gordus and Willard in 1957.[242] The total yield of organic products—consisting mainly of CH_3Br and CH_2Br_2—formed by the $^{79}Br(n,\gamma)^{80}Br$ reaction was 18%, if 0.5 mol % Br_2 was present as the source for ^{80}Br. The organic yields for the isomeric $^{80m}Br \rightarrow {}^{80}Br$ transition were found to be between 0 and 8%, depending upon which molecule contained the ^{80m}Br atom (Table XX). The isomeric transition contributes to the formation of highly charged $^{80}Br^{n+}$ ions ($n \leq 12$).[243] After charge distribution to the other atoms in the molecule, the molecule will blow up, due to coulombic repulsion. In case of $CH_3{}^{80m}Br$, the parent molecule was broken into the

TABLE XX.[242] **Organic Yields (%) for the Reactions of Recoil ^{80}Br Particles with CH_4**

parent compound	$H^{80m}Br$	$CH_3{}^{80m}Br$	$C_2H_5{}^{80m}Br$	$CCl_3{}^{80m}Br$	$CH_3{}^{80m}Br$	$Br^{80m}Br$
recoil energy, eV	1	10	10	10	22	24
organic yield, %	<0.1	4	3	8	8	8

fragments as CH_3^+, CH_2^+, CH^+, C^+, CH_3Br^+, CH_2Br^+, $CHBr^+$, CBr^+, Br^{n+}, and H^+.[243,244] The amount of kinetic energy and the charge of the ^{80}Br ions depend on the numbers and types of the other atoms in the molecule. If it is assumed that the ions must all be reduced to a 1+ (or possibly 2+) state through charge-transfer collisions prior to reacting, the differences between the organic yields for differing parent molecules (Table XX) cannot be explained by variences in the charges of the Br^{n+} ions.

Investigations by Rack and Gordus[245,246] with rare gas moderators showed that the organic yield for the ^{79}Br(n,γ)^{80}Br reaction (measured by them as 13% in the presence of 0.5 mol % Br_2) dropped to 0 at 100% moderation, indicating that the reactions with CH_4 occurred as a result of the recoil kinetic energy of ^{80}Br atoms, although 18% of the ^{80}Br particles are in the 1+ charge state.[247] Similar yields as reported above were also found by Spicer and Gordus:[248] organic yield of 12% for the ^{79}Br(n,γ)^{80}Br reaction in CH_4 and 7% for the ^{80m}Br(IT)^{80}Br reaction, when extrapolating to 0 mol % $Br^{80m}Br$. Numakara et al.[249] found that in the $CH_4/Br^{80m}Br$ system the yield of $CH_2Br^{80}Br$ increased from 2 to 3% upon the addition of Kr. This finding suggests the partial formation of $CH_2Br^{80}Br$ via a thermal ionic process in highly moderated systems.

In CH_4, the ^{81}Br(n,γ)^{82m}Br reaction also leads to an organic yield of some 13%.[250] In the case of the ^{82m}Br(IT)^{82}Br decay the organic yield from $Br^{82m}Br$ decreases from 7% (6% $CH_3{}^{82}Br$, 1% $CH_2Br^{82}Br$) to 2% (1% $CH_3{}^{82}Br$, 1% $CH_2Br^{82}Br$) on high moderation with Ar.[251-253] Yagi and Kondo[254-261] published a series of papers on the same subjects: to explain the results for the $H^{80m}Br/CH_4$ and $H^{82m}Br/CH_4$ systems, they suggested that the charge complex (CH_4Br^+), formed in the primary step resulted in an ion cluster with surrounding molecules in the subsequent step, thus generating the final products.[258,259,261] Differences in product yields between the reactions of ^{80}Br and ^{82}Br—activated by the isomeric transitions—with gaseous CH_4, were attributed to the consecutive, two-step internal conversion process in the cascade deexcitation of ^{80m}Br, where an intermediate level with a half-life of 7.4 ns exists.[262] The transition from this level to the ground state is converted for only 61%, whereas the first transition to the metastable level and the transition $^{82m}\mathrm{Br} \rightarrow {}^{82}\mathrm{Br}$ are converted for 100%.[256,260]

TABLE XXI. **Parameters of Kinetic Theory**[a]

reaction system	α	*I* (total)	*I* (CH_3Br, CD_3Br)	ref
^{79}Br(n,γ)^{80}Br + CH_4	0.266	0.043	0.04	265
	0.3	0.057		245
^{79}Br(n,γ)^{80}Br + CD_4	0.280	0.020	0.015	265
^{80m}Br(IT)^{80}Br + CH_4	0.266		0.018	249
^{82m}Br(IT)^{82}Br + CH_4	0.098		0.004	246

[a] Expressed in Units of α_{kr}.

TABLE XXII. **Decay Characteristics of ^{78}Kr and ^{77}Kr**

decay	^{78}Kr 14.8 h) $\xrightarrow{100\%\ EC}$ ^{78}Br (16.4 h)
	^{77}Kr (1.2 h) $\xrightarrow[16\%\ EC]{84\%\ \beta^+}$ ^{77}Br (54 h)
charge	^{76}Br: 100% + *n* (1 < *n* < 13)
	^{77}Br: 35% + *n* (1 < *n* < 13)
	15% 0, 50% 1−
recoil energy	^{78}Br: 100% EC, max 7.25 eV
	^{77}Br: 16% EC, max 56.9 eV
	84% β^+, max 36.4 eV
	av 10.4 eV

CH_4/CD_4. Spicer and Gordus[248] found an isotope effect in the organic yields due to reactions of ^{80}Br with CH_4 and CD_4. For the ^{79}Br(n,γ)^{80}Br activation, the organic yields were 12.0 and 6.4%, respectively, and for the ^{80m}Br(IT)^{80}Br decay, 6.8 and 4.5%. Nicholas and Rack[246] found no isotope effect for the organic yields from CH_4 and CD_4 with ^{82}Br, but this may be due to rare gas sensitized radiation damage.[252] A detailed investigation was carried out by Tachikawa et al.[263,264] In the case of the ^{80m}Br(IT)^{80}Br decay, the $CH_3{}^{80}Br$ yield was found to be 3.5%, with the $CD_3{}^{80}Br$ yield at 1.6%. Both yields dropped to 0.5% on moderation with Xe, indicating an isotope effect of 2.7 (= (3.5 − 0.5)/(1.6 − 0.5)) for the reactions of energetic ^{80}Br atoms. The 0.5% yields at high moderation are due to thermal reactions of $^{80}Br^+$ ions. A similar isotope effect was found for the reactions of ^{82}Br atoms, generated by the ^{82m}Br(IT)^{82}Br transition, although the absolute yields are a factor of 1.5 higher than for ^{80}Br. No isotope effect was found for $CH_2Br^{80}Br$ or $CD_2Br^{80}Br$. In both cases the yield was 1.1%, which remains constant on moderation with Xe, thus establishing that these compounds are formed by thermal $^{80}Br^+$ ions.

Kinetic Theory. Several papers have dealt with the determination of parameters that can be derived by applying the Estrup–Wolfgang kinetic theory.[57,58] In Table XXI data are given on α, the average logarithmic energy loss and on *I*, the reactivity integral. The differences found between the ^{82m}Br(IT)^{82}Br and the other data may be attributable to an additional yield due to kinetic energy independent processes that become noticeable at high moderation.[266] The low values of *I* barely suggest the probability of hot reactions by recoil Br atoms. However, the kinetic theory still appears to be an adequate framework for the data derived by the addition of moderators.[246]

^{235}U Fission. Fission of ^{235}U by thermal neutrons results in the formation of two types of recoil Br particles:

(1) Primary Br species, generated directly by the fission of a ^{235}U nucleus.

(2) Secondary Br species, brought about by the decay of the corresponding Se atoms, these being produced either by a primary or secondary process. In the reaction with CH_4, the ratio of organic yields derived by the secondary and primary reactions were measured as 1.1 for ^{84}Br, 0.1 for ^{86}Br, and with no secondary yield being detected for ^{87}Br.[267]

^{76,77}Br. More recently, the reactions of ^{76}Br and ^{77}Br—formed by the decay of ^{76}Kr and ^{77}Kr—with CH_4 have been studied.[268,269] In contrast with ^{80}Br and ^{82}Br that are produced in a nuclear reactor, a cyclotron is needed for the production of the Kr isotopes, e.g., ^{76,77}Se(^{3}He,3n)^{76,77}Kr, ^{79}Br(p,4n)^{76}Kr, and ^{79}Br(p,3n)^{77}Kr. The initial charges and recoil energies for the two Br

TABLE XXIII. Organic Yield (%) for (n,γ) Produced ^{80}Br in Br_2 Scavenged Gaseous Halomethanes

	OY	ref
CH_3F	8.5[a]	272, 273, 274
CD_3F	5.8[a]	272
CH_2F_2	3.2	275
CHF_3	1.5	275
CF_4	0.4	275
CH_3Cl	5.0; 3.0[b]	274, 276
CH_3Br	4.3; 2.8; 4.0;[c] 3.9	274, 275
CF_3Br	0.8; 1.3	271, 275
CH_2ClBr	1.4[d]	279

[a] Extrapolated to 0% Br_2. [b] 2.12% CH_3Br, 0.22% CH_2ClBr, 0.65% CH_2Br_2. [c] 3.0% CH_3Br, 1% Br_2. [d] 0.30% CH_2ClBr, 0.17% CH_2Br_2, 0.90% CH_2BrI (I_2 scavenger).

isotopes are given in Table XXII. At a pressure of 2.5 MPa, the yield of both $CH_3{}^{76}Br$ and $CH_3{}^{77}Br$ are 4.5%.[268] As the recoil energies of the Br^+ ions are too low to explain these results via a direct reaction:

$$Br^+ + CH_4 \rightarrow CH_3Br + H^+$$

it was suggested that a reaction between an excited intermediate molecule ion and CH_4 proceeds:

$$Br^+ + CH_4 \rightarrow [CH_4Br^+]^*$$

$$[CH_4Br^+]^* + CH_4 \rightarrow CH_3Br + CH_5{}^+$$

This suggestion can also explain the observation that the CH_3Br yields in unmoderated CH_4 increase only slightly (25%) over an 10^3 increase in pressure from 3 kPa to 3 MPa.

The CH_3Br yields decrease on moderation, but above 80 mol % of Ar or Kr, the yields increase to 12% for $CH_3{}^{76}Br$ and to 5% for $CH_3{}^{77}Br$. Brominating complexes, such as $ArBr^+$ and $KrBr^+$, were hypothesized to explain the results at high moderation.

