CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS

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I. Introduction

The chemical effects of nuclear transformations are mainly the chemical reactions of energetic (hot), electronically excited, and thermal radioactive recoil atoms, produced by nuclear reactions and of hot, excited, and thermal ions, produced by nuclear decay (α, β^-, β^+, IT, EC). The study of the reactions of recoil particles began in the 1930s, when Szilard and Chalmers (*1*) 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. Obviously, the C—I bond was broken after the nuclear reaction. The literature on hot (or recoil) chemistry is so extensive that only some topics can be discussed in this article. The selection is such that there is little overlap with existing review articles. General reviews can be found in references (*2–7*). More specialized articles reviewed the reactions of radioactive T (*8*), F

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(*9–11*), Cl (*12*), I (*13*), N (*14*), Si (*9*), other polyvalent atoms (*15*), and of muonium (*16*). Reviews have also been published on the reactions of recoil atoms with arenes (*17*), (halo)ethylenes (*18*), and (halo)-methanes (*19*). The capture of π^- in hydrogenated species is sometimes considered as a part of recoil chemistry (*20*), and so also are reactions of species formed after decay of multiply labeled (T, ^{14}C) molecules (*21–23*), for example,

$$CT_4 \xrightarrow{\beta^-} [CT_3{}^3He]^+ \xrightarrow{fast} CT_3{}^+ + {}^3He$$

II. Reactions of Thermalized Recoil Atoms

The thermalization of energetic recoil atoms in excess moderator is a useful tool to measure kinetic parameters for abstraction, substitution, and addition reactions. For thermal experiments, the bulk (>90%) of the sample must consist of a compound that is (1) inert for hot and thermal reactions with the recoil atom and (2) able to supply the radioactive atom. For example, Ne, CF_4, C_2F_6, SF_6 + Ar, CF_2Cl_2, and CF_3Cl meet these requirements for radioactive recoil F and Cl atoms.

A. Thermal Reactions of ^{18}F Atoms

The compounds SF_6, CF_4, and C_2F_6 are mainly used for the production and moderation of ^{18}F atoms. These compounds are not absolutely inert for reactions with hot ^{18}F atoms, but the product yields are low: 2% (*24*), 7.4%, and 14% (*11*), respectively.

1. Hydrogen Abstraction

The first experiments were carried out by Williams and Rowland (*25*), using SF_6 as the bath gas, with tracers of C_2H_2 and HI. For these mixtures, the following reactions were considered.

$$^{18}F + C_2H_2 \longrightarrow H^{18}F + C_2H \qquad (1)$$

$$^{18}F + C_2H_2 \longrightarrow CH{=}CH^{18}F \qquad (2)$$

$$CH{=}CH^{18}F + HI \longrightarrow CH_2{=}CH^{18}F + I \qquad (3)$$

$$^{18}F + HI \longrightarrow H^{18}F + I \qquad (4)$$

The following equation can be derived for the fractional yield Y of $CH_2{=}CH^{18}F$:

$$\frac{Y_{\text{total}}}{Y_{CH_2=CH^{18}F}} = \frac{k_1 + k_2}{k_2} + \frac{k_4[HI]}{k_2[C_2H_2]}$$

If a third reactant (RH) is present, an additional reaction can take place:

$$^{18}F + RH \longrightarrow H^{18}F + R \tag{5}$$

This leads to the equation:

$$\frac{Y_{\text{total}}}{Y_{CH_2=CH^{18}F}} - \frac{k_4[HI]}{k_2[C_2H_2]} = \frac{k_1 + k_2}{k_2} + \frac{k_5[RH]}{k_2[C_2H_2]}$$

Both equations predict straight lines for graphs of $Y^{-1}_{CH_2=CH^{18}F}$ versus $[HI]/[C_2H_2]$ with slopes of k_4/k_2 and k_5/k_2, respectively.

The second group of experiments was performed by Root and coworkers (*26–29*), using C_2F_6 as the bath gas and C_3F_6 as the reference compound. From the reaction

$$^{18}F + C_3F_6 \longrightarrow C_3F_6{}^{18}F \tag{6}$$

and a total hot yield of 14% for pure C_2F_6, the following equation can be derived:

$$\frac{0.86}{Y_{H^{18}F}} = \frac{k_5 - k_6}{k_5} + \frac{k_6}{k_5}\left(\frac{1}{1 - [C_3F_6]}\right)$$

The formed $H^{18}F$ is quantitatively absorbed on the sample vessel walls, from which it is removed by extraction with a K_2CO_3 solution (*28, 30*).

Some of the absolute rate constants for H abstraction, measured by both groups, are given in Table I. In the cases of H_2 and CH_4, the agreement with recommended literature survey values for ^{19}F atoms is very good. For C_2H_6, only one ^{19}F value has been published. The results for the deuterated compounds are compared with ^{19}F isotopic ratios.

2. *Reactions with* CH_3X *and* CF_3X

Thermal ^{18}F-for-X substitution yields have been measured in SF_6–CH_3X mixtures. Extrapolated to zero CH_3X concentration, the absolute yields are found to increase with decreasing C—X bond energies (*34*): 0.11 ± 0.2, 0.27 ± 0.02, and 0.45 ± 0.15% for X = Cl, Br, and I,

TABLE I

RATE CONSTANTS FOR THERMAL H ABSTRACTION BY ^{18}F AND ^{19}F ATOMS AT 283 K[a]

Compound	^{18}F (ref. *25*)[b]	^{19}F (ref. *29*)[c]	^{19}F
H_2	1.3 ± 0.2	1.29 ± 0.05	1.35[d]
D_2	0.7 ± 0.2	0.56 ± 0.02	—
H_2/D_2	1.8 ± 0.6	2.30 ± 0.12	2.00 ± 0.04[e]
CH_4	3.8 ± 0.4	4.0 ± 0.2	4.3[d]
CD_4	2.2 ± 0.4	1.94 ± 0.11	—
CH_4/CD_4	1.7 ± 0.4	2.06 ± 0.16	1.5 ± 1.0[f]
C_2H_6	12.9 ± 1.1	14.9 ± 2.1	12.9[g]
C_2D_6	—	9.3 ± 0.6[h]	—

[a] Absolute constants in 10^{10} liters mol^{-1} sec^{-1}.

[b] Relative to ^{18}F addition to C_2H_2: $k^{283} = (9.2 \pm 0.7) \times 10^{10}$ liters mol^{-1} sec^{-1} (*31*).

[c] Relative to ^{18}F addition to C_3F_6: $k^{283} = (6.0 \pm 0.3) \times 10^{10}$ liters mol^{-1} sec^{-1}.

[d] Calculated from recommended literature survey data of H_2 (1.5×10^{10} liters mol^{-1} sec^{-1}) and CH_4 (4.8×10^{10} liters mol^{-1} sec^{-1}) at room temperature (*32*).

[e] Recommended literature survey data (*32*).

[f] Calculated from $(1.0 \pm 0.3) \exp(0.96 \pm 0.84)/RT$. At 300 K, a ratio of 1.8 was measured (*32*).

[g] Relative to H abstraction from CH_4: $k^{283} = 4.3 \times 10^{10}$ liters mol^{-1} sec^{-1} (*33*).

[h] At 300 K.

respectively. The remaining ^{18}F activity—about 98%, when corrected for a contribution of 2% for hot reactions with SF_6—is the result of thermal H abstraction from CH_3X. Rate constants for the substitution reactions were calculated from the rate constants of the H-abstraction reactions (Table II). Since no thermal ^{18}F-for-X substitution was observed for CH_3Br and CF_3I, although their bond energies are similar to those of CH_3Br and CH_3I, respectively, the absolute substitution yields apparently do not depend only on bond energies. This effect can be understood if the substitution proceeds via an inversion mechanism: the H atom in CH_3 can relax rapidly enough to permit formation of the necessary trigonal pyrimidal intermediate, with ^{18}F and X in the apical positions (*36*).

TABLE II

ABSOLUTE RATE CONSTANTS[a] FOR THERMAL ^{18}F ATOMS (*31, 34, 35*)

Reaction	k^{283}
$^{18}F + CH_3Br \rightarrow HF + CH_2Br$	$(3.7 \pm 0.4) \times 10^{10}$ [b]
$^{18}F + CH_3I \rightarrow HF + CH_2I$ $^{18}F + CH_3I \rightarrow IF + CH_3$	$(10.5 \pm 0.9) \times 10^{10}$ [b]
$^{18}F + CF_3I \rightarrow IF + CF_3$	$(9.8 \pm 1.0) \times 10^{10}$ [c]
$^{18}F + CH_3F \rightarrow CH_3F + F$	$(0.66 \pm 0.24) \times 10^7$
$^{18}F + CH_3Cl \rightarrow CH_3F + Cl$	$(2.2 \pm 0.8) \times 10^7$ [d]
$^{18}F + CH_3Br \rightarrow CH_3F + Br$	$(10.2 \pm 1.8) \times 10^7$
$^{18}F + CH_3I \rightarrow CH_3F + I$	$(48 \pm 18) \times 10^7$

[a] In liters mol^{-1} sec^{-1}.
[b] Relative to ^{18}F addition to C_2H_2 with $k^{283} = (9.2 \pm 0.7) \times 10^{10}$ liters mol^{-1} sec^{-1}.
[c] Literature values for ^{19}F are: (8 ± 3) and $(11 \pm 5) \times 10^{10}$ liters mol^{-1} sec^{-1} at 296 and 293 K, respectively (*32*).
[d] Relative to H abstraction from CH_3Cl by ^{19}F atoms: $k = (2.0 \pm 0.6) \times 10^{10}$ liters mol^{-1} sec^{-1} (*35*).

