Chem. Rev. **1981**, *81*, 267–290

Reactions of Radioactive Recoil Atoms with Arenes

G. A. BRINKMAN

Chemistry Department, National Institute of Nuclear and High Energy Physics (NIKHEF) (formerly IKO), P.O. Box 4395, 1009 AJ Amsterdam, The Netherlands

Received September 17, 1980

Contents

G. A. Brinkman, born in 1933, is a senior researcher of the Chemistry Department of the National Institute of Nuclear and High Energy Physics, NIKHEF (formerly Institute for Nuclear Physics Research (IKO)) in Amsterdam. He joined the department as a student of the University of Amsterdam in 1955 and received his Ph.D. degree in 1961 on a thesis about the absolute standardization of radioisotopes with liquid scintillators. After some further research on absolute standardization (long-lived isotopes ^{40}K, ^{87}Rb, and ^{176}Lu, and the development of the "sum-peak-method), his major interest was focused on organic hot atom chemistry, in particular on reactions of radioactive recoil atoms: T, ^{11}C, ^{18}F, ^{34m}Cl, ^{38}Cl, and (recently) Mu with liquid aromatic compounds.

I. Introduction

Free-radical substitution reactions on aromatic compounds proceed mainly through the formation of an intermediate σ complex. The ultimate product yields depend on (1) the site of attack of the free radical—that is mainly predicted by the relative energies in the σ-complex intermediates—and (2) the mechanism through which the σ-complex rearomatizes to the substituted compound.

Attack of the radical in general takes place at the position of a hydrogen atom and, in the case of substituted arenes, this can then lead to the formation of ortho, meta, and para isomers or to a return to the starting product by elimination of the original radical. Attack at the position of a nonhydrogen substituent (ipso attack) can lead to ipso substitution (recently reviewed by Traynham[1] and Tiecco[2]) or to a return to the starting product or to a 1,2 shift of one of the substituents. A return to the original arene by elimination of the attacking radical is normally hard to detect; the observed radiochlorine-for-chlorine exchange in chlorobenzenes, is a special example of the observation of such a reaction.[3-8] A typical example of a 1,2 shift is the formation of 2-bromo-1-chloro-4-nitrobenzene by the photochlorination of *p*-bromonitrobenzene.[9]

For the attack of H, Cl, and CH_3 radicals on chlorobenzene and toluene, relative energies of the four isomeric σ complexes are calculated by Gandour with the MINDO/3 method.[10] Due to competition reactions (e.g., H abstraction by Cl atoms from toluene) the calculations do not always conform with the experimental results. Furthermore, such calculated relative energies can give only qualitative information on the production of specific σ complexes, but they cannot predict the course of the subsequent rearomatization.

0009-2665/81/0781-0267$06.00/0

TABLE I. Production and Properties of Some Recoil Atoms

isotope	production	threshold energy, MeV	recoil energy, MeV	half-life	decay mode (energies in MeV, max β energies)
^{34m}Cl	$^{35}Cl(n,2n)^{34m}Cl$	13.1	$<{}^{1}/_{18}(E_n - 13.1)$	32.0 min	β^+ (1.35-2.47-4.50) γ (1.18-2.13-3.30)
^{38}Cl	$^{37}Cl(n,\gamma)^{38}Cl$	0	$<0.53 \times 10^{-3}$	37.3 min	β^- (1.11-2.77-4.81) γ (1.64-2.16)
^{18}F	$^{19}F(n,2n)^{18}F$	10.9	$<{}^{1}/_{10}(E_n - 10.9)$	110 min	β^+ (0.64)
^{18}F	$^{19}F(\gamma,n)^{18}F$	10.9	$<{}^{1}/_{19}(E_\gamma - 10.9)$		
^{11}C	$^{12}C(n,2n)^{11}C$	20.3	$<{}^{2}/_{13}(E_n - 20.3)$	20.4 min	β^+ (0.96)
^{14}C	$^{14}N(n,p)^{14}C$	0	0.042	5730 y	β^- (0.16)
T	$^{3}He(n,p)T$	0	0.20	12.3 y	β^- (0.019)
T	$^{6}Li(n,\alpha)T$	0	2.73	12.3 y	β^- (0.019)
Mu	decay π^+	0	$\geqslant 4.2$	3.2 μs	β^+ (52)

The direct loss of one of the substituents or of a hydrogen atom and the abstraction by one of the reactants present are considered as the two main reaction channels.[1] A possible third reaction channel for a σ complex—the addition to another aromatic molecule leading to dimerization or even further polymerization—is hardly discussed in common radical substitution reactions, but it is one of the most important pathways in the radiation and recoil atom chemistry of aromatic compounds.[11,12]

Free-radical abstraction reactions with aromatic compounds have been reported. Dorrepaal and Louw[13,14] found that the first step in the formation of dichlorobenzenes by the reaction of chlorine atoms with gaseous chlorobenzene is the abstraction of a H atom, yielding HCl, followed by reaction with Cl_2:

$$\cdot Cl + C_6H_5Cl \rightarrow \cdot C_6H_4Cl + HCl$$

$$\cdot C_6H_4Cl + Cl_2 \rightarrow C_6H_4Cl_2 + \cdot Cl$$

Aromatic hydrogen abstraction by a fluorine atom is energetically very possible, but, at least in the gas phase, addition prevails. Moehlmann et al.[15] reported a value of 3 for the addition/abstraction ratio with benzene whereas from the experiments of Cramer et al.,[16] in the presence of large amounts of O_2, a value >1.5 can be deduced. When toluene is used as the target compound, benzylic hydrogen abstraction by fluorine atoms is a favorite reactive channel.[17] In the case of hydrogen atoms, the observed formation of HD from gaseous C_6D_6[18] and CH_4 from $C_6H_5CH_3$[19] proceeds through an intermediate σ complex that can rearomatize through direct elimination of the molecules or through abstraction by a second hydrogen atom.

II. Recoil Atom Chemistry

Radioisotopes are often used in inorganic chemistry as tracers for the elucidation of reaction mechanisms. It is then assumed that these isotopes behave in exactly the same manner as their nonradioactive counterparts. In addition, tritium is also used for the determination of isotope effects and can provide information about rate-determining steps in complicated reactions. A far less known application of radiochemistry in the study of organic reaction mechanisms is the use of translational excited radioisotopes, produced by a nuclear reaction (recoil chemistry).

A. Production of Recoil Atoms

Table I compiles the nuclear reactions through which the isotopes that are extensively discussed in this article are produced: by thermal neutrons (n_{th}) in a nuclear reactor, by fast neutrons ($E \geq 10$ MeV) from a cyclotron, or with high energy photons from an electron accelerator. For the production of positive pions, the precursors of positive muons, high-energy proton or photon beams ($E > 140$ MeV) are used. Radioisotopes produced in a nuclear reaction receive an enormous amount of kinetic (recoil) energy that can be calculated by applying the laws of conservation of energy (mass) and of impulse. The recoil energies are incorporated in Table I. Depending on the nuclear reaction and the recoil energy, the high energetic radioisotopes can be produced as neutral or as ionized particles, whereas they loose their recoil energy by (ionizing) collisions with the molecules of the surrounding medium. In the case of Cl, F, and H ions, it is assumed that during their deceleration these particles become neutralized[11,20], and that they reach the chemical reactive zone (<20 eV)—where chemical reactions leading to stable radioactive compounds can take place—as neutral ground-state atoms with only an excess of kinetic energy.[21] However, Können et al. found that in gas-phase collisions of halogen atoms with energies above 5 eV ionization may occur, but no absolute cross sections were given.[22] In the case of recoil bromine, iodine, and astatine, ground-state and electronically excited atoms as well as ions must all be considered to be present as reacting species in the reactive zone, and it is experimentally very difficult to attach the final labeled products to the results of a specific reaction. Whereas this article deals with reactions of recoil atoms, only a short literature review will be given on the reactions of the three heaviest recoil halogens with aromatic compounds.

B. Special Features of Recoil Chemistry

The research of the reactions of translational excited atoms is called "hot atom chemistry". Hot atoms can be produced by a variety of methods: photolysis, nozzle techniques,[23] sputtering, neutralization of high-energy ion beams in chemical accelerators,[24-26] and, as mentioned above, nuclear reactions.[11,12] This review deals with the research of radioactive recoil atoms, but comparisons with reactions of thermal atoms will be made when possible.

1. Hot Reactions

Recoil particles with energies above about 20 eV will not lead to radioactive, stable chemical compounds. After being slowed down below this energy, the recoil particle enters the chemical reactive zone from the high-energy side and can give rise to the formation of labeled fragmentation products, to ring opening and C–C bond scission, and to hot abstraction, displacement, and addition reactions.[27] A real hot hydrogen replacement reaction in substituted benzenes should result in a statistical ortho, meta, and para distribution, because directive effects of the substituent should have no influence on the direction of attack of the fast-moving hot atom.

2. *Thermal Reactions*

Recoil atoms that do not react in the hot zone will become thermalized by multiple collisions and will further behave as thermal atoms, giving rise to diffusion-controlled chemical reactions. However, if the reaction constant is not too small, reaction can also occur in the epithermal zone, with transfer of some extra excitation energy to an intermediate complex. In condensed phases, the recoil atom can loose its last amount of kinetic energy in a cage at the end of its track and can then react by thermal combination with radicals formed in this cage.[28]

3. *Scavengers*

Scavengers are often added to the irradiated system to distinguish between hot or thermal reactions. A scavenger is a compound that has a much higher rate constant ($>10^2$–10^3) for reaction with a thermal recoil atom than the medium itself, so that it will surpress those thermal reactions even when it is present in low concentrations ($<10^{-2}$). This means that scavengers can only be used if the collision efficiency for the thermal reaction is smaller than 10^{-3}. Similarly, scavengers can also distinguish between reactions of excited and thermal radicals and complexes. Scavengers that are commonly used in liquid-phase recoil chemistry are halogens (Br_2, I_2), unsaturated compounds, DPPH (diphenylpicrylhydrazil),[7] and in the gas phase compounds with an unpaired electron (O_2, NO).

4. *Carrier-Free Nature*

It must be realized that in recoil experiments the number of radioactive atoms is very low whereas the reaction of almost a single radioactive atom can be followed due to extremely high efficient detection techniques. The labeled products are also present in very low—carrier-free—concentrations and can therefore not be identified by normal UV, NMR, etc. techniques, but they can only be detected via the decay of the radioactive label. Chemical identification of the labeled products can take place by addition of mass amounts of the expected products (carriers) before the chemical separation.

III. Experimental Aspects

A. Irradiations

The recoil radioisotopes are produced through the irradiation of the aromatic compounds sealed in small glass or quartz ampoules. For prevention of reactions of thermal recoil atoms or labeled radicals with dissolved oxygen, the air in the samples is in general removed by using the freeze–thaw technique. For the experiments with radiochlorine or radiofluorine, halogenated aromatic compounds were irradiated; in the case of tritium ^3He was used for gas-phase experiments and LiF, Li_2CO_3, or lithium containing glass powder for condensed-phase experiments. Energetic negative muons were produced outside the target area and magnetically deflected into the ampoule. A serious problem in the study of recoil chemistry is formed by radiation-induced side reactions: the accompanying—often intensive—radiation fields may result in the formation of radicals that can react with thermal recoil atoms or labeled radicals or molecules. Therefore, the influence of radiation damage must be evaluated for all systems.