At very high pressures (>3 MPa) the CH_3Br and the C_2H_5Br yields increase, which was explained by the onset of cage reactions due to autoradiation effects, caused by the Auger electrons emitted after the electron capture event. These increases in yields reached maximum values in the solid phase (liquid N_2 temperature):[268] 36.5% ($CH_3{}^{76}Br$), 13.8% ($CH_3{}^{77}Br$); 15.9% ($C_2H_5{}^{76}Br$), 18.9% ($C_2H_5{}^{77}Br$).

The differences in yields between ^{76}Br and ^{77}Br are correlated with differences in the initial charges and the kinetic energies of the two types of recoil particles.

Se(p,n)^{76,77,82}Br. Proton irradiations of CH_4 + 20 mol % H_2Se resulted in the formation of labeled CH_3Br, with yields of (5.5 ± 0.1)%, (6.8 ± 1.3)%, and (3.1 ± 1.3)% for ^{76}Br, ^{77}Br, and ^{82}Br, respectively.[270] Due to the high initial kinetic energies, the Br isotopes react as neutral species. However, radiolysis and increased temperature during the irradiations require a more detailed discussion.

B. Reactions with Halomethanes

1. Gaseous Phase

(n,γ) Reactions. The first experiments with gaseous halomethanes were performed in 1953 by Rice et al.,[271] who found an organic yield of 7% for the $^{79}Br(n,\gamma)^{80}Br$ reaction with CF_3Br. However, this yield was mainly due to the reactions of thermal ^{80}Br atoms with impurities and radicals, as the addition of 0.5 mol % Br_2 reduced this yield to 1%. Organic yields for scavenged halomethanes are given in Table XXIII. Alfassi et al.[276] found that in CH_3Br thermal reactions account for the major proportion of the organic yield, i.e., 12.8% for unscavenged CH_3Br, which decreases to only 3.5% in the presence of 0.5 mol % Br_2. Minor differences were found in the organic yields, brought about by Br isotopes produced via several (n,γ) reactions in CH_3F:[272] ^{80}Br, (8.5 ± 0.3)%; ^{80m}Br, (10.0 ± 0.3)%; $^{82+82m}$Br, (7.5 ± 0.3)%. These differences are due to fluctuations in the kinetic energy spectra of the Br atoms. The addition of He and Ar reduces all these yields to 0 at 100% moderation, indicating that the reactions occur entirely as a result of the recoil energies of the Br atoms. Apart from differences between the Br isotopes, a large isotope effect was also found between CH_3F and CD_3F. The organic yields for the latter compound are ^{80}Br, (5.8 ± 0.3)%; ^{82}Br, (7.5 ± 0.3)%; $^{82+82m}$Br, (5.0 ± 0.3)%[272] and the average H/D isotope effect is 1.46. From the data given in Table XXIII it can also be seen that double atom substitution is an important reaction channel (at least in chloromethanes), and the yield of the (H + Cl) substitution in CH_2ClBr is even higher than the total yields of single atom substitution reactions.

TABLE XXIV. Organic Yields (%) for IT Produced ^{80}Br and ^{82}Br in Br_2 Scavenged Gaseous Halomethanes

	^{80}Br		^{82}Br	
	OY	ref	OY	ref
CH_3F		271	5.8	4
CH_2F_2	1.5	275		
CHF_3	0.8	275		
CF_4	0.3	275		
CH_3Cl[a]	2.5	275	4.5	4
CH_2Cl_2	2.0	275		
$CHCl_3$	2.5	275		
CCl_4	0.5	275		
CH_3Br[b]	2.4	275	3.9	274
CH_3Br	5.1	280	3.9	278
CH_3Br			5.9	281
CF_3Br	1.4	275		
CH_2Br_2			8.2	282

[a] When $CF_3{}^{80m}Br$ was used as the precursor, the OY is 3%.[283] [b] When $H^{80m}Br$ and $H^{82m}Br$ were used as the precursors, the OY are 4.5 and 5.1%, respectively.

(IT) Reactions. In Table XXIV a compilation is given of organic yields for the reactions of ^{80}Br and ^{82}Br—produced via isomeric transitions from ^{80m}Br and ^{82m}Br—with gaseous halomethanes. Most experiments have been performed with $Br^{80m}Br$ and $Br^{82m}Br$ as the sources of the recoil particles. The only experiment with HBr as the precursor[283] does not result in lower yields, as observed with CH_4 (Table XXIV). Differences in the organic yields generated by ^{80m}Br and ^{82m}Br in CH_3Br were explained by the higher reactivity of ^{80}Br (activated by the two-step internal conversion), in contrast with ^{82}Br, activated via the one-step process.[280] Extrapolation to 100% moderation of yield curves for $CH_3{}^{82}Br$ and $CH_2Br{}^{82}Br$, measured for CH_3Br mixed with 0–80 mol % He, Ar, Xe, and Br_2, resulted in 0 product yields.[278,281] Both products are formed via excess kinetic energy processes, in contrast with products formed from CH_4, where isomeric processes are also involved. However, using $CF_3{}^{80m}Br$ as the precursor for the production of ^{80}Br, the moderation curves level off above 80 mol % Ar and do not extrapolate to 0, but to 0.8% for CH_3Cl, 0.4% for CH_3F, 1.9% for CH_3Br, and

TABLE XXV.[270] **Absolute Product Yields (%) in Proton Irradiated Mixtures**[a]

gas mixture	proton current (nA)	CH_3Br			CH_2XBr		
		^{76}Br	^{77}Br	^{82}Br	^{76}Br	^{77}Br	^{82}Br
CH_3F + 15% H_2Se	250 nA	83 ± 3	73 ± 2	70 ± 2	5.9 ± 0.6	5.3 ± 0.7	5.0 ± 0.5
CH_3F + 22% $(CH_3)_2Se$	250 nA	20 ± 1	20 ± 1	19 ± 2			
CH_3F + 82% H_2Se	250 nA	4.5	4.2	2.8			
CH_3F + 21% $(CF_3)_2Se$[b]	250 nA	34 ± 5	32 ± 1	24 ± 2			
CH_2Cl + 20% H_2Se	250 nA	63 ± 6	63 ± 1	53 ± 9	1.6 ± 0.6	1.7 ± 0.7	1.9 ± 0.4
CH_3Cl + 21% $(CH_3)_2Se$	150 nA	18 ± 3	18 ± 3	17 ± 2			
CH_3Br + 20% H_2Se	200 nA	39 ± 2	35 ± 2	32 ± 4	0.8 ± 0.2	1.1 ± 0.2	0.6 ± 0.1

[a] The CF_3Br yields are (7 ± 4)% $CF_3{}^{76}Br$, (4.6 ± 0.8)% $CF_3{}^{77}Br$, and (4.8 ± 1.0)% $CF_3{}^{82}Br$. [b] Pressure 109 kPa.

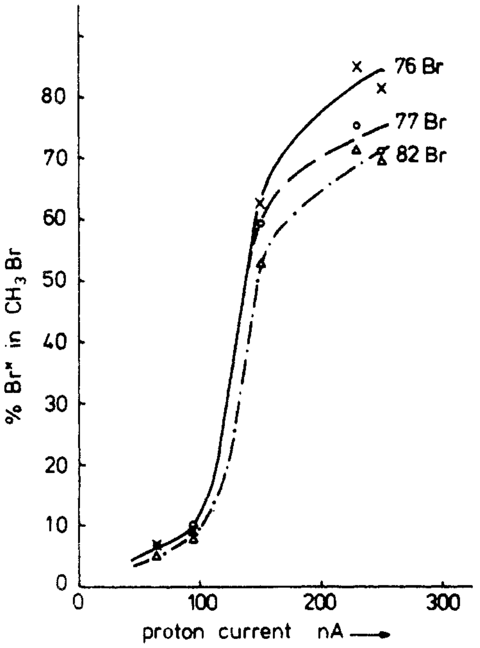

Figure 7. Effect of the proton current on the CH_3Br^* yield in a mixture of CH_3F + 20 mol % H_2S. (Pressure 109 kPa, irradiation time 10 min).[270]

3.8% for CH_3I (to 0% for CCl_4[283]). The production of these fractions was explained by the formation of an excited $[CH_3X^{80}Br]^+$ ion, that—after stabilization—can react by proton or halide ion transfer. Similarly as for (n,γ) reactions in CH_3F and CD_3F, a large isotope effect was also observed for IT produced ^{82}Br: the organic yields—corrected for thermal ionic processes—were 6.5% and 3.5% for CH_3F and CD_3F, respectively.[272]

Se(p,n)^{76,77,82}Br. De Jong et al.[270] produced ^{76}Br, ^{77}Br, and ^{82}Br by the irradiation of gaseous Se compounds (H_2Se, $(CH_3)_2Se$, and $(CF_3)_2Se$) with protons. For these radioisotopes, the yields of CH_3Br^* from pure $(CH_3)_2Se$ are 21, 21, and 18%, respectively, and the yields of CF_3Br^* from $(CF_3)_2Se$ are 34, 34, and 26%, respectively (irradiation: 250 nA protons, 10 min). These nuclear reactions produce Br isotopes with high kinetic energies that react as neutral atoms. When the reactions in mixtures of gaseous Se compounds with halomethanes were studied, it was hoped that additional information regarding the reactions of hot Br atoms could be gained. In general, the results are very difficult to interpret, as radiolysis occurs during the irradiations, especially for mixtures with $(CF_3)_2Se$. Figure 7 shows the yields of CH_3Br (as a function of the proton current) for a mixture of CH_3F and 20 mol % H_2Se. Table XXV gives the product yields of Br-for-X and Br-for-H substitution in CH_3X at high proton currents. Apart from the occurrence of radiolysis, temperature effects can also be involved in the product formation as the temperature of the vessels—not cooled—can be increased by 50–100 K during the irradiations. The high CH_3Br^* yields are of interest for efficient in-beam production of labeled CH_3Br, but no conclusions can be drawn in relation to the reaction mechanisms of hot Br atoms.

TABLE XXVI.[285–288] **Absolute Hydrogen and Halogen Substitution Yields (%) Following the ^{76,77}Kr → ^{76,77}Br Reactions**

	hydrogen substitution			halogen substitution		
	^{76}Br	^{77}Br	$^{76}Br/^{77}Br$	^{76}Br	^{77}Br	$^{76}Br/^{77}Br$
CH_4	2.3	3.7	1.3			
CH_3F	0.40	0.54	1.4	1.9	3.9	2.0
CH_2F_2	0.16	1.0	6.2	0.35	2.6	7.4
CHF_3	0.06	0.19	3.2	0.26	1.4	5.4
CF_4				0.27	1.3	4.8
CH_3Cl	0.22	0.19	0.9	1.2	3.5	2.9
CH_3Br	0.24	0.33	1.4	1.4[a]	4.7	3.5
CH_3I				1.4[a]		
	F substitution			Br, Cl substitution		
	^{76}Br	^{77}Br	$^{76}Br/^{77}Br$	^{76}Br	^{77}Br	$^{76}Br/^{77}Br$
CF_4	0.27	1.3	4.8			
CF_3Cl				0.36	0.94	2.6
CF_3Br	0.40	1.1	2.7	0.60	0.82	1.4

[a] Extrapolated to 0 decay time.