3. *Addition*

Addition reactions of ^{18}F atoms with alkenes and alkynes were reviewed in 1978 by Rowland *et al.* (*37*). In the case of C_2H_4 as the reactant in excess CF_4, the excited $C_2H_4{}^{18}F$ radicals can either decompose (to $C_2H_3{}^{18}F$) or become collisionally stabilized and react with added HI (to $C_2H_5{}^{18}F$) (*38, 39*). A plot of the decomposition/stabilization ratio (D/S = $Y_{C_2H_3{}^{18}F}/Y_{C_2H_5{}^{18}F}$) versus the inverse pressure results in a straight line. The half stabilization pressure (D/S = 1) found is 19.2 ± 1.3 kPa, corresponding to a lifetime of the excited $C_2H_4{}^{18}F$ radical of 1 nsec. The total yield for thermal addition of ^{18}F to C_2H_4 is about 65%, the remaining yield being due to thermal H abstraction. Rate constants measured by this method are given in Table III.

In the case of C_2H_2, addition accounts for 86% of the total activity (*41*). The yield of $C_2H_3{}^{18}F$ in the SF_6–C_2H_2–HI system does not vary in the pressure range of 33–530 kPa, indicating that decomposition of the $(C_2H_2{}^{18}F)^*$ radical to $C_2H^{18}F$ is negligible.

Using C_3H_6 as the bath gas, the ratio of terminal to central attack (resulting in $CH_3CH^{18}FCH_3$ and $CH_3CH_2CH_2{}^{18}F$, respectively) is 1.4, regardless of pressure (65–530 kPa) (*42*). The radical formed after

TABLE III

ABSOLUTE RATE CONSTANTS[a] FOR THERMAL ^{18}F ADDITION REACTIONS AT 283 K

Compound	Ref. (37, 40) k^{283}	Ref. (37, 40) Standard	Ref. (29) k^{283}	Ref. (29) Standard
C_2H_2	10.2	C_2H_4	9.4 ± 0.7	H_2, D_2, CH_4, CD_4, C_2H_6
C_2H_4	8.4	C_2H_2	7.7 ± 0.6	C_2H_2
CHCl=CHCl	10.2	CH_4	9.2 ± 0.7	RH, RD, C_3F_6
CFCl=CFCl	1.7	C_2H_2	1.5	C_2H_2
C_3F_6	1.2	CH_4	0.94 ± 0.05	H_2, CH_4, CHF_3
$CH{\equiv}CCH_3$	10.2	C_2H_2	—	—
$CH{\equiv}CCF_3$	3.6	C_2H_2	—	—

[a] In liters mol^{-1} sec^{-1} × 10^{-10}.

central addition can undergo unimolecular decomposition at lower pressures:

$$(CH_3CH^{18}FCH_2)^* \longrightarrow CH_3 + CH^{18}F{=}CH_2 \tag{7}$$

The terminal/central attack ratios for $H_2C{=}C{=}CH_2$, $H_2C{=}CHC_2H_5$ (*37*), and $HC{\equiv}CCH_3$ (*40*) are 1.9, 1.4, and 3.7, respectively.

With C_2F_4 in excess SF_6, the excited $C_2F_4{}^{18}F$ radicals decomposed by C—C bond scission (*43*):

$$(C_2F_4{}^{18}F)^* \longrightarrow CF_2 + CF_2{}^{18}F \tag{8a}$$

$$CF_2{}^{18}F + HI \longrightarrow CHF_2{}^{18}F + I \tag{8b}$$

The half-stabilization pressure is 30 kPa, indicating a lifetime of 2 nsec. Selectivities for addition to other fluoroethylenes are given in Table IV (*44*). The product yields reflect the behavior of C_2H_4 and C_2F_4, i.e., (1) C—C scission as a decomposition mode of an excited $C_2H_nF_{4-n}{}^{18}F$ radical 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 energy (480 kJ mol^{-1}); and (2) the next most energetic decomposition mode of these radicals is the loss of an H atom, which is also an exothermic reaction.

The CH_2 end of $CH_2{=}CHCl$ is 2.5 times as reactive toward addition of thermal ^{18}F as is the CHCl end (*45*). The decomposition of the excited $CH_2CHCl^{18}F$ radical is extremely rapid (Cl loss), with no stabilization at 500 kPa. Excited $CHCl^{18}FCHCl$ radicals, formed after the

TABLE IV *(44)*

SELECTIVITY IN THERMAL ^{18}F ADDITION TO ETHYLENES

Olefin	Relative yield per C atom			Relative total addition yield
	CH_2	CHF	CF_2	
$CH_2{=}CH_2$	1.0	—	—	1.0
$CH_2{=}CHF$	0.8	0.6	—	0.70
$CH_2{=}CF_2$	1.1	—	0.2	0.65
trans-CHF=CHF	—	0.3	—	0.30
$CHF{=}CF_2$	—	0.4	0.1	0.25
$CF_2{=}CF_2$	—	—	0.1	0.20

addition of ^{18}F to *cis*- and *trans*-CHCl=CHCl, also decompose very rapidly (98% at 270 kPa), or some 50 times as fast as $CFCl^{18}FCFCl$ (50% at 270 kPa) (*37*).

4. *Reactions with Organometallic Compounds*

Rowland and co-workers have investigated the reactions of thermal ^{18}F atoms with organometallic compounds (Sn, Ge, Hg) (*31, 46–50*). In Table V, product yields and rate constants are given for organotin compounds and $(CH_3)_2Hg$. The yields of $CH_3{}^{18}F$ from $(CH_3)_4Sn$ and of $CH_2{=}CH^{18}F$ from $(CH_2{=}CH)_4Sn$ are independent of the pressure in the range between 65 and 400 kPa, indicating that the abstraction reactions take place in a time that is considerably shorter than 0.1 nsec (*47*). In both cases, the abstraction is a direct thermal reaction, in contrast with neopentane, from which $CH_3{}^{18}F$ is only formed via a hot reaction (*49*). Apart from $CH_2{=}CHCH_2{}^{18}F$, produced from $(CH_2{=}CH\text{-}CH_2)_4Sn$, $CH_2{=}CH^{18}F$ was also detected. The yield of this product decreased linearly as a function of $1/P$ from 0.5% to 65 kPa to zero at infinite pressure, which proves that it is formed through decomposition of excited $SnC_{12}H_{20}{}^{18}F$ radicals (*51*). The decomposition rate of these radicals is 10^3 times as high as that calculated with the RRKM theory. This is attributed to the lack of internal energy equilibration beyond the central C—Sn—C bonding in a time range of 0.1–1 nsec. There seems to be a bottleneck of energy transfer because of that bonding. A similar non-RRKM behavior was also found for $(CH_2{=}CHCH_2)_4Ge$ (*49*), but no $CH_2{=}CH^{18}F$ was observed from $(CH_2{=}CHCH_2)_2Si(CH_3)_2$ (*50*).

TABLE V (*46–50*)

YIELDS (%) AND RATE CONSTANTS[a] FOR REACTIONS OF THERMAL ^{18}F ATOMS WITH ORGANOMETALLIC COMPOUNDS

Compound	Labeled product	Yield	*k*
$(CH_3)_3SnH$	CH_3F	5	—
$(CH_3)_4Sn$	CH_3F	8.5	2.3
	HF	—	24
$(CH_3)_2Hg$	CH_3F	9.6	2.8 ± 0.2
	Total[b]	—	28 ± 3
$(C_2H_5)_4Sn$	C_2H_5F	2	—
$(CH_2{=}CH)_4Sn$	$CH_2{=}CHF$	16	13 ± 2
	Total[c]	—	72 ± 12
$(n\text{-}C_3H_7)_4Sn$	C_3H_7F	0.8	—
$(CH_2{=}CHCH_2)_4Sn$	$CH_2{=}CHCH_2F$	0.5	—
$(CH_3)_3SnC_6H_5$	CH_3F	5.3	—

[a] In 10^{10} liters mol^{-1} sec^{-1}.

[b] $HF + CH_3F + CH_3HgF$.

[c] Addition + H abstraction + $CH_2{=}CH_2$ abstraction and substitution.

B. THERMAL REACTIONS OF ^{38}Cl ATOMS

For the production and moderation of recoil ^{38}Cl atoms, CF_3Cl and CF_2Cl_2 are in use as bath gases. Hot reactions with both gases account for only 3 and 6% of the total yields, respectively (*51, 52*).

