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Reactions of Radioactive Recoil Atoms with (Halo)ethylenes

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I. Introduction

This article is mainly dealing with the reactions of radioactive recoil F, Cl, T, and Mu atoms with ethylene and haloethylenes. The study of the reactions of recoil bromine and iodine is complicated by their lower reactivities and the possible involvement of neutral atoms and positive ions in ground and electronically excited states. The reactions of recoil ^{11}C atoms with ethylene are extensively studied, but the results are absolutely different from those obtained with nonradiocarbon atoms. No publication deals with ^{15}O, and only one deals with ^{38}S, although the knowledge about reactions of nonradioactive O and S atoms with ethylene is quite well developed. The study about the reactions of N atoms is limited to one publication about ^{13}N; the nonradioactive research is limited to the measurements of rate constants.

In fact, this article deals with the reactions of three kinds of atoms: translationally excited (hot) and thermal radioactive atoms and thermal nonradioactive atoms (in the case of H atoms, some experiments with photolytically produced hot H atoms are mentioned). Atoms that are released through a nuclear reaction receive a large amount of kinetic (recoil) energy, in general on the order of kiloelectronvolts. Chemical reactions that lead to labeled stable products can only take place after the moderation of the energetic recoil atoms (by collisions with surrounding atoms and molecules) to energies that are in the electronvolt range. In practice, it means that no differences are expected in the chemical reactions of isotopic atoms (belonging to the same element) that are produced by different nuclear reactions and that have received different amounts of recoil energy, because the energy distributions at lower energies will be all the same (an exception may be formed by ^{38}Cl atoms produced from ^{37}Cl with thermal neutrons[1]). The production of the radioisotopes and their nuclear physical behavior will be mentioned in the following chapters.[2] Atoms recoiling in inert[3] media are slowed down to thermal kinetic energies ($^3/_2kT$ = 3.7 kJ mol^{-1} = 0.039 eV mol^{-1} at 298 K) and can then react with noninert compounds that are added in low concentrations (<5 mol %). The interest in thermal reactions of radioactive atoms is recently encouraged by the wish of radiochemists to apply their techniques and specialized knowledge to the study of the reactions of halogen atoms, produced by the de-

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composition of Freons in the stratosphere by ozone, with simple molecules. Such studies must yield similar results as studies with thermal nonradioactive atoms, which can be produced by a number of techniques: thermal dissociation, microwave discharge, radiolysis, photolysis, etc., but qualitative and quantitative differences are sometimes observed. However, in some aspects the results that can be obtained with thermalized radioisotopes are unique in a sense that information can easily be derived about reactions that lead to isotopic substitution, e.g., ^{34m}Cl-for-Cl in C_2Cl_4 and the chlorodechlorination of chlorobenzene.[4]

In the reaction of a halogen or a hydrogen atom with ethylenes three reactions can be distinguished: (1) *abstraction*, which leads to compounds such as HX, TX, X_2 (X = halogen) that are not observed as such by recoil chemistry techniques and to the formation of HT; (2) *substitution*, which can proceed in a fast direct process (without the formation of a long-lived radical) by a high energetic recoil atom (in such a process no cis–trans isomerization of dihalo compounds is expected; with less energetic atoms, addition/elimination reactions may also lead to substitution); (3) *addition* to unsaturated π bonds. The subsequent reactions of the excited ethyl radical may involve (a) elimination of a H or X atom, which results in the formation of the initial or another ethylene (in general the atom with the weakest C bond will be lost)—this process may be preceded by a 1,2 migration of one of the atoms; the eliminated atom may start another cycle of addition/elimination reactions, but with another energy spectrum; (b) elimination of HX, resulting in the formation of an ethylene radical; (c) other fragmentation reactions, such as C–C bond scission; (d) dimerization with another ethylene molecule and possible further polymerization; (e) abstraction of a H or X atom from another ethylene molecule, resulting in a stable ethane; (f) reaction with scavengers (O_2, I_2, HI, H_2S); (g) reaction with another radical (as observed in radiolytical experiments).

Most of the research is focused on gaseous systems. In the studies with thermal atoms reaction rate constants, lifetimes (or half-stabilization pressures vs. unimolecular decomposition of ethyl radicals) are measured. In the liquid phase, reactions in an excited solvent cage, in particular with recoil halogen atoms, must be taken into account.

II. Fluorine

Abstraction of a H atom by F is always an exothermic process and proceeds very rapidly. In alkanes it is the only possible reaction, but in unsaturated compounds addition to the unsaturated bonds decreases the abstraction yield considerably. The total reaction energy for abstraction, E_T, is given by

$$E_{\mathrm{T}} = D(\mathrm{H{-}F}) - D(\mathrm{H{-}R}) + E_{\mathrm{a}} + 3RT$$

in which $3RT$ corresponds to the initial rotation plus translational energies of the reactants and E_a is the activation energy ($\sim$4 kJ mol^{-1} for C_2H_4).[5] For C_2H_4 the value of E_T is 132.1 kJ mol^{-1}, with D(H–F) = 565.8 and $D(H{-}CH_3)$ = 445.5 kJ mol^{-1}. Part of the energy (F_ν) is released as vibrational energy of HF

$$F_\nu = \frac{1}{E_{\mathrm{T}}}\sum n_i E_i$$

in which n_i is the fractional population of the i^{th} vibrational level of energy E_i ($\sum_{\nu=0}^{\nu_{\max}} n_i = 1$).

Values of n_i can be calculated from HF infrared emission spectra. Published values of F_ν and n_i are given in Table I. The energy of the level with $\nu = 3$ is 136 kJ mol^{-1}, somewhat higher than the value of E_T. If it is assumed that the values of D(H–F) and $D(H{-}C_2H_3)$ are correct, Bogan et al.[5] suppose that the $\nu = 3$ levels, observed by Vasiljev et al.[6] and Moehlmann et al.,[7] are populated by HF molecules that are formed in reactions of F atoms with H_2, which is produced by the recombination of H atoms generated by decomposition of excited C_2H_4F radicals. The F_ν data are averaged values, because the vibrational and rotational states can be filled up close to the limit of the available energy E_T, but some stabilization energy is retained in the radical.[5] The highest state for C_2H_4 is that with $\nu = 2$, $J = 12$, at 445.4 kJ mol^{-1}. Parson et al.[8] found highly vibrationally excited HF and DF by measuring their angular distribution and translational energy as they were formed from reactions of F atoms with C_2H_4 and C_2D_4 at relative kinetic energies of 8.3 and 8.1 kJ mol^{-1}. Abstraction of halogen atoms is usually endothermic and has not been reported for haloethylenes, but Cl, Br, I, and CH_3 abstraction from arenes was observed through the detection of the C_6H_5 radical.[8]

Substitution reactions of thermal F atoms were followed through measurements of the infrared emission spectra of vibrationally excited fluoroethylenes.[9-11] The experimentally observed relative intensities of the emission bands are in very good agreement with populations calculated by assuming a statistical distribution of the vibrational energy over the molecule, at least when a Cl or Br atom is substituted. If the leaving entity is a H atom (from C_2H_4[8-11]) or a CH_3 group (from C_3H_6), then the experimental results differ from the calculated intensities. It seems that the excess energy is statistically distributed in the transition state, but the distribution becomes distorted before the products completely separate. This is then due to the existence of an energy barrier of 13 and 33 kJ mol^{-1} for H and CH_3 loss, whereas such a barrier height is zero in case of the halides. The substitution pattern for chloroethylenes is given in Table II. The only product observed in reactions with $CH_2{=}CCl_2$ is $CH_2{=}CFCl$. It is not known if the addition of the F atom is solely at the CCl_2 end or if F migration takes place (there is a high probability for H abstraction). With C_2HCl_3 all three isomeric C_2HFCl_2 compounds are observed, and if no atom migration in the intermediate takes place, then the product distribution indicates that F addition at the CHCl site is three times as likely as at the CCl_2 site. With *cis*- and *trans*-CHCl=CHCl the original configuration is favored. The *cis*-CHF=CHCl isomer is about 3.3 kJ mol^{-1} more stable than the trans isomer. If the activated complex has an internal energy of 210 kJ mol^{-1}, statistically distributed, and if the barrier to the cis product is 8–13 kJ mol^{-1} lower than that to the trans product, then a cis/trans ratio of 1.8–2.4 can be expected for both starting compounds.[12] The observed preference for retention of the original configuration indicates that the complex lifetime is comparable with

TABLE I. HF Fractional Vibration Energy (F_ν) and Population of Vibrational Levels from $F + C_2H_4 \rightarrow HF + C_2H_3$

F_ν	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	ref
0.49	0.08	0.43	0.48		5
		0.40	0.54	0.06	6
0.38	[a]	0.56	0.41	0.03	7

[a] For further calculations the authors suppose $n(\nu = 0) = {}^1/_2 n(\nu = 1)$.