No effect of the proton current on the yields of CH_2XBr^* was found for irradiations of CH_3X. The Br*-for-H substitution yields decrease when going from CH_3F to CH_3Br, which was ascribed to the more efficient moderation properties of the heavier gases. From mixtures of 20 mol % H_2Se with CF_4, CF_3H, and CF_3Br, labeled CF_3Br was formed in yields (averaged over the three isotopes) of 0.3, 0.2, and 20%, respectively. For CF_3Br an additional yield of 12% CF_2BrBr^* was also measured. In these three mixtures, high yields of unidentified gaseous products were found (13, 30, and 13%, respectively), another indication of the complexity of these irradiations.

^{76,77}Kr → ^{76,77}Br. De Jong et al.[285–288] measured product yields of ^{76}Br and ^{77}Br, generated from ^{76}Kr and ^{77}Kr, with 10 halomethanes (Table XXVI). In all the cases only two products were observed from single substitution reactions. Large isotope effects were found, in particular for the substitution of halogen atoms. It was mentioned before, that reactions of very energetic ^{76}Br and ^{77}Br atoms (from proton irradiation of Se) result in a yield of 0.2% CF_3Br^* in gaseous CF_4. This means that the 1.3% $CF_3{}^{77}Br$ yield in CF_4, produced from the $^{77}Kr \rightarrow {}^{77}Br$ decay, must be generally formed by the reactions of $^{77}Br^-$ ions. On the basis of scavenger and moderator effects, it can be deduced that the substitution of halogens occurs via reaction of Br^+ and Br^-

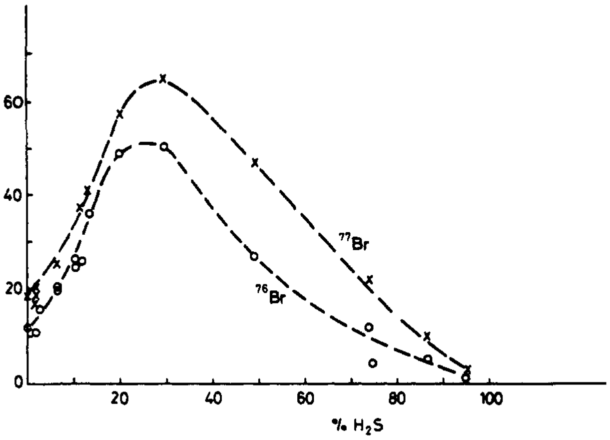

Figure 8. The yield of CH_3Br^* as a function of the H_2S concentration.[285,288]

ions, whereas the substitution of H atoms is merely due to reactions of Br^+ ions. The small isotopic ratios for H substitution were ascribed to differences in the kinetic energies between ^{76}Br and ^{77}Br; the higher ratios found for the substitution of halogens—the ratios increase as the halogens become heavier—were thought to originate from reactions of $^{77}Br^-$ ions. In the case of ^{76}Br, only Br^+ ions are present. Thermodynamic considerations lead to the conclusion that electronically excited Br^+ ions, $Br^+(^1D_2)$ and $Br^+(^1S_0)$, are at least partly responsible for the thermal halogen substitution. The substitution of halogens is favored above that of H atoms, which is to some extent due to the fact that the Br^+ ions primarily react with the lone pair electrons of the halogen atom in a halomethane. The product yields, which are due to reactions of Br^+ ions, decrease as near-resonance conditions for charge-transfer reactions of Br^+ ions are approached, which explains these yields in CH_3Cl being lower than in CH_3F and CH_3Br.

In the case of CH_3Br and CH_3I, exchange reactions with HBr* (absorbed on the walls of the reaction vessels) were found, the extent of which is influenced by pressure, exposure time, temperature, and glass surface. The addition of H_2S (Figure 8) and related compounds such as CH_3SH, $(CH_3)_2S$, H_2Se, or CH_3OH leads to an increase in the exchange yield, due to the formation of a gas-phase cluster of Br^+ or Br^- with the gas molecules, in which clusters HBr* can be formed. $(CH_3)_2O$ has no effect on the CH_3Br^* yield, which is a consequence of efficient near-resonance charge transfer, and no HBr* will be formed. HBr* formation is also inhibited in the presence of propene, which reacts with Br^+ ions via addition to a bromonium ion, inducing a cationic polymerization.

2. *Liquid Phase*

In Table XXVII organic yields are compiled for the reactions of (n,γ) produced ^{80}Br and (IT) produced ^{82}Br with liquid and solid halomethanes, it being notable that the yields are far higher than those for gas-phase experiments. This effect is apportioned to the occurrence of reactions in a cage, formed at the end of the track of energetic recoil particles, or by Auger cascades. In contrast with the gas-phase experiments there are barely any isotope effects for the yields measured for (n,γ) and (IT) reactions.

Berg et al.[274] measured individual product yields in liquid CH_3F/Br_2 mixtures, both for (n,γ) produced ^{80}Br and (IT) produced ^{82}Br. Although the total organic and Br-for-F and -H substitution yields do not vary greatly when proceeding from 0% to 100% Br_2, the products formed through displacement of 2, 3, or 4 atoms differ considerably, i.e., extrapolated to 0% Br_2:

	$CFBr_3$	CBr_4	$CHBr_3$
$^{79}Br(n,\gamma)^{80}Br$	0.1	0.5	2.4
$^{82m}Br(IT)^{82}Br$	0.1	3.6	5.8

	CH_2Br_2	CH_3Br	CH_2FBr
$^{79}Br(n,\gamma)^{80}Br$	3.8	7.0	8.6
$^{82m}Br(IT)^{82}Br$	2.8	6.4	9.6

Cages formed either by energetic recoil atoms or by Auger cascades result in variances in the yields of some of the labeled products, but due to the complexity of these systems, it is not possible to obtain more specific information regarding the relative contributions of molecular, ionic, and radical reactions. Relatively high yields of products formed by double displacement reactions were also detected in Br_2 scavenged liquid CF_2Cl_2 (1Cl, 2%; 2Cl, 0.8%; 1F, 0.4%; and 1F + 1Cl, 0.2%) and in $CFCl_3$ (1Cl, 6% and 2Cl, 2%).[289] Assuming that part of the labeled products are formed through reactions of radicals in an excited cage, it has been summized that a relationship between individual product yields and G values derived from γ irradiations exists. G values for the CF_2Cl_2/Br_2 system are 1Cl, 6.7; 2Cl, 0.8; and 1F 0.2, and for $CFCl_3/Br_2$: 1Cl, 7.0; 2Cl, 0.7; 1F, <0.05,[290] illustrating that there are discrepancies between the radiolysis and recoil yield patterns. An evaluation of average logarithmic energy losses (the α parameters in Estrup-Wolfgang kinetic theory, as discussed in section II for liquid $CHBr_3/C_6H_6/Br_2$ mixtures indicates that moderative collisions with C_6H_6 involve the entire molecule, whereas collisions with $CHBr_3$ have a more atom-atom character.[299]

TABLE XXVII. Organic Yields (%) for (n,γ) Produced ^{80}Br and (IT) Produced ^{82}Br in Condensed Halomethanes

	^{79}Br-(n,γ)^{80}Br		^{82m}Br-(IT)^{82}Br			
	liq	solid	liq	solid	scavenger	ref
CH_3F	24[a]		28		Br_2	273, 274
CF_2Cl_2			3.4		Br_2	289, 290
$CFCl_3$			8		Br_2	289, 290
CCl_4	27	50	39		Br_2	291, 292, 293
CCl_4	26	10	25	10	Br_2	294, 295
CCl_4	23		42–49[c]		Br_2	296, 297
CH_3Br	40				Br_2	298
CH_2Br_2	50				Br_2	297
CH_2Br_2	60			59	Br_2	213, 298
$CHBr_3$	58			65	Br_2	213, 297
$CHBr_3$	65				Br_2	298
$CHBr_3$	42				Br_2	299
$CHBr_3$	61				–	300
CF_3Br	11				Br_2	271
CCl_3Br	40	75			–	291
CCl_3Br	39				Br_2	298
CCl_2Br_2	40	75			–	291
CBr_4	88	93			–	291

[a] Similar yields for $^{82}Br(n,\gamma)^{82m+82g}Br$. The yield of 24% at density of 0.5 g cm^{-2} increases to 36% at 1.1 g cm^{-3}. [b] 29% for ^{81}Br-(n,γ)^{82}Br, 33% for $^{38m}Br(IT)^{80}Br$.[292] [c] Probably too high, see ref 295.

VII. Iodine

Arrhenius parameters for the reactions of ground-state $(^2P_{3/2})$ I atoms with halomethanes are given in

TABLE XXVIII. Arrhenius Parameters for the Reactions of Ground-State I($^2P_{3/2}$) Atoms with (Halo)methanes[8]

H abstraction			I abstraction		
compd	A, 10^{10} L mol^{-1} s^{-1}	ΔE kJ mol^{-1}	compd	A 10^{10} L mol^{-1} s^{-1}	ΔE kJ mol^{-1}
CH_4	60	143	CH_3I	14	83
CH_3I	25	131	CH_2I_2	28	63
CHF_3	4.0	152	CHI_3	56	40
			CI_4	63	17
			CF_3I	2.6	72

TABLE XXIX. Production Modes for Radioactive Recoil Iodine Isotopes

$^{127}I \xrightarrow{n,\gamma} {}^{128}I$ (25 min)
^{129}I (1.7 × 10^7 years) $\xrightarrow{n,\gamma} {}^{130m}I$ (9 min)
^{129}I (1.7 × 10^7 years) $\xrightarrow{n,\gamma} {}^{130}I$ (12.3 h)
$^{127}I \xrightarrow{n,2n} {}^{128}I$ (12.8 days)
$^{127}I \xrightarrow{\gamma,n} {}^{126}I$ (12.8 days)
^{129}I (1.7 × 10^7 years) $\xrightarrow{n,2n} {}^{128}I$ (25 min)
^{130m}I (9 min) $\xrightarrow{IT} {}^{130}I$ (12.3 h)
^{125}Xe (16.8 h) $\xrightarrow{\beta^+} {}^{125}I$ (60 days)
^{123}Xe (21 h) $\xrightarrow{EC,\beta^+} {}^{123}I$ (13.3 h)
$^{235}U \xrightarrow{n,f}$ (8.1 days)
$^{235}U \xrightarrow{n,f} {}^{133}I$ (20.8 h)
$^{235}U \xrightarrow{n,f} {}^{135}I$ (6.7 h)
$^{131,133,135}Xe \xrightarrow{\beta^-} {}^{131,133,135}I$