1. *Abstraction*

Stevens and Spicer (*53*) measured the yields for abstraction from H_2 (3.7% $H^{38}Cl$) and from D_2 (1.3% $D^{38}Cl$) in excess CF_2Cl_2. In purely thermal systems, with nonradioactive Cl atoms, an HCl–DCl isotope effect in the range 9–10 has been measured at 300 K. Based upon extrapolation of thermal data, the observed ^{38}Cl isotope effect of 2.8 indicates that the effective temperature in the recoil experiment is 800–900 K. Lee and Rowland (*54*) measured rate constants for thermal H abstraction from CH_4 and C_2H_6, in competition with addition to C_2H_3Br. At 243 K they found these constants to be $(1.9 \pm 0.4) \times 10^7$ and 2.7×10^{10} liters mol^{-1} sec^{-1}, respectively, in agreement with average values obtained with thermal nonradioactive Cl atoms of 2.4×10^7 and 3.6×10^{10} liters mol^{-1} sec^{-1}, respectively (*55*). Abstraction of CH_3 and C_2H_5 was observed from $(CH_3)_4Pb$ and $(C_2H_5)_4Pb$, respectively (*56*). In the former case, the yield of $CH_3{}^{38}Cl$ was 18% [the rate constant is $(1.8 \pm 0.3) \times 10^{10}$ liters mol^{-1} sec^{-1}], whereas $H^{38}Cl$ accounts

TABLE VI

RELATIVE REACTION RATES FOR THERMAL ^{38}Cl ADDITION

Reactant	Relative rate	Reference
$^{38}Cl + HI \rightarrow H^{38}Cl$	(1.0)	
$^{38}Cl + H_2S \rightarrow H^{38}Cl$	0.75 ± 0.10	*57*
$H_2C{=}CH_2$	1.7 ± 0.1	*57*
$H_2C{=}CHCH_3$	1.2 ± 0.1	*58*
$HC{\equiv}CH$	1.6 ± 0.3	*59*
$HC{\equiv}CCH_3$	1.9 ± 0.1	*60*
$H_2C{=}CHF$	1.3	*45*
$H_2C{=}CHBr$	1.2; 1.7[a]	*61*

[a] The limiting total reactivity at high pressure.

for 75% of the total activity [rate constant (7.8 ± 1.4) × 10^{10} liters mol^{-1} sec^{-1}].

2. *Addition*

Rates of addition to alkenes and alkynes, relative to H abstraction from HI, are given in Table VI. The reactions of thermal ^{38}Cl atoms with traces of C_2H_4 in a CF_2Cl_2 or $CFCl_3$ matrix lead to high yields (90%) of $C_2H_4{}^{38}Cl$ (*57, 62, 63*). The excited radical can decompose by Cl loss, but that causes the ^{38}Cl atom to be available again for reaction. A minor reaction channel is the elimination of $H^{38}Cl$. Extrapolation of the $H^{38}Cl$–$C_2H_4{}^{38}ClI$ (I_2 scavenged experiment) to $1/P = 0$ results in a ratio of 0.06, indicating that H abstraction also takes place: the addition/abstraction ratio is 15.5 ± 0.5 (*62*). Relative to the rate of H abstraction from C_2H_6, evaluated as (3.4 ± 0.4) × 10^{10} liters mol^{-1} sec^{-1} at 298 K, the rate constant for removal of Cl atoms by addition to C_2H_4 is (1.0 ± 0.1) × 10^{11} liters mol^{-1} sec^{-1} (*63*). Correction for back reaction of C_2H_4Cl leads to an absolute rate constant of (1.14 ± 0.12) × 10^{11} liters mol^{-1} sec^{-1}. Thermal reactions of ^{38}Cl with C_3H_6 result in the formation of 86% $C_3H_6{}^{38}Cl$ (*58*). The terminal/central addition ratio depends upon the HI concentration and varies between 6.5 and 12.3. This is explained by ^{38}Cl migration from $CH_3CH^{38}ClH_2$ to $CH_3CHCH_2{}^{38}Cl$, with a rate constant of 10^7 sec^{-1}. The original terminal/central ratio is 6. Allylic H abstraction accounts for no more than 14% of the total number of reactions. Thermal ^{38}Cl atoms react almost quantitatively with C_2H_2 (*59*). The addition takes place in not more than two to five collisions. The reaction with propyne also proceeds almost entirely by addition, with less than 5% H abstraction (*60*). The

TABLE VII

RELATIVE ^{38}Cl-FOR-Cl SUBSTITUTION YIELDS IN 1 : 1 : 1 MIXTURES OF *o*-, *m*-, AND *p*-C_6H_4ClX[a]

	Ortho	Meta	Para
$C_6H_4Cl_2$ (*69*)			
Hot	35 ± 1	25 ± 1	40 ± 1
Thermal	42 ± 2	2 ± 2	56 ± 2
C_6H_4ClF (*70*)			
Hot	38 ± 1	26 ± 1	36 ± 2
Thermal	55 ± 4	1 ± 2	44 ± 3
$C_6H_4ClCH_3$ (*67*)			
Hot	46 ± 4	20 ± 4	34 ± 1
Thermal	55 ± 6	6 ± 2	39 ± 4

[a] Dose: 7.5 kGy.

terminal/central ratio is 8 ± 1, but there is no indication of a 1,2 shift as observed with C_3H_6.

The addition of ^{38}Cl to $CH_2{=}CHF$ occurs preferentially at the CH_2 end by a factor of two (*45*). A major proportion of both $C_2H_3F^{18}Cl$ radicals are stabilized at a pressure of 500 kPa, their lifetimes being 1 nsec.

In the presence of HI, the reactions of ^{38}Cl with $CH_2{=}CHBr$ produce both $CH_2{=}CH^{38}Cl$ and $CH_2{}^{38}ClCH_2Br$ (no $CH_3CH^{38}ClBr$) in pressure-dependent yields, indicating a long-lived (0.1–1 nsec) excited $C_2H_3{}^{38}ClBr$ radical (*54, 61*). The proposed mechanism shows very little preference for addition to the CH_2 site versus CHBr. The observation that no $CH_3CH^{38}ClBr$ is found is explained by a 1,2-Br shift after the formation of $CH_2CH^{38}ClBr$, the "anti-Markovnikov" product.

cis- and *trans*-$CHCl{=}CHCl$ were used in hot-atom chemistry experiments as scavengers for thermal ^{38}Cl atoms (*52, 64, 65*). The lifetime of the $CHClCHCl^{38}Cl$ radical is 0.5–0.7 nsec. With either isomer as the reactant, the loss of a Cl atom from this radical leads to $CHCl{=}CH^{38}Cl$ with a trans/cis ratio of 0.50. Similar experiments with C_2Cl_4 as a scavenger resulted in yields of $C_2Cl_3{}^{38}Cl$ between 9 and 92%, owing to radiation-induced reactions (*52*).

3. ^{38}Cl-*for*-Cl *Exchange*

The hot substitution of a Cl atom in liquid chlorobenzenes by recoil ^{34m}Cl and ^{38}Cl atoms accounts for 4–6% of the total activity. Apart

TABLE VIII

HOT AND THERMAL ^{34m}Cl-FOR-Cl SUBSTITUTION YIELDS (%) IN EQUIMOLAR MIXTURES OF *o*-DICHLOROBENZENES (*71*)

1:1 Mixtures		Hot yields		Thermal yields	
A	B	A	B	A	B
$C_6H_4Cl_2$	C_6H_4ClF	15 ± 1	6 ± 1	11 ± 3	6 ± 2
$C_6H_4Cl_2$	$C_6H_4ClCH_3$	8 ± 1	8 ± 1	0	13 ± 1
$C_6H_4Cl_2$	$C_6H_4ClCF_3$	12 ± 1	4 ± 1	22 ± 4	1 ± 1
C_6H_4ClF	$C_6H_4ClCH_3$	3 ± 1	5 ± 1	6 ± 1	13 ± 1
C_6H_4ClF	$C_6H_4ClCF_3$	9 ± 2	7 ± 2	31 ± 2	0
$C_6H_4ClCH_3$	$C_6H_4ClCF_3$	4 ± 1	11 ± 1	29 ± 1	0

from the substitution by energetic Cl atoms, there is a high yield of a thermal ^{38}Cl-for-Cl exchange reaction that can be completely suppressed by 1–2 mol % Br_2 or I_2. In C_6H_5Cl, this thermal yield is 30% and increases to 50% at high radiation doses (*66*). Comparable high exchange yields were observed in $C_6H_4Cl_2$ (*70*), $C_6H_4ClCH_3$, and C_6F_5Cl (*67, 68*). The thermal exchange reaction rates are influenced by the position of the second substituent. Table VII gives relative hot and thermal substitution yields for equimolar mixtures of the three isomers of some substituted chlorobenzenes: the rate constants for the thermal reactions are substantially lower for the meta isomers. Not only the position of the second substituent affects the thermal exchange rates, but also the nature of that substituent, as can be seen in Table VIII, for equimolar mixtures of two ortho-substituted chlorobenzenes. The "hot" yields are those measured in the presence of 2 mol % I_2, the "thermal" yields are the differences between the yields measured in mixtures without and with I_2. From the thermal data it can be concluded that the sequence of the rate constants for thermal Cl-for-Cl exchange is $CH_3 > Cl > F > CF_3$. Similar values were found for equimolar mixtures of the meta isomers (*72*). The effect of the substituent X on the thermal exchange rate in C_6H_4ClX compounds is in the same order as the σ_m^+ and σ_p^+ Hammett constants, indicating the electrophilic nature of the reaction. The thermal exchange yield in C_6F_5Cl is (15 ± 1)%, but in equimolar mixtures with C_6H_5Cl thermal exchange is only found with C_6H_5Cl, the thermal yield of $C_6F_5{}^{34m}Cl$ being zero (*72*). The strong electron withdrawal properties will decrease the rate of the formation of a π-complex in C_6F_5Cl.