TABLE II.[9] Substitution Products from Reaction of Thermal F Atoms with Chloroethylenes

compound	product (yield, %)
$CCl_2{=}CH_2$	$CFCl{=}CH_2$ (100)
cis-$CHCl{=}CHCl$	*cis*-$CHF{=}CHCl$ (69) *trans*-$CHF{=}CHCl$ (31)
trans-$CHCl{=}CHCl$	*cis*-$CHF{=}CHCl$ (37) *trans*-$CHF{=}CHCl$ (63)
$CHCl{=}CCl_2$	$CHF{=}CCl_2$ (74) *cis*-$CHF{=}CHCl$ (13) *trans*-$CHF{=}CHCl$ (13)
$CCl_2{=}CCl_2$	$CHF{=}CCl_2$ (100)

the time for internal rotation. Parson et al. have measured the angular distribution and the translational energy of C_2H_3F and C_2D_3F by addition reactions with C_2H_4 and C_2D_4. The recoil energies have a broad distribution, peaking at about half the available energy.[8]

Abstraction and substitution products could be simultaneously recorded in one experiment, and the abstraction/substitution ratios could be determined: C_2H_4, 3; C_2H_3Cl, 4; C_2H_3Br, 2; $CCl_2{=}CH_2$, 14; *cis*-$CHCl{=}CHCl$, 7; C_2HCl_3, 3. Fluoroethylenes, excited by triplet mercury photosensitization, decompose by molecular elimination of HF either by[13,14] geminal elimination

$$[CF_2{=}CHF]^* \rightarrow HF + CF_2{=}C{:}$$

or by 1,2-H migration

$$[CHF{=}CHF]^* \rightarrow CH_2F{=}\dot{C}F \rightarrow HF + CH{\equiv}CF$$

The reactions of energetic and thermal ^{18}F recoil atoms with gaseous ethylene and fluoroethylenes have been thoroughly studied.[15] Product yields for hot ^{18}F atoms recoiling in C_2H_4 were determined by extrapolation to 100 mol % C_2H_4 in C_2H_4/CF_4 (or SF_6) mixtures, with a little HI present.[16] At 200 kPa the yields are 25% $C_2H_5{}^{18}F$, 10% $C_2H_3{}^{18}F$, and 6% $CH_3{}^{18}F$ (total 41%).[17] The total amount of organic ^{18}F products is diminished markedly compared with thermal reactions, which means that extra $H^{18}F$ is formed, either through hot abstraction or by decomposition of excited products. The yield of $C_2H_3{}^{18}F$ also increases at higher C_2H_4 concentrations, either through hot ^{18}F-for-H substitution or through hot addition followed by fast decomposition. The amount of $C_2H_5{}^{18}F$, formed via ^{18}F addition followed by H abstraction from HI, decreases. $CH_3{}^{18}F$ can be formed from two excited products

$$[CHF{=}CH_2]^* \rightarrow CH^{18}F \xrightarrow{HI} CH_3{}^{18}F \qquad (a)$$

$$CH_2{}^{18}F{-}\dot{C}H_2]^* \rightarrow CH_2{}^{18}F \xrightarrow{HI} CH_3{}^{18}F \qquad (b)$$

It is known that CHF reacts quantitatively with C_2H_4 to give c-C_3H_5F. In experiments without HI, in a 1:1 mixture of C_2H_4/SF_6, 2% $CH_3{}^{18}F$ was obtained via 0.8% $CH^{18}F$ (a) and 1.2% $CH_2{}^{18}F$ (b).

In mixtures with a 20-fold excess of CF_4 or SF_6 the recoil ^{18}F atoms are thermalized before they can react with C_2H_4. The amount of $H^{18}F$ (thermal abstraction) is about 40%, and the remaining 60% ^{18}F atoms react through addition. The excited $C_2H_4{}^{18}F$ radical (~200 kJ mol^{-1}) can decompose

$$C_2H_4{}^{18}F^* \xrightarrow{D} C_2H_3{}^{18}F + H$$

or can become stabilized by collisions and react with HI

$$C_2H_4{}^{18}F^* \xrightarrow{S} C_2H_4{}^{18}F \xrightarrow{HI} C_2H_5{}^{18}F$$

(if no HI is present the stabilized radicals can give rise to wall or polymerization reactions). The ratio $C_2H_3{}^{18}F/C_2H_5{}^{18}F = D/S$ is pressure dependent; the "half-stabilization pressure" ($D/S = 1$) in C_2H_4/CF_4 mixtures is about 18 kPa, which means that the lifetime of the excited $C_2H_4{}^{18}F$ radical is about 10^{-9} s.

The product distribution in C_2F_4 is totally different from that found in C_2H_4. This behavior can very well be explained by the energetics of the decomposition pathways of some reactions with thermal ^{18}F atoms:

$$^{18}F + C_2H_4 \rightarrow C_2H_4{}^{18}F \rightarrow H + C_2H_3{}^{18}F \qquad \Delta H = -29 \text{ kJ mol}^{-1}$$

$$^{18}F + C_2H_4 \rightarrow C_2H_4{}^{18}F \rightarrow CH^{18}F + CH_2 \qquad \Delta H = +217 \text{ kJ mol}^{-1}$$

In unmoderated C_2F_4 three primary hot reactions can be distinguished.[18a] (1) hot abstraction—the $F^{18}F$ yield was not determined; (2) hot substitution:

$$^{18}F + C_2F_4 \rightarrow C_2F_3{}^{18}F^*$$

the excited molecule can be stabilized or can decompose by splitting into $CF_2 + CF^{18}F$; in the presence of HI the carbenes can react by insertion:

$$C_2F_3{}^{18}F^* \xrightarrow{S} C_2F_3{}^{18}F \ (\sim 1.5\%)$$

$$C_2F_3{}^{18}F^* \xrightarrow{D} CF_2 + CF^{18}F \xrightarrow{HI} CHF^{18}FI \ (\sim 13\%)$$

(3) hot addition:

$$^{18}F + C_2F_4 \rightarrow C_2F_4{}^{18}F^*$$

followed by

$$\begin{aligned} C_2F_4{}^{18}F^* &\xrightarrow{S} C_2F_4{}^{18}F \xrightarrow{HI} C_2HF_4{}^{18}F \\ &\xrightarrow{D} CF_2 + CF_2{}^{18}F \xrightarrow{HI} CHF_2{}^{18}F \end{aligned}$$

Both products account for about 30–60% of the total ^{18}F activity.

On addition of inert SF_6 the recoil ^{18}F atoms react more as thermal atoms, and when extrapolated to infinite dilution with SF_6 the following effects were noticed: (1) The yield of $CHF_2{}^{18}I$ drops to zero, which proves that the direct ^{18}F-for-F substitution is a hot process. (The endothermicity of the decomposition reaction of $C_2F_3{}^{18}F$ is 318 kJ mol^{-1}.) (2) The yield of $CHF_2{}^{18}F$ drops to about half of the yield in unmoderated C_2F_4. The decomposition/stabilization ratio in the thermal system is pressure dependent, the half-stabilization pressure is about 30 kPa, and the average decomposition rate of $C_2F_4{}^{18}F$ is about 2×10^9 s^{-1}.

Smail et al.[18b] have also investigated the reactions of recoil ^{18}F atoms with fluoroethylenes with a composition between C_2H_4 and C_2F_4, with the pure compounds, and with those diluted with a 20-fold excess of inert SF_6. It is not surprising to observe that the product yields reflect the behavior of both C_2H_4 and C_2F_4:

(a) C–C scission as a decomposition mode of an excited compound is important if a CF_2 group is present, because the C–F bond energy in CF_2 (522 kJ mol^{-1}) is high compared with the ethylenic C–F bond (480 kJ mol^{-1}).

(b) The next most energetic decomposition mode for an ethyl radical is the loss of a H atom, which is also an exothermic reaction with extreme values for

$$F + CH_2{=}CF_2 \rightarrow CH_2F{-}CF_2 \rightarrow H + CHF{=}CF_2 \ (\Delta H = -12 \text{ kJ mol}^{-1})$$

$$F + CH_2{=}CHF \rightarrow CHF_2{-}CHF \rightarrow H + CF_2{=}CHF \ (\Delta H = -88 \text{ kJ mol}^{-1})$$

(c) The loss of a F atom is always a thermoneutral reaction but must always be considered as a possible participating reaction channel.

(d) The studies in the presence of a 20-fold excess of SF_6 were performed at a pressure of about 0.5 MPa, which means that the excited ethyl radicals are predominantly stabilized (the half-stabilization pressure in C_2HF_3 is only 6 kPa).

(e) It must be realized that in undiluted ethylenes a more endothermic reaction is sometimes preferred, e.g., the formation of $CH_2{}^{18}F$ (+75 kJ mol^{-1}) instead of H loss (−12 kJ mol^{-1}) from $CH_2{}^{18}FCF_2$.

(f) From experiments with C_2HF_3 in excess SF_6 the $CHF^{18}FCF_2H/CH_2FCF_2{}^{18}F$ ratio is 3.4. If no other reactions are involved, such as 1,2 migration or polymerization, then it can be concluded that attack is preferentially at the CHF site. In $CH_2{=}CF_2$ the ratio $CH_2{}^{18}FCHF_2/CH_3CF_2{}^{18}F$ is 5. The results of experiments on the intramolecular selectivity in ^{18}F addition are shown in Table III.

(g) Intermolecular competition experiments in excess SF_6 gave the initial rate constants for addition; e.g., in a 1:1 mixture of C_2H_4 and C_2F_4 the ratio $C_2H_5{}^{18}F/C_2HF_4{}^{18}F$ is 0.25. Other relative rate constants can be calculated from results compiled in Table III. Reactions of ^{18}F with *trans*-CHF=CHCl give a cis/trans ratio for $CHF{=}CH^{18}F$ of 1.2, independent of the pressure between 60 and 470 kPa.[19]

Milstein et al. have used a mixture of $SF_6/C_2H_4/HI$ (95/4/1) for competition experiments with O_2, NO, SO_2, N_2, and CO.[20] Reaction rates of thermal ^{18}F atoms with these additives relative to addition to C_2H_4 were determined by measuring a decrease in the $CH^{18}F{=}CH_2$ yield. Reaction rates of $CH_2{}^{18}F{-}CH_2$ radicals were determined relative to H abstraction from HI by measuring a decrease in the $CH_2{}^{18}F{-}CH_3$ yield.[20] C_2H_4 was used as a scavenger in one of the first hot atom experiments of recoil ^{18}F atoms with CH_4.[21] In combination with small amounts of I_2 all thermal ^{18}F atoms react through the formation of $C_2H_3{}^{18}F$ or $CH_2{}^{18}FCH_2I$:

$$^{18}F + C_2H_4 \rightarrow C_2H_4{}^{18}F^* \xrightarrow{D} C_2H_3{}^{18}F$$

$$\xrightarrow{S} C_2H_4{}^{18}F \xrightarrow{I_2} CH_2{}^{18}FCH_2I$$

TABLE III.[17] Intermolecular and Intramolecular Selectivity in Thermal ^{18}F Atom Addition to Ethylene

olefin	normalized yield for olefinic carbon atom[a] CH_2	CHF	CF_2	total addition yield (corrected)[a]
$CH_2{=}CH_2$	1.0			1.0
$CH_2{=}CHF$	0.7 (0.8)	0.6		0.70
$CH_2{=}CF_2$	0.8 (1.1)		0.2	0.65
trans-CHF=CHF		0.3		0.30
$CHF{=}CF_2$		0.4	0.1	0.25
$CF_2{=}CF_2$			0.14 (0.2)	0.20

[a] Yield per carbon atom of the stabilized radical (relative to CH_2 in ethylene as 1.0). Numbers in parentheses are the yields after approximate correction for decomposition of excited radicals.