B. Product Analysis

For determination of the individual yields of labeled products four separation techniques are involved: (a) separation of labeled organic products (organic yield) from inorganic activities (inorganic yield) by shaking the irradiated organic liquid with an aqueous solution; (b) separation of gaseous and low-boiling (<573 K) organic compounds by GLC techniques (small mass amounts of compounds that are to be expected as labeled products are often added before injection; the identification of labeled products follows then from their simultaneous elution from the GLC with the added carrier); (c) separation of high-boiling compounds (polymers) by thin-layer chromatography or by gel filtration (e.g., by Sephadex LH20 columns, eluted with $CHCl_3$); (d) determination of the position of T or ^{14}C in labeled molecules by chemical decomposition and further analysis.

The detection of the radioisotopes can be performed with all kinds of radiation detectors. The effluent of the GLC can discontinuously be trapped by several techniques and counted afterwards (off line) or the effluent can be radioassayed continuously (on line) with suitable window or windowless proportional counters or well-type NaI(Tl) crystals. The effluent of Sephadex columns can be counted off line and also on line with flow-through scintillation detectors. Special precautions must be taken in case more than one radioisotope is present in the sample, e.g., ^{11}C, ^{18}F, and ^{34m}Cl after a fast neutron irradiation of C_6H_4FCl. The radioassay of tritium with windowless flow-through proportional counters or in the case of $CHCl_3$ solutions in gel filtration experiments with a liquid scintillation detector demands special quenching corrections.

IV. Reactions of Recoil Atoms

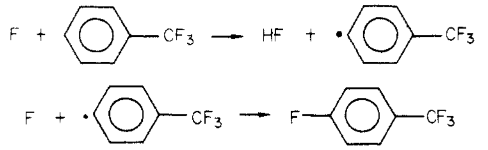
A. Fluorine

Liquid-phase reactions of fluorine atoms with aromatic compounds have exclusively been studied with recoil ^{18}F atoms, and as a consequence the only comparison with the results of the reactions of thermal fluorine atoms are those measured in gas-phase experiments. In 1976 a review article on thermal gas-phase reactions of fluorine atoms was published by Jones and Skolnik.[29] The article of about 30 pages contained only half a page on the reaction with aromatic compounds (six references). Since 1975 five more papers were published on the same subject. The main conclusions that can be drawn from these gas-phase contributions with regard to the overall reactivity and addition, substitution, and abstraction reactions are the following:

(a) Thermal fluorine atoms are very reactive toward aromatic compounds; for benzene, one out of two collisions leads to reaction. (This can be concluded from relative rate constants of thermal ^{18}F atoms toward CH_4, C_2H_2, and C_6H_6 (1:2.5:3.75)[16] as well as from relative rate constants for hydrogen abstraction from CH_4, C_6H_6, SiH_4, and GeH_4 (1:1:6.5:6),[30] in combination with a value of 3 measured for substitution of hydrogen relative to abstraction in C_6H_6.[15]) The collision efficiency with SiH_4 and GeH_4 is almost 1.

(b) Addition of a fluorine atom to benzene—resulting in the monofluorocyclohexadienyl radical—was first observed by Cochran et al.[31] Cramer et al. found that such radicals are formed with high yields: about 50% in benzene and about 30% in toluene and benzotrifluoride.[16] In a collision with another aromatic molecule dimerization will probably take place, whereas a reaction with oxygen can lead to hydrogen abstraction.

(c) Fast substitution reactions, proceeding through the unimolecular decomposition of a reactive complex, have been observed by Shobatake et al.,[32] Moehlmann et al.,[33] and Moss et al.[34] The vibrational energy is statistically distributed over the fluorobenzene after the substitution of H, Cl, Br, I, or CH_3 by a F atom. In chlorotoluenes only the fluorotoluenes were detected, indicating that a Cl atom is more easily substituted than a CH_3 group (nonstatistical energy distribution is observed in substitution of H and CH_3 in olefinic substrates). Fluorine substitution in fluorobenzene by thermal ^{18}F atoms proceeds for less than 0.3%.[16] Gas-phase substitution of hydrogen atoms has been reported by several groups, but a discussion is hampered because of contradictive results. Vasek, Jeffrey, and Sams[35-37] have studied the fluorination of bromobenzene, fluorobenzene, and benzotrifluoride. The total yields and the *o*:*m*:*p* distribution depend strongly on the relative amount of F_2. The authors suggest that the mechanism of the substitution proceeds as



Cramer et al.[16] found a yield of 7% fluorobenzene in a mixture of 3000 torr of SF_6 and 50 torr of C_6H_6 (thermal recoil ^{18}F atoms), which value increased to 60% on the addition of 500 torr of O_2. Cipollini et al.[17] also get high yields in a mixture of 760 torr of CF_4 and 2 torr of C_6H_6 (radiolysis), but addition of 18 torr of O_2 had absolutely no influence on the product yield. Some of the results are given in Table II.

(d) Hydrogen abstraction has been observed by Moehlmann et al.[15] and Smith et al.,[30] through the measurement of vibrational modes of HF. From the abstraction ratios given in both references the relative rate constant per hydrogen atom for methane, the methyl group in toluene, and benzene can be calculated as about 12:3:1. Abstraction of CH_3, Cl, Br, and I from substituted benzenes was observed through the appearance of $\cdot C_6H_3$.[33]

TABLE II. Thermal Atomic Fluorination of Gaseous Aromatic Compounds (C_6H_5X)

X	additive	relative yields *o*	*m*	*p*	absolute yield, %	ref
H					9	16, *a*
	65 kPa of O_2				60	
F		37	15	48	7	16, *b*
	O_2	4	53	43	38	
CF_3		22	55	22	4.5	16, *c*
	O_2	13	61	26	38	
H					0.68[d]	17, *e*
	O_2				0.75	
CH_3		36	30	40	1.91	17, *f*
	O_2	36	30	40	1.92	
Br		38	16	46		35
F		30	20	50		36

[a] 400 kPa of SF_6, 6.5 kPa of C_6H_6. [b] 400 kPa of SF_6, 5.2 kPa of C_6H_5F. [c] 400 kPa of SF_6, 1.3 kPa of $C_6H_5CF_3$. [d] *G* values. [e] 100 kPa of CF_4, 0.26 kPa of C_6H_6. [f] 100 kPa of CF_4, 0.26 kPa of $C_6H_5CH_3$.

TABLE III. X-Substitution Yields (%) by Recoil ^{18}F Atoms in *p*-C_6H_4FX and C_6F_5X[45,46]

X	X-substitution yield *p*-C_6H_4FX	C_6F_5X	bond strength, kJmol^{-1} [a] C_6H_5-X	C_6F_5-X
H	2.1	1.8	460	477
F	2.3	1.9	523	477
Cl	6.3	9.6	397	385
I	2.1	5.1	268	276
CH_3	1.5	0.9	418	439
CF_3	1.0	1.6		251
CN	nm	1.1		
CHO	2.2	nm		
OCH_3	3.2	nm	410	
NH_2	1.1[b]	nm	435	

[a] "Handbook of Chemistry and Physics", 60th ed.; CRC Press: Cleveland, OH; 1979/1980; F-241. [b] *o*- and *m*-$C_6H_4FNH_2$.

Recoil ^{18}F atom experiments in the liquid phase are mainly performed with fluorobenzenes that contain the ^{19}F atoms needed for the nuclear reaction. In case of nonfluorinated arenes, addition of perfluorobenzene or perfluorobiphenyl provides the necessary amount of fluorine atoms. The first ^{18}F experiment was performed 25 years ago by Aten et al.[38] and dealt, like some other investigations,[39,40] with the determination of the inorganic yield. Anbar and Neta[41] measured the yield of labeled substituted products in various fluorobenzenes using distillation as the separation technique.[42] More detailed information was gained by van Dulmen and Aten[43] in their investigations with perfluorobenzene and perfluorotoluene, by Berei and Vasâros[44] with fluoro- and chlorobenzene, and by Brinkman et al.[45-47] and Bakker et al.[48] submitting information on benzene, 10 fluorobenzenes, and 21 substituted fluorobenzenes. "Regarding the very high reactivity of thermal fluorine atoms towards gaseous arenes, it can be expected that recoil ^{18}F atoms react with gaseous and liquid arenes as hot atoms and that they will not become thermalised".

1. Substitution

Table III lists the substitution yields for several atoms and groups by recoil ^{18}F atoms. In general, the yields are in the order of 1–3%, whereas bond strengths do not seem to be involved to a large extent. It was proposed that these reactions proceed by hot fluorine atoms.[46] The rather high yields for chlorine substitution—also observed with *p*-chlorobenzotrifluoride (5.7%)—were not well understood. As was mentioned before, thermal substitution of Cl, Br, I, and CH_3 was observed in the gas phase, but no yields or cross sections were given.[32-34] (Molecular fluorination of liquid bromobenzene resulted also in fluorobenzene, a compound that was not detected in the fluorination of liquid chlorobenzene, whereas in the case of liquid iodobenzene no recognizable products were found.[49]) Substitution of fluorine and hydrogen atoms by recoil ^{18}F atoms will be discussed separately.

a. Fluorine substitution

Cramer[16] has measured a thermal ^{18}F-for-F substitution yield in gas-phase experiments of 0.26% for *m*-difluorobenzene and of less than 0.1% for benzotrifluoride (per fluorine atom). In recoil ^{18}F chemistry the fluorine substitution yield in gaseous monofluorobenzene is 3.6%, not much different from the results obtained in the liquid phase: (3.1 ± 0.2)%.[45,50] The yield per fluorine atom bound to the aromatic ring decreases somewhat by enhanced fluorine substitution in the liquid phase: from 3.1% for monofluorobenzene to about 2% for penta- and hexafluorobenzene, with an average value for all the fluorinated benzenes of (2.3 ± 0.2)%. This value for aromatic bound fluorine atoms is in the same order as substitution yields of fluorine in trifluoromethylarenes: 1.6% per fluorine atom in benzotrifluoride and 2.6% in *p*-chlorobenzotrifluoride. In the solid phase only perfluorobenzene was investigated, and the substitution yield per fluorine atom is (3.0 ± 0.2)%.[43] It seems that for recoil ^{18}F atoms the fluorine substitution yield in arenes does not depend very much on: (a) the phase (gas or liquid), (b) the number of fluorine atoms, or (c) the nature of the C-F bond (aromatic or aliphatic). All these observations led to the conclusion that the observed substitution yields with recoil ^{18}F atoms were obtained through a hot reaction,[20] which means that a very fast reaction is involved, without the formation of an intermediate π or σ complex. Hot substitution reactions should proceed without any selectivity and should result in a statistical distribution, e.g., in pentafluorobenzene, but unfortunately this kind of information is still lacking. Scavengers such as I_2, unsaturated compounds, and DPPH do not affect the fluorine substitution yields. This is not surprising, because the arenes are "self-scavenging" toward fluorine atoms.[45-48]

b. Hydrogen Substitution

The lowest yield for the substitution of a hydrogen atom bound to the ring of liquid aromatic compounds is 1.3%, the highest yield is 2.3%, and averaged over 17 compounds a value of (1.6 ± 0.1)% can be calculated. With gaseous monofluorobenzene (at 373 K) a yield of 0.9% per hydrogen atom was measured. In two liquid fluorotoluenes the substitution yield per benzylic hydrogen atom was also 0.9%.[45,46] No benzylic hydrogen substitution was observed in the reaction of thermal fluorine atoms with gaseous toluene,[17,51] which means that the substitution by recoil ^{18}F atoms is mainly a hot process. However, more information is obtained from the relative yields of the ortho, meta, and para isomers formed with monosubstituted compounds (Table IV). In the absence of Br_2 or I_2 the substitution is, within experimental error, almost statistical for the three investigated compounds, typical for a hot process. However, in the case of monofluorobenzene there is a deviation from a statistical distribution,[45] the ortho yield being somewhat lower and the para yield somewhat higher. This is more or less confirmed by the agreement between measured substitution yields in *o*- and *m*-difluorobenzenes and calculated yields (Table V). The calculations were performed by applying the additivity principle on the yields measured in monofluorobenzene. The substitution pattern is absolutely different from that observed in the gas-phase fluorination of monofluorobenzene and benzotrifluoride by thermal atoms (Table I) and from fluorination with molecular F_2 of liquid fluorobenzene (*o*:*m*:*p* 22:13:65),[49] benzotrifluoride (16:64:20[49] and 26:61:30[52]), and chlorobenzene (40:16:46[49] and 23:8:69[53]).