4. *Discussion–Conclusions*

The accurate determination of rate constants for the reactions of ^{19}F atoms is often hampered by the presence of reactive F_2 and by the occurrence of side reactions. The measurement of the absolute concentration of F atoms is sometimes a further problem. The use of thermalized ^{18}F atoms is not subject to these handicaps, and reliable and accurate results for abstraction and addition reactions are obtained. The studies of the reactions of ^{18}F atoms with organometallic compounds are unique, inasmuch as such experiments have not been performed with ^{19}F atoms. In the case of addition reactions, the fate of the excited intermediate radical can be studied by pressure-dependent measurements. The non-RRKM behavior of tetraallyltin and -germanium compounds is very interesting inasmuch as not many other examples are known. The next phase in the ^{18}F experiment should be the determination of Arrhenius parameters for selected reactions, i.e., those occurring in the earth's atmosphere, since it is expected that the results will be more precise than those obtained with ^{19}F atoms.

As a consequence of the occurrence of cage reactions in the liquid phase, which cannot be suppressed by small amounts of scavengers, studies of the reactions of thermalized recoil atoms are, in general, not possible. The investigations of thermal exchange reactions of ^{34m}Cl and ^{38}Cl atoms with chlorobenzenes are an exception to this rule. It must also be noted that X-for-X exchange reactions can only be studied with radioactive (or enriched) isotopes. In order to gain more information regarding the role of a second substituent on the rate of exchange, further experiments with varying substitutents will have to be conducted. Similar types of experiments should also be performed with recoil Br and I atoms. The observation (*73*) that recoil T atoms do not react with liquid CCl_4 indicates the viability of the study of reactions of thermal T atoms with compounds present in low concentrations in CCl_4.

III. Stereochemistry in Substitution Reactions

A. Tritium

An important aspect of hot-atom chemistry concerns the stereochemistry of substitution reactions, particularly if the reactions proceed via retention or (Walden) inversion. Cross sections for the reactions of energetic T atoms with CH_4, calculated by trajectory studies, show that T-for-H substitution with inversion is a feasible but minor process at low energies (*74*). Chou *et al.* (*75*) investigated the reactions of photolytically produced T atoms (1.8–3.2 eV) with CH_3F. The threshold energy is much lower for the T-for-F substitution (1.3 eV) than for the T-for-H substitution (1.8 eV). Furthermore, the ratio of the yields of both reactions (0.6 at 2.7 eV) is far smaller than unity, as has been measured for energetic T atoms originating from a nuclear reaction (*76*). It was suggested that at low energies the T-for-F substitution involves the preferential loss of F along a linear T—C—F axis, leading to Walden inversion (*75*). Similar experiments with CHF_3 resulted in higher threshold energies (1.9 eV for both H and F substitution) and lower reactivity for the T-for-F substitution ($CTF_3/CHTF_2 \simeq 7$), indicating the absence of inversion during the F-substitution reaction (*77*). Such a reaction involves two heavy F substituents, which would not readily adjust to changes in configuration. Retention of configuration is expected to be even more efficient for the T-for-H substitution reaction in CHF_3.

Substitution reactions at asymmetric C atoms in optically active molecules were first studied with glucose, galactose, and alanine, and it was proved that retention was preserved during the substitution of H atoms bound at these asymmetric atoms (*78–80*). However, it was not possible from the results of these solid-phase experiments to establish the mechanism. More direct information was obtained with gas-phase experiments (Table IX). Only for $C_2H_5CHOHCH_3$ and $(CHFCl)_2$ was substitution at the asymmetric C atom studied; for the other compounds, the total T-for-H (all H atoms) substitution yields were measured. Even if all the T activity in *meso*-$(CH_3CHCl)_2$, formed from reactions with *dl*-$(CH_3CHCl)_2$, were in the asymmetric position, the gas-phase preference for retention of configuration is more than 93% (*84*). In gaseous 1,3-dimethylcyclobutane, the yield of the inverted isomer is less than 1% (*85*). Since only 2 out of the 12 H atoms are bonded in asymmetric positions, more than 94% of the H substitution at the asymmetric C atom occurs with retention of configuration (if it is assumed that T-for-H substitution yields are equal for all 12 H atoms). It is even probable that this small inversion yield arises from secondary isomerization of the excited product and not from the primary event itself. In the condensed phases of $(CHFCl)_2$ and $(CH_3CHCl)_2$, the inversion yields are higher than in the (scavenged) gas phases. This is thought to be due to the decomposition of excited, labeled isomers by Cl loss, followed by caged recombination, in competition with racemization of the radical (*82, 83*).

TABLE IX

INVERSION FOR T-FOR-H SUBSTITUTION REACTIONS[a]

Sample	Phase[b]	Inversion (%)	Sample	Phase	Inversion (%)
d-$C_2H_5CHOHCH_3$ (*81*)	G	10 ± 3	*dl*-$(CH_3CHCl)_2$ (*84*)	G	1.3 ± 0.1
l-$C_2H_5CHOHCH_3$	G	9 ± 4		L	3.1 ± 0.8
				L(I_2)	2.3 ± 0.6
dl-$(CHFCl)_2$ (*82*)	G	15.3 ± 1.1	*meso*-$(CH_3CHCl)_2$	S(I_2)[c]	4.3 ± 1.0
	G(O_2)	2.1 ± 1.4		G(O_2)	0
	L(I_2)	16.4 ± 0.3	*cis*-$(CH_3)_2$-*c*-C_4H_8 (*85*)		
				G(O_2)	1.0 ± 0.1
meso-$(CHFCl)_2$	G	8.6 ± 0.5		L	6.7
	G(O_2)	0.7 ± 0.4		L(I_2)	0.9
	L(I_2)	5.4 ± 0.2	*trans*-$(CH_3)_2$-*c*-C_4H_6[d]	G(O_2)	0.8 ± 0.1
dl-$(CHFCl)_2$ (*83*)	G(I_2)	4		L	6.7
	L(I_2)	20		L(I_2)	0.2
meso-$(CHFCl)_2$	G(I_2)	4			
	L(I_2)	8			

[a] Inversion + Retention = 100%.
[b] G: gas, L: liquid. (O_2), (I_2): O_2 or I_2 scavenger present.
[c] S: solid.
[d] $(CH_3)_2$-*c*-C_4H_6: 1,3-dimethylcyclobutane.

B. CHLORINE

1. Gaseous Phase

The ^{38}Cl and ^{39}Cl-for-Cl substitution in gaseous *meso*- and *dl*-$(CH_3CHCl)_2$ (scavenged with butadiene) proceeds with almost complete (≥93%) retention of configuration (*86*). In the absence of butadiene, (26 ± 2)% inversion was measured for *dl*-$(CH_3CHCl)_2$ and (15 ± 2)% for the meso compound. Decomposition of labeled products will occur if they possess over 6 eV of excitation energy. Radical reactions appear then in the formation of both diastereomers, with some preference for the more stable meso compound. Virtually complete retention of configuration was also found in gaseous *dl*-$(CHFCl)_2$ (91%) and *meso*-$(CHFCl)_2$ (92%) when scavenged with I_2 (*91*).

In contrast with these experiments, a high degree of inversion (81%) was observed for the substitution by recoil ^{38}Cl and ^{39}Cl atoms of the Cl atom bound at the asymmetric C atom in gaseous *d*- and *l*-CH_3CH-$ClCOCl$ (*88*). In the gas phase, the gauche prime configuration is present in high concentrations. This conformation provides a relatively unhindered approach to an attack of the asymmetric C atom from the rear (with respect to the 2-Cl atom), resulting in Walden inversion upon substitution. This theory is upheld by the finding that in $(CH_3)_2CHCHClCOCl$, where the approach is sterically hindered, the amount of inversion is only $(41 \pm 1)\%$. In *d*- and *l*-$CH_3CHClCH_2OH$, the inversion decreases from 80% at a pressure of 38 kPa to 42% at 100 kPa (*89*). Infrared spectroscopy shows that an increase in pressure results in the appearance of a 3470 cm^{-1} absorption band (O—H stretching in a dimer) and in a decrease of the 3600 cm^{-1} band (O—H stretching in the monomer). As the extent of aggregation by hydrogen bonding increases, the chances for unhindered rear attack, leading to inversion, decrease (see Notes Added in Proof, p. 133).