In order to prevent the possible complication of H abstraction, C_2F_4 was investigated as a scavenger for thermal ^{18}F atoms, but the ease with which C_2F_4 polymerizes under the prevailing irradiation conditions was a serious drawback for its application.[22a] A better scavenger was found in C_3F_6, which gives a series of $C_6F_{13}{}^{18}F$ products on addition of ^{18}F, followed by dimerization and chain termination by allylic F abstraction from C_3F_6.[22b]

III. Chlorine

Reactions of Cl atoms with olefins were reviewed in 1974 by Nonhebel and Walton.[23] The addition of thermal Cl atoms to unsaturated bonds forms the main reaction channel at room temperature, but the relative rate for H abstraction increases at elevated temperatures. The rate constant for addition to gaseous C_2H_4, CHCl=CHCl, and C_2HCl_3 is about 4×10^{10} L mol^{-1} s^{-1}, while it is 1.3×10^{10} L mol^{-1} s^{-1} for C_2Cl_4.[24-26] Relative addition rates of Cl atoms to liquid chloroethylenes were measured by Poutsma et al.[27] (Table IV). These rates decrease slowly with enhanced chlorination. The addition prevails at the less chlorinated C atom: at the CH_2 site in $CCl_2{=}CH_2$ and at the CHCl site in C_2HCl_3. Larger variations in these relative addition rates are observed on dilution with C_6H_6 and CS_2. From the work of Russell it is known that arenes and sulfur compounds can act as complexing solvents for thermal Cl atoms and can give rise to considerable changes in reaction rates.[28] Knox and Riddick[25] arrived at the conclusion that in the excited chloroethyl radical, formed after a thermal addition reaction, free rotation about the C–C bond exists, which excludes the formation of a more stable, chlorine-bridged radical that would hinder the free rotation and slow down the rate of subsequent decomposition.[29] The most important decomposition channel of excited chloroethyl radicals is the loss of a Cl atom. The rate of this decomposition mode depends, among others, on the C–Cl bond strength in the radical.[30] Goldfinger et al. have calculated bond energies in chloroethyl radicals and in chloroethanes by use of the experimental results of such studies.[31] In several publications attempts were reported on the application of the Marcus–Rice theory about the decomposition of activated products with respect to the decomposition of excited chloroethyl radicals.[25b,29,32] It was concluded that the attempts to correlate theoretical and experimental data were disappointing, partly due to the use of a much oversim-

TABLE IV.[27] Relative Rates of Addition of Cl Atoms to Liquid Chloroethylenes

	solvent[a]			
compound	pure	80% C_2FCl_2	80% C_6H_6	80% CS_2
$CCl_2{=}CH_2$	1.2	1.3	3.9	7.0
cis-$CHCl{=}CHCl$	1.2	1.1	1.5	1.8
trans-$CHCl{=}CHCl$	1.0	1.0	1.0	1.0
$CHCl{=}CCl_2$	0.7	0.7	0.7	0.9
$CCl_2{=}CCl_2$	0.4	0.4	0.08	0.05

[a] Volume percent.

plified model and partly due to a lack of experimental data over an extensive pressure range.

Cis–trans isomerization of CHCl=CHCl was studied by several investigators.[25,33] In the gas phase, Knox et al.[25] found a trans/cis ratio of 0.28 for the decomposition of the excited trichloroethyl radical, irrespective of if it was formed from either the cis or the trans compound. No isomerization was observed in liquid chloroethylenes with a little Cl_2 present, which was due to a fast reaction of the ethyl radical with Cl_2, yielding chloroethanes.[27] In more recent experiments the angular distribution of translational excited chloroethylenes and their vibrational energy distribution were investigated.[12,34,35] These studies are dealing with the behavior of excited vinyl chloride, formed after the addition of a Cl atom to C_2H_3Br and C_2D_3Br and after the subsequent loss of the Br atom. The results on the angular distribution are consistent with the idea that the primary attack of the Cl atom is at the C=C bond and not at the C—Br bond. The observed symmetrical distribution around 90° indicates that the C_2H_3BrCl radical persists at least for a few rotational periods ($\geq 5 \times 10^{-12}$ s). In view of extensive evidence for anti-Markovnikov addition, it was concluded that the reaction involved a 1,2-Cl migration; this step would be the rate-limiting process:

$$Cl + CH_2{=}CHBr \rightarrow CH_2Cl{-}\dot{C}HBr \rightarrow \dot{C}H_2{-}CHClBr \rightarrow CH_2{=}CHCl + Br$$

The translational energy distribution of the C_2H_3Cl molecules corresponds to a random energy distribution in the intermediate C_2H_3ClBr radical.

By use of infrared chemiluminescence techniques the population of some vibrational modes (800–1800 cm^{-1}) of excited C_2H_3Cl and C_2D_3Cl could be determined.[12,35] The CH (CD) rocking mode at 1280 (994) cm^{-1} contained much more energy than would be predicted on the basis of statistical distribution of energy. The observed populations were explained by (a) the existence of a potential barrier in the exit channel leading to an extra excess of translational energy or (b) if less than 10^4 vibrational states are available, a nonstatistical distribution will be observed. Olbrechts has studied the loss of a Cl atom from nonexcited chloroethyl radicals that were produced through H abstraction from chloroethanes.[36] Grabowski et al. observed the isomerization of *cis*- and *trans*-CHCl=CHCl through the photo-induced formation of an intermediate T_1 triplet state of the ethylene, common for both isomers, in which the equilibrium configuration is twisted 90° about the C=C bond.[37] Reiser et al. have investigated the reactions of mono-, di-, and trichloroethylenes that were highly excited by multiple infrared absorption.[38] The dominant mode of decay is the elimination of HCl. Comparison of HCl/DCl ratios from CHD=CHCl and $CH_2{=}CDCl$ shows that the preferred mode of decomposition is the gem or αα elimination of H(D)Cl. Free rotation about the C=C bond in excited CHCl=CHCl also leads to cis–trans isomerization.

Polymerization in liquid chloroethylenes–Cl_2 mixtures was only observed to a minor extent for CHCl=CHCl at an olefin/Cl_2 ratio of about 30–40, but the polymerization vanished at a ratio of 8.

Three radioactive Cl isotopes are in use in recoil chemistry: $^{35}Cl(n,2n)^{34m}Cl$, $t_{1/2} = 32.4$ min; $^{37}Cl(n,\gamma)^{38}Cl$, $t_{1/2} = 37.3$ min; and $^{40}Ar(\gamma,n)^{39}Cl$, $t_{1/2} = 56$ min. Due to the complex cascade of γ transitions through which the newly formed isotopes, initially in very high excited states, reach the ground state and the time scales involved in the cascade, it is not sure which recoil energies should be given to the isotopes. In the case of ^{34m}Cl all the recoil atoms receive in their last transition a recoil energy of at least 18.5 eV, in the case of ^{38}Cl 41% can receive an energy between 4 and 6 eV,[1,39] but in the case of ^{39}Cl a reasonable fraction can receive an energy of 2.2 eV.[40]

Small amounts of C_2H_4 (with some I_2) were used as a scavenger in a study of the reactions of recoil ^{39}Cl atoms with alkanes. The thermalized Cl atoms were detected as $CH_2{}^{39}Cl{-}CH_2I$:

$$^{39}Cl + CH_2{=}CH_2 \rightarrow CH_2{}^{39}Cl{-}\dot{C}H_2 \xrightarrow{I_2} CH_2{}^{39}Cl{-}CH_2I^{41}$$

Reactions of thermal recoil ^{39}Cl atoms with C_2H_4 were more systematically studied in a 20-fold excess of CF_2Cl_2 or CF_3Cl in the presence of HI or I_2.[42,43] (Only 1–2% of the recoil ^{39}Cl atoms react with CF_2Cl_2 or CF_3Cl by Cl or F substitution,[44] because both compounds are inert toward reactions with thermal Cl atoms.) Thermal H abstraction from C_2H_4 (+20 kJ mol^{-1}) is a process with a yield lower than 6% ($H^{38}Cl$), because the most important reaction channel is the thermal addition to the unsaturated bond (−90 kJ mol^{-1}, $k = 5$–6×10^{10} L mol^{-1} s^{-1}).[42,43] The excited $C_2H_4{}^{38}Cl$ radical may become stabilized by collisions and can then react with added I_2 ($CH_2{}^{38}ClCH_2I$) or HI ($CH_2{}^{38}ClCH_3$). The radical may also decompose through one of the four available reaction channels:

(a) $$C_2H_4{}^{38}Cl^* \rightarrow C_2H_3{}^{38}Cl + H$$

This is a slightly endothermic reaction and cannot occur after the addition of a thermal ^{38}Cl atom.[43]

(b) $$C_2H_4{}^{38}Cl^* \rightarrow CH_2{}^{38}Cl + CH_2$$

The yield of this reaction, observed by the presence of $CH_3{}^{38}Cl$, formed by H abstraction from HI, is less than 1%.[42]

(c) $$C_2H_4{}^{38}Cl^* \rightarrow C_2H_3 + H^{38}Cl$$

The high pressure rate constant for this reaction is determined as $(8 \pm 3) \times 10^8$ s^{-1}.[42]

(d) $$C_2H_4{}^{38}Cl^* \rightarrow C_2H_4 + {}^{38}Cl$$

The rate constant for this reaction was measured in a competitition experiment with H abstraction from HI and is 10^{10} s^{-1}.[42]

$$^{38}Cl + HI \rightarrow H^{38}Cl + I$$

TABLE V. Trans/Cis CHCl=CHCl Ratios for Reactions of Recoil Cl Atoms with Both Compounds

sample composition	reactant cis	reactant trans	absolute yield, %	ref
gas, excess CH_3Cl	0.50 ± 0.02	0.55 ± 0.01	not measured	46
Ar (1.3)[a]	0.49 ± 0.04	0.61 ± 0.02	30	49
Ar (1.3), O_2 (6.5)	0.61 ± 0.03	0.71 ± 0.03	25	49
Ar (1.3), O_2 (20)	0.67 ± 0.05	0.75 ± 0.05	18	49
Ar (1.3), O_2 (6.5), butadiene (6.5)	0.72 ± 0.03	0.95 ± 0.04	7	49
liquid[b]	0.60 ± 0.02	1.33 ± 0.02	16	47, 52
solid	0.43 ± 0.10	2.00 ± 0.10	not measured	47

[a] Pressure in kPa in parentheses. [b] Averaged values from all the data in ref 47 and 52; these include results from ^{34m}Cl and ^{38}Cl recoil atoms in the pure liquids and in the presence of small amounts of I_2 or DPPH.