TABLE IV. Hydrogen Substitution by Recoil ^{18}F Atoms in Liquid Aromatic Compounds

		relative yields			absolute total	
compound	additive	*o*	*m*	*p*	yield, %	ref
C_6H_5F		31	40	29	11.9	44
		31	46	23	9.0	45
		38	35	27	8.8	48
C_6H_5F	1% I_2	44	29	27	15.9	44
	1% I_2	43	28	29	11.9	45
	2% Br_2	42	28	30	12.5	48
C_6H_5Cl		37	35	28	nm	45[a]
	1% I_2	40	31	29	14.8	44[b]
	1% I_2	44	29	27	nm	45[a]
$C_6H_5CF_3$		41	38	21	9.9	45
	1% I_2	32	43	25	12.8	45

[a] Mixture with 10% perfluorobiphenyl. [b] Mixture with 50% perfluorobenzene.

TABLE V. Additivity for Hydrogen Substitution by Recoil ^{18}F Atoms

		yields, %	
compound	product	calcd[a]	exptl
o-$C_6H_4F_2$	1,2,3-$C_6H_3F_3$	2.7	2.9
	1,3,4-$C_6H_3F_3$	3.9	3.7
m-$C_6H_4F_2$	1,2,3-$C_6H_3F_3$	1.1	1.4
	1,2,4-$C_6H_3F_3$	3.2	3.2
	1,3,5-$C_6H_3F_3$	2.4	2.0

[a] Calculated from relative *o*, *m*, *p* yields in C_6H_5F, given in ref 45.

The addition of small amounts of Br_2 or I_2 has a remarkable effect on the hydrogen substitution yields. First, the total yield is increased in monosubstituted benzenes with, on the average (35 ± 4)% and in disubstituted benzene with (27 ± 9)%. Second, this increase is very selective, favoring the ortho and para isomers for monofluorobenzene (and comparable effects in *m*-difluorobenzene) and the meta and para isomers in benzotrifluoride (Table VI). Third, the change in the ortho:meta:para yield ratio observed in gaseous monofluorobenzene due to added I_2 is equal to the change in the liquid phase. It must be concluded that a special thermal process, in which Br_2 or I_2 has a definite role, leads to enhanced substitution. In order to explain these findings, several reaction pathways were discussed,[45,48] but the most likely explanation is the formation of a long-lived ^{18}F-containing σ complex, for which rearomatization two alternatives were proposed: (1) hydrogen abstraction by Br_2 (I_2)[45] or (2) the

TABLE VI. Hydrogen Substitution Yield Ratios (with/without Br_2 or I_2) for Recoil ^{18}F Atoms

compound	additive	yield ratios			ref
		$C_6H_4F_2$			
		o	m	p	
C_6H_5F	1% I_2	1.89	0.96	1.26	44
	1% I_2	1.88	0.79	1.67	45
	2% Br_2	1.61	1.12	1.54	48
		av 1.8 ± 0.1	1.0 ± 0.1	1.5 ± 0.1	
		$C_6H_3F_3$			
		123	124	135	
m-$C_6H_4F_2$	1% I_2	1.42	1.84	0.70	45
	2% Br_2	1.94	1.70	0.67	48
		av 1.7 ± 0.2	1.8 ± 0.1	0.7 ± 0.1	
		$C_6H_4FCF_3$			
		o	m	p	
$C_6H_5CF_3$	1% I_2	1.0	1.5	1.5	45

formation of [^{18}F]fluorobromo(iodo)cyclohexadiene that subsequently eliminates HBr (HI), either almost directly or later during GLC analysis.[48] The increase found in the thermal ^{18}F-for-H substitution yield on the addition of oxygen to gaseous systems could only be explained by some reaction of oxygen with a long-lived ^{18}F-containing cyclohexadienyl radical.[16]

2. Polymerization and Fragmentation

The formation of polymeric species (tars) is very well-known in molecular fluorination of aromatic compounds, and this has prevented systematic research, until the controlled reaction—by a stream of a N_2/F_2 mixture flowing through a diluted solution of arenes in inert solvents—was developed.[49,53] In recoil ^{18}F chemistry van Dulmen and Aten were the first investigators who reported the formation of high yields of polymerization and fragmentation products[54] in liquid perfluoroarenes.[43] In Figure 1 a radiogas chromatogram is shown for liquid pentafluorobenzene in which a number of unidentified labeled products can be distinguished. At the moment the following trends and conclusions have been noticed:[43-48]

(a) The first step in the formation of these ^{18}F-containing compounds is the addition of a ^{18}F atom, thereby forming an excited cyclohexadienyl radical.

(b) The addition of 1% I_2 has no effect on the total yield of polymerization and fragmentation products, which means that dimerization must be a very fast process. (The effect of the addition of 2% Br_2 is not straightforward; for some compounds the yield of polymeric species as well as the maximal polymer chain length is decreased; for other compounds no changes were observed.)

(c) In the presence of 2% Br_2 the maximal polymer chain length corresponds to at least four cyclohexadienyl units (this is also observed in unscavenged perfluorobromobenzene). This means that polymerization up to 4 units is a very fast process and that a large amount of excitation energy must be involved (as will be discussed in the chapter on the polymerizastion by recoil chlorine and tritium atoms, the yields of these labeled compounds are drastically influenced by the addition of I_2 or other scavengers). It was therefore proposed that the formation of polymers is initiated by hot atoms.

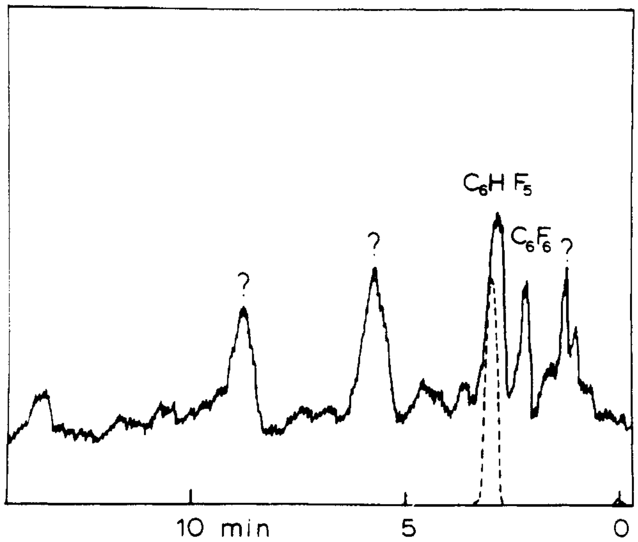


Figure 1. Radiogas chromatogram of irradiated C_6HF_5 (^{18}F): (—) log radioactivity signal, (- - -) mass signal. Column: silicon gum rubber on firebrick.[45]

(d) The yields of polymers and fragmentation products increases with enhanced fluorination from about 15 and 0% for benzene to almost 40–50 and 20%, respectively, for perfluorobenzenes, at the cost of the inorganic fractions. It seems that there are other reaction channels—besides the dimerization reaction—for excited [^{18}F]fluorocyclohexadienyl radicals: (i) as will be further discussed in the next section (dealing with inorganic ^{18}F yields), it seems likely that $H^{18}F$ is formed by fast elimination from such a radical; (ii) as the number of hydrogen atom attached to the ring decreases, the possibility of $H^{18}F$ elimination diminishes and ring opening and fragmentation reactions can occur (it has been proposed that "reduced aromaticity" enhances this kind of reaction,[46] but from the moment that the cyclohexadienyl radical is formed, its further reactions are predicted by arguments such as energy randomization through the molecule, bond strength, collisional stabilization, etc.).

(e) The yield of polymerization products for gaseous monofluorobenzene (3%) is much lower than for the liquid phase (18%). In the liquid phase excitation energy can easily be transferred to neighboring molecules. In the gas phase unimolecular decomposition—by $H^{18}F$ elimination from a $\cdot C_6H_4F^{18}F$ radical—can be more important and will result in a lower polymer yield in the case of C_6H_5F. Unfortunately, no product yields are reported for gas-phase experiments with perfluorobenzenes. In the solid phase also only one experiment was performed: perfluorobenzene with a polymer yield of 47%, somewhat lower than the 57% yield obtained in the liquid phase.[43]

(f) The yield of polymerization products is low for the three monofluoroanilines (about 10%) and very low for perfluorobenzonitrile (18%) when compared with the other compounds. The behavior of the anilines was explained by the efficient hydrogen-donating properties of the NH_2 group, yielding $H^{18}F$, either by a direct reaction with a ^{18}F atom or with ^{18}F already bound to an aniline molecule. The polymer yield was calculated from the total organic yield (~12%) which was determined through extraction with an aqueous solution containing 3 mol % NaOH and 3 mol % NaF, and it cannot be excluded that carrier-free, labeled organic

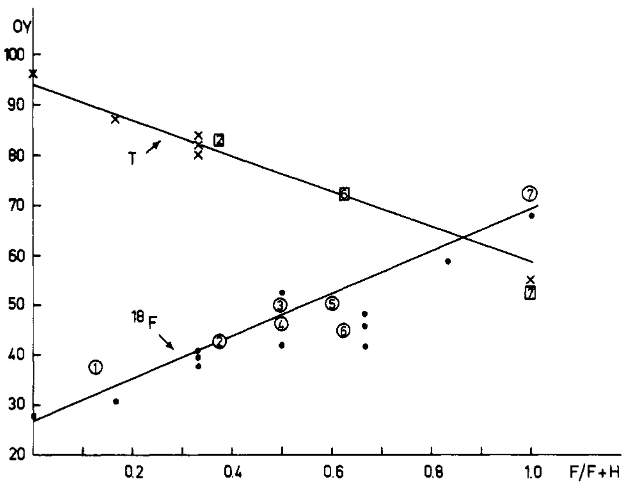


Figure 2. Absolute organic yields (%) for the reactions of T and ^{18}F with fluorinated benzenes and toluenes: (●) $C_6H_xF_{6-x}$ + ^{18}F, (×) $C_6H_xF_{6-x}$ + T, (1) *p*-$C_6H_4FCH_3$ + ^{18}F, (2) $C_6H_5CF_3$ + ^{18}F (T), (3) *p*-$C_6H_4FCF_3$ + ^{18}F, (4) *p*-$C_6F_4HCH_3$ + ^{18}F, (5) *m*-$C_6H_4(CF_3)_2$ + ^{18}F, (6) $C_6F_5CH_3$ + ^{18}F (T), (7) $C_6F_5CF_3$ + ^{18}F (T).[46] Yields of T are indicated by numbers in squares.

products are extracted into the aqueous phase.