2. *Condensed Phases*

The ^{38}Cl-for-Cl substitution yields in *dl*- and *meso*-$(CH_3CHCl)_2$ are 10 times as high in the condensed phases as in the gas phase (*86*). The inversion in the liquid phase for both isomers is 28% at 298 K and 30% at 217 K, independent of the presence of scavengers, whereas it is 50 and 38% in the solid phase for the dl and meso isomers, respectively (*87*). These findings confirm the recombination of a ^{38}Cl atom with a $CH_3CHClCHCH_3$ radical in a solvent cage. Such a process will not be affected by normal concentrations of scavengers. The increase of inversion at lower temperatures is consistent with a slightly higher activation energy for the combination process than for the racemization of the radicals. Caged radical recombination reactions could also explain the observations that in *d*- and *l*-$CH_3CHClCOCl$ the total substitution yield increases (from 1.2% to 4.3%) and the inversion decreases (from 80% to 50%) when going from the gaseous to the liquid phase (*88*). In *dl*- and *meso*-$(CHFCl_2)$, the ^{38}Cl-for-Cl substitution yields increased by a factor of about three, and the inversion increases from 9 to 30%, when going from the gaseous to the liquid phase (*87*). These effects were not explained by caged recombination between a ^{38}Cl atom and a CHFClCHF radical but by the formation of a caged complex: "i.e., an electronically unstable intermediate, which is held together by the surrounding solvent molecules for a time sufficient for configurational changes to occur" (*87*).

3. *Solutions*

An interesting behavior of the retention/inversion ratio in *dl*- and *meso*-$(CH_3CHCl)_2$ was observed upon dilution with several compounds (Fig. 1) (*91*). This effect was assigned to the relative concentrations of

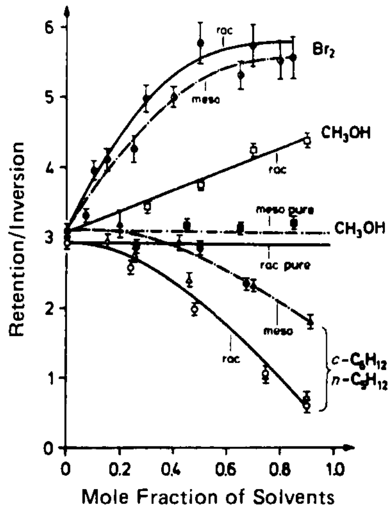


FIG. 1. Solvent effect on the stereochemical course (ratio retention/inversion) of ^{38}Cl-for-Cl substitution in *rac*- and *meso*-2,3-DCB. Key: ⊗: *rac*-DCB-Br_2; □: *rac*-DCB-CH_3OH; △: *rac*-DCB-*n*-C_5H_{12}; ○: *rac*-DCB-*o*-C_5H_{12}; ◑: *meso*-DCB-Br_2; ■: *meso*-DCB-CH_3OH; ▲: *meso*-DCB-*n*-C_5H_{12}; ●: *meso*-DCB-*o*-C_5H_{12}. [Reprinted with permission from ref. (*91*). Copyright 1972 American Chemical Society.]

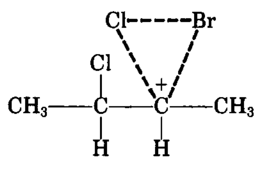
the three possible conformers (RT, RG, and RG′), these concentrations depending on the type and amount of the additive. A similar effect on the retention/inversion ratio was found for $(CH_3CHCl)_2CH_2$ (*92*), but in this case each of the dl and meso compounds has only one preferred conformation, with minor amounts of the others, whereas the conformation population is barely affected by the nature of the solvent. Furthermore, only small changes in the retention/inversion ratio were observed in the case of $(CH_3CHCl)_2$ when going from the liquid to the solid phase (dl from 2.78 to 2.57, meso from 2.45 to 2.21), whereas distinct changes in the relative conformer concentrations were to be expected. Alterations in the retention/inversion ratios were similarly observed in *dl*- and *meso*-$(CHFCl)_2$ and in *d*- and *l*-$CH_3CHClCH_2OH$ (*93, 94*). It was proposed that the dielectric properties of the solvent, or more precisely the quantity $(\varepsilon - 1)/(2\varepsilon + 1)$, causing differences in the solute–solvent interactions, control the substitution mechanism to a large degree. A strong interaction prevents the intermediate radical from obtaining planarity, maintaining the configuration that is obtained in the primary substitution step (*94*). For liquid *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane, the retention is 76%

(*95*) and the addition of 80 mol % $n\text{-}C_7H_{16}$, $c\text{-}C_6H_{12}$, or $n\text{-}C_5H_{11}OH$ increases this value to 80%. In contrast with the other experiments, no dependence was found on the dielectric constants of the various hydrogen-containing solvents. This was attributed to a much higher activation energy being required for achieving planarity in the case of the $c\text{-}C_4F_6Cl$ radical than for the other radicals. The addition of 80 mol % $n\text{-}C_7F_{16}$ decreases the retention from 76 to 55 and 72% for the cis and trans isomers, respectively. The different behavior of C_6F_{16}, which has the same dielectric constant as C_7H_{16} and $c\text{-}C_6H_{12}$, has been attributed to the self-scavenging of ^{38}Cl by H abstraction from the hydrogen-containing solvents.

C. Fluorine, Bromine, and Iodine

No inversion of configuration was found in the case of ^{18}F-for-F substitution in gaseous *dl*- and *meso*-$(CHFCl)_2$, in accord with the results obtained with the same compounds for recoil T and ^{38}Cl atoms (*96*).

The isomeric transitions $^{80m}Br \xrightarrow{IT} {}^{80}Br$ and $^{125}Xe \xrightarrow{IT} {}^{125}I$ result in highly positively charged ^{80}Br and ^{125}I ions. In a study with gaseous $(CH_3CHCl)_2$, it was safely assumed that both species react as singly charged Br^+ and I^+ ions (*97*). Electrophilic ^{80}Br and ^{125}I-for-Cl substitution leads to *erythro*- and *threo*-2-bromo(iodo)-3-chlorobutanes. In the pure systems, the retention/inversion ratios were 2.5 for ^{80}Br (for both the dl and meso isomers) and 1.9 for ^{125}I (for the dl isomer). Extrapolation of these ratios to 100 mol % moderator (Ar for ^{80}Br and Xe for ^{125}I) result in the following ratios: 3.3 (^{80}Br/meso), 0.3 (^{80}Br/dl), and 0.5 (^{125}I/dl); the attack of the thermal ions proceeds preferentially from the front and results in the formation of a halocarbocation with a three-centered bond structure and which retains the original configuration:



After the formation of the carbocation, two competing processes occur in the moderated systems: racemization and Cl^+ transfer. In the case of the meso compound, front attack leads to the thermodynamically stable erythro form, whereas in the dl system, the less stable threo diastereomer is formed, which readily leads to racemization.

Dilution of liquid $(CH_3CHCl)_2$ with several additives results, in the

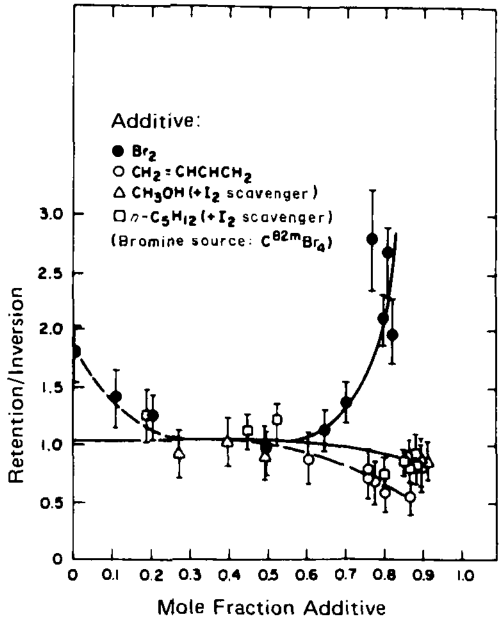


FIG. 2. ^{82}Br-for-Cl exchange in *dl*-2,3-dichlorobutane solutions following ^{82m}Br(T) ^{82}Br. [Reprinted with permission from ref. (*98*). Copyright 1976 American Chemical Society.]

case of Cl substitution by neutral ^{80m}Br atoms [produced by the ^{79}Br(n,γ)^{80m}Br reaction], in curves similar to those plotted for ^{38}Cl (Fig. 1), indicating that direct hot reactions are involved (*98*). In Fig. 2, results are shown for ^{82}Br, produced via the $^{82m}\mathrm{Br} \xrightarrow{\mathrm{IT}} {}^{82}\mathrm{Br}$ decay. Auger radiolysis leads to the formation of $CH_3CHClCHCH_3$ radicals, which can react with a neutral ^{82}BR atom. The stereochemistry depends on the time needed to obtain a planar configuration of the radical, this time interval depending on the neutralization time of the $^{82}Br^+$ ion and the density of the solvent.

D. Conclusions

Hot T-for-H substitution occurs mainly with retention of configuration. Inversion seems theoretically possible only when very light substituents are bound to that C atom at which the substitution takes place. Unfortunately, it appears to be impossible to prove inversion experimentally. During Cl substitution in gaseous compounds by recoil Cl atoms, the configuration is mainly retained in the case of simple molecules, but for larger molecules the situation becomes more complex. If unhindered approach can take place from the rear of the atom that is to be substituted, inversion is the main reaction channel. Such a situation can occur if one of the possible conformations is significantly more abundant than the others. However, the degree of inversion can be affected by steric hindrance. Many more experiments are needed in order to gain further insight into the significance of the parameters predicting the substitution process, such as conformational effects and steric hindrance. In the condensed phase, more experiments are needed to obtain information regarding the importance of cage reactions. In particular, experiments in liquid mixtures can provide more information about the time scale of the reactions and the interactions of radicals with the surrounding molecules. As noted in the previous section on thermal Cl-for-Cl substitution, hot X-for-X substitution reactions as discussed in this article can be studied only with radioactive atoms. Although not further discussed, the electrophilic substitution reactions by thermal $^{80}Br^+$ and $^{125}I^+$ ions are of special importance in these cases where other methods, such as ion cyclotron resonance and high-pressure mass spectroscopy, cannot provide the necessary information on the stereochemical course of the reaction.