C_2H_3Br has been used as a competitive reactant in studies of the abstraction of H atoms from alkanes by thermal ^{38}Cl atoms.[45] The excited $C_2H_3Br^{38}Cl$ radical decomposes by the loss of the Br atom with a rate constant of 10^{10} s^{-1}. From beam experiments Cheung et al. measured a rate constant $\geq 2 \times 10^{11}$ s^{-1}.[34] The rate-determining step in the loss of the Br atom is the 1,2 migration of a H or Cl atom in the $CH_2{}^{38}ClCHBr$ complex.[34,46] *cis*- and *trans*-CHCl=CHCl were used as scavengers for thermal ^{38}Cl atoms in the recoil chemistry of CH_3Cl, CF_3Cl, and CF_2Cl_2.[44,46,47] The lifetime of the excited $CHCl^{38}ClCHCl$ radical is 5–7 × 10^{-10} s (or the rate constant for Cl or ^{38}Cl loss is 1.5–2 × 10^9 s^{-1}). The loss of a Cl atom from this radical leads to $CHCl{=}CH^{38}Cl$ with a trans/cis ratio of 0.50; this ratio was found at pressures between 2.5 and 85 kPa and from either isomer as the reactant. The ratio of 0.5 is rather different from the trans/cis ratio of 0.28 measured by Knox and Riddick with thermal nonradioactive Cl atoms for both reactants.[25] In that experiment differences may be involved in addition and decomposition rates of the Cl atoms to the trans or the cis isomer, because the cis isomer is 2 kJ mol^{-1} more stable than the trans form.[48] Experiments—in which radiation-induced reactions were absolutely involved—with the cis compound as a scavenger resulted in trans/cis ratios between 0.38 and 0.64. Taking C_2Cl_4 instead of *cis*-CHCl=CHCl as a scavenger in similar experiments gave yields of $C_2Cl_3{}^{38}Cl$ between 9 and 92%.[44]

In less moderated experiments (2.5-fold excess of He) the trans/cis ratio was 0.49 for the cis compound as the reactant and 0.55 for the trans compound. The small difference may reflect a minor contribution from a direct hot ^{38}Cl-for-Cl substitution reaction, which proceeds with retention of the original stereochemical configuration. Such a conclusion was partly based on the observation of low yields of $C_2HCl_2{}^{38}Cl$, formed through hot ^{38}Cl-for-H substitution.[47] Trans/cis ratios that differed more from the thermal value of 0.5 were observed in the presence of large amounts of butadiene as a scavenger (Table V). The total yield of the labeled cis and trans products is decreased considerably due to reactions of thermal Cl atoms and less excited $C_2H_2Cl_2{}^{38}Cl$ radicals with butadiene. But the relative yield of hot reactions leading to these labeled compounds, either by hot ^{38}Cl-for-Cl substitution or hot addition and fast decomposition, is increased. In general, it may be concluded that the higher the energy, the closer the trans/cis ratio comes to unity.[49,50] The results obtained by Leurs with ^{38}Cl atoms, produced through nuclear decay [$^{38}S(\beta,\gamma)^{38}Cl$], and the CHCl=CHCl compounds agree with the former observations.[51]

TABLE VI.[53] Relative and Absolute Yields of *cis*-$CHCl{=}CH^{34m}Cl$ from the Reactions of ^{34m}Cl Recoil Atoms with Liquid CCl_3CH_3 and $CHCl_2CHCl_2$

irradiated compound	yield of *cis*-$CHCl{=}CH^{34m}Cl$ relative[a]	yield of *cis*-$CHCl{=}CH^{34m}Cl$ absolute[b]
CCl_3CH_3	39.7 ± 2.3	1.0
$CHCl_2CH_2Cl + I_2$	44.9 ± 2.0	0.8
$CHCl_2CH_2Cl$ + 3% n-C_6H_{12}	43.6 ± 1.9	not measured
$CHCl_2CHCl_2$	42.8 ± 1.3	1.2
$CHCl_2CHCl_2 + I_2$	47.5 ± 2.7	1.0

[a] *cis*- + *trans*-$CHCl{=}CH^{34m}Cl$ = 100. [b] Absolute yields in %.

Experiments were performed with ^{34m}Cl atoms, produced by the $^{35}Cl(p,pn)^{34m}Cl$ reaction, recoiling in gaseous C_2Cl_4. The proton beam causes considerable radiation problems, and the results were irreproducible.[52] A high yield of 69% $C_2Cl_3{}^{34m}Cl$ in pure C_2Cl_4 is reduced by addition of 10 mol % of unsaturated compounds (e.g., to 8% by cycloheptatriene), whereas the yield of polymeric species increases. The addition of some aniline enhances the inorganic fraction. Even in the most "energetic" experiments with gaseous *trans*-CHCl=CHCl, the trans/cis product ratio never exceeds unity, but in condensed phases the situation is changed, as can be noticed in Table V. Wai and Rowland mention the possible involvement of caged recombination reactions between ^{38}Cl atoms and C_2H_2Cl radicals as a possible reaction channel next to the addition/elimination combination.[47] Brinkman et al. proposed that an addition/elimination sequence in an excited cage results in a trans/cis ratio of 1.0 (their summed yield is 13%), whereas the remaining fraction (3%) is explained by a direct hot ^{34m}Cl-for-Cl substitution reaction.[52] In the elimination reaction there is a 1:1 possibility that the ^{34m}Cl atom is lost. If a new cycle is started, with a thermal ^{34m}Cl atom, more of the cis isomers can be expected, but, as will be discussed later, dimerization and further polymerization are another efficient reaction channel for liquid phase experiments. *cis*- and *trans*-$CHCl{=}CH^{34m}Cl$ were also detected in ^{34m}Cl recoil experiments with liquid chloroethanes, but their combined yield never exceeds 3%.[53] The formation of both compounds in $CHCl_2CH_3$ and CH_2ClCH_2Cl can easily be explained through hot ^{34m}Cl-for-H substitution, followed by HCl loss from an excited ethane molecule, and in $CHCl_2CH_2Cl$ similarly after hot ^{34m}Cl-for-Cl substitution. The formation of the $CHCl{=}CH^{34m}Cl$ isomers from CCl_3CH_3, CCl_3CH_2Cl, and $CHCl_2CHCl_2$ requires a much more complex reaction sequence. Some of the data are given in Table VI.

Product yields for the reactions of recoil ^{34m}Cl atoms with all the chloroethylenes (except C_2H_3Cl) in the liquid phase are given in Table VII (the yields are

TABLE VII.[52] Absolute Product Yields (%) from the Reactions of Recoil ^{34m}Cl Atoms with Chloroethylenes

target compound	^{34m}Cl for Cl[a] (1)	^{34m}Cl for H[a] (2)	^{34m}Cl + Cl addition[a] (3)	C-C bond scission[a] (4)	other compounds	polymers	inorganic
$CH_2=CCl_2$	4	1	3	0.3	2	29	61
cis-$=CHCl=CHCl$	17	2	6	2.0	2	44	27
$=CHCl=CHCl$	14	2	5		1	49	29
C_2HCl_3	18	2	7	0.8	2	50	20
C_2Cl_4 [b]	24		6	1.3	1	36	32

[a] From $C_2H_nCl_{4-n}$: (1) $C_2H_nCl_{4-n}$; (2) $C_2H_{n-1}Cl_{5-n}$; (3) $C_2H_nCl_{6-n}$; (4) CH_mCl_{4-m}. [b] References 20 and 21.

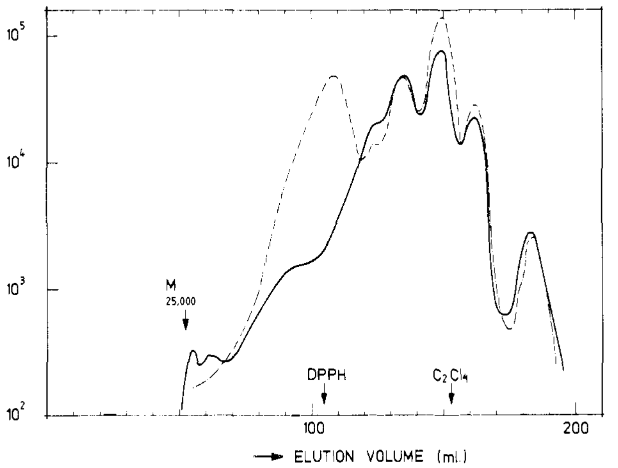

Figure 1. Radiogelfiltration chromatogram from the reactions of recoil ^{38}Cl with C_2Cl_4: (—) C_2Cl_4; (------) C_2Cl_4 + DPPH.

hardly changed on addition of a little I_2).[52] Black and Morgan have performed similar experiments with recoil ^{38}Cl atoms.[54] With the exception of $CCl_2=CH_2$ the yields of products formed by similar reactions are almost equal for all the target compounds. The formation of the products obtained by ^{34m}Cl-for-H substitution can be explained either through a direct hot substitution process or through caged recombination between a ^{34m}Cl atom and a vinyl radical.[47,51] The major fraction of the labeled products is formed by the subsequent reactions of excited or thermalized ethyl radicals: (a) 14–20% by Cl loss from an excited radical (a ^{34m}Cl atom can also be lost and react again by thermal addition) (a small fraction of the ^{34m}Cl-for-Cl substituted compounds can also be formed by a direct hot reaction and by caged recombination); (b) 1–2% by C–C bond scission of excited radicals; (c) 5–7% chloroethanes (with a ^{34m}Cl and a Cl atom more than the target compound), formed by Cl abstraction from a neighbor molecule or by reaction with a free Cl atom; (d) a large fraction of the radicals reacting with another ethylene molecule and further polymerizing, yielding high boiling products. These fractions were analyzed in more detail by liquid chromatography, using Sephadex LH20 columns.