3. *Abstraction and Inorganic Products*

Abstraction of an atom or a group by a thermal or hot ^{18}F atom does in general not lead to a product that can be recognized as such, because—with the exception of CH_3 and CF_3 groups—all the other abstraction products will be extracted by the aqueous solution and contribute to the inorganic yield. No effort was undertaken to determine $CH_3{}^{18}F$ or $CF_3{}^{18}F$ yields. However, it can be expected that those yields are low and in the same order of magnitude as their displacement yields (~1%), because in the reactions of recoil ^{38}Cl atoms with benzotrifluoride the displacement and the abstraction yields of the CF_3 group were both 1.1%,[55] whereas 3.2% CH_3T and 4.9% C_6H_5T were measured in the reactions of recoil tritium atoms with toluene.[56]

In fluorobenzenes (with no other substituents than hydrogen and fluorine atoms) the inorganic yield decreases linearly—as a function of the fraction of fluorine atoms—from 72% for benzene to 32% for perfluorobenzene.[45] (In ref 48 lower yields are given for deoxygenized samples, but the data used in ref 45 and 46 will be used.) If thermal hydrogen abstraction is an important reaction channel, then it should be expected that through the introduction of CH_3 groups the inorganic fraction should increase considerably due to benzylic hydrogen abstraction, but this does not happen, as can be seen in Figure 2: no extra inorganic activities are formed with the fluorotoluenes. Two reaction mechanisms were proposed:[45] (a) hot hydrogen abstraction—if the hot abstraction yield is not much different for aromatic and benzylic hydrogen atoms, than it is easily understood that the inorganic yields for compounds containing CH_3 or CF_3 groups fit very well on the curve in Figure 2; (b) elimination of $H^{18}F$ from an excited ^{18}F complex—in this case only the number of hydrogen atoms bound to the aromatic ring should predict the inorganic yield. Taking into consideration the opposite effect found with recoil tritium atoms (Figure 2, discussion in the chapter on tritium reactions), this reaction channel is considered to be of great importance.

TABLE VII. Thermal Atomic Chlorination of Gaseous C_6H_5X Compounds

	relative yields			
X	*o*	*m*	*p*	ref
Cl	32	24	44	17, *a*
CH_3	40	22	38	
F	3	74	23	13, *b*
Cl	7	68	25	
CF_3	6	58	36	

[a] Radiolysis of 13 kPa of CCl_4, 0.26 kPa of C_6H_5X at 310 K. [b] Photolysis of Cl_2 at 378 K.

B. Chlorine

Only four publications report on gas-phase arene studies with thermal chlorine atoms that are produced by several techniques: moderation of energetic recoil ^{38}Cl atoms,[5] radiolysis of CCl_4,[17] and photolysis of Cl_2.[13,14] Dorrepaal and Louw proved that the primary reaction of photolytically produced chlorine atoms is the abstraction of hydrogen, followed by secondary reactions that can lead to chlorinated aromatic compounds. In these experiments the reaction partner is Cl_2, whereas in the case of the radiolysis experiments several partners are available, such as Cl, Cl_2, CCl_4, and phenyl radicals. Differences between the reaction partners are probably responsible for the observed differences in the ortho, meta, and para yields, measured in substituted benzenes by both techniques (Table VII). The hydrogen abstraction mechanism is confirmed by the observation that in the radiolysis of CCl_4–C_6H_6 mixtures high yields of benzotrichloride are found, a compound that can only be formed by the recombination of $\cdot CCl_3$ and $\cdot C_6H_5$ radicals.[17] The relative yields of benzylchloride and chlorotoluenes found in the radiolysis of CCl_4–$C_6H_5CH_3$ mixtures leads to a rate constant for benzylic hydrogen abstraction that is a factor of 3.5 larger than for phenylic abstraction.[17] In the liquid phase other substitution reactions have been observed. Chlorodebromination was reported in six publications between 1890 and 1954.[57] The reaction mechanism involving chlorine atoms was thought to proceed through a rearrangement of an initial loose π complex—as was observed by Bühler et al.[58]—or through a relative stable σ complex.[3,59,60] Ipso substitution is now supposed to be a very likely reaction mechanism, which involves an ipso cyclohexadienyl transition state.[1,2,10] Thermal chlorodeiodination and denitration were observed by Milligan et al., whereas chlorodechlorination was observed with radioactive ^{36}Cl atoms formed by the photolysis of $Cl^{36}Cl$.[3] (The replaced nonradioactive chlorine atom can again react by ipso attack, but how many of these reactions cycles are involved before hydrogen abstraction takes place cannot be measured with radiochlorine.)

Many publications on chlorine recoil chemistry deal with the measurements of total organic yields, through which important information can be gained by applying scavenger experiments and competition experiments in mixtures.[61–67] A computer analysis of the data obtained for a two-component mixture can give hot and thermal yields for the pure compounds A and B and relative reactivities for hot ($S = \sigma_A/\sigma_B$ and thermal ($S' = \sigma_{A'}/\sigma_{B'}$ reactions. In Table VIII S and S' values are given for some binary mixtures.[66,67] More detailed information is obtained by the determination of individual product

TABLE VIII. Relative Reactivities of Chlorobenzene Mixtures for First (S) and Second (S′) Zone Reactions[65d,66]

compound		$S = \sigma_A/\sigma_B$	$S' = \sigma_{A'}/\sigma_{B'}$
A	B		
CH_3OH	C_6H_5Cl	1.1	9
C_2H_5OH		1.3	17
n-C_6H_{14}		3.0	26
c-C_6H_{12}		1.8	33
CH_3OH	o-$C_6H_4ClCH_3$	0.8	21
C_3H_7OH		1.9	11
C_4H_9OH		3.0	63

yields using gas chromatographic and gel filtration techniques. Yield determinations for non-chlorine-containing arenes are normally performed in mixtures with CCl_4 by extrapolating to 0 mol % CCl_4.[4-8,68-73]

1. Substitution

Table IX compiles the substitution yields in liquid arenes for several atoms and groups by recoil ^{38}Cl atoms, and it is obvious that there are two classes of substituents. The first class (F, CH_3, NH_2) contains the compounds for which the substitution process is endothermic. The yields are not affected by scavengers and are in the same order of those observed with recoil ^{18}F atoms, and it seems therefore that a hot process is involved.[5] There is general agreement about the involvement of hot substitution reactions in recoil chlorine chemistry; however, there are several possible reaction mechanisms: (a) a direct hot one-step substitution reaction;[4,6] (b) a hot addition reaction, followed by the decomposition of the formed excited cyclohexadienyl radical;[4,5] (c) recombination between the recoil chlorine atom and radicals trapped in a solvent cage (not in the gas phase).[65,66,73] In gas-phase experiments with fluorobenzene, hydrogen substitution seems to proceed entirely via a direct substitution process, but fluorine substitution—the yield for this reaction being a factor of 10–15 higher—cannot be explained by such a process.[5]

The substitution yields of the second class of compounds (Table IX) are lowered on the addition of scavengers, which proves that besides hot substitution—with yields of some percent—a thermal reaction mechanism is also involved. Whereas most of the available information deals with the (thermal) substitution of chlorine and hydrogen atoms, this subject will be discussed separately.

a. Chlorine Substitution

The thermal substitution yield in chlorobenzene for recoil ^{38}Cl atoms is in the order of 20–30% (Table X), but in two kinds of experiments quite different yields were measured. A high thermal yield of about 50% was found at high radiation doses, which effect was explained by radiation-induced conversion of a part of the inorganic ^{38}Cl fraction into ^{38}Cl atoms, that to a large extent will react by ipso substitution.[8] Low thermal yields of 11–15% were found with recoil ^{34m}Cl atoms; this effect was attributed to higher recoil energies for ^{34m}Cl atoms (≥18.5 eV) than for ^{38}Cl atoms (41% between 6 and 8 eV, 59% above 36.9 eV). Due to the differences in the nuclear reactions, the complex cascade of γ transitions through which both isotopes reach the ground state, and the time scales involved in the cascade and in all kinds of chemical reactions, it is at the moment unfeasible to discuss the observed effects in more detail.

Several mechanisms were proposed for aromatic chlorine substitution by thermal recoil chlorine atoms: (i) formation of a π complex that can lead to substitution via a concerted one-step mechanism;[6] (ii) ipso substitution;[5,8] (iii) caged recombination between a radiochlorine atom and a phenyl radical.[73]

Thermal substitution yields depend to a large extent on the kind and amount of added compounds. (i) The effect of small concentrations (≤1 mol%) of bromine or iodine is illustrated in Table X (chlorine has no effect[69]). The observation that iodine decreases the ^{38}Cl-for-Cl substitution yield much more than 50% was considered as an indication that iodine does not abstract a ^{38}Cl atom from an ipso σ complex but that it reacts directly with thermal chlorine atoms, either free or loosely bound in a π complex.[6] (ii) A decrease of the $C_6H_5{}^{38}Cl$ yield to the level as measured in bromine- and iodine-scavenged chlorobenzene was also observed on the addition of low concentrations (1–4 mol%) of organic compounds such as diphenylpicrylhydrazyl (DPPH), cycloheptatriene (CHT), and 2,3-dimethyl-2-butene (DMB), which are also efficient scavengers for thermal chlorine atoms in aromatic systems.[7,8] (iii) Competition experiments were performed with compounds that react with thermal chlorine atoms at a rate constant comparable with that of ipso substitution. An example of this class of compounds is pentane, which reacts with thermal chlorine atoms, free or bound in a π complex, by hydrogen abstraction. About 20 mol % pentane halves the yield of $C_6H_5{}^{38}Cl$ in chlorobenzene. (iv) Addition of compounds that are inert toward thermal chlorine atoms (e.g., perfluoroheptane and perfluorobenzene) has no decreasing effect on the substitution yield, but rather enhances it. Within the model of cage reactions this was explained by the properties of a cage wall consisting of these inert perfluoro compounds.