IV. Muonium Chemistry

Muonium (Mu) is the lightest hydrogen-like atom ($m_{Mu} = 0.11\ m_H$) available for chemical research; it has a positive muon (μ^+, $\tau = 2.2$ μsec) as the nucleus. The muon spin resonance (μSR) technique is described in several review articles (*16, 99–102*). Most of the research is performed in the condensed phases, but because of the development of the "surface muon beams" (*103, 104*), experiments in the gaseous phase have received more attention. At present three muonic fractions can be detected: (1) f_{Mu}, free muonium; (2) f_D, free μ^+, or Mu bound in a diamagnetic compound; and (3) f_R, Mu bound in a paramagnetic compound. In liquid phases, there is quite often a missing fraction, $f_L = 1 - f_{Mu} - f_D - f_R$.

A. Gaseous Phase

During the deceleration process in matter, a μ^-, formed through the decay of a π^-, generally captures an atomic electron, resulting in Mu formation. In compounds where the ionization potentials are higher than that of Mu (13.6 eV), no (or only partial) neutralization takes place: $f_{Mu} = 0$ for He, 0.07 for Ne, 0.74 for Ar, and 1 for Kr and Xe (*105*).

TABLE X

REACTION RATES AND ISOTOPIC RATIOS FOR GAS-PHASE REACTIONS OF Mu (*111*)

Reactant	Reaction type	k_{Mu} (300 K) ($\times 10^{10}$ liters mol^{-1} sec^{-1})	k_{Mu}/k_H
F_2	Abstraction	1.46 ± 0.11	9.2 ± 3.1
Cl_2	Abstraction	5.30 ± 0.15	3.5 ± 0.8
Br_2	Abstraction	2.4 ± 3	5.3 ± 1.5
HBr	H abstraction, H exchange	0.91 ± 0.15	3.0 ± 1.0
C_2H_4	Addition	0.4 ± 0.05	5.8 ± 0.8
O_2	Spin exchange	15.8 ± 2.4	2.5 ± 0.4
NO	Spin exchange	18.3 ± 2.0	2.7 ± 0.3

The addition of 0.09 mol % Xe to He increases f_{Mu} to 0.75 (*106*). Similar effects were found on the addition of small amounts of Xe, CH_4, and NH_3 to Ne (*105*). This demonstrates the importance of the neutralization process right down to thermal energies. Neutralization may also proceed through a reaction with $Ne\mu^+$:

$$Xe + Ne\mu^+ \rightarrow Xe^+ + Ne + Mu \quad (107)$$

In gaseous N_2, H_2O, NH_3, n-C_6H_{14}, c-C_6H_{12}, $(CH_3)_4Si$, CH_2Cl_2, and $CHCl_3$, f_D = 0.1–0.25 and f_{Mu} = 0.9–0.75 (an exception in CCl_4: $f_D = f_{Mu} = 0.5$). The f_D fraction is supposed to be formed by hot reactions of μ^+ or of Mu (*108*). In collisions with paramagnetic molecules, fast spin exchange can take place. Cross sections at room temperature are reported for O_2: (5.9 ± 0.6) (*109*) and (7.8 ± 0.4) (*110*) $\times 10^{-16}$ cm^2; while for NO: (7.1 ± 1.0) (*109*) and (10.3 ± 0.4) (*110*) $\times 10^{-16}$ cm^2. In Table X, the rate constants are listed for the reactions of Mu with several gaseous compounds and also the isotopic k_{Mu}/k_H ratios. If the reactions are diffusion controlled, an isotope effect of $k_{Mu}/k_H = (m_H/M_\mu)^{1/2} = 3$ is to be expected. Ratios higher than 3, as for F_2 and C_2H_4, point to tunneling effects (*111*), as has been corroborated (for F_2) by theoretical calculations (*112*).

B. Liquid Mixtures

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 compounds 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–$CHCl_3$, from 0.16 to 0.56 in C_6H_6–CH_3OH (*100*), and from 0.16 to 0.61 in C_6H_6–*c*-C_6H_{12} (*113*)] was taken as evidence for hot Mu reactions. In binary mixtures of C_6H_6 with C_6H_5Br, $C_6H_5NH_2$, and *p*-$C_6H_4F_2$, the values of f_D and of f_R (C_6H_6Mu and the isomeric C_6H_5XMu) were measured as a function of the relative concentration (*114*). The relative reaction rates of Mu do not differ to a large extent from those measured for thermal H atoms (*115*); these Mu results do not contribute much to the discussion on hot/thermal reactions. The partial rate factors, relative to C_6H_6, differ for $C_6H_5NH_2$ (ortho 1.9, meta 1.2, and para 1.7) from those measured with thermal T atoms [4.7, 1.36, and 2.0, respectively (*116*)].

In mixtures of C_6H_6 and CH_3I, the values of f_D and f_R deviate significantly from the proposed linearity for hot reactions (*117*). The results indicate that both compounds compete in reactions with thermal Mu, CH_3I being the more efficient. More information was obtained by investigations of Roduner (*118*) 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 $(8.9 \pm 0.6) \times 10^9\ M^{-1}\ \text{sec}^{-1}$, 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 $4 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$, 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 f_D values were measured (*113*). Roduner (*118*) has also measured f_R values, in particular at low CCl_4 concentrations (Fig. 3). Since it was proved 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: $\mu^+ + e^- \rightarrow \text{Mu}$. The rate constant of $2.7 \times 10^{12}\ M^{-1}\ \text{sec}^{-1}$ for the reaction of CCl_4 with electrons shows that Mu is formed within a picosecond after the creation of the last spur.

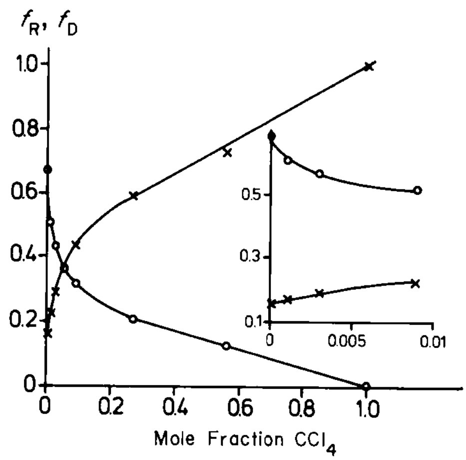


FIG. 3. $f_R(0)$ and $f_D(X)$ in C_6H_6–CCl_4 mixtures. [By permission of E. Roduner, ref. (*118*).]

For most of the hydrocarbons it has been found that f_D = 0.6–0.7, f_{Mu} = 0.1–0.2, and f_L = 0.1–0.2 (*100, 119*). These data were taken as evidence that hot abstraction (MuH) is of comparable efficiency for all of these compounds and that only 10–20% of the hot Mu atoms become thermalized and contribute to f_M. The data for f_D are not much different from those obtained for the reactions of recoil T atoms with C_4H_{10}: HT (40%), C_4H_9T (20%) (*120*). In n-C_6F_{14}, similar yields were found: f_D = 0.64 and f_{Mu} = 0.20, whereas F abstraction is a less probable process (*121*).

C. Formation and Reactions of Muonic Radicals

Before the first muonic radicals were observed in 1978 by Roduner *et al.* (*122*), rate constants had been measured for the addition of Mu to unsaturated compounds in aqueous solution (Table XI). If k_{Mu}/k_H is larger than 3, tunneling may be important, since otherwise differences in the vibrational zero-point energy in the transition state can decrease this ratio (*128*). In the case of maleic acid, the Arrhenius parameters were determined as $A = (2.3 \pm 0.2) \times 10^{13}\ M^{-1}\ \mathrm{sec}^{-1}$ and E = 18.8 ± 1.7 kJ mol^{-1}. Rate constants were also measured for addition to the CN triple bond (*127*).

TABLE XI

REACTION CONSTANTS[a] FOR ADDITION OF Mu IN AQUEOUS SOLUTIONS AT 298 K

Compound (*123, 124, 125*)	k_{Mu}	k_{Mu}/k_H
Maleic acid	1.1×10^{10}	18
Fumaric acid	1.4×10^{10}	16
Ascorbic acid	1.8×10^{9}	16
Dihydroxyfumaric acid	4.5×10^{7}	0.5
Acrylamide	1.9×10^{10}	1.1
Acrylic acid	1.6×10^{10}	
Acrylonitrile	1.1×10^{10}	2.8
Methyl metacrylate	1.0×10^{10}	

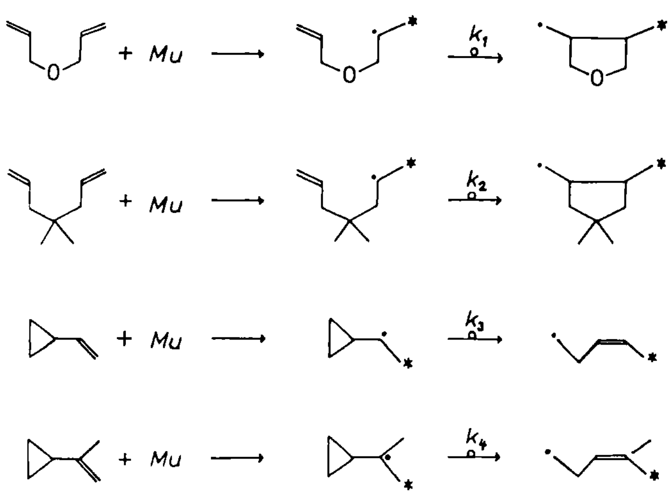
[a] In $mol^{-1} sec^{-1}$.