From Figure 1 it is obvious that the polymerization process can involve many steps (DPPH scavenges thermal ^{38}Cl atoms).[55] The origin of the 20–32% inorganic ^{34m}Cl fraction is not well understood. Some additional experiments are reported on C_2Cl_4 (first investigated by Aten and van Dulmen[56-58]) by the addition of small amounts of several compounds (Table VIII). A decrease in the $C_2Cl_3{}^{34m}Cl$ yield can be explained either through addition of ^{34m}Cl atoms to another unsaturated compound (in the case of CHT accompanied by an increase in the yield of high boiling compounds) or to H abstraction, leading to an increase of the inorganic yield (C_6H_{14}).

TABLE VIII.[52] Effect of Additives on the Absolute Product Yields (%) for the Reactions of Recoil ^{34m}Cl Atoms with Liquid C_2Cl_4

products		1% I_2	10% C_6H_{14}[a]	10% C_6H_6[b]	10% CHT[c]
$CCl_3{}^{34m}Cl$	2.1	0.7	0.3	1.2	0.4
$C_2Cl_3{}^{34m}Cl$	23	25	17	21	4.6
$C_2Cl_5{}^{34m}Cl$	5.6	0.5	<0.2	0.8	<0.2
$CHCl_2{}^{34m}Cl$			1.0	0.4	0.7
$C_2HCl_2{}^{34m}Cl$			0.7	0.2	0.4
$C_2HCl_4{}^{34m}Cl$			2.4	0.7	1.0
inorganic	32	27	39	21	32
polymers	37	47	37	55	61

[a] Contains 1.3% $C_6H_{13}{}^{34m}Cl$. [b] Contains 3.1% $C_6H_5{}^{34m}Cl$. [c] CHT = cycloheptatriene.

IV. Tritium

The reactions of thermal H atoms with ethylenes were reviewed in 1973 by Jones, MacKnight, and Teng.[59] Reports about abstraction of H atoms from C_2H_4 are rather controversial: whereas in the older publications positive results were reported, in the more recent investigations it was concluded that H abstraction is negligible when compared to addition at the double bond. Falconer et al. determined the abstraction/addition ratio as $\leq 3 \times 10^{-4}$.[60] The addition reaction leads to a highly excited ethyl radical, which then contains an excess of energy of 166 kJ mol^{-1}. The rate constant for the addition reaction has been measured by many investigators and is for low pressures (<1 kPa) in the order of 2×10^8 L mol^{-1} s^{-1} and for the high pressure limit 5–8 × 10^8 L mol^{-1} s^{-1}. Recently, Lee et al. measured a rate constant of $(6.7 \pm 1.9) \times 10^8$ L mol^{-1} s^{-1} (50–100 kPa, 298 K)[61] and Sugawara et al. measured one of $(7.2 \pm 0.5) \times 10^8$ L mol^{-1} s^{-1} (high pressure limit, 298 K).[62] The excited ethyl radical can decompose into the initial compounds or can be stabilized by collisions and undergo further reactions (in most of the systems studied through combination with another C_2H_5 radical to yield C_4H_{10} or with an H atom to form C_2H_6 that can dissociate into two CH_3 radicals). Experiments were also performed with D atoms and with deuterated ethylenes. Turner et al. found that addition of a D atom to C_2H_4 led subsequently to decomposition into H + C_2H_3D, but no C_2HD_3 was observed after reaction of H atoms with C_2D_4.[63] These results for both experiments were dedicated to differences in C–H(D) bond energies. Sugawara et al. found practically no isotope effects for the rate constants for addition of H and D atoms to C_2H_4, C_2H_3D, and C_2D_4[62] (Table IX). However, poor agreement was found between the experiments and calculations using the activated complex theory and also by a treatment of the RRKM theory on the unimolecular decomposition of ethyl radicals.

H atom addition to fluorinated ethylenes proceeds

TABLE IX.[62] High Pressure Limit of Arrhenius Parameters for H and D Addition to Ethylenes

	A, 10^{10} L mol^{-1} s^{-1}	E, kJ mol^{-1}	k_{298}, 10^{8} L mol^{-1} s^{-1}
H + C_2H_4	2.77	9.0	7.4
D + C_2H_4	2.05	9.2	5.9
H + C_2H_3	2.59	8.9	7.3
D + C_2H_3	2.11	9.1	5.3
H + C_2D_4	2.77	9.1	7.1
D + C_2D_4	2.17	9.3	5.1

TABLE X. Relative Addition and H-Abstraction Rates for Thermal H Atoms with Fluoroethylenes

	addition			H abstraction
	ref 66	ref 67[a]	ref 68	ref 66
C_2H_4	1.00	1.00	1.00	0
C_2H_3F	0.80	0.44	0.47	0.36
$CH_2{=}CF_2$	1.45	0.36	0.33	02.33
cis-CHF=CHF	0.70	0.06		0.68
trans-CHF=CHF	1.15	0.09		1.27
C_2HF_3	1.65	0.05	0.082	0.56
C_2F_4	1.69	0.08	0.075	

[a] Discrepancies with the Data given in ref 66 are discussed in ref 67.

largely to the less fluorinated carbon atoms.[64] The major reaction products of the radicals obtained from C_2H_3F, $CF_2{=}CH_2$, and C_2H_3F are formed by disproportionation and combination reactions with other radicals, whereas decomposition through HF elimination is a less important reaction channel. Reactions with C_2F_4 also resulted in a large number of products.[65] Penzhorn et al.[66] have measured relative rate constants of thermal H atoms for addition to and H abstraction from fluoroethylenes. These values are compared in Table X with data of Kilcoyne et al.[67] and Sugawara et al.[68]

The rate constant for abstraction of an F atom is much smaller than that for addition or H abstraction, if the process occurs at all. Some absolute rate constants, derived by Teng and Jones are given in Table XI.[65b,c] In the case of the reactions of thermal H atoms with C_2H_3Cl, the probability of the abstraction of the Cl atom is twice as large as for addition followed by Cl loss.[69] Oldershaw has reviewed in 1977 the reactions of hot H atoms (produced by the photolysis of HI, DI, and H_2S and containing translational energies of 0.9–1.9 eV) with C_2H_4.[70] In the reaction a "superhot" C_2H_5 radical is produced that has a lifetime that is too short for stabilization at normal pressures and that decomposes by the elimination of a H atom. The net result of this process is the moderation of the hot H atom. The probability of H atom abstraction from C_2H_4 is also, for hot H atoms, a matter of disagreement between several research groups.[70] Hase et al. calculated reactive cross sections vs. translational and vibrational energy for H atom addition to C_2H_4 to form vibrationally excited C_2H_5 radicals.[71] Replacing the H through a D atom causes no major changes in the reactive cross sections. Rennert and Wijnen studied the reactions of hot H atoms with C_2H_3Cl and found the ratios for addition:H abstraction:Cl abstraction as 1:2.15:1.47.[72]

TABLE XI.[65b,c] Arrhenius Parameters for Reactions of H Atoms with Fluoroethylenes

	A, 10^{7} L mol^{-1} s^{-1}	E, kJ mol	k_{298}, 10^{7} L mol^{-1} s^{-1}
H + $C_2H_4 \rightarrow [C_2H_5]^{\ddagger}$	77	3.1	23
H + $C_2H_3F \rightarrow$	12	3.8	2.6
$[C_2H_4F]^{\ddagger} \rightarrow$ $C_2H_2F + H_2$	1.1	4.5	0.17
H = $CH_2{=}CF_2 \rightarrow$	11.8	6.8	0.75
$[C_2H_3F_2]^{\ddagger} \rightarrow$ C_2H_2F + HF	6.2	8.6	0.19

TABLE XII.[77,78] Product Yields (Relative HT = 100) for the Reactions of Recoil T Atoms with Gaseous *cis*- and *trans*-CHCl=CHCl

	pure		$+O_2$		$+O_2$	
products	cis	trans	cis	trans	cis	trans
HT	100	100	100	100	100	100
C_2HT	226	217	226	167	53	58
C_2H_3T	12	8		5	11	7
C_2H_2TCl	720	770	520	510	96	108
cis-CHCl=CTCl	39	13	31	14	13.5	2.1
trans-CHCl=CTCl	18	27	15	28	2.6	10.7
retention of configuration	68	68	67	67	84	84

Reactions of recoil T atoms with ethylenes are restricted to only seven publications. The reactions with gaseous C_2H_4 (O_2 scavenged) lead to the formation of 9.8% HT, 1.5% C_2HT, and 43.7% C_2H_3T, whereas 45% of the total activity was not identified.[73,74] Most of the HT yield and a minor fraction of the C_2H_3T yield is formed by hot abstraction and substitution reactions. C_2H_3T is formed mainly through H atom loss from excited C_2H_4T radicals (one-third of such reactions lead to the loss of a T atom and is followed by a second—thermal—addition reaction). C_2HT is formed through H_2 elimination from excited C_2H_3T, and an equal amount of HT is then also released. In unscavenged C_2H_4 the addition of T may lead to dimerization and further polymerization, which can be inhibited by added O_2, because in reactions of recoil T with gaseous C_3H_6, polymeric products were observed, whereas their yields drop to almost zero in the presence of O_2.[75] Siefert and Tang observed $CHT{=}CF_2$ as a major product in the reactions of recoil T atoms with *cis*- and *trans*-CHF=CHF.[76] Pressure and scavenger studies indicated that $CHT{=}CF_2$ is formed via the decomposition of an excited radical, formed by an addition reaction. The reaction sequence includes a 1,2-F shift via a bridged intermediate.