Table XXVIII. Some rate constants for the collisional removal of excited ($^2P_{1/2}$) I atoms—0.95 eV above the groundstate—are CH_4 (5.5 × 10^7 and 6 × 10^7 L mol^{-1} s^{-1}, respectively[301,302]) CF_4 (2.8 × 10^5), CF_3H (2.8 × 10^7), and CF_3I (2.1 × 10^5).[301] A large isotope effect, in the vicinity of a factor of 50, was found in the rate constants for the reactions of ($^2P_{1/2}$) I atoms with CH_4 and CD_4: 6.6 × 10^{10} [303] and 1.3 × 10^9 [304] L mol^{-1} s^{-1}, respectively. A similar isotope effect was observed for the reactions of ($^2P_{1/2}$) atoms with CH_3I and CD_3I: 1.6 × 10^8 and 2.7 × 10^6 L mol^{-1} s^{-1}, respectively.[305-308] Substitution of D for H in CH_3I will have only a minimal effect on the rate of I abstraction:

$$I(^2P_{1/2}) + CH_3I(CD_3I) \rightarrow I_2 + CH_3(CD_3)$$

This means that the value of 2.7 × 10^6 L mol^{-1} s^{-1} is the upper limit for the abstraction reaction. The efficient quenching of excited I atoms by CH_3I

$$I(^2P_{1/2}) + CH_3I \rightarrow I(^2P_{3/2}) + CH_3I^*$$

is explained by the resonant transfer of electronic to vibrational and rotational energy.[308]

Several radioactive isotopes are available for the study of the reactions of recoil I particles (Table XXIX). Depending on their production mode, they differ in the initial amount of recoil energy and charge, whereas ground-state and electronically excited states of neutral atoms and of ions can also be involved. Reactions such as (n,γ), (n,2n), (γ,n), and direct fission of ^{235}U result in isotopes with high kinetic energy. Nuclear decay, via either electron capture or a highly converted isomeric transition, generally proceeds through the capture (EC) or emission (IT) of a K electron, after which an Auger cascade starts, transforming the atom into a highly charged positive ion. The effect of such a cascade on the charge state was investigated by Carlson et al..[309,311] The $^{123m}Xe \xrightarrow{IT} {}^{123}Xe$ decay gives rise to a charge distribution of the Xe^{n+} ions between $n = 1$ and $n = 22$, with a maximum at $n = 8$.[311] The creation of a K vacancy can also be brought about by irradiation with X-rays of an appropriate energy (Figure 9). If such an irradiation is achieved with iodinated molecules, a rapid electron transfer from the other atoms to the I^{n+} ion takes place, followed by a coulombic explosion, resulting in several ions with excess kinetic energy. In the case of CH_3I, the average charges and energies of the ions are C^{2+} (40 eV), H^+ (34 eV), I^{5+} (8.9 eV).[310]

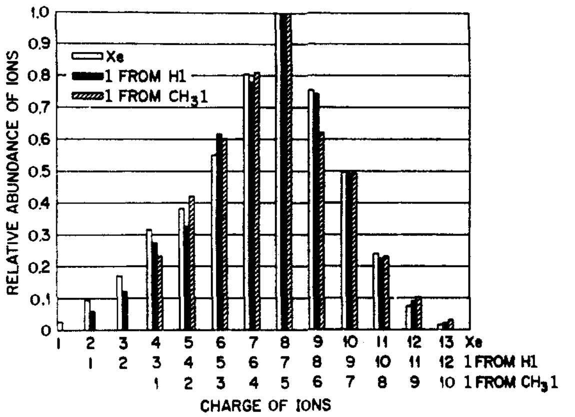

Figure 9. Comparison of the charge spectra for the heavy ion as a result of X irradiation of Xe, HI, and CH_3I. Reproduced with permission from ref 311. Copyright 1966, American Institute of Physics.

The study of the chemical reactions of recoil particles began 50 years ago, when Szilard and Chalmers[312] showed that after neutron irradiation of C_2H_5I, the majority of the ^{128}I activity—formed by the $^{127}I(n,\gamma)^{128}I$ reaction—could be extracted as $^{128}I^-$ ions and obviously the C–I bond is broken after the nuclear reaction. Several review articles have been published on the recoil chemistry of iodine.[3,41,313]

A. Reactions with Methane

(n,γ) (IT). The first studies were published in 1952 by Willard and co-workers who found that I_2, produced by the $^{127}I(n,\gamma)^{128}I$ reaction, led to 50% $CH_3{}^{128}I$ in gaseous CH_4 + 0.05 mol % I_2.[314-316] This yield was constant at ratios of P_{CH_4}/P_{I_2} above 500. This surprisingly high yield was not ascribed to hot reactions of ^{128}I recoil atoms, as excessive concentrations of inert gases did not reduce the $CH_3{}^{128}I$ yield to 0. Other additives, such as I_2, CH_3I, or NO (with ionization potentials lower than that of I), are far more effective in reducing the amount of $CH_3{}^{128}I$, indicating that reactions of $^{128}I^+$ ions are important. As the $I^+ + CH_4 \rightarrow CH_3I + H^+$ reaction is endothermic by 420 kJ mol^{-1}, it was concluded that electronically excited I^+ ions are responsible for these high yields.

More thorough investigations by Rack and Gordus[317] of the effects of the addition of rare gases on the yield of $CH_3{}^{128}I$ provided further information regarding the status of the reacting iodine species (Figure 10). In the presence of 1.5 × 10^{-2} mol % I_2 and of 8 × 10^{-2} mol % CH_3I, the yield of $CH_3{}^{128}I$ in CH_4 is 54%, decreasing to 36% at infinite moderation with Ne, Ar, and Kr, illustrating that 18% is formed as a result of hot ^{128}I reactions. The yield of 11% at 100 mol % Xe moderator (IP 12.13 eV) can only be explained by reactions of $^3P_0$ (11.25 eV) and $^3P_1$ (11.33 eV) I^+ ions, as the reactions of ground-state I^+ ions (10.45 eV) with CH_4 are endothermic. I^+ ($^1D_2$) ions (12.15 eV) will react by near resonance charge transfer with Xe, which process

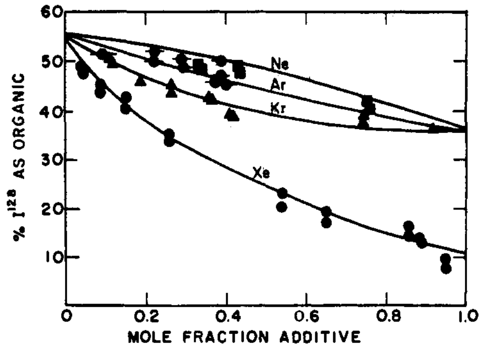

Figure 10. Percent ^{128}I formed as organic activity in CH_4/inert gas mixtures containing CH_3I and I_2. Reproduced with permission from ref 317. Copyright 1961, American Institute of Physics.

TABLE XXX.[319] **Organic Yields (%) for the Reactions of Recoil Iodine with CH_4 and CD_4**

system	hot yield	thermal yields		total yield
		$I^+(^1D_2)$	$I^+(^3P_1,^3P_0)$	
$(n,\gamma)^{128}I + CH_4$	18.5	25.0	11.0	54.5
$(n,\gamma)^{130}I + CH_4$	16.5	9.5	16.5	42.5
$(IT)^{130}I + CH_4$	9.7	5.6	10.3	25.6
$(n,\gamma)^{130}I + CD_4$	15.3	9.5	16.5	41.3
$(IT)^{130}I + CD_4$	10.5	5.6	10.3	26.4

is endothermic by 0.029 eV. The remaining 25% $CH_3{}^{128}I$ is then formed by reactions of I^+ ($^1D_2$) ions with CH_4. These conclusions were further consolidated by the addition of other gases: N_2 and CF_4, having ionization potentials above the 12.16 eV barrier of I^+ ($^1D_2$), gave the same results as Ne, Ar, and Kr. CH_2F_2 behaves in the same way as Xe, although the IP is 12.15 eV, indicating that the 25% additional inhibition by CH_2F_2 is due to a thermal I^+ ($^1D_2$) + CH_2F_2 reaction.[318] Similar investigations of the reactions of I particles—generated via $^{129}I(n,\gamma)^{130+130m}I$ and $^{130m}I(IT)^{130}I$—with CH_4 led to the organic yields as given in Table XXX. The hot yields of (n,γ) induced ^{128}I and ^{130}I are almost equal, the discrepancies in the thermal yields from I^+ ions being ascribed to differences in internal conversion coefficients of the nuclear capture gamma rays.[319] No isotope effects were found for reactions with CH_4 and CD_4. In contrast with the findings of Rack and co-workers, Kuhry et al. reported a yield of (46 ± 3)% for the $^{127}I(n,\gamma)^{128}I$ process and of (44 ± 3)% for that of $^{129}I(n,\gamma)^{130m}I$. These yields remained constant over the entire moderation range with Ne and Ar,[320] with only a trace amount of I_2 (5.4×10^{-7} mol) and no CH_3I being present.

^{123}Xe $\xrightarrow{EC,\beta^+}$ ^{123}Xe, ^{125}Xe $\xrightarrow{EC}$ ^{125}I. The reactions of ^{123,125}I—produced via the decay of the corresponding Xe isotopes—with CH_4 differ in several respects from those of (n,γ) produced isotopes. The ^{123}I atoms formed by electron capture (77%) are initially in a I^{n+} state, where n = 2 to 16 (peaking at I^{9+}) with a maximum kinetic energy of 34 eV. Of all the ^{123}I atoms formed via β^+ emission (23%), two-thirds are formed in the I^- state, from which they are unlikely to form organic compounds.[321] ^{125}Xe decays 100% via electron capture, the maximum energy of the ^{125}I ions is 10 eV. Once the I^{n+} ions have attained a charge of 1+, they have reached thermal equilibrium with their surrounding. This is confirmed by the observation that no hot I-for-H substitution reactions take place: Ne and Ar have no effect on the $CH_3{}^{125}I$ yield, which remains a constant 58% over the whole moderation range.[322] Moreover, the yield

TABLE XXXI.[328] **Fission Yields and Decay Data for I Isotopes**

	^{131}I	^{133}I	^{135}I
total (cumulative) fission yield from ^{235}U, barns	16.0	36.0	36.9
direct fission yield, %	0.3	2.3	48.1
indirect fission yield, %	99.7	97.7	51.9
half-life	6.7 h	20.7 h	8.1 days

of $CH_3{}^{123}I$ was found to increase from 52% in pure CH_4 to 63% at total Ne, Ar, and Kr moderation.[321]