All these experiments do not give a definite answer to the question whether thermal ^{38}Cl-for-Cl substitution proceeds through diffusion-controlled reactions or in a reaction cage.[73] The preference of thermal chlorine

TABLE IX. X-Substitution Yields (%) by Recoil ^{38}Cl Atoms in C_6H_5X[a]

F(523)	Cl (398)	Br (334)	I (268)	CH_3 (418)	CF_3	NH_2 (435)	NO_2[b]
2.5, 3.1	24.5, 5.9		7.2, 5.0	0.6	1.1		14.8[c]
3.1, 2.3	29.3, 4.6	13.8, 1.9	9.9, 3.6	1.7, 1.7		1.1, 1.1	13.1, 3.1[d]
	33.0, 4.7[e]						11.6, 5.4[f]

[a] The first yield is for unscavenged, the second yield for scavenged systems. [b] Bond energies in kJ mol^{-1} in parentheses. [c] Scavenged with 1% I_2 or Br_2.[4,55] [d] Scavenged by dilution with n-C_5H_{12}.[5] [e] Scavenged with 1% I_2.[6] [f] Scavenged with 0.5% I_2.[70]

TABLE X. Chlorine Substitution Yields by Recoil ^{34m}Cl and ^{38}Cl Atoms in Chlorobenzenes

compound	scavenger	Yield, % ^{34m}Cl	Yield, % ^{38}Cl
C_6H_5Cl		11.0[a]	26.4[a]
	I_2	6.0	5.9
		15.4[b]	33.0[b]
	I_2	7.4	4.7
o-$C_6H_4Cl_2$		19.1[b]	35.0[a]
	I_2	8.7	10.2
			30.5[c]
	I_2		15.7
m-$C_6H_4Cl_2$		10.1[b]	30.0
	I_2	9.1	7.0
p-$C_6H_4Cl_2$			36.6[c]
(333 K)			19.1

[a] 1% I_2, ref 4. [b] 1% I_2, ref 6. [c] 0.5% I_2, ref 71.

atoms for ipso attack is not predicted by MINDO/3 calculations of the relative energy contents of the various dichlorocyclohexadienyl radicals, which stabilities are ordered as $p > m > o >$ ipso.[10] For the ultimate formation of the labeled products a second step is involved: the elimination of a hydrogen or chlorine atom. In the case of ipso substitution there is a 50% chance of exchange, but it is not known what the chances are for hydrogen or chlorine elimination in the cases of ortho, meta, or para addition.

Some interesting results were obtained with Cl-for-Cl exchange in substituted chlorobenzenes. Kardos et al. found the absolute substitution yields in *o*-, *m*-, and *p*-chloronitrobenzenes by recoil ^{38}Cl atoms to be 15.6, 12.6, and 16.3%; these values decreased to 9.1, 3.9, and 8.3% on the addition of 0.5 mol % iodine.[71] In a 1:1:1 mixture of the three dichlorobenzenes the relative ortho, meta, and para substitution yields with recoil ^{34m}Cl atoms were found to be 42:24:34, which changed into 39:34:27 on the addition of 1 mol % iodine.[6] Such a selective substitution behavior was previously observed in the photochemically induced chlorodebromination of bromochlorobenzenes: Milligan et al. found a ratio of 36:7:57.[60] This was attributed to a complex mechanism in which a bromine atom attacks the carbon-bound bromine atom of a Cl_2–arene complex.[74]

Few solid-phase experiments have been performed. In the case of chlorobenzene the chlorine substitution yield is somewhat lower than in the liquid phase.[69] In the case of solid *o*- and *p*-dichlorobenzenes the yields are 15.7 and 17.8%, almost equal to the yields in iodine-scavenged liquids (Table X). This effect is ascribed to a lack of mobility of the radical, hindering radical recombination. In a mixture of C_6F_6 with 5 mol % CCl_4, the yield of $C_6F_5{}^{38}Cl$ is 16.1% in the liquid phase, but only 0.2% in the solid phase. Cluster formation (or microcrystals) were proposed to explain these results.[73]

b. Hydrogen substitution

The substitution yield for phenylic hydrogen atoms by recoil chlorine atoms depends on the substituent and is, for instance, 1.5, 1.4, 0.7, and 0.4% per hydrogen atom for fluoro-, chloro-, bromo-, and iodobenzene (the yields for phenylic and benzylic hydrogen substitution per atom are almost the same in toluene.[68]) These values are lowered with more than 50% on the addition of scavengers, indicating that hot and thermal processes are involved.[5] The mechanism for the hot reaction is supposed to be direct addition of an energetic recoil chlorine atom, forming an excited σ complex, which then collapses to the substitution product or loses the incoming chlorine atom.[4,5] The small orientation effects observed in the ortho, meta, and para products are then originating from the second step. The thermal mechanism may involve a π-to-σ-complex reaction sequence.[5] The ortho, meta, and para -yield ratios are different for the hot and thermal processes. Coenen et al. found that Hammett plots gave straight lines with slopes of $\rho^+ = -0.56$ (hot) and $= -1.43$ (thermal), indicating an electrophilic character for both processes. The smallest value of ρ^+ found for the hot process is in agreement with a higher reactivity and lower selectivity.[5]

TABLE XI

Hydrogen Substitution Yields by Recoil ^{38}Cl Atoms in Chlorobenzene at a Dose of 7.5 kGy[a]

additive (mol %)	yield, % o	yield, % m	yield, % p	yield, % total
	3.1	2.6	1.9	7.6
1% DPPH[b]	2.15	1.78	1.45	5.38
3.5% CHT[c]	1.69	1.55	1.09	4.33
4% DMB[d]	1.77	1.63	1.18	4.58
av	1.87	1.65	1.24	4.76
0.5% I_2	4.30	2.75	3.15	10.20
G Values for Hydrogen Substitution by Radiolysis of Chlorobenzene				
	0.10	0.03	0.10	0.23[e]
	0.11	0.035	0.11	0.255[f]
0.05% I_2	0.10	0.03	0.10	0.23[e]
1% I_2	0.24	0.04	0.34	0.62[f]

[a] 7.5 kGy = 0.84 kJ mol^{-1}. [b] Diphenylpycrylhydrazyl. [c] Cycloheptatriene. [d] 2,3-Dimethylbutene. [e] Reference 74. [f] Reference 75.

At high doses another effect was observed in chlorobenzene: the total hydrogen substitution yield of 7.6% decreases to 4.8% in the presence of low concentrations of organic scavengers, but increases to 10.2% in the presence of iodine (Table XI); this effect was explained by radiation-induced rearomatization of c-$C_6H_5Cl_2I$.[8] A comparable iodine effect was observed in the radiolysis of chlorobenzene: the *G* values (number of molecules produced per 100 eV = 1.6×10^{-7} J absorbed energy) are more than doubled for *o*- and *p*-dichlorobenzene, but does not alter for the meta isomer.[75,76] Only one gas-phase experiment was reported for a mixture of fluorobenzene and 10–20 mol % CCl_4. The hydrogen substitution is almost statistical (o:m:p = 38:38:24), and is independent of the pressure in the range of 1–100 kPa. With increasing mole fraction of argon moderator the yields, 0.5% per hydrogen atom, decrease linearly to 0, clearly indicating a single hot substitution mechanism.[5] The hydrogen substitution yields in solid benzene and chlorobenzene are somewhat higher than in the liquid phase.[70]

2. Polymerization

The formation of 10–30% high boiling products formed by the reaction of recoil ^{38}Cl atoms with liquid arenes was first reported by Stöcklin et al.[69] For monosubstituted benzenes the yields are in the order of 20–25%, with the exception of bromobenzene (45.8%) and aniline (4.6%),[5] and are generally lowered on the addition of bromine or iodine. The formation of these products was explained through the addition of a recoil

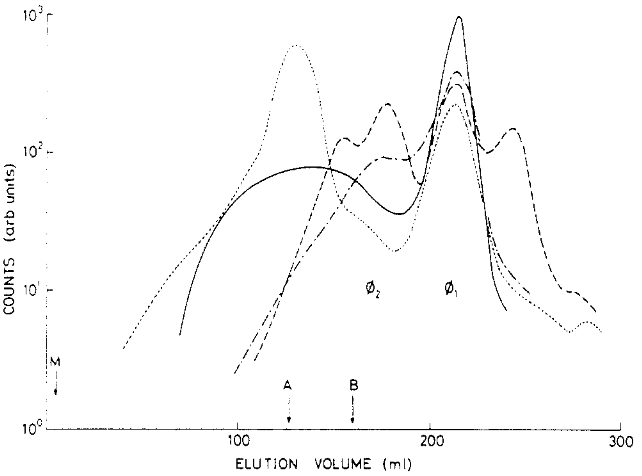


Figure 3. Radiogel filtration chromatogram from the reactions of recoil ^{38}Cl with C_6H_5Cl: (—) C_6H_5Cl, (-·-) (C_6H_5Cl + 1% DPPH), (----) C_6H_5Cl + 3.5% CHT, (······) C_6H_5Cl + 0.5% I_2. Positions of mass peaks: M (mol weight 25000), A (DPPH), B (CHT), ϕ_2 (dimers), ϕ (monomers).[8]

chlorine atom, forming the labeled chlorocyclohexadienyl radical.[5,71] From the observation that iodine had not much effect on the polymer yields in chlorobenzene, it was concluded that hot recoil atoms must be the precursors for the polymerization process.[6] However, the effect of iodine on the composition of the polymer fraction is quite more complex. By applying gel-filtration techniques, it was found that the addition of iodine decreased the yield of dimers and higher polymers from about 25 to 13%, whereas the monomer peak contains, besides the normal chlorine and hydrogen substitution products, about 20% of unknown labeled compounds which were not eluted from gas chromatographic columns at 393 K.[8] The formation of c-$C_6H_5Cl\ ^{38}ClI$ was suggested, but no information about the existence and thermal stability of di- or trihalocyclohexadienes is available. The total chain length of the polymer fraction is shortened on the addition of iodine, the main fraction consisting of dimers—in this case also for monochlorobenzene—that probably contain iodine. Consequently, iodine does not prevent the addition reaction of recoil ^{38}Cl atoms, indicating that a hot process is involved, but iodine prevents dimerization and further polymerization to a large extent, indicating the thermal nature of these processes, in contradiction to the polymerization induced by recoil ^{18}F atoms in which case the formation of compounds containing up to four units was not influenced by added bromine.[48]

The gel filtration chromatogram changes completely if 1 mol % of DPPH is used as a scavenger instead of iodine (Figure 3). The monomer peak consists mainly of hot substitution products. A broad peak, containing the majority of the radioactive compounds, is the consequence of radical–radical reactions between thermal ^{38}Cl atoms or labeled cyclohexadienyl radicals and DPPH. A quite different chromatogram is obtained with 3.5 mol % CHT. In this case addition of atoms and radicals to the unsaturated compounds takes place; this is often followed by further polymerization[8] with benzene and/or CHT molecules. There are indications that the polymer yield increases with enhanced halogenation of the substrate as was also observed in recoil ^{18}F chemistry. With recoil ^{34m}Cl atoms the yields are about 30% chlorobenzene, 44% dichlorobenzenes, and 65% chloropentafluorobenzene.[6] Some conclusions are discussed in the next section.

In gas phase experiments with fluorobenzene and CCl_4 the yield of high boiling compounds increases with pressure and temperature from almost zero at 0.1 kPa and 295 K to about 60% at 250 kPa and 473 K, the latter value being much higher than the yield in the liquid phase (25%).[5] In the case of benzene, with 5 mol % CCl_4, the polymer yield in the solid phase is not much different from that in the liquid phase. With aniline as the substrate molecule, the ^{38}Cl-labeled polymer yield is extremely low (4.6%) and reflects the special behavior of this compound, as was also observed with recoil ^{18}F atoms.