Product yields, relative to HT, from the reactions of recoil T atoms with *cis*- and *trans*-CHCl=CHCl are given in Table XII.[77,78] The differences between the yields given in the references for O_2-scavenged gaseous systems may be due to differences in pressure or in scavenger amounts. It is difficult to draw conclusions from relative product yields when going from one system to another, because it is not known if in this case the HT yield is constant. C_2H_2TCl is formed by addition of a T atom, followed by the loss of a Cl atom; this mechanism is confirmed by the absence of C_2HT in the liquid phase where fast deexcitation of excited C_2H_2TCl will take place.[78] The high retentions of the original stereochemical configuration of C_2HTCl_2 are explained through a fast T-for-H substitution reaction, whereas the low yields of the isomerized compounds can be caused by rotation around the double bond in excited C_2HTCl_2 (activation energy about 200 kJ mol^{-1})[79]

TABLE XIII. Absolute Product Yields (%) from the Reactions of Recoil T Atoms with Liquid Chloroethylenes

target compound	polymers	T⁺	HT	T for H[a] (1)	T for Cl[a] (2)	T + Cl addition[a] (3)	other C1 + C2 compounds
$CH_2=CCl_2$	60	12	4	11	5	2	6
cis-CHCl=CHCl	68	9	5	6	1	3	8
trans-CHCl=CHCl	65	8	5	6	1	8	7
C_2HCl_3	65	12	1	3	11	3	5
C_2Cl_4	57	3			17	8	15

[a] From $C_2H_nCl_{4-n}$: (1) $C_2H_{n-1}TCl_{4-n}$; (2) $C_2H_nTCl_{3-n}$; (3) $C_2H_nTCl_{5-n}$.

or by H atom loss from a highly excited $C_2H_2TCl_2$ radical (instead of Cl atom loss).

In Table XIII absolute yields are given for the reactions with liquid chloroethylenes:[80]

(1) The main yield (on the average 63%) consists of high boiling compounds, formed through addition of a T atom, followed by dimerization and subsequent polymerization steps. In Figure 2 a gel-filtration radiogram is given for the reactions with *cis*-CHCl═CHCl. Addition of some I_2 prevents excessive polymerization.

(2) About 10% of the total number of T atoms are extractable with water (T^+). This fraction could be due to abstraction of Cl atoms, but in that case the much lower yields for C_2Cl_4 is not well understood.

(3) H-abstraction leads to 5% HT for the dichloroethylenes and to about 1% for trichloroethylenes. These low yields, compared with HT yields from saturated hydrocarbons, demonstrate the preference for the addition reaction.

(4) Low yields are also found for the T-for-H substitution reactions. The retention of the original configuration of *cis*- and *trans*-CHCl═CHCl (~90%) means that the substitution reaction is a very fast process and does not proceed through a long-lived intermediate ethyl radical.

(5) The yields of products formed by T-for-Cl substitution are rather low; in addition to the possibility of a fast direct reaction, such compounds can also be formed through a T addition/Cl elimination process. In the case of ^{34m}Cl recoil atoms, the ^{34m}Cl addition/Cl elimination reaction sequence proceeds to the extent of 15–25% (Table VII).[52] Addition of a recoil T atom leads probably to a very high excited radical that in the condensed phase reacts with another molecule prior to decomposition by Cl loss. In the case of the CHCl═CHCl compounds, twice the yield of C_2HT (2 × 1.6%) is formed from excited C_2H_2TCl molecules.

(6) The yield of ethanes—formed by addition of a T atom followed by abstraction of a Cl atom (2–8%)—are not very different from the yields of compounds that are formed by comparable reactions with recoil ^{34m}Cl atoms (3–7%).[52]

(7) The irradiation of C_2HCl_3 yields (5.5 ± 0.1)% CHT═CCl_2 and (2.9 ± 0.1)% *trans*- and (2.1 ± 0.1)% *cis*-CFCl═CHCl. This means that there is no preference for a particular site of attack, either at the CHCl or at the CCl_2 group. Also the formation of the labeled C_2HTCl_4 compounds, as discussed above, gives a 1:1 distribution (1.7 ± 0.1)% $CHTClCCl_3$ and (1.6 ± 0.1)% $CTCl_2CHCl_2$).

(8) The last column of Table XIII gives the summed yields of all other $C_1 + C_2$ compounds, and these yields are not much different from those from ^{34m}Cl experiments. Some compounds measured for *cis*-CHCl═CHCl are 0.4% CH≡CT, 1.7% CH_2═CHT, 0.5% CHT═CCl_2, 1.0% *trans*-CHCl═CTCl, 0.2% C_2TCl_3, 0.2% CH_2TCCl_3, 0.3% $Cl_3CCHTCl$, and 0.9% Cl_2CH-CCl_2T.

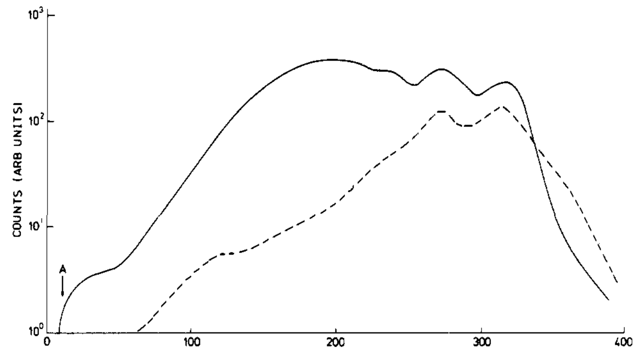

Figure 2. Radiogel filtration chromatogram from the reactions of recoil T with *cis*-CHCl═CHCl (1): (—) 1; (- - -) 1 + 2% I_2.

(9) With *cis*-CHCl═CHCl as the target compound (5.6 ± 0.2)% *cis*- and (1.0 ± 0.2)% *trans*-CHCl═CHT are measured, whereas with the trans compound (6.2 ± 1.2)% trans and (1.0 ± 0.2)% cis are formed. Both isomers are also found with Cl_2C═CH_2 and C_2HCl_3 (total yields 1.1 and 5.1%). The trans/cis ratios are 1.5 and 1.4, not different from values of 1.5 Cl_2C═CHCl and of 1.3 $Cl_2CHCHCl_2$ found with ^{34m}Cl (Table VI). Differences in relative yields of some products as given in ref 78 and 80 may be due to the very low product yields.

Steinkruger et al. determined C–H bond energies for some chloro- and fluoroethylenes by comparing HT yields, obtained from these ethylenes, with DT yields from C_2D_4.[81]

V. Muonium

Muonium (Mu) is the lightest hydrogen atom that is available for chemical research ($m_{Mu} \simeq {}^1/_9 m_H$) as it contains a positive muon (μ^+) as the nucleus. The short half-life of μ^+ ($t_{1/2}$ = 3.8 μs) does not prevent such research. The experimental techniques that are used in muonium chemistry (μSR techniques) are based on the detection of the angular distribution rate of high energy positive decay electrons ($\mu^+ \rightarrow e^+ + \nu_e + \nu_\mu$) that are preferentially emitted in the direction of the spin of the muon that is precessing in a magnetic field.[82] At the moment three 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 are determined relative to P_D in liquid CCl_4, but in general $P_{Mu} + P_D + P_R < 1$, whereas no explanations are available for the "missing fractions".[2,82] Radical signals were only recently discovered by Roduner et al.

in compounds such as acetone, tetramethylethylene, and benzene.[83,84] Fleming et al. have investigated the reactions of thermal Mu with gaseous C_2H_4 in excess N_2 moderator.[85] It is assumed that Mu reacts through addition to the unsaturated bond, but no search was undertaken for the detection of the muonic ethyl radical. By pressure variation, the relaxation rate λ, which is given by $\lambda = \lambda_0 + k[C_2H_4]$, in which λ_0 is a background signal and k the bimolecular rate constant, could be determined, because the measured time-dependent μSR signal is proportional to $e^{-\lambda t}$. The measured rate constant at 300 K was $(4.0 \pm 0.5) \times 10^9$ mol^{-1} s^{-1}, almost a factor of 6 higher than the comparable rate constant for the reactions of thermal H atoms with C_2H_4, as measured by Lee et al.[61] and Sugawara et al.[62] On the basis of simple kinetic considerations of a collisional controlled reaction an isotope effect of 2.9 $(=(m_H/m_{Mu})^{1/2})$ could be expected. The activation energy for the reaction of Mu was measured as (4.9 ± 0.1) kJ mol^{-1} by varying the temperature between 300 and 500 K. This is almost a factor of 2 lower than determined for the corresponding H atom[62] and forms a strong indication that tunneling is a dominant process for the addition of Mu to C_2H_4 at ambient temperatures. The reactions of Mu with all the liquid chloroethylenes (except C_2H_3Cl) are investigated. Even after the detection of 10^7 "good" events, no muonic chloroethyl radicals were detected, which means that $P_R < 0.02$.[86] From ESR studies it is known that the comparable hydrogen chloroethyl radicals do exist.[87] Rather high values of the diamagnetic compounds were measured. The P_D values are not much different from those reported for normal hexenes and cyclohexenes[88] (Table XIV). (A radical signal was observed for liquid tetramethylethylene.[82-84]) The experiments with T recoiling in liquid chloroethylenes do not give any explanation for these high P_D values: (1) H or Cl abstraction is of minor importance for recoil T. (2) Fast addition of Mu ($< 10^{-11}$ s) followed by Cl loss ($<10^{-9}$ s) could lead to a detectable diamagnetic compound, but this reaction sequence is hardly observed with recoil T. (3) Addition followed by dimerization and further polymerization accounts for about 60% of the reactions of recoil T, but in the case of Mu such processes would lead to the loss of the polarization.