1. Alkenes

Roduner *et al.* (*128*) studied the formation of muonic radicals in 24 monoolefins and in 9 dienes. Hyperfine coupling constants (A_μ) were measured for 44 radicals (11 compounds gave two radicals each). For comparison with the corresponding protonic constants A_p, the values of A_μ must be multiplied by the ratio of the magnetic moments: $A'_\mu = (\mu_p/\mu_\mu)A_\mu = 0.3141A_\mu$. The isotopic effect A'_μ/A_p is found to be of the order of 1.4 (see also comments below in Section C,2). The terminal and nonterminal olefins yield primary, secondary, and tertiary alkyl radicals with $A_\mu = 330$, 300, and 270 MHz, respectively. Allylic radicals were usually formed from dienes with $A_\mu = 160\text{–}190$ MHz. The assignment of the radicals is based on more extensive investigations of ethene, propene, 2-methylpropene (*128*), and tetramethylethylene (*129*). The regioselectivity of Mu addition is similar to that of H atoms, in that it occurs (1) at the unsubstituted C atom for terminal olefins, with the exception of allyl ethers, (2) preferentially at the less substituted C atom for nonterminal olefins, and (3) at the end C atoms for dienes to yield the thermodynamically more stable allyl type radicals.

In methyl-substituted dienes, the following yields were found: $f_D = 0.2\text{–}0.3$, $f_R = 0.45\text{–}0.35$, and $f_L = 0.35$ (*130*). The missing fraction of muon polarization f_L is thought to be due to muonic radicals having lost spin polarization during encounters with other paramagnetic species in the spur of the muon track. If Mu is the precursor for the formation of radicals, then its lifetime must be less than 20 psec. Comparing the selectivities, the activation energies, and the rate constants for addition between Mu and H leads to the conclusion that Mu is close to thermal energy at the moment of its addition. However, μ^+ cannot be excluded as the precursor (*131*), in which case its lifetime is less than 2 nsec, because the precession frequency is 100 times lower than that of Mu. The hyperfine coupling constants A_μ decrease with increasing temperature for $CH_2Mu\dot{C}H_2$, $CH_2Mu\dot{C}HCH_3$, and $CH_2Mu\dot{C}(CH_3)_2$, which is evidence of a higher barrier against rotation about the C—C bond than that for H and D atoms. This is a consequence of higher zero-point vibrational amplitudes, which result in a more effective van der Waals radius of Mu (*128*) (see Notes Added in Proof, p. 133).

In Table XII, A_μ values are given along the f_R, f_D and relative rates λ for a selection of chloroolefins (C_4H_9Cl). The tentative assignments of the radicals are based on the data of other olefins, e.g., the A_μ values for both radicals from 1-chloro-3-butene being similar for terminal and nonterminal Mu addition to allyl propyl and diallyl ethers (*128*). The relaxation rates are somewhat high, indicating slow addition rates. In the case of 2-chloro-2-butene, no radicals were observed, but this may be due to even higher relaxation rates (similarly no radicals were observed for chloroethylenes). Ring closure and ring fission were observed for muonic radicals (*132*). The Arrhenius parameters are in good agreement with literature values for the corresponding protonic radicals, supporting the view that the substitution of H by Mu in a CH_3 group neighboring the reactive center changes hardly the rate constants.



log (A/sec^{-1})	E/kJ mol^{-1}
(9.5 ± 0.3)	(16.7 ± 1.9)
(10.1 ± 0.3)	(24.7 ± 1.9)
(11.0 ± 0.6)	(22.3 ± 3.0)
(14.5 ± 0.4)	(43.5 ± 2.7)

TABLE XII

RADICALS FROM CHLOROOLEFINS (C_4H_7Cl) AT ROOM TEMPERATURE (*121*)

Olefin	Radical	A_μ (MHz)	λ (μsec)$^{-1}$	f_R	f_D
$CH_2{=}CHCH_2CH_2Cl$	$CH_2Mu\dot{C}HCH_2CH_2Cl$	318.4	0.75 ± 0.01	0.13 ± 0.02	0.52 ± 0.01
	$\dot{C}H_2CHMuCH_2CH_2Cl$	332.1	3.1 ± 0.6	0.23 ± 0.02	
$CH_2{=}CHCHClCH_3$	No radical	—	—	—	0.60 ± 0.01
$CH_3CH{=}CHCH_2Cl$	$CH_3CHMu\dot{C}HCH_2Cl$	302.5	2.3 ± 0.1	0.056 ± 0.006	0.57 ± 0.01
	$CH_3\dot{C}HCHMuCH_2Cl$	276.7	1.2 ± 0.3	0.046 ± 0.005	
$CH_3CH{=}CClCH_3$	$CH_3CHMu\dot{C}ClCH_3$	235.0	4.4 ± 0.2	0.31 ± 0.02	0.47 ± 0.01
$CH_2{=}C(CH_3)CH_2Cl$	$CHMu\dot{C}(CH_3)CH_2Cl$	265.5	—	0.20 ± 0.02	0.60 ± 0.02
$CHCl{=}C(CH_3)_2$	$CClMu\dot{C}(CH_3)_2$	79.0	—	0.16 ± 0.02	0.52 ± 0.02

TABLE XIII (*133, 134*)

ADDITION OF Mu TO MONOSUBSTITUTED ARENES

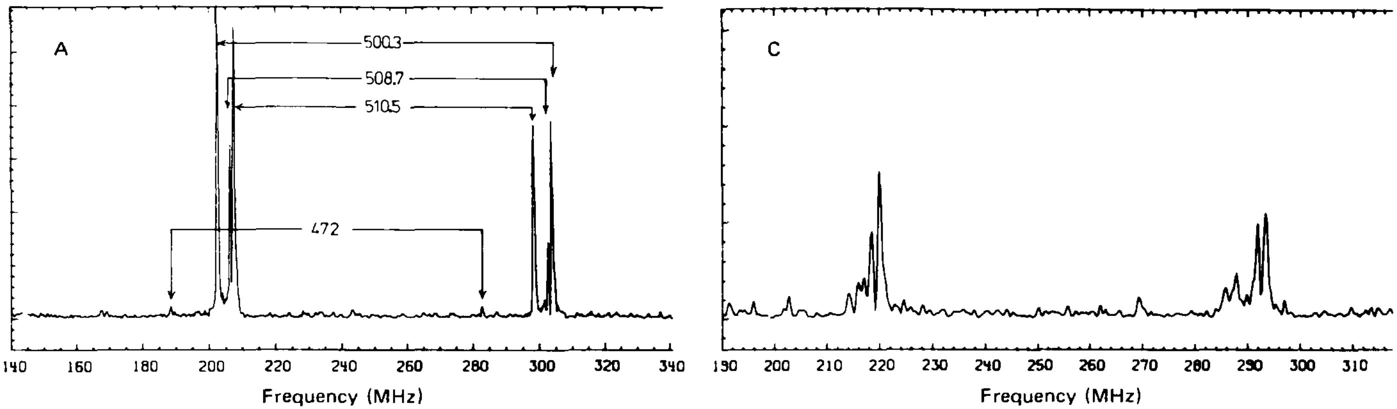
	A_μ (MHz) and relative ortho/meta/para ratios (%)			Σf_R	f_D	f_L
$C_6H_5CH_3$	498.6	509.3	496.4			
	48	35	17	0.50	0.25	0.25
C_6H_5F	485.7	511.8	511.8			
	42	44	14	0.43	0.19	0.38
$C_6H_5CF_3$	500.3	510.5	508.7			
	37	44	19	0.42	0.24	0.34
C_6H_5Cl	487.3	509.4	485.3			
	39	44	17	0.28	0.33	0.39
$C_6H_5CCl_3$	477.5[a]	155.7	477.5[a]			
	a	36	*a*	0.16	0.67	0.17

[a] Ortho and para isomers possibly degenerate.