In the case of ^{125}I, the yield of 58% in pure CH_4, decreases to 18% at full moderation with Kr and Xe. Accordingly with the above developed discussion on ^{128}I recoil atoms, this means that 18% of the $^{125}I^+$ ions react in the $^3P_0$ and $^3P_1$ excited states. The remaining yield of 40% is not formed through reactions of I^+ ($^1D_2$) ions (as charge transfer to Kr is endothermic by 1.8 eV), but by I^+ ($^1S_2$) ions (14.58 eV).[322]

Differing conclusions are drawn by Welch and coworkers for the reactions of $^{123}I^+$.[321,323,324] The yield of $CH_3{}^{123}I$ increases from 52% in pure CH_4 to 63% at total moderation with N_2, Ne, and Ar, and also with Kr. Infinite moderation with Xe decreases the yield to 31%, and this decrease is consistent with the near resonant charge exchange of the I^+ ($^1D_2$) state as discussed by Rack and Gordus.[317] The addition of 4 mol % neopentane decreases the 52% $CH_3{}^{123}I$ yield to 10%, due to efficient charge exchange by ground-state and excited I^+ ions. The addition of 10 mol % C_2H_6 decreases the yield to 20%. This is not due to a rapid deactivation of a state other than I^+ ($^1D_2$), as the addition of 90% Xe to the CH_4/C_2H_6 mixture does not change the 20% $CH_3{}^{123}I$ yield. The rapid deactivation was proposed to be due to charge exchange between I^+ ($^1D_2$) and C_2H_6 ($\Delta H = -0.51$ eV). The $CH_3{}^{123}I$ yield decreases to zero at 100% C_2H_6. As charge exchange with I^+ ($^3P_0$) and I^+ ($^3P_1$) are endothermic by 0.40 and 0.32 eV, respectively, the effect was explained by the formation of HI, either directly or via the formation of an excited C_2H_6I or $C_2H_6I^+$ intermediate.

The addition of Ne, Ar, Kr, or N_2 to CH_4/Xe mixtures results in enhanced $CH_3{}^{123}I$ formation. All these observations can be better understood if it is proposed that Xe undergoes resonance charge transfer with I^+ ($^1D_2$) and that the reactive species leading to the formation of $CH_3{}^{123}I$ is a molecular ion AI^+, with A being CH_4, Ne, Ar, Kr, Xe, or N_2.[321]

Increasing the pressure of pure CH_4 to 20 MPa results in a decrease of the $CH_3{}^{123}I$ yield to 10%. The following product yields were measured for solid CH_4: CH_3I (24.3%), C_2H_5I (7.8%), C_3H_7I (1.8%), C_4H_9I (1.6%). Reactions with radicals and ions in a cage formed by the recoil iodine and the electrons from Auger cascades led to the formation of the higher alkyl iodides.

^{235}U(n,f)I, Te $\xrightarrow{\beta^-}$ I. Thermal neutron induced fission of ^{235}U results in the formation of two types of recoil I species: (1) direct fission produced I particles, containing a very high amount of kinetic energy (70–80 MeV), which at the end of their range will react as neutral atoms,[325] and (2) indirect fission I particles formed by β^- decay of directly or indirectly produced Te isotopes. The kinetic energy of these I recoil particles is considerably lower (eV range) and they are mainly positively charged. The reactions with gaseous CH_4 yield CH_3I as the most predominant product. The

TABLE XXXII. **I-for-X Substitution Yields in CH_3X**

I-for-X	X =	H	F	Cl	Br	I
$^{127}I(n,\gamma)^{128}I$[334]						
hot, absolute yields (%)		19.0	11.2	4.1	0.7	0.2
$^{235}U(n,f)$, direct[328]		2.1	5.0	9.3	14.1	nm[a]
$^{235}U(n,f)$, indirect[329]		0.36	1.4	1.7	2.3	nm
relative yields		0.36	1.4	1.7	2.3	nm
I-for-H	**X =**	**H**	**F**	**Cl**	**Br**	**I**
$^{235}U(n,f)$, direct[328]		2.0	2.1	1.7	1.3	1.0
$^{235}U(n,f)$, indirect[329]		0.36	0.40	0.36	0.30	0.29

[a] nm = not measured.

relative yields are much higher for directly than for indirectly produced I.[326,327]

Table XXXI gives relevant data for three I isotopes. Kikuchi and Church[328,329] deduced from moderator experiments with Ar that the ratio of labeled CH_3I formed by directly and indirectly produced I was 5.6. By adding C_2H_4 to CH_4, labeled c-C_3H_5I was also produced (compared to the CH_3I yield: 13% via direct and 6% via indirect fission), due to the addition of :CHI, formed by H_2 elimination from excited CH_3I.[330] The addition of O_2 to CH_4/C_2H_4 mixtures made it possible to distinguish between addition reactions of singlet and triplet :CHI.[331] ^3CHI is primarily generated by independently produced fission I, whereas ^1CHI is formed by β^- decay produced I.

B. Reactions with Halomethanes

Gas Phase. Several investigations deal with the reactions of recoil I particles with gaseous CH_3I, which quite often serves as the source for ^{126}I and ^{128}I, produced via (γ,n) and (n,γ) reactions, respectively. A particular problem with CH_3I is the occurrence of thermal exchange reactions that can mask the yield of hot substitution reactions. From competition experiments with CH_3I/I_2 mixtures, a rate constant for the exchange with CH_3I was determined as 10^2 L mol^{-1} s^{-1}.[332] Cross and Wolfgang[333] used $I^{129}I$ as a scavenger in experiments with ^{126}I. The yield of $CH_3{}^{129}I$ is a direct measure of the exchange reaction with CH_3I. The real hot ^{126}I-for-I substitution yield was determined as 4%, in accord with those measured for (n,γ) produced ^{128}I.[318,332] Extrapolating to 0 mol fraction of CH_3I and correcting for 1.1% failure of bond rupture, Yoong et al.[334] found a yield of 0.2% $CH_3{}^{128}I$. Apart from I-for-I substitution, I-for-H substitution yielding CH_2I_2, was also observed with fission produced $^{131,133,135}I$.[335] From moderator experiments with Ar it was deduced that CH_2I_2 was formed by hot reactions of directly produced I isotopes, but that other reactions were involved in the case of indirectly produced I particles, as this part of the CH_2I_2 yield did not change upon the addition of Ar. Table XXXII gives the absolute ^{128}I-for-X substitution yields in CH_3X (X = H, F, Cl, Br, I).[334] There is a linear dependency between these yields and the "energy degradation factor", defined as $4\,M_aM_n/(M_a + M_n)^2$, where M_a is the mass of the hot atom and M_n that of the target molecule. These results differ from relative I-for-X substitution yields, determined for I isotopes produced from direct and indirect fission of ^{235}U.[328,329]

Condensed Phases. High organic yields (60–100%) were found for the reactions of (n,γ) produced ^{128}I with liquid CH_3I.[336–340] These yields are difficult to reproduce and depend upon the degree of purification, temperature, time of irradiation, and the presence of scavengers. Simultaneous extraction of inorganic ^{128}I activities caused by stirring the CH_3I sample during the irradiation with an aqueous Na_2SO_3 solution, resulted in a decrease of the organic yield from 99% to 50%, validating the importance of thermal exchange reactions in the liquid phase.[341] Extrapolation of the organic yield to irradiation time 0 decreased it from 98% (45 min) to 57%.[340] The yield of organically bound ^{131}I in a mixture of CH_3I with 10^{-3} mol % $I^{131}I$, increased linearly with the irradiation time,[337] the exchange reaction apparently proceeding via labeled I_2. The organic yield of 57% consists of $CH_3{}^{128}I$ (46–48%) and of $CH_2I^{128}I$ (8–11%).[336,337] The addition of 10 mol % I_2 decreases the $CH_3{}^{128}I$ yield to 34%, but the $CH_2I^{128}I$ yield remains unaffected.[337] Brusted et al.[338] measured relative yields of $CH_3{}^{128}I$ (90%), $CH_2I^{128}I$ (9%), and inorganic ^{128}I (1%), when CH_3I was irradiated at room temperature. Upon cooling, the $CH_2I^{128}I$ yield remains constant, but the $CH_3{}^{128}I$ yield decreases to 45% at melting point, whereas the inorganic fraction became 44%. Ayres and Rack[340] found that the organic yield did not change when proceeding from room temperature (57%) to the solid phase at 77 K, but Levey and Willard[337] observed an increase to 65% at 83 K, whereas Glückauf and Fay[336] measured a decrease to 49% at 78 K. Iyer and Martin[342] irradiated mixtures of CH_3I, C_3H_7I, and I_2, in which one of the three compounds was labeled with ^{129}I, with thermal neutrons. They came to the conclusion that recoil ^{130}I particles are more likely to react with CH_3I than with C_3H_7I by a factor of 2–3, and that in 10% of the neutron captures in ^{129}I there is either an immediate recombination of ^{129}I with the organic residue of the parent molecules or there is no bond rupture at all.

Thermal neutron irradiation of a mixture of 1.8 mol % CH_3I in n-C_5H_{12} gave the following relative product yields: CH_3I (42%), C_2H_5I (9%), C_3H_7I (6%), C_4H_9I (2%), and $C_5H_{11}I$ (40%).[343] The high yields of $CH_3{}^{128}I$ could not be explained by the failure of bond rupture, recombination of parent partners or thermal exchange reactions. The relative distribution of the ^{128}I activity differs little from the distribution of ^{131}I measured after an irradiation with a ^{60}Co source of a similar mixture of 1.8 mol % CH_3I in n-C_5H_{12}, containing a trace of $I^{131}I$: 54, 5, 4, 1, and 36%, respectively. The ^{128}I results were thus explained by the reactions of radicals produced by electrons originating from (1) the interactions of ^{128}I recoil particles with other molecules or (2) an Auger cascade connected with converted transitions from excited ^{128}I levels to the ground state:

$$e^- + CH_3I \rightarrow CH_3 + I^-$$

There are only a limited number of articles available concerning reactions of recoil I particles with halomethanes other than CH_3I. Results with gaseous CH_3F, CH_3Cl, and CH_3Br have been mentioned previously. Parks and Rack[344] measured organic yields for selected polyhalomethanes with IT produced ^{130}I and (n,γ) produced (^{130}I + ^{130m}I) in the presence of 0.03 mol % I_2. The respective yields (%) are CH_2Cl_2 (54, 44,), $CHCl_3$ (30, 24), $CFCl_3$ (16, 11), CCl_4 (1.9, 2.5), CCl_3Br (1.9, -). The observed results were ascribed to differences in product stabilities, which were in turn related to variations in steric interaction among substituents of the product molecules.

TABLE XXXIII. Rate Constants for $O(^1D)$ Atoms at 298 K[a]

	k^{349}		k^{349}	k^{350}	k^{351}
CH_4	9.0	CF_2Cl_2	15.6	8.7	8.4
CH_2F_2	4.3	$CFCl_3$	18.0	13.2	13.8
CHF_3	3.2	CCl_4	28.2	18.6	19.8
CF_4[b]	1.0	CHF_2Cl	7.8	5.7	
CF_3Cl	7.8	$CHFCl_2$	15.6	11.4	

[a] 10^{10} L mol^{-1} s^{-1}. [b] No chemical reaction, but physical quenching.