At the moment there is no explanation for the absence of the radical signal, nor for the high value of the diamagnetic signal.

VI. Bromine, Iodine

From experiments of photolysis of Br_2[89] and of radiolysis of HBr[90] in the presence of C_2H_4, it was concluded that Br atoms react through addition to the double bond. When radioactive bromine was used, it was found that the rate constant for the exchange reaction in *cis*- and *trans*-BrCH═CHBr

$$^{82}Br + CHBr{=}CHBr \rightarrow CHBr{=}CH^{82}Br + Br$$

is twice as large as the rate constant for cis–trans isomerization.[91] The addition of bromine atoms to CHD═CHD leads to a very rapid geometrical isomerization, which is about a factor of 100 faster than the formation of HBr through H abstraction from HBr by the bromoethyl radical.[92] I atoms do not seem to add readily to olefins.[92] With radioactive iodine, it was found that the rate constant for the exchange reaction with *cis*- and *trans*-ICH═CHI is a factor of 100 larger than the rate constant for cis–trans isomerization.[93] This finding is compatible with a planar structure of the radical intermediate.[94]

TABLE XIV.[86,87] Diamagnetic Yields (P_D) for Reactions of Muonium with Olefins

hexane	0.62	1,3-cyclohexadiene	0.38
1-hexene	0.50	C_2Cl_4	0.66
1-hexyne	0.43	C_2HCl_3	0.64
cyclohexane	0.68	*cis*-CHCl=CHCl	0.67
cyclohexene	0.55	*trans*-CHCl=CHCl	0.58
1,4-cyclohexadiene	0.47	$CH_2{=}CCl_2$	0.46

The reactions of recoil ^{128}I atoms, produced with thermal neutrons in a nuclear reactor by the $^{127}I(n,\gamma)^{128}I$ reaction, with ethylene at a pressure of 100 kPa (and 3 kPa) results in the formation of 10% (19%) $CH_3{}^{128}I$, 4% (16%) $C_2H_3{}^{128}I$, and 4% (6%) $C_2H_5{}^{128}I$.[95,96] The initiating step in the formation of $CH_3{}^{128}I$ is the ion–molecule reaction

$$^{128}I^+(^3P_0 \text{ or } ^3P_1) + C_2H_4 \rightarrow C_2H_4{}^{128}I^+$$

The formation of $C_2H_3{}^{128}I$ is dependent on the presence of I_2 and appears to be due to the reaction

$$^{128}I^+ + C_2H_4 \rightarrow C_2H_3{}^{128}I + HI$$

$C_2H_5{}^{128}I$ is formed through a hot reaction via an excited $C_2H_4{}^{128}I$ radical.

VII. Carbon, Silicon

Most of the knowledge about the reaction mechanisms of C atoms with ethylene is obtained through investigations with ^{11}C recoil atoms.[97] ^{11}C ($t_{1/2}$ = 20.3 min) can be produced from natural carbon by (n,2n), (p,pn), and (γ,n) reactions and from ^{14}N via a (p,α) reaction. The other common radiocarbon isotope that could be of interest, produced via $^{14}N(n,p)^{14}C$, is less suited for this type of research, because its long half-life (5730 y) requires long irradiation times for its production. This may lead to severe radiation damage in a nuclear reactor. In C_2H_6 the main radioactivity is shared between C_2H_2 and C_2H_4 (Table XV).[98] Acetylene is formed through insertion into C–H bonds by high-energy $^{11}C(^3P)$ and low-energy $^{11}C(^1D)$ atoms:

$$^{11}C + H_3C{-}CH_3 \rightarrow [H^{11}C{-}CH_2{-}CH_3]^* \rightarrow H^{11}C{\equiv}CH + CH_3 + H$$

Ethylene is preferentially formed by high-energy $^{11}C(^1D)$ atoms:

$$^{11}C + CH_3{-}CH_3 \rightarrow [H^{11}C{-}CH_2{-}CH_3]^* \rightarrow {}^{11}CH + C_2H_5$$

$$^{11}CH + H_3C{-}CH_3 \rightarrow [H_2{}^{11}C{-}CH_2{-}CH_3]^* \rightarrow H_2{}^{11}C{=}CH_2 + CH_3{}^{99}$$

Both mechanisms will also contribute to the formation of labeled C_2H_2 and C_2H_4 in the reactions of ^{11}C recoil atoms with C_2H_4, but addition of both $^{11}C(^3P)$ and $^{11}C(^1D)$ atoms to the unsaturated bond forms another very important reaction channel and gives rise to the formation of several unsaturated compounds[100,101] (Table XV). A reaction scheme of the $^{11}C/C_2H_4$ system

TABLE XV.[97,100,101] Product Yields (%) for Reactions of Recoil ^{11}C Atoms

	C_2H_6[a]			C_2H_4[b]		
	gas	gas (O_2)	liquid	gas	gas (O_2)	liquid
CO	1	18				
CH_4	2		4			
C=C	24	17	16	1	2	2
C≡C	31	31	17	39	35	18
C—C—C	13	3	12			
C—C=C	5	6	13	3	2	4
C=C=C				17	16	12
C—C≡C				5	4	4
cyclopropane				3		2
C=C—C≡C				10	10	3
C=C—C—C—C				1		10
C=C=C—C—C				3		4
C≡C—C—C—C				7		7

[a] Absolute yields. [b] Gaseous yields.

is given in Figure 3. It is supposed that the reactions of $^{11}C(^1D)$ atoms lead mainly to the production of allene and methylacetylene, whereas acetylene and the C_5 products are preferentially formed from $^{11}C(^3P)$ atoms. The compound with the highest yield, allene, can be formed through C–H insertion as well as through an addition reaction (Figure 4). Both mechanisms (in which only one ethylene molecule is proposed to be involved) are in agreement with the observation that in an equimolar mixture of C_2H_4/C_2D_4 the formed allene consists of almost 90% of a 1:1 mixture of C_3H_4 and C_3D_4.[102] For the elucidation of the exact reaction mechanism, the intramolecular distribution of the ^{11}C atom (central or end) in the allene molecule was determined. The total time needed for the degradation of the allene molecule was 210 min, which meant that only a fraction of 8×10^{-4} of the initial ^{11}C atoms were available for radioassay.[100] The results of such experiments indicated that 64% of the ^{11}C atoms were in the central position; this increased to 74% in a highly moderated system, which indicated that the C–H insertion reaction is the more energetic reaction channel. Besides the reactions of bare ^{11}C atoms the reactions of ^{11}CH and $^{11}CH_2$ may also participate in the final product formation:

$$^{11}CH + H_2C{=}CH_2 \rightarrow H_2{}^{11}C{=}CH{=}CH_2 \rightarrow \text{products}$$

$$^{11}CH_2 + H_2C{=}CH_2 \rightarrow \text{c-}^{11}CC_2H_6 \rightarrow H_3{}^{11}CCH{=}CH_2$$

Reactions of ^{12}C atoms with olefins have been investigated by Skell et al.[104,105] The nonradioactive C atoms were generated in a carbon arc and trapped in a paraffin matrix at 77 K. By addition of olefins at different time intervals the reactions of C(^3P, ^1D, ^1S) could be studied. The addition of C(^3P) atoms is stereospecific (e.g., in *cis*- and *trans*-2-butene) in accordance with its triplet state, but the addition of the formed cyclopropylidene to a second olefin molecule, to form a spiropentane, yields equal amounts of the different stereoisomers (Figure 5). No other products arising from reactions of single carbon atoms were observed. C(^1S) atoms also add to the double bond, but the excited cyclopropylidene intermediate carbene decomposes into an allene, with a yield of about 45%[105] (Figure 5). C(^1D) atoms lead to the formation of a singlet cyclopropylidene intermediate. This compound reacts with a second olefinic molecule forming other products, but no allenes are detected. A striking difference with the results obtained with ^{11}C recoil atoms is the lack of the formation of acetylene.

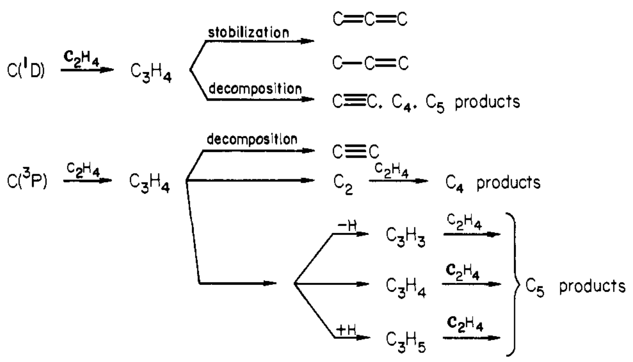

Figure 3. Reaction scheme of $^{11}C(^1D)$ and $^{11}C(^3P)$ with C_2H_4.[101]

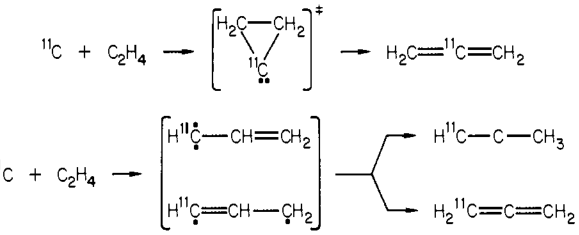

Figure 4. Formation modes of [^{11}C]allene.[100]

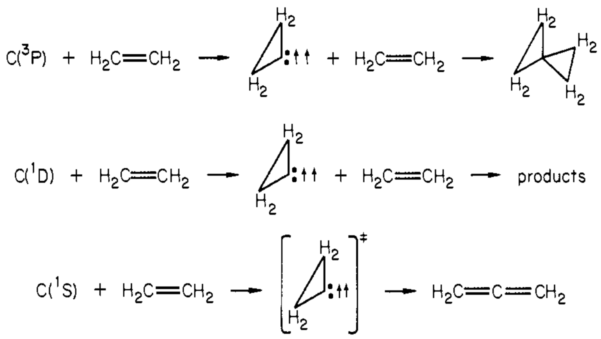

Figure 5. Reactions of carbon atoms with C_2H_4.[105]