3. *Abstraction and Inorganic Products*

Not much is known about abstraction reactions by recoil chlorine atoms because in most cases the compounds formed can not be identified as they are extracted by the aqueous solution and do not elute from gas chromatographic columns. The only value that is available is a yield of 1.1% $CF_3\ ^{38}Cl$ from benzotrifluoride.[68]

The inorganic fraction is 30–35% for chlorobenzene and is supposed to be formed by hot hydrogen abstraction because this yield is not changed considerably on the addition of DPPH (37%), CHT (39%), or DMB (40%), which compounds are excellent scavengers for thermal chlorine atoms.[8] The inorganic fraction is 60–70% for benzene, fluorobenzene, and toluene; the extra yield may be due to thermal hydrogen abstraction (in the case of chlorobenzene ipso substitution prevails above abstraction). Such thermal abstraction was already proved to operate in the gaseous phase and is further underscribed by the observation of high yields of HCl in the radiolysis of chlorobenzene (G = 1–2).[75] With recoil ^{34m}Cl atoms the following inorganic yields were measured: 45% for chlorobenzene, 32 and 42% for *o*- and *m*-dichlorobenzene. The low inorganic yield found for chloropentafluorobenzene (16%) is possibly the result of hot abstraction reactions, because no thermal F or Cl abstraction is expected; thermal chlorine atoms react by addition (the polymer yield is 65%), because no thermal ^{34m}Cl-for-Cl substitution is observed.[6]

4. *General Conclusions*

Whereas all recoil ^{18}F atoms react as hot atoms, in the case of chlorine thermal reactions are also involved. Although dose effects seem important and differences exist between the reactions of ^{34m}Cl and ^{38}Cl atoms, some general conclusions about the reactions with arenes can be made.

Reactions of hot chlorine atoms lead to: (a) substitution of atoms and groups, (b) abstraction of atoms and groups, (c) addition and further thermal polymerization.[77]

Arranged according to decreasing rate constants, the reactions of thermal chlorine atoms led to (a) radical recombination (DPPH), addition to unsaturated hydrocarbons (CHT, DMB), and reaction with I_2, (b) ipso substitution with chlorobenzene, (c) benzylic hydrogen abstraction, (d) addition to perhalobenzenes, followed by polymerization.

C. Tritium

The literature about the reactions of thermal hydrogen atoms (H, D, T) with arenes is more comprehensive than that for fluorine and chlorine and deals with gaseous, liquid, and solid phases, but also with aqueous solutions. Gas-phase reactions were reviewed by Jones et al. in 1973,[78] but many contributions have been published since then. In case of benzene the following total rate constants at 298 K are measured: 1.7,[79] -3.7,[80,81] -5.7,[82] -1.3,[83] and 1.8[84] × 10^7 L mol^{-1} s^{-1}. Knutti et al. have given a detailed discussion on these data, which are very low as compared with cyclohexadiene and cyclohexene, for which the rate constants are about 70 and 30 times larger.[84] The main conclusion is that the primary reaction of thermal hydrogen atoms is addition to the aromatic ring, but it is not quite clear if a measured isotope effect, $k_D/k_H = 1.9$, found for the reactions with benzene and deuteriobenzene, is due to this primary reaction or to secondary reactions.[82,84] Those latter reactions can be very complex and include exchange, further addition, and cleavage of the benzene ring, whereas the product distribution depends on pressure and on relative benzene and hydrogen concentrations.[83] Reactions with toluene are almost a factor of three faster than with benzene,[80,84] which is not due to benzylic hydrogen abstraction, because the addition/hydrogen abstraction ratio in toluene is larger than 6,[80,85] but probably due to enhanced reactivity of the ortho position.[84] However, MINDO/3 calculations by Gandour predict that the *p*-methylcyclohexadienyl radical is energetically more stable than the ortho isomer.[10] Benson et al. found that hydrogen addition to benzene and to the methyl position in toluene (ipso attack) have about equal rate constants.[86,87] Gas-phase reactions with substituted benzenes are slightly electrophilic, as was found by the correlation of rate constants with Hammett substituent constants.[81] A similar conclusion was derived by the reactions of thermal tritium atoms with substituted liquid benzenes[88] and toluenes[89] and also by the reactions of hydrogen atoms with substituted benzenes in aqueous solution.[90] A review on the reactions in aqueous solution was published by Neta.[91] The rate constants for hydrogen atoms were found to be 0.53[92] and 1.1 × 10^9[80] L mol^{-1} s^{-1} for benzene, 2.6 × 10^9 L mol^{-1} s^{-1} for toluene,[80] and in the order of (0.7–2.6) × 10^9 L mol^{-1} s^{-1} for many other arenes.[90,93] The rate constants for benzene is still a factor of 10 below the diffusion-controlled limit of about 1 × 10^{10} L mol^{-1} s^{-1}.[94] Brett et al. performed a series of experiments with tritium atoms in aqueous solution.[95–97] The relative reactivities of substituted benzenes C_6H_5X toward these tritium atoms were X = H 1.0, F 1.0, Cl 1.1, Br 1.1, CH_3 2.2, CF_3 0.35. Relative T-for-X substitution yields were I:H:Br:Cl = 8.1:1:0.31:0.12. Ortho addition in toluene and anisole was found to be very high (70%), but this is not confirmed by reactions in organic liquids.[88] As a consequence of additional reactions of hydrogen atoms with substituent groups (NO_2, CN, CHO), these compounds do not fit the Hammett plot.[90] In the solid phase primary cyclohexadienyl radicals were observed by Bennett et al., and also radicals due to abstraction of the tertiary hydrogen atom from cumene and the α hydrogen atom from benzyl alcohol, but not the benzylic radical in toluene,[98] in agreement with conclusions derived in the other phases that benzylic hydrogen abstraction is not an important reaction channel. Addition is preferentially at ortho positions,[98] which was also observed for several substituted benzenes embedded at 77 K in an adamantane matrix, whereas in perfluorobenzene addition at C–F sites was also observed.[99,100]

TABLE XII. Product Yields (%)[a] for the Reactions of Recoil T Atoms with Benzene[112]

phase	HT	C_6H_5T	polymers	1,3-C_6H_7T	1,4-C_6H_7T	c-C_6H_9T
gas	12	68	20			
liquid	12	40	40	3	4	1
solid	8	56	25	3	6	1

[a] Without inorganic activity (4% for the liquid phase).

Whereas the reactivity of hydrogen atoms with liquid arenes is only a factor of about 10 below the diffusion-controlled limit, it can be expected that a large fraction of recoil tritium atoms will react as hot atoms, or at least as epithermal atoms, before being totally thermalyzed and that therefore low concentrations of scavengers will not affect the primary reactions of these atoms. Reactions of recoil tritium atoms are reviewed by Stöcklin[11] and Tang,[101] but the reactions with aromatic compounds forms only a minor fraction of the total research. After some studies with substituted benzenes[102–104] a more systematic investigation was started between 1960 and 1965; these studies dealt with benzene, perdeuteriobenzene, and halobenzenes, liquid and solid phases, and the effect of scavengers (Br_2, I_2, DPPH) and mixtures.[105–109] After the discovery in 1965 of rather high yields of tritiated polymers, a more detailed discussion was started on the reactions with benzene in the three aggregation states,[110–112] but absolute product yields could not be calculated before the determination of the inorganic (water-extractable T^+ fraction) in 1980.[113,114] In the gas phase the recoil tritium atoms are produced by the ^{3}He(n,p)T reaction and in the liquid phase via ^{6}Li(n,α)T by adding LiF-, Li_2CO_3-, or inert lithium-containing glass powder (with grain diameters smaller than 30–40 μm, the range of the 2.7-MeV recoil tritons) to the sample. Two special complications are involved in recoil tritium studies. First, the long half-life of tritium (10.2 y) demands for relatively long irradiation times and/or high neutron fluxes and therefore high radiation doses are involved. The dose delivered to the sample can be much higher due to ionizations by protons, tritons, and α particles, but it is difficult to estimate which fractions of the energies are absorbed in the lithium compounds and which in the sample. Another complication that has delayed this type of research is the determination of the amount of tritium in labeled compounds because tritium emits only β^- particles with maximal energies of 19 keV, which makes the detection rather difficult.

1. Benzene

In Table XII average product yields are given, taken from Table I in ref 112 (these yields do not include the inorganic fraction, which is about 4% for liquid benzene). The information about gas-phase experiments is very scarce. In aliphatic gas-phase recoil chemistry the yield of HT formed by a direct reaction is a function of the C–H bond energy and is for simple alkanes about

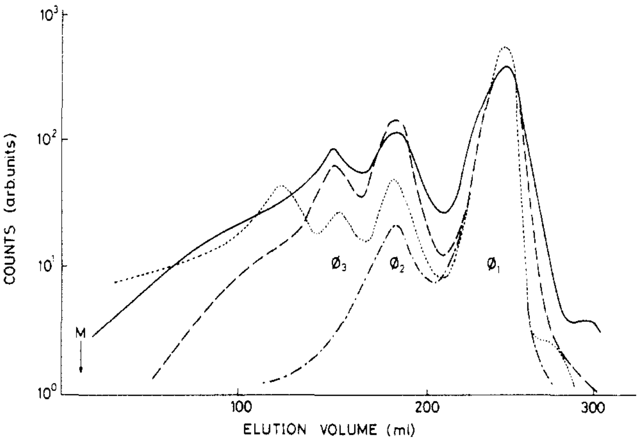


Figure 4. Radiogel filtration chromatogram from the reactions of recoil T with C_6H_6: (—) C_6H_6, (·····) C_6H_6 + 2% DPPH, (- - -) C_6H_6 + 2% CHT, (-·-·) C_6H_6 + 2% I_2. Positions of mass peaks: M (mol weight 25 000), ϕ_3 (trimers), ϕ_2 (dimers), ϕ_1 (monomers).[114]

4.7% per hydrogen atom.[115] The lower yields for gaseous benzene (2% per atom) can be attributed to a higher C–H bond energy and/or to the scavenging of lower energetic tritium atoms by addition to benzene.[111] For simple alkanes the yield for hydrogen substitution, also proceeding through a direct process at an average excitation energy of 5 eV, is about 22% per molecule, much lower than for benzene, in which case an addition complex again forms an extra reaction channel. The formation and subsequent reactions of the intermediate σ complex depend on the surroundings that influence the tritium energy spectrum and the rapidity of collisional deexcitation. Thermal hydrogen atom scavengers do not affect the relative HT/C_6H_5T yields, unless in moderated systems. The available gas-phase information alone is not enough to determine the reactions involved, but when condensed-phase experiments are included, a more detailed scheme is proposed in which tritiated compounds are produced through three categories of reactions:[112] (a) by fast reactions of hot tritium atoms, resulting in (i) abstraction to form HT, (ii) substitution to form C_6H_5T, (iii) addition to form excited $\cdot C_6H_6T$ radicals; (b) by reactions of excited $\cdot C_6H_6T$ radicals, resulting in (i) deexcitation, (ii) further addition, (iii) hydrogen transfer:

$$\cdot C_6H_6T + C_6H_6 \rightarrow c\text{-}C_6H_7T + \cdot C_6H_5$$

$$\cdot C_6H_6T + C_6H_6 \rightarrow C_6H_5T + \cdot C_6H_7$$

(c) by reactions of thermal $\cdot C_6H_6T$ radicals with molecules or other radicals.