2. *Arenes*

The first muonic cyclohexadienyl radical detected was C_6H_6 Mu (*122*). Later, many others were found, e.g., those originating from all the liquid CH_3- and F-substituted arenes (*133*). Furthermore, 24 monosubstituted arenes were studied, and the relative yields of Mu addition at the ortho, meta, and para positions were determined (*134*) (Table XIII). The assignment of these three isomeric radicals is determined via reactions with the *p*-deutero-substituted analogs (*137, 138*), where (1) at a magnetic field of 0.3 T there is a slight shift in the A_μ values in the sequence para > meta > ortho (Fig. 4), and (2) at a magnetic field of 0.1 T the signals from addition at C(H) atoms are split, but not from those pertaining to C(D) atoms (Fig. 4). In most cases, ortho addition occurs at a rate somewhat higher than the statistical probability, even in the presence of a bulky substituent. It is difficult to correlate the deviations from statistics with any substituent properties. In several cases, ipso substitution was observed (Fig. 4 and reference *133*). Muonic radicals were also detected in solid benzene (*135*) and durene (*136*).

For some of these compounds, the protonic hyperfine coupling constants are known. The isotopic A'_μ/A_p ratio is 1.21 for radicals produced by addition to C_6H_6 and to the ortho position of $C_6H_5CH_3$ and 1.15–1.18 for several fluorobenzenes (*133*). Quantum chemical calculations that include averaging over 33 vibrational modes in C_6H_7–C_6H_6Mu have shown that the dynamics account quantitatively ($A'_\mu/A_p = 1.16$) for the



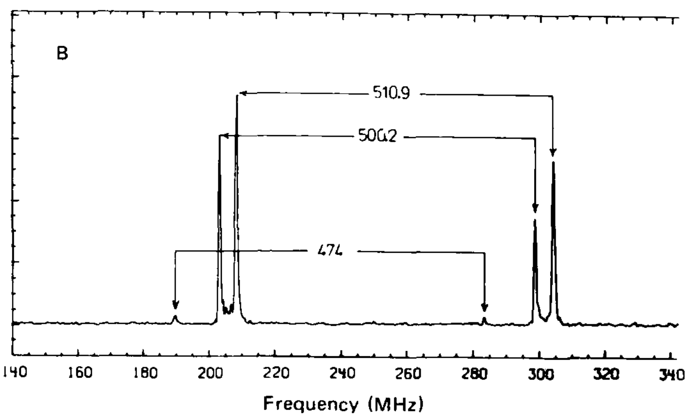


FIG. 4. Fourier spectra of $\cdot C_6H_5MuCF_3$ [0.3 T (A)] and of p-$\cdot C_6H_4DMuCF_3$ [0.3 T (B) and 0.1 T (C)] radicals, with their A_μ values indicated (ref. *134*).

$C_6H_5CF_3$	$C_6H_4DCF_3$	Shift	Assignment
500.3 MHz	500.2 MHz	−0.1 MHz	ortho
510.5	510.9	+0.4	meta
508.7	510.9	+2.2	para
471	473	—	ipso

isotope effect (*137*). The normal C—Mu stretching frequency and the two out of plane vibration frequencies are, in particular, responsible for the isotopic effect.

The value of f_D for monosubstituted arenes range between 0.15 (C_6H_6) and 0.76 (C_6H_5SH). In the series of halobenzenes, it increases from 0.19 (F) to 0.52 (I) (*134*). As discussed in Section IV,B, radical formation in mixtures of C_6H_6 involves the thermalization of μ^+ and subsequent combination with end-of-track electrons ($\leq$ 1 psec), followed by addition (10 psec) (*118*). The compounds with high f_D values undergo efficient dissociative electron capture, increasing from C_6H_5F to C_6H_5I, inhibiting the formation of Mu and of muonic radicals.

3. *Reactions of Muonic Radicals*

On addition of small amounts of benzoquinone to benzene, the relaxation rates increase linearly with concentration, in accord with a pseudo-first-order reaction between C_6H_6Mu and BQ (*136*). In the case of $C_6H_5CH_3$, the rate constants for the reactions of the *o*- and *m*-$C_6H_5MuCH_3$ radicals with BQ are comparable, but they differ considerably for the three isomers formed from $C_6H_5OCH_3$ (*138*) (Table XIV). The rate constant for the reaction of C_6H_6Mu with 2,3-dimethyl-1,3-butadiene is 7×10^5 mol^{-1} sec^{-1} at room temperature (*139*), whereas for C_6H_7 it is less than 12 mol^{-1} sec^{-1}. The large isotope effect is due to direct Mu transfer from C_6H_6 to C_6H_{10}, a reaction that is considerably faster than H transfer from C_6H_7, owing to the much higher zero-point vibrational energies in the muonic radical. For the dimerization reaction of the $C_6H_5CHCH_2Mu$ radical with styrene, a rate constant of 1.3×10^5 mol^{-1} sec^{-1} at room temperature has been reported (*131*). (Mu adds at the C=C bond in styrene, and not at the ring.)

4. *Miscellaneous*

Apart from addition to alkenes and arenes, other addition reactions have also been observed:

Styrene	$C_6H_5\dot{C}HCH_2Mu$	A_μ = 213.3 (*134*)
Phenylacetylene	$C_6H_5\dot{C}{=}CHMu$	421.2 (*134*)
Furane	c-$\dot{C}_4H_8OMu$	379.2 (*140*)
Acetone	$(CH_3)_2\dot{C}OMu$	26.0 (*122*)
Methyl methacrylate	$CH_2Mu\dot{C}(CH_3)COOCH_3$	270 (*140*)
Cyclohexanone	c-$\dot{C}_6H_{10}OMu$	21.4 (*140*)
Nitrobenzene	$C_6H_5\dot{N}OOMu$	38.7 (*134*)
Azobenzene	$C_6H_5NMu\dot{N}C_6H_5$	21.2 (*121*)

TABLE XIV (*138*)

RATE CONSTANTS FOR THE REACTION OF MUONIC CYCLOHEXADIENYL-TYPE RADICALS WITH QUINONES AT 293 K

Compound	Substitution of the radical	k_{BQ} (10^8 M^{-1} sec^{-1})	k_{DQ} (10^8 M^{-1} sec^{-1})	k_{BQ}/k_{DQ}
Benzene	—	2.6 ± 0.4[a]	0.62 ± 0.09	4.2 ± 0.9
Benzene-d_6	—	—	0.56 ± 0.08	—
Toluene	ortho	3.4 ± 0.9	0.52 ± 0.05	6.5 ± 1.8
	meta	3.5 ± 1.5	0.79 ± 0.13	4.4 ± 2.2
Anisole	ortho	10.5 ± 1.3	1.2 ± 0.3	8.8 ± 2.5
	meta	4.2 ± 0.5	0.66 ± 0.08	6.4 ± 1.1
	para	20	—	—

[a] See ref. *117*.

5. *Conclusions*

Despite its short mean life of 2.2 μsec, many chemical reactions of the hydrogen-like Mu atom can be studied. From investigations with recoil T atoms, it was suggested that Mu atoms could also react while possessing an excess of kinetic energy (hot reactions). Later investigations in C_6H_6–c-C_6H_{12} mixtures showed that addition to C_6H_6 is a thermal reaction. The relative addition rates to the ortho, meta, and para positions in monosubstituted benzenes, although not as conclusive, also point in the same direction. As free μ^+, MuCl, and $CMuCl_3$ cannot be distinguished in liquid CCl_4, it could not be deduced whether the value of $f_D = 1$ was due to hot abstraction (MuCl), hot substitution ($CMuCl_3$), or to nonneutralization of the μ^+. From experiments with CCl_4–C_6H_6 mixtures, it is now believed that CCl_4 scavenges spur electrons, preventing the formation of Mu.

The discovery of muonic radicals in 1978 by Roduner opened up a broad field of interesting experiments. Aromatic substitution is normally studied by the measurement of the yields of stable products. This includes not only the site of addition of the reactant, but also the splitting off of the atom that is substituted. With the MuSR technique only the first step is studied exclusively. Another development concerns the measurements of the reactions of muonic radicals: dimerization, ring opening, and ring closure. The observations of different reaction rates of the three isomeric muonic cyclohexadienyl radicals from anisole with quinones also opens a new field of investigation.

Absolute and relative reaction rates of Mu were measured for several compounds. Some of the results can be explained only by the acceptance of tunneling reactions.

Obviously the field of MuSR reaction studies is still in its infancy. Many more experiments must be performed in order to reach firm conclusions.

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NOTES ADDED IN PROOF

(Page 115): Not only does steric hindrance predict the retention/inversion ratio, but also the nature of the leaving group. In halopropionyl halides the degree of inversion for ^{34m}Cl-for-X substitution is

$$72\%\ (X = F),\ 79\%\ (X = Cl),\ \text{and}\ 78\%\ (X = Br)$$

Furthermore, the mass of the incoming atom is also important, as can be seen by the extent of inversion for ^{18}F-for-X substitution for the propionyl halides:

$$30\%\ (X = F),\ 35\%\ (X = Cl),\ 39\%\ (X = Br)$$

[Reference: To, K. C., Wolf, A. P., *et al., J. Phys. Chem.* **87,** 4929 (1984).]

(Page 124): The height of the barriers for internal rotation has been determined as 2.71 kJ mol^{-1} for both the $CMuH_2CH_2$ and $CMuD_2CD_2$ radicals, but is only 0.35 and 0.38 kJ mol^{-1} for the CDH_2CH_2 and CHD_2CD_2 radicals, respectively.

[Reference: Ramos, M. J., McKenna, D., *et al., J. Chem. Soc. Faraday Trans.* **I80,** 255, 267 (1984).]