VIII. Polyvalent Atoms

A. Oxygen

For most halomethanes the major reaction of ground-state $O(^3P)$ atoms is H abstraction.[345] Arrhenius parameters for the reactions with CH_4, CH_3F, CH_3Cl, and CH_3Br are $A = 2.0, 0.8, 1.8$, and 3.0×10^{10} L mol^{-1} s^{-1} and $\Delta E = 37.8, 40.5, 30.6$, and 31.6 kJ mol^{-1}.[346] In the case of CF_3Br, Br abstraction takes place: $A = 0.9 \times 10^{10}$ L mol^{-1} s^{-1} and $\Delta E = 55.9$ kJ mol^{-1}, whereas in CH_3I and CF_3I, I abstraction seems the main reaction channel, the rate constants for reaction with CF_3I being $k_{298} = 6.6 \times 10^9$ L mol^{-1} s^{-1}.[8,347,348] Rate constants for reactions of $O(^1D)$ atoms (first excited level, 1.98 eV above ground state) were evaluated up until 1977 by Schofield.[349] These data, together with some more recent values[350] are compiled in Table XXXIII. In all cases there are very rapid chemical reactions involved (with the exception of CF_4).[352] The reactions of $O(^1D)$ atoms with CH_4 at 100 kPa result mainly in the formation of C_2H_6 (70%), due to the recombination of CH_3 radicals:[353]

$$O(^1D) + CH_4 \rightarrow CH_3 + OH$$

$$2CH_3 \rightarrow C_2H_6$$

Molecular elimination of H_2 occurs to the extent of 9%:

$$O(^1D) + CH_4 \rightarrow H_2 + H_2CO$$

At enhanced pressures, increasing amounts of CH_3OH are detected:

$$O(^1D) + CH_4 \rightarrow [CH_3OH]^*$$

$$[CH_3OH]^* \rightarrow CH_3 + OH$$

$$[CH_3OH]^* + M \rightarrow CH_3OH + M$$

The lifetime of the excited CH_3OH molecule is determined as 0.8 ps. In the case of chloromethanes,[354] $O(^1D)$ atoms also insert into C–H bonds. The highly excited chloromethanols decompose by HCl elimination:

$$O(^1D) + CHCl_3 \rightarrow [CCl_3OH]^* \rightarrow HCl + CCl_2O \quad (\Delta H = -648 \text{ kJ mol}^{-1})$$

$$O(^1D) + CH_2Cl_2 \rightarrow [CHCl_2OH]^* \rightarrow HCl + CHClO \quad (\Delta H = -606 \text{ kJ mol}^{-1})$$

$$O(^1D) + CH_3Cl \rightarrow [CH_2ClOH]^* \rightarrow HCl + CH_2O \quad (\Delta H = -560 \text{ kJ mol}^{-1})$$

With fluoromethanes, $O(^1D)$ atoms react by insertion into a C–H bond, and the highly excited fluoromethanes decompose by HF elimination:[355]

$$O(^1D) + CHF_3 \rightarrow [CF_3OH]^* \rightarrow HF + CF_2O \quad (\Delta H = -648 \text{ kJ mol}^{-1})$$

$$O(^1D) + CH_2F_2 \rightarrow [CHF_2OH]^* \rightarrow HF + CHFO \quad (\Delta H = -619 \text{ kJ mol}^{-1})$$

$$O(^1D) + CH_3F \rightarrow [CH_2FOH]^* \rightarrow HF + CH_2O \quad (\Delta H = -598 \text{ kJ mol}^{-1})$$

The fluoromethanols possess about 540 kJ mol^{-1} excitation energy, whereas the critical barrier for HF elimination is only in the order of 125 kJ mol^{-1}.

In the case of chlorofluoromethanes the major reaction channel for $O(^1D)$ atoms is Cl abstraction forming ClO (about 30–60% of the total cross section for removal of $O(^1D)$ atoms[348,356]). It is reasoned that ClO is formed by abstraction, rather than by an insertion reaction followed by decomposition of an excited molecule. Physical quenching leading to $O(^3P)$ accounts for 30% of the total cross section in CF_3Cl and CF_2HCl, and with CF_2HCl this proceeds via a dissociative excitation channel, yielding $CF_2 + HCl + O(^3P)$.[348] The reaction of $O(^1D)$ with CF_3Br results in rapid formation of BrO, while it is assumed that reaction with CF_3I yields IO.[348]

There is only one rate constant known for reactions of $O(^1S)$ atoms (second excited state, 4.22 eV above ground level): $k_{298} = 1.6 \times 10^7$ L mol^{-1} s^{-1} for CH_4.[349] It has not been established whether a chemical reaction or physical quenching is involved. There is no information regarding the reactions of recoil ^{15}O atoms ($t_{1/2}$ = 2 min) with (halo)methanes.

B. Sulfur

Ground-state $S(^3P)$ atoms do not react with methane, but their yield can be quantitatively determined by the amount of CO formed from reaction with COS:

$$S(^3P) + COS \rightarrow CO + S_2$$

$S(^1D)$ atoms (first excited state, 1.35 eV above ground level) can be produced by photolysis of COS. The rate constant for chemical reactions with CH_4 is 4.0×10^{10} L mol^{-1} s^{-1} and that for physical quenching to the ^3P ground state is 1.1×10^8 L mol^{-1} s^{-1}.[301] The ratio of both rate constants (about 400) is much larger than for other hydrocarbons. Little et al. found the rate constant of $S(^1D)$ atoms with CH_4 to be 0.076 relative to C_2H_4, with which compound $S(^1D)$ reacts at almost every collision.[357]

The main reaction of $S(^1D)$ atoms with CH_4 is insertion yielding vibrationally excited mercaptan:[358,359]

$$S(^1D) + CH_4 \rightarrow [CH_3SH]^*$$

Variation of the concentration of HS radicals with CH_4 pressure suggests that H abstraction can also take place:

$$S(^1D) + CH_4 \rightarrow CH_3 + HS$$

The excited mercaptan can—depending on pressure—stabilize or decompose:

$$[CH_3SH]^* \rightarrow CH_3SH \quad (\Delta H = -29 \text{ kJ mol}^{-1})$$

$$[CH_3SH]^* \rightarrow CH_3S + H \quad (\Delta H = +33 \text{ kJ mol}^{-1})$$

$$[CH_3SH]^* \rightarrow CH_2 + H_2S \quad (\Delta H = +4 \text{ kJ mol}^{-1})$$

$$[CH_3SH]^* \rightarrow CS + 2\ H_2 \quad (\Delta H = -79 \text{ kJ mol}^{-1})$$

HS and CS have been observed as transients in flash photolysis–kinetic absorption spectroscopic studies.[359] Other evidence of the existence of several decomposition channels are the observation of the presence of CH_3SSCH_3, CH_3SCH_3, C_2H_6, H_2, and CS_2.[358]

Radiosulfur can be produced by: $^{34}S(n,\gamma)^{35}S$, $^{35}Cl(n,p)^{35}S$, $^{40}Ar(\gamma,2p)^{38}S$, or $^{40}Ar(p,3p)^{38}S$. Due to a combination of low cross sections, lack of abundance of starting material and long half-lives (^{35}S $t_{1/2}$ = 87 days, ^{38}S $t_{1/2}$ = 2.9 h), high radiation doses are involved in all radiosulfur production modes. This means that considerable radiation damage of the target compounds can be expected together with decomposition of existing labeled products, particularly of radiation sensitive organic sulfur compounds (mercaptans). Pânek and Mudra[360] found $H_2{}^{35}S$ and $CH_3{}^{35}SH$ upon neutron irradiation of a mixture of HCl (as a source of ^{35}S) and CH_4. Addition of Ar as a moderator for energetic ^{35}S atoms caused the $CH_3{}^{35}SH$ yield to increase, indicating that not only hot reactions lead to the formation of the mercaptans. Kremer,[361] experimenting with ^{38}S has observed—in $CH_4/H_2S/AR$ mixtures—the formation of $H_2{}^{38}S$ and $CH_3{}^{38}SH$, the latter product being ascribed to $^{38}S(^1D)$ atoms. H_2S serves as a necessary agent by scavenging radiation induced radicals. In experiments with ^{38}S in C_3H_8/Ar mixtures, 23% $H_2{}^{38}S$ and 3.2% $C_3H_7{}^{38}SH$ were found only if H_2S was present, whereas without its presence, all the ^{38}S activity was found on the walls of the irradiation vessel.[362] Changing the CH_4/Ar ratio from 1.5 to 0.08 (total pressure 90 kPa, 5% H_2S present), the $H_2{}^{38}S$ yield remained constant—~19%—but the $CH_3{}^{38}SH$ yield decreased from (4.9 ± 0.8)% to (2.7 ± 0.5)%. Extrapolated to 100% Ar, this yield would become 2.5%. This was interpreted as an indication that the $CH_3{}^{38}SH$ yield in pure CH_4 is formed by hot and thermal reactions in approximately equal proportions. However, the results are almost irreproducible and—as mentioned before—all conclusions are premature, as most of the ^{38}S activity (75–80%) is found on the walls of the irradiation vessel. The fate of this activity is unknown, apart from the fact that it differs from the results with photolytically produced S atoms.

C. Nitrogen

Only a limited number of publications deal with the measurements of rate constants for ground-state $N(^4S)$ atoms with (halo)methanes[8] (at 500 K: $\leq 4 \times 10^6$ L mol^{-1} s^{-1} for CH_4, CH_3F, CH_3Cl,[363] 1.25×10^7 L mol^{-1} s^{-1} for CHD_3,[363] and at room temperature $(0.6 - 1.3) \times 10^5$ L mol^{-1} s^{-1} for CH_4.[364] Only one value has been reported for the reactions of $N(^2D)$ atoms (the first excited state, 2.38 eV above ground level) with CH_4: 1.8×10^8 L mol^{-1} s^{-1},[365] but this value may be too high by a factor of 2.[366] The exact reaction mechanism has not been determined, but is probably more complex than a one-step reaction, forming HCN as the major product.[366,367] No data are available for the reactions of $N(^2P)$ atoms (the second excited state, 3.57 eV above ground level).