The yields of HT, C_6H_5T, and the polymers do not change on the addition of CHT and DPPH to liquid C_6H_6, which means that abstraction and substitution reactions proceed by hot tritium atoms. As will be discussed later in more detail I_2 decreases the yield of polymers from 35 to 5% via a reaction with thermal $\cdot C_6H_6T$ radical and not via a reaction with thermal tritium atoms. This means that addition also proceeds by hot tritium atoms and furthermore that no excited radicals are involved in the dimerization reaction b.ii.

The composition of the high boiling products was first determined by reverse-phase gas chromatography and distillation techniques[110,116,117] and later by thin-layer chromatography[118,119] and gel filtration.[114] In Figure 4 a radio gel filtration chromatogram is given for benzene, pure and with DPPH and I_2 as scavengers. With DPPH a high boiling peak consisting of DPPH addition products can be distinguished, but with I_2 hardly any high boiling species are formed. The effect of I_2 on the product yields has a long history: in 1962 Pozdeev et al. found that the amount of C_6H_5T was increased about 50%, which was ascribed to energy transfer from an excited $\cdot C_6H_6T$ complex to a benzene–iodine complex.[106] In 1968 Avdonina et al. showed that iodine decreased relative polymer yields from about 1.0 to 0.2.[117] It was only in 1980, after the determination of the inorganic yields in benzene and fluorobenzenes, that the effect of iodine could be quantized: the yield of the polymers decreases about 30%, whereas the inorganic fraction and of C_6H_5T each increase about 15%.[113,114] An explanation of these observations was given by assuming the formation and subsequent decomposition of c-C_6H_6TI, as was already proposed by Garland et al.:[111]

$$C_6H_6 + T \rightarrow \cdot C_6H_6T^* \xrightarrow{M} \cdot C_6H_6T$$

$$\cdot C_6H_6T + I_2 \rightarrow c\text{-}C_6H_6TI + I$$

$$c\text{-}C_6H_6TI \rightarrow \begin{array}{l} 50\%\ C_6H_5T + HI \\ 50\%\ C_6H_6 + TI \end{array}$$

(Iodocyclohexadiene has not been reported in literature.)

Product yields for solid benzene differ from liquid-phase results by an increased yield of C_6H_5T of about 30% on account of a decrease in the yield of the polymers[107,112,120] (Table XII). Reactions of excited radicals can take place in liquid drops formed at the end of the recoil tritium path and then resembles liquid-phase reactions. However, further reactions of cyclohexadienyl radicals can be different for both phases and lead to the observed shifts in the benzene and polymer yields.

A minor fraction of the tritium activity is found in 1,3- and 1,4-cyclohexadienes and in cyclohexene. In the liquid phase the two first compounds are formed through hydrogen abstraction by excited cyclohexadienyl radicals, because the ratio of the 1,4/1,3 compounds is about 1.4, whereas it is 2.7 for thermal radicals.[112] In the solid phase the ratio is 2.1, and the cyclohexadienes are then thought to be formed through reactions with diffusive hydrogen atoms. Both compounds are not observed in the gaseous phase because of unimolecular decomposition of the excited radicals. Cyclohexene could be formed in radiolysis processes via hydrogen atom capture by hexadienes.

2. Substituted Benzenes

a. Fluorobenzenes[113,114]

A systematic study was made of the reactions of recoil tritium atoms with the fluorobenzenes; it showed that an almost linear relationship exists between the product yields and the number of fluorine substituents (Figure 2) similar to that observed with recoil ^{18}F atoms.

(i) The T-for-F/T-for-H substitution yield ratio is almost constant for all the investigated compounds. When calculated from benzene and perfluorobenzene this value is about 0.4 (Table XIII), whereas an average value of about 0.3 was determined for mono-, di-, and tetrafluorobenzenes. This constancy reflects the hot nature of the substitution processes, for which bond energies are not of primary importance.

TABLE XIII. Product Yields (%) for the Reactions of Recoil T Atoms with Liquid C_6H_6 and C_6F_6[114]

	HT	T^+	C_6H_5T (C_6F_5T)	polymers	c-C_6F_6TI (?)
C_6H_6	13	4	46	37[a]	
$C_6H_6 + I_2$	13	24	56	7	
C_6F_6		43	20	37[b]	
$C_6F_6 + I_2$		55	20	3	22

[a] Includes 2% c-C_6H_7T and c-C_6H_9T. [b] Includes 2% fragmentation products.

(ii) The high inorganic yield in C_6F_6 can hardly be explained by hot fluorine abstraction, and it was supposed to be formed by TF elimination from excited cyclohexadienyl radicals, whereas the reversed effect (high inorganic ^{18}F yields in less substituted fluorobenzenes) was thought to proceed through $H^{18}F$ elimination.

(iii) The yield of polymers is about 35% for benzene and for perfluorobenzene, but in the latter case this fraction consists for about one-third out of compounds that are formed by polymerization reactions of fragmentation products. A fragmentation yield of about 10% is also measured in the reactions of recoil ^{18}F atoms with perfluorobenzene, and fragmentation seems therefore a significant decomposition channel for highly excited perfluorocyclohexadienyl radicals. The effect of the addition of iodine is also similar for both compounds: the yields of the polymers decrease from 35% to about 5%. In the case of benzene it was proposed that iodotritiohexadiene was formed. This decomposes in equal yields of HT and C_6H_5T, whereas in the case of perfluorobenzene the formation of iodotritioperfluorocyclohexadiene was suggested; this compound is possibly more stable, because c-C_6F_5HCl, c-C_6F_7Cl, c-$C_6F_6Cl_2$, and c-C_6F_7Br have been prepared.[121]

b. Alkylbenzenes

Sokolowska has compared relative hydrogen abstraction yields from aliphatic (HT_{al}) and aromatic (HT_{ar}) compounds. Per hydrogen atom the yield of HT_{al} from hexane, heptane, and cyclohexane is a factor of 2.7 higher than the HT_{ar} yield from benzenes.[122,123] This value differs somewhat from a ratio of 2.0 that can be calculated by using average HT_{al} yields from smaller hydrocarbons (methane–butane)[115] and a value of HT_{ar} = 2.3% for benzene. From data published by Sokolowska on the reactions of recoil tritium atoms with toluene, an intramolecular ratio of HT_{al}/HT_{ar} 2.3 can be calculated; this value is intermediate between the above-mentioned ratios of 2.7 and 2.0. The total HT yield from toluene is therefore about 27%, twice as large as the HT yield from benzene; this increase is at the expense of a decrease in the yield of polymers from 43% (benzene) to 30% (toluene).

The substitution yield of phenylic hydrogen atoms in toluene is a factor of two higher than of benzylic hydrogen atoms: Ache et al. found in gaseous toluene a value of 0.47 for H_{al}/H_{ar} (per hydrogen atom) and Ciranni et al. measured a value of 0.58 for liquid toluene, which ratio became 0.62 (0.44) for liquid ethylbenzene (cumene).[124,125] Relative ortho, meta, and para substitution yields for the above-mentioned compounds are given in Table XIV, together (for comparison) with substitution yields in phenylacetic acid.[126] The distribution among the various positions is quite statistical, with the exception of ethylbenzene and cumene, for which compounds substitution at the meta position is hampered.

TABLE XIV. Relative Hydrogen Substitution Yields for Recoil T Atoms with Substituted Benzenes

	relative yields		
compound	*o*	*m*	*p*
toluene (gas)[124]	44	36	20
toluene (liquid)[125]	36	43	21
ethylbenzene (liquid)[125]	64	15	21
cumene (liquid)[125]	68	<1	31
phenylacetic acid (solid)[126]	38	38	24

TABLE XV. Relative Substitution Yields (Cl = 1.0) for Halogen and Hydrogen Atoms in Halobenzenes by Recoil Tritium Atoms[128]

substitution of	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I	ref
halogen	0.46	1.0	1.63	2.14	109
		1.0	1.5	2.6	128
	0.39	1.0	1.58	2.6	104
hydrogen (per atom)		1.16	1.0	0.28	128

Krasnyanskii et al. determined the abstraction yield of the methyl group from toluene (CH_3T) as 3.2% and the substitution yield (C_6H_5T) as 4.9%, whereas not much different results were reported for some other alkylbenzenes.[127]

c. Halobenzenes

Relative substitution yields of halogen atoms in liquid halobenzenes increase when going from fluorine to iodine (Table XV); this effect was explained by decreasing bond energies.[109,128] These relative yields do not differ for halo substitution in solid *o*-halobenzoic acids.[104] Ortho-substitution yields for other groups were measured in orthobenzoic acids, relative to Cl, for OH (0.2), NH_2 (0.2), NO_2 (0.3), and COOH (0.6). Simirskii et al. have measured relative hydrogen substitution yields in halobenzenes (Table XV).[128] Absolute yields can be calculated from known values for fluorobenzene.[113,114] The halogen and total hydrogen substitution yields are then 2.7–40% (C_6H_5F), 6–35% (C_6H_5Cl), 10–30% (C_6H_5Br), and 14–9% (C_6H_5I). A detailed discussion is not possible due to a lack of information about inorganic and polymer yields.

d. Miscellaneous

Tritium particles produced by the $^3He(n,p)T$ or $^6Li(n,\alpha)T$ reactions possess a recoil energy of several MeV, and they are ionized as long as their velocity is above the velocity of the electrons in the Bohr orbital, which means that for a hydrogen matrix this critical energy of a tritium particle is about 25 keV. Beams of T^+ ions with an energy above this value can also become neutralized during their moderation, and it can therefore be expected that when such a T^+ beam is stopped in a certain compound, the tritiated product composition will be the same as with recoil tritium atoms. Ascoli et al.[24] found through the reactions of 40 keV T^+ ions with solid *m*-iodobenzoic acid a product yield similar to that determined with recoil tritium atoms.[104] Furthermore, intramolecular tritium distribution in phenylacetic acid was found to be equal for 40 keV T^+ ions, recoil atoms, and also 40 keV HT^+ ions,[126,129] which proves that the HT^+ particles dissociate in their collisions with the target molecules. By the irradiation of successive solid layers of benzene with a beam of T^+ ions supplementary information can be gained about the processes of moderation, and chemical stabilization of high energetic particles.[129-131]

Several publications deal with the reactions of recoil tritium atoms in mixtures of arenes and hydrocarbons. In the simplest case there exists additivity, which means that individual product yields are linear functions of the relative concentrations of both compounds. Deviations from linearity were observed in mixtures of benzene and cyclohexane; this phenomenon was explained by preferential energy transfer from excited cyclohexane to benzene molecules, preventing decomposition of the former molecules.[108a] By similar experiments pyridine seemed to be a better energy acceptor than benzene.[108b] However, these experiments were performed before the discovery of the formation of polymers. Inclusion of these yields results in linear functions for benzene and hydrocarbons,[122,123] and as a consequence there is no necessity for the postulate of energy transfer to aromatic molecules.[111] Another postulate about energy transfer was introduced by Pozdeev et al., who explained the increase in the yield of C_6H_5T on the addition of iodine to benzene by the transfer of energy from an excited $\cdot C_6H_6T$ radical to a benzene/iodine complex.[106] The idea of the protective action of such a complex was also used to explain deviations from additivity in iodine scavenged benzene/cyclohexane mixtures.[117] As an alternative explanation of the effect of iodine on the C_6H_5T yield in benzene, the elimination of HI from c-C_6H_6TI was proposed as the actual reaction channel.[110,114]

D. Muonium

Positive and negative muons ($\mu^\pm$) are the decay products of charged pions:

$$\pi^\pm \xrightarrow{t_{1/2} = 37\text{ ns}} \mu^\pm + \nu_\mu$$

$$\mu^\pm \xrightarrow{t_{1/2} = 3.2\ \mu\text{s}} e^\pm + \nu_e + \nu_\mu$$

(ν_e and ν_μ are the electron and muon neutrinos). Muons can be observed on earth in cosmic radiation because they are formed by the decay of pions that are produced in the upper atmosphere by nuclear reactions of high energetic protons arriving from outer space. However, the main research is performed at some specialized institutes that are equipped with high-energy accelerations: JINR (Dubna), LBL (Berkeley), SIN (Villigen), and TRIUMF (Vancouver).