Reactions of recoil ^{31}Si atoms ($t_{1/2}$ = 2.62 h, produced via the $^{31}P(n,p)^{31}Si$ nuclear reaction) have been investigated in 1:1 gaseous mixtures of PH_3 and C_2H_4).[106] Five volatile labeled products were observed (total yield 7%): $^{31}SiH_4$, $CH_3CH_2{}^{31}SiH_3$, and $^{31}SiH_3CH_2CH_2PH_2$ (major product) and two unknown compounds. Addition of SiH_4 up to 15 mol % results in a linear decrease of the yield of $^{31}SiH_3CH_2CH_2PH_2$ and a linear increase of $H_3{}^{31}SiSiH_3$, indicating that SiH_4 and C_2H_4 compete for reaction with a common intermediate. A plausible reaction scheme starts with $^{31}SiH_2$ as that intermediate:

$$^{31}SiH_2 + SiH_4 \rightarrow H_3{}^{31}SiSiH_3$$

$$^{31}SiH_2 + C_2H_4 \rightarrow \text{c-}^{31}SiH_2CH_2CH_2$$

$$\text{c-}^{31}SiH_2CH_2CH_2 + PH_3 \rightarrow {}^{31}SiH_3CH_2CH_2PH_2$$

VIII. Oxygen, Sulfur, Nitrogen

Oxygen. ^{15}O ($t_{1/2}$ = 2 min) is the radioisotope of choice for chemical studies, but its very short half-life has prevented the research on reactions with olefins. ^{15}O can be produced by $^{16}O(x,xn)^{15}O$ nuclear reactions (x = fast neutron, charged particle, or photon) and through the $^{14}N(d,n)^{15}O$ reaction. Rate constants of ^{16}O atoms with C_2H_4 were measured for the ^3P ground state and the ^2D and ^1S excited states as 4.8×10^8, 2.4×10^{11}, and 6×10^{11} L mol^{-1} s^{-1}.[107] Besides addition, the reactions of $O(^3P)$ with C_2H_4 can also lead to H substitution, yielding $CH_2{=}CHO$.[108] Huie and Herron[107a] have reviewed the reactions of $O(^3P)$ atoms with ethylene and with a series of mixed (F, Cl, Br) haloethylenes. The reactions with such C_2X_4 compounds lead mainly to fragmentation products, probably by addition of the O atom to the double bond, followed by C—C bond scission ($X_2C{=}O$ and X_2C:). Few stable products are observed.[107b] Rate constants of $O(^3P)$ atoms with fluoroethylenes are measured by Sugawara et al.[109] Reactions of $O(^1D)$ atoms with propylene result in an excited intermediate that decomposes at ambient pressure and becomes stabilized at high pressures of about 15 MPa.[110] Decomposition of such primary addition products has also hampered the research of the reactions of ^{15}O recoil atoms with ethylenes. The attack of an $O(^1D)$ atom on C_2H_4 corresponds to a symmetric concerted addition, whereas the $O(^3P)$ path corresponds to an asymmetric approach, forming an open ring adduct ($\angle CCO = 105°$), in which the barrier for rotation is calculated as about 20 kJ mol^{-1}.[111]

Sulfur. Two radioisotopes are available for research: ^{35}S ($t_{1/2}$ = 87 d), produced with thermal neutrons in a nuclear reactor by either the $^{34}S(n,\gamma)^{35}S$ or the $^{35}Cl(n,p)^{35}S$ reactions, and ^{38}S ($t_{1/2}$ = 2.9 h), produced by $^{40}Ar(p,3p)^{38}S$ or $^{40}Ar(\gamma,2p)^{38}S$ reactions. Due to combination of low cross sections, low abundance of starting material, and long half-lives, high radiation doses are involved in all radiosulfur production modes. In the only published recoil experiment of ^{38}S atoms with C_2H_4 (55 kPa of C_2H_4, 35 kPa of Ar, 4 kPa of H_2S), liquid colorless droplets were observed after the irradiation on the walls of the glass ampule.[112] Rate constants of S atoms with C_2H_4 are measured for the ^3P ground state and the ^2D and ^1S excited states as 0.9×10^9, 4.2×10^{10}, and 7.8×10^7 L mol^{-1} s^{-1}.[113] Thermal $S(^3P)$ atoms react only by addition of the episulfide. On the other hand, with addition reactions of other triplet species, e.g., CH_2, the addition of $S(^3P)$ is stereospecific as is observed with *cis*- and *trans*-$HFC{=}CHF$ and $HClC{=}CHCl$.[114,115] This is a consequence of a high barrier for rotation of the terminal methylene in the intermediate biradical (~100 kJ mol^{-1}). The reactions of $S(^1D)$ atoms with C_2H_4 lead to fast C–H insertion and addition; almost every collision leads to reaction.[116] The yields of vinylmercaptan and of the episulfide are each about 40% of the total $S(^1D)$ atoms. In the case of reactions with *cis*- and *trans*-$HCCl{=}HCCl$ no gaseous products were observed, because polymerization reactions seem to prevail.[114,115] Dzantiev et al. have found that reactions of energetic H atoms, formed by photolysis of H_2S, lead to a H abstraction/H addition ratio for C_2H_4 of 0.25.[117] In the already mentioned experiment of ^{38}S recoil atoms with C_2H_4, only 3.3% $H_2{}^{38}S$ and 2.3% [^{38}S]episulfide were detected, but no $H_2C{=}CH^{38}SH$ was formed. Most of the ^{38}S activity (94.4%) sticks to the walls of the irradiation vessel. When a neutron-irradiated KCl crystal (production of ^{35}S) is heated to 623 K in an atmosphere of C_2H_4, ^{35}S atoms diffusing from the crystal surface lead to the formation of labeled episulfide.[118] Unlabeled episulfide was also formed by the irradiation of a sulfur surface with a KrF laser.[119]

Nitrogen. The best available isotope ^{13}N ($t_{1/2}$ = 10 min) can be produced from ^{14}N, and also through the $^{12}C(d,n)^{13}N$ and $^{16}O(p,\alpha)^{13}N$ reactions. Rate constants of thermal ground and electronically excited nitrogen atoms with C_2H_4 are for $N(^4S, ^2D)$ 6×10^7 ($<3 \times 10^5$), and 3.6×10^{10} L mol^{-1} s^{-1}, respectively.[120-123] Formation of HCN was observed for both $N(^4S)$ and $N(^2D)$ atoms, but the exact reaction mechanism is uncertain (a C_2H_4N addition intermediate was proposed). One recoil experiment is reported. In pure C_2H_4 50% $HC^{13}N$ was found, whereas on the addition of 5% NO to C_2H_4 the formation of 44% $HC^{13}N$ and 38% $N^{13}N$ + ^{13}NO resulted. It was concluded that $HC^{13}N$ was formed by reactions of $^{13}N(^2D)$ atoms and ^{13}NO was formed by reactions of $^{13}N(^4S)$ atoms.[124]

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Notes Added in Proof

Fluorine. Experimental results obtained for the

$$F + C_2H_4 \rightarrow \cdot C_2H_4F \rightarrow H + C_2H_3F$$

reaction at higher collision energies (crossed molecular beam studies) indicate that deviations from statistical energy distributions are not entirely caused by the presence of an exit channel barrier.[125] Trajectory calculation studies indicate that the nonstatistical vibrational and translational energy distribution arises from the centrifugal potential at the exit-channel saddle point and the potential energy released in that channel (80% of the energy goes into translation).[126,127]

Muonium. Recent experiments at SIN showed the existence of muonic monochloroalkyl radicals in two out of four investigated chlorobutenes:[128] 3-chloro-1-butene, no radical, $P_D = 0.60 \pm 0.01$; 1-chloro-1-butene, no radical, $P_D = 0.61 \pm 0.02$; 3-chloro-2-methyl-1-propene, radical at 265 MHz, $P_R = 0.20 \pm 0.01$, $P_D = 0.60 \pm 0.02$; 1-chloro-2-methyl-1-propene, radical at 79 MHz, $P_R = 0.16 \pm 0.02$, $P_D = 0.52 \pm 0.02$.

Carbon. Using Ne as a moderator and O_2 as a scavenger, Ferrieri et al. concluded that energetic $^{11}C(^1D)$ atoms insert into the double bond of C_2H_4 to yield $H_2C{=}^{11}C{=}CH_2$, while this reaction does not proceed with thermal $^{11}C(^1D)$ atoms. $^{11}C(^3P)$ atoms undergo both double bond and C—H insertion to yield $H_2C{=}^{11}C{=}CH_2$ and $H_2{}^{11}C{=}C{=}CH_2$, respectively:[129]

$$^{11}C(^1D)^* + C_2H_4 \rightarrow H_2C{=}^{11}C{=}CH_2$$

$$^{11}C(^1D) + C_2H_4 \rightarrow H_2C{=}^{11}C{=}CH_2$$

$$^{11}C(^3P) + C_2H_4 \rightarrow c\text{-}^{11}\ddot{C}{-}CH_2{-}CH_2 \rightarrow H_2C{=}^{11}C{=}CH_2$$

$$^{11}C(^3P) + C_2H_4 \rightarrow H^{11}\dot{C}—CH{=}CH_2 \rightarrow H_2{}^{11}C{=}C{=}CH_2$$

Silicon. The major product formed in the reaction of ^{31}Si recoil atoms with a 1:1 mixture of PH_3 and C_2H_4 is not $^{31}SiH_3CH_2CH_2PH_2$ as proposed in ref 106, but $PH_2{}^{31}SiH_2CH_2CH_3$.[130]

Oxygen. The major reaction channel for $O(^3P)$ atom colliding with C_2H_4 is H atom elimination to give the C_2H_3O radical,[131,132] as was also pointed out in ref 108. No 1,2-H migration occurs in the intermediate complex. Three distinct reaction channels for $O(^3P)$ with C_2H_3Br lead to H + C_2H_2BrO, Br + C_2H_3O, and CH_2Br + CHO.[8]

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