Several earlier publications deal with "active nitrogen", formed when N_2 at low pressure is subjected to a condensed discharge.[368] This active nitrogen consists almost primarily of $N(^4S)$ atoms, with minor contributions of $N(^2D)$ atoms (0.6%) and $N(^2P)$ atoms (0.25%).[369] HCN is the only product that has been detected from the reactions of active nitrogen with CH_4.[370] In CH_3Cl, the main products are HCN and HCl:[371]

$$N + CH_3Cl \rightarrow [N{\cdot}CH_3Cl] \rightarrow HCN + HCl + H$$

The products from the reactions with CH_2Cl_2 and $CHCl_3$ can be explained by[372]

$$\begin{aligned} N + CH_2Cl_2 \rightarrow [N{\cdot}CH_2Cl_2] &\rightarrow HCN + HCl + Cl \\ &\rightarrow CNCl + HCl + H \\ &\rightarrow CN + 2\ HCl \\ N + CHCl_3 \rightarrow [N{\cdot}CHCl_3] &\rightarrow CNCl + HCl + Cl \\ &\rightarrow HCN + Cl_2 + Cl \\ &\rightarrow CN + HCl + Cl_2 \end{aligned}$$

In the case of CCl_4, the reaction occurs via

$$N + CCl_4 \rightarrow [N{\cdot}CCl_4] \rightarrow CNCl + Cl_2 + Cl$$

The chemical form of ^{13}N ($t_{1/2}$ = 10.0 min), produced in various nuclear reactions, was reviewed in 1979 by Tilbury.[373] The most utilized nuclear reactions are $^{14}N(n,2n)$, $^{14}N(p,pn)$, $^{14}N(\gamma,n)$, $^{12}C(d,n)$, and $^{16}O(p,\alpha)$.

Methane. In the first publications dealing with the reaction of recoil ^{13}N with CH_4, $HC^{13}N$ was reported as the major compound and $CH_3C^{13}N$ as a secondary product.[374,375] No $^{13}NH_3$ was observed, and this was interpreted as proof that H abstraction was not an important reaction channel.[374] However, later it became obvious that $^{13}NH_3$ was indeed formed, but it was not detected in these earlier experiments as only the gas phase was investigated by GLC techniques and $^{13}NH_3$ had adhered to the walls of the brass target irradiation vessels used. Tilbury et al.,[376] using a flowing CH_4 gas target, found 95% $^{13}NH_3$, 2% $CH_3{}^{13}NH_2$, less than 3% $HC^{13}N$, and no $CH_3C^{13}N$ whatever. The irradiated gas was bubbled through water and it was not ascertained if $^{13}NH_3$ is directly formed in the irradiation vessel or through reactions of some intermediate compound with water. Straatman and Welch[377] found, depending on irradiation conditions (beam intensity, irradiation time, gas pressure), 34–80% $^{13}NH_3$, less than 2.6% $CH_3{}^{13}NH_2$, and 2–53% of an unidentified compound.

Halomethanes. The main product found from the reactions of recoil ^{13}N atoms with CH_3Cl and CH_3Br was $HC^{13}N$, whereas $ClC^{13}N$ was also detected in $CHCl_3$.[378] The yield of $HC^{13}N$ was influenced by the state of the wall materials of the irradiation vessels. Where the walls were conditioned by extensive irradiations of the alkyl halides (coated with polymers, produced by radiolysis) gaseous $HC^{13}N$ was detected. However, as was mentioned in the case of CH_4, no $^{13}NH_3$ was detected, due to the experimental conditions. Welch and Straatman found for $CHCl_3$ 5.3% $^{13}NH_3$ and 43% $C^{13}N^-$, and in CH_2Cl_2 7.2 and 35%, respectively.[379] In CCl_4, only $ClC^{13}N$ was observed[378] and in CF_4, only one product was detected, which was thought to be $FC^{13}N$.[380]

D. Carbon

Recoil C atoms can react as hot or thermal ground-state $C(^3P)$ atoms, and also as hot or thermal electronically excited $C(^1D)$ or $C(^1S)$ atoms (1.26 and 2.68 eV, respectively, above ground state). Thermal reactions of these three types of C atoms have been the subject of several publications.[8,381,382] Thermal $C(^3P)$ atoms are almost inert for reactions with CH_4; H ab-

TABLE XXXIV. **Absolute Product Yields (%) for the Reactions of Recoil ^{11}C Atoms with CH_4**[a]

	gaseous CH_4					
product	b	b	0.12% O_2	2% C_2H_2	1.2% C_2H_4	solid CH_4
CO	<0.2	<0.2	20.4	<0.2	<0.2	<0.2
CH_4	13.9	6.9	<0.15	1.9	<0.2	4.5
C_2H_2	17.7	14.0	32.3	32.8	25.2	28.1
C_2H_4	12.4	6.6	30.5	29.5	23.5	27.2
C_2H_6	23.9	29.4	<0.5	6.0	3.4	11.3
C_3H_8	11.2	20.2	<0.2	<0.2	1.7	4.5
C_3H_4[c]	3.0		<1.0	<0.2	<0.2	<0.2
higher boiling	17.9	22.9	15.8	29.8	46.2	24.4

[a] Radiation dose 4–5 × 10^{-4} eV/molecule.[391] [b] Radiation dose 8.3 × 10^{-4} eV/molecule. [c] Allene.

straction is an endothermic reaction (ΔH = 98 kJ mol^{-1}). Published rate constants for CH_4 differ considerably: $<3.8 \times 10^4$,[383] $<3 \times 10^6$,[384] and $<1.2 \times 10^6$ [385]) L mol^{-1} s^{-1}. Thermal $C(^1D)$ atoms interact through physical relaxation processes with rare gases, H_2O, and N_2, but a rapid chemical reaction (with almost unit collisional efficiency) takes place on collision with CH_4. The two reported rate constants differ by a factor of 6: 1.9×10^{10} [384] and 1.3×10^{11} [386] L mol^{-1} s^{-1}. Braun et al.[384] quantitatively measured the formation of C_2H_2 via its 151-nm absorption band, suggesting a mechanism proceeding through a short-lived excited state of C_2H_4:

$$C(^1D) + CH_4 \rightarrow [C_2H_4]^* \rightarrow C_2H_2 + H_2 \ (\Delta H = -535 \text{ kJ mol}^{-1})$$

Reaction rates of thermal $C(^1S)$ atoms are generally much lower than those of $C(^1D)$ atoms. Reported rate constants for CH_4 are 1.8×10^7,[387] $<6 \times 10^9$,[388] and $<6 \times 10^8$ [382] L mol^{-1} s^{-1}. H abstraction is exothermic by 161 kJ mol^{-1}, but energy transfer may also be viable reaction channel. With regard to the reactions of thermal C atoms with halomethanes, only rate constants for reactions of $C(^1S)$ atoms with CCl_4 are reported: 1.6×10^{10} [389] and 2.0×10^{10} [382] L mol^{-1} s^{-1}. The exact reaction mechanism is not known, but Cl abstraction is probably involved, as it is exothermic by 279 kJ mol^{-1}. All the knowledge of the reactions of recoil C atoms with (halo)methanes has been obtained by investigations using ^{11}C ($t_{1/2}$ = 20.3 min) rather than ^{14}C ($t_{1/2}$ = 5730 years). ^{11}C can be produced by several nuclear reactions: $^{12}C(n,2n)$, $^{12}C(p,pn)$, $^{12}C(\gamma,n)$, $^9Be(^3He,n)$, $^{11}B(p,n)$, $^{14}N(p,\alpha)$, $^{16}O(\gamma,\alpha n)$, ^{20}Ne(p,spall.).

Methane. The first experiments with CH_4 were performed by Mackay and Wolfgang in 1961.[390] Even in systems to which no oxygen was purposely added, high yields of ^{11}CO were observed. Therefore, the first published data were given for CH_4 to which 2% O_2 was added as a scavenger for thermal ^{11}C atoms and radicals and also for surpressing radiation induced reaction of labeled unsaturated compounds. The observed labeled products were (yields as % of total volatile activity) CO (26.8%), CH_4 (1.5%), C_2H_6 (3.1%), C_2H_4 (28.0%), and—as the most striking result—C_2H_2 (30.0%). C_2H_2 was assumed to be formed through insertion of ^{11}C into a C–H bond:

$$^{11}C + CH_4 \rightarrow [H^{11}C - CH_3]^* \rightarrow H^{11}C{\equiv}CH + 2\ H \text{ (or } H_2)$$

More detailed information was gained by Wolf and co-workers. In Table XXXIV the product yields are given for CH_4 entirely free of oxygen (at different doses), for CH_4 scavenged with O_2, C_2H_2, and C_2H_4, and also for solid CH_4.[391] The effect of the radiation dose was held to be due to reactions of H atoms and CH_3 radicals, produced by concomitant radiolysis of CH_4, e.g., with labeled C_2H_4:

$$H + C_2H_4 \rightarrow \cdot C_2H_5$$

$$H + \cdot C_2H_5 \rightarrow C_2H_6$$

$$\cdot CH_3 + \cdot C_2H_5 \rightarrow C_3H_8$$

TABLC XXXV. **Acetylene-^{11}C Yields from Deuterated Methanes and 1:1 Mixtures**[393,394]

	% of total acetylene-^{11}C		
system	C_2H_2	C_2HD	C_2D_2
CH_3D	48.8	51.2	<2.0
CH_2D_2	12.4	70.8	16.8
CHD_3	<2.0	48.9	51.1
CH_4/CD_4	56.6	<3.0	43.3
CH_3F/CD_3F	51.5	3.8	44.7
CH_3Cl/CD_3Cl	61	5	34
C_6H_6/CD_4	22.4	5.0	72.6

Scavengers such as O_2, C_2H_2, and C_2H_4 react with the H atoms and CH_3 radicals and prevent the reactions with $^{11}CH_2{=}CH_2$. Part of the C_2H_6 yield may also be formed by $^{11}CH_2$ insertion into the C–H bonds of CH_4. Welch and Wolf[392] measured product yields in CH_4 + 4.5% O_2 as a function of pressure between ~7 kPa and 19 MPa. With increasing pressure, the yield of CO decreased from some 38% to 20%, whereas both the yields of C_2H_2 and C_2H_4 increased from about 15% to 32%. These trends led to the assumption of an initial formation of a collision complex between an energetic ^{11}C atom and CH_4, $[^{11}CCH_4]^*$, which could, depending on the pressure, fragment to products that can react with O_2 to form CO, undergo collisional deexcitation, and decompose to form C_2H_2 or allow the formation of C_2H_4.

A clearer insight into the reaction mechanisms that lead to labeled C_2H_2 was obtained by experiments with partly deuterated methanes and with equimolar mixtures of CH_4/CD_4 and CH_3F/CD_3F.[393,394] The results are compiled in Table XXXV, and they confirm the hypothesis that C_2H_2 is formed by an intramolecular process—as was originally put forward by Mackay and Wolfgang—and not by methyne insertion. In the latter case, a distribution of 25% C_2H_2, 50% C_2HD, and 25% C_2D_2 should be expected for the CH_4/CD_4 mixture. The measured C_2H_2/C_2D_2 ratios of 1.27 in CH_4/CD_4 and of 1.16 in CH_3F/CD_3F mixtures prove the existence of isotope effects. Two types can be involved: (1) insertion isotope effect of the ^{11}C atom, (2a) C–H homolytic bond scission isotope effect, and (2b) C–C homolytic bond scission isotope effect (only in higher hydrocarbons and not in CH_4).