The negative charged particles behave in matter like heavy electrons ($m_\pi = 273m_e$, $m_\mu = 207m_e$). After being slowed down to almost thermal velocities they are captured in atomic orbitals with an average quantum number of $n = 14$, and in their fast cascade to the 1s orbital ($\sim 10^{-12}$ s) Auger electrons and mesonic X-rays are emitted. In atoms with low nuclear charges the lifetime of negative muons in the 1s orbital is in the order of a microsecond, which means that chemical reactions of such mesonic atoms can take place. Whereas the radii of electronic orbitals are inversely proportional to the mass of those particles, the radius of the muonic 1s orbital is about 200 times smaller than that of an electron. As a consequence, the muon is so close to the nucleus that the outer electrons—that predict the trajectory of chemical reactions—judge a muonic atom of nuclear charge Z as one of charge $Z - 1$. The muonic hydrogen atom ($p^+\mu^-$) behaves like a neutron and can freely penetrate into the electron cloud of other atoms.[132] The muonic ^{4}He atom ($\alpha^{++}\mu^-e^-$) can chemically be considered as a heavy hydrogen atom[133] and the muonic neon atom as a fluorine atom.[134] The existence of these atoms have been proved, and the value of the observed residual asymmetry (discussed below) seems to be intense enough to encourage further chemical research.

Positively charged pions and muons can be considered as light hydrogen atoms and, similarly to recoil tritium atoms that are slowed down in matter, they can pick up an electron and form neutral pionium (π^+e^-) or muonium (μ^+e^-) atoms. Due to a combination of particular properties only the chemical reactions of positive muons (with spin $^1/_2$) can be followed in practice, but not the reactions of positive pions (zero spin): (a) muons arising from pion decay are 100% polarized opposite to their momentum in the pion center of mass frame; (b) the spin direction is maintained during the slowing down and the neutralization of the muons and during fast chemical reactions of muonium atoms; (c) the decaying muon emits the electron that is detected in muon chemistry, preferentially in the direction of the muon spin.

Information about the chemical state of the muon can be gained by the measurements of the asymmetry of the decay positrons. The asymmetry a is defined by the positron emission probability that is proportional to $(1 + a \cos \theta)$, where θ is the angle between the muon spin and the positron momentum. The coefficient a is a function of the positron energy and has a value of about $^1/_3$ for a 100% polarized muon beam. At the moment three different kinds of signals from decaying positive muons can be detected by the so-called μSR (muon spin resonance) technique: (a) Muons in free muonium (μ^+e^-) precess in low magnetic fields at a rate of 1.4 MHz G^{-1} (the muonium signal h_M). Muonium was first detected in 1960 in argon gas by Hughes et al.[135]. (b) Bare muons precess at the nuclear Larmor frequency of 13.55 kHz G^{-1}. Due to the absence of a magnetic interaction between a muon and electrons in diamagnetic molecules, muonium bound in such compounds precesses at the same frequency as bare muons (the diamagnetic signal h_D). (c) Muonium atoms incorporated in organic free radicals give rise to two precession frequencies in transverse magnetic fields of a few kG. The muon hyperfine coupling constant is the sum of these frequencies and is independent of the strength of the magnetic field (the radical signal h_R). In practice the fractional polarization signals in solid and liquid compounds are compared with liquid CCl_4 as a standard, for which the diamagnetic signal is taken as 1.0. The use of CCl_4 is justified by the fact that it gives the same asymmetry coefficient as is found in copper and alumina, but it is not known if this signal is due to bare muons or to bound muonium. The observation that tritium recoiling in liquid CCl_4 results in an inorganic yield (T^+) of 99.5% can be an indication that positive muons in CCl_4 are not becoming neutralized.[21]

It is outside the scope of this review to discuss more thoroughly the physical background of the behavior of

TABLE XVI. Diamagnetic Yields (h_D) and Rate Constants (k) for the Reactions of Muonium with Arenes

	h_D		rate constants, mol^{-1} s^{-1} × 10^{-9}		
compounds	ref 150-152	ref 149, 155	k_1	k_2	organic yields for ^{38}Cl recoil atoms, %
C_6H_6	0.15	0.21	0.3	3.1	
C_6H_5F	0.26	0.24	0.7	2.3	
C_6H_5Cl	0.35	0.34	0.9	2.0	
C_6H_5Br	0.51	0.47	1.6	1.6	
C_6H_5I	0.59	0.55	1.5	2.0	
$C_6H_5CH_3$	0.26		0.8	2.6	0.30 ± 0.02[5]
$C_6H_5C_2H_5$	0.31		1.1	2.5	
$C_6H_2(CH_3)_4$	0.31		1.1	2.3	
$C_6H_5CH_2Cl$	0.34		2.5	2.5	0.38 ± 0.01[156]
$C_6H_5CHCl_2$	0.49		4.1	2.4	0.55 ± 0.01
$C_6H_5CCl_3$	0.68		6.5	2.5	0.63 ± 0.01

muons and muonium atoms in magnetic fields as well as the experimental techniques that are in use for the detection of these particles. There exists already an impressive number of reviews on these subjects,[136-142] and an excellent introduction to muonium chemistry was recently published by Percival.[143]

Chemically important properties such as atomic radii, ionization potentials, and bond energies are almost equal for all the hydrogen particles. However, it can be expected that large differences in atomic masses ($m_{Mu} = 0.038m_T$) will be reflected in thermal isotope effects. For thermal reactions tunneling must be considered to contribute considerably to the rate of muonium reactions, which can result in large isotope effects.[144-146] Furthermore, the velocities of hot atoms and the amount of energy transferred during collisions are different for isotopes possessing the same amount of kinetic energy, and this can lead to variations in the individual product yields of hot reactions.

1. The Diamagnetic Signal

The first determination of the value of the diamagnetic signal in benzene was performed by Swanson in 1958: $h_D = 0.20 \pm 0.05$.[147] Other experiments resulted in yields of 0.12 ± 0.02, 0.13 ± 0.01, 0.15 ± 0.03, 0.21 ± 0.05,[148] and 0.21 ± 0.01.[149] The observation that the reactions of recoil tritium atoms with benzene lead to an inorganic yield of less than 4% may be an indication that the main fraction of the diamagetic muon signal is due to the formation of molecular compounds (HMu, C_6H_5Mu). The possibility of addition of muonium to aromatic compounds, forming muonic cyclohexadienyl radicals, was first suggested by Brodski.[144] Firsov developed a kinetic reaction scheme that included five possible reactions of muonium atoms: formation of molecular products (hydrogen abstraction), formation of radical products (in unsaturated compounds), spin exchange, depolarization, and nuclear decay.[150,151] By applying the results of these calculations on experimentally obtained h_D values for pure compounds and for mixtures, the rate constants for the formation of molecular (k_1) and radical (k_2) products could be obtained (Table XVI).[152-154] Reaction rates of hydrogen atoms with benzene in aqueous solutions are measured as 0.53 and 1.1 × 10^9 L mol^{-1} s^{-1},[80,92] about a factor of 3 lower than k_2 for muonium atoms. A difference of a factor of 3 between the values for hydrogen and muonium should be expected for diffusion-controlled reactions because the rate constant is inversely proportional to the square root of the mass. For an exact comparison of such isotopic reaction rates it must be realized that tunnelling effects can cause large differences.[144-146] There is good agreement between the values of h_D determined in JINR and SIN.[149,155] The increase in the diamagnetic yield, when going from fluoro- to iodobenzene, is, of course, correlated with the specific halogen atom, but at the moment it is not possible to assign the observed effect to either halogen abstraction or substitution. The increase in the diamagnetic yield on enhanced α-chlorination in toluene is surprisingly equal to organic yields as measured for the reactions of recoil ^{38}Cl atoms with these compounds (Table XVI),[156] in which case thermal ^{38}Cl-for-Cl exchange seems to be an obvious reaction channel.

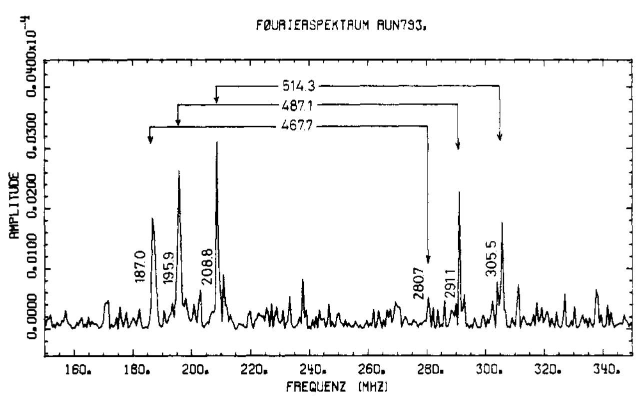


Figure 5. μSR precession frequencies observed in *m*-difluorobenzene corresponding to three isomeric muonic radicals.[149]

2. The Radical Signal

Much effort was devoted into the search of muonium radicals in low magnetic fields (<10 G), but without success. Roduner et al. found out that the reason of the nonobservation of these radicals laid in the neglect of a term in the Hamiltonian that describes the system. The search was thereafter more successful by the irradiation of unsaturated compounds in high magnetic fields (>1 kG).[157,158] The first muonic cyclohexadienyl radical was detected in liquid benzene—later on followed by its observation in solid benzene—through a hyperfine coupling constant (hfc) of 514.6 MHz. In toluene two radicals were detected at 490.7 and 510.8 MHz; these signals are assigned to ortho and para muonium addition according to the behavior of thermal hydrogen atoms.[158] The theory on the evolution of the spin polarization in muonic radicals was further developed by Roduner et al.[158-160] The progress in the experimental and computational techniques makes it now possible to determine in a single irradiation