From a close inspection of the product yields obtained from C_2H_6 and C_2D_6, Ache et al.[394] concluded that effect (1) and (2a + 2b) distribute almost equally to the experimental measured isotope effect, and it seems probable that for CH_4/CD_4 both effects are also operative.

Formation of C_2H_4 from hydrocarbons is held to proceed exclusively from insertion of ^{11}CH into C–H bonds:[395]

$$^{11}CH + CH_4 \rightarrow H_2{}^{11}C{-}CH_3 \rightarrow H_2{}^{11}C{=}CH_2 + H$$

TABLE XXXVI.[403] **Absolute Product Yields (%) for the Reactions of Recoil ^{11}C Atoms with N_2/CH_3X (4:1)**[a]

	products								
CH_3X	CO	CH_4	CO_2	C_2H_2	C_2H_4	HCN	CH_3CN	CH_2X_2	wall act.
CH_3Cl	12.9	0.6		2.0		29.6		23	31
CH_3Br	28		1.6	17.6	1.2	40			8
CH_3I	9		1.0	24	0.4	33	0.5		33

[a] Dose: 0.26 eV/molecule. Pressure: 67 kPa.[403]

However, in the case of CH_4, this compound can also be formed via ^{11}C insertion, followed by collisional stabilization of the excited $H^{11}C-CH_3$ complex, and H migration. Moderation studies with mixtures of hydrocarbons and rare gases yielded more information about hot and thermal reactions of recoil ^{11}C atoms and also of the involvement of $^{11}C(^3P)$ and $^{11}C(^1D)$ atoms (excess Xe leads to deexcitation of $C(^1D)$ atoms).[396] At the moment the final conclusions regarding the reactions of recoil C atoms with hydrocarbons in the absence of moderator(1) and in the presence of excess moderator(2) can best be described with a quotation of Wolf:[397]

"(1) At the upper end of the energy range where the carbon atoms become chemically reactive

(a) ^3P carbon insertion reaction results in acetylene formation and ^3P carbon abstraction reaction results in ethylene formation but this is a minor pathway for ethylene formation

(b) ^1D carbon insertion decomposition reaction results in ethylene formation.

(2) At the lower end of the energy range

(a) ^3P carbons in the thermal and near thermal range are scavenged by O_2. Rate of reaction with organic substrates is so low to be noncompetitive

(b) ^1D carbons still undergo insertion decomposition and ultimately yield ethylene. The insertion intermediate may also begin to fragment to yield acetylene."

$^{11}CH_4$ can be produced in high yields by proton irradiation of N_2 (via the $^{14}N(p,\alpha)^{11}C$ nuclear reaction) with some percent H_2.[398-401] The initial formed ^{11}CN and $^{11}C{=}N{=}N$ compounds can—depending upon the radiation conditions—almost be quantitatively converted by radiolytically processes into $^{11}CH_4$.

Halomethanes. Reactions of recoil ^{11}C atoms with gaseous CF_4 lead to the formation of 10% low boiling products (5% CO, <1.2% C_2F_2, <2.5% C_2F_4), 10% higher boiling gaseous products, and 80% nonvolatile products which remain on the walls of the irradiation vessels.[402] In solid CF_4 20% labeled CF_4 and 11% C_2F_6 were measured, whereas 56% of the activity was incorporated in nonvolatile products. It is therefore obvious that recoil ^{11}C atoms react with CF_4 in a different way than with CH_4. Recoil ^{11}C atoms react efficiently with CF_4, but they do not seem to insert into C–F bonds.[402] This can also be concluded from experiments with mixtures of CF_4 and O_2. Extrapolated to 100% CF_4, 78% ^{11}CO, and 27% $^{11}CO_2$ are found. The latter compound is not formed by reaction of ^{11}C with O_2, as that yields ^{11}CO, and therefore it must be formed via a reaction of O_2 with an intermediate originating from a reaction of ^{11}C with CF_4. Further analysis of the experimental results led to the conclusion that the reactivity of recoil ^{11}C atoms toward O_2 to form ^{11}CO, and toward CF_4 to form the reactive intermediate, is almost equal. Results obtained from CF_4/C_2H_4 mixtures were also in accord with the former finding regarding a reactive intermediate. All these results led to the hypothesis that the reactive intermediate is ^{11}CF, which can be formed via two mechanisms:

(1) insertion, followed by decomposition:

$$^{11}C + CF_4 \rightarrow F^{11}C - CF_3 \rightarrow {}^{11}CF + CF_3$$

(2) direct F abstraction:

$$^{11}C + CF_4 \rightarrow {}^{11}CF + CF_3$$

However, the similarities observed between products and product yields obtained with SF_6 and fluorocarbons favor the second mechanism. In gaseous CHF_3, 0.5% C_2HF_3 and 0.8% CHF_3 were found, whereas in solid CHF_3 these yields were 2.6 and 7.9%, respectively.[402] The observations that (1) ^{11}C atoms insert into C–H bonds of CH_4, but (2) abstract F atoms from CF_4, and (3) regarding the relative inertness of C–C bonds, led to the suggestion that C atoms—being electron deficient species—preferentially attack at positions where electrons are readily available.[402]

Wagner[403] investigated the reactions of recoil ^{11}C atoms—produced from N_2—with CH_3X (X = Cl, Br, I), and his results are given in Table XXXVI. The low yields of C_2H_4 can be explained by assuming that no ^{11}CH is formed, but that C atoms abstract preferentially an X atom from CH_3X, as was already proposed by Taylor et al.[404] for reactions of recoil ^{11}C atoms with alkyl chlorides. In the presence of O_2, ^{11}CCl may easily be oxidized to ^{11}CO. The high yield of $^{11}CH_2Cl_2$ can partially be explained by a reaction through ^{11}CCl, but as was concluded from the dependence of the yield on the radiation dose, and from the low yield (3%) in the presence of O_2, its formation through reactions of ^{11}C atoms with HCl—produced by radiation induced chain reactions—seems more probable:[403]

$$^{11}C \xrightarrow{HCl} {}^{11}CHCl \xrightarrow{HCl} {}^{11}CH_2Cl_2$$

The yield of HCN does not change appreciably for doses between 0.005 and 0.15 eV molecules, but the yield of C_2H_2 decreases in the case of CH_3Cl from 18 to 2%. The addition of 4.5% O_2 has the following effects: (1) The wall activity decreases to a yield lower than 10%, indicating that this yield is due to thermal ^{11}C atoms. (2) The main product (70–80%) is ^{11}CO. (3) The yield of $H^{11}CN$ is decreased to 5–10%.

Note Added in Proof. The yields of ^{11}C-labeled CO, CO_2, C_2H_4, and C_2H_2 were measured for 13 (halo)methanes[405,406] (Table XXXVII).

The CO yields were enchanced, whereas the C_2H_4 yields were dramatically reduced by the presence of a halogen atom. These product yields add further evidence to the mechanism of formation of C_2H_4 via the insertion of energetic ^{11}CH into C–H bonds, followed by the decomposition of the complex.

The presence of halogen atoms appear to divert $^{11}C(^1D)$ from forming ^{11}CH by formation of ^{11}CX and/or

TABLE XXXVII.[405,406] **Principal ^{11}C Products as Percent of Volatile Activity from CH_nX_{y-n} + 4.5% O_2**

target	yields			
	CO	CO_2	C_2H_4	C_2H_2
CH_4	33	3.7	25	30
CH_3F	42	14	6	24
CH_2F_2	61	22	1.4	3.9
CHF_3	68	26	<0.5	<0.5
CF_4	69	27	0	0
CH_3Cl	56	3.2	4.0	27
CH_2Cl_2	57	4.7	<1.0	10
$CHCl_3$	68	3.6	<0.5	<0.5
CCl_4	73	5.7	0	0
CH_3Br	68	3.0	4.2	25
CH_2Br_2	70	6.4	2.1	12
$CHBr_3$	79	5.0	<0.5	<0.5
CH_3I	51	2.1	3.4	28
CHF_2Cl	75	22		
$CHFCl_2$	65	14		
CF_3Cl	41	51		
CF_3I	67	31		
CF_2Cl_2	53	25		
CCl_3Br	79	3		

TABLE XXXVIII. $^{11}CH_4$ Yields from Proton-Irradiated Targets

target	nuclear reaction	yield, %	ref
NH_4Br	$^{14}C(p,\alpha)^{11}C$	7.5	407
N_2/H_2 (400/1)	$^{14}C(p,\alpha)^{11}C$	38	408, 409
N_2/H_2 (1/4.7)	$^{14}C(p,\alpha)^{11}C$	83	408, 409
N_2/HBr (1/4)	$^{14}C(p,\alpha)^{11}C$	23	403
N_2/HI (1/1)	$^{14}C(p,\alpha)^{11}C$	50	403
NH_3 (solid)	$^{14}C(p,\alpha)^{11}C$	13–20	410
NaCl	$^{23}Na(p,spal)^{11}C$	73[a]	411
NaBr	$^{23}Na(p,spal)^{11}C$	81[b]	411
Al	$^{27}Al(p,spal)^{11}C$	100[c]	411

[a] Dissolved in liquid NH_3. [b] Dissolved in liquid CH_3NH_2. [c] Dissolved in HCl.

TABLE XXXIX.[403,412,413] **Yields of ^{11}C Labeled Halomethanes Produced by $^{14}N(p,\alpha)^{11}C$ Reactions**

target	dose, eV/mol	yield, %			
		CH_3X	CH_2X_2	CHX_3	CX_4
N_2/HCl (1/1)	0.3	7	11	1.3	
N_2/HBr (1/1)	0.3	10	13		
N_2/HI (1/1)	0.3	28			
NH_4Cl	0.1		8.1	1.4	1.4
NH_4Cl	50		<0.1	<0.1	2.7
NH_4Br	0.2	3.0	0.5		
NH_4Br	75	10	1.6		
NH_4I	0.3	16			
NH_4I	37	<0.1			

spin conversion of $^{11}C(^1D)$ to $^{11}C(^3P)$. The yield of C_2H_3Cl in the case of CH_3Cl was a mere 0.3%.

Production of $^{11}CH_xX_{4-x}$. High yields of $^{11}CH_4$ can be derived from the reaction of ^{11}C atoms—produced by the $^{14}N(p,\alpha)^{11}C$ reaction or by spallation of ^{23}N and ^{27}Al by 3-GeV protons—with inorganic compounds (Table XXXVIII). Labeled halomethanes were produced from N_2/HX mixtures and from NH_4X. The yields are sensitive to dose and dose rates (Table XXXIX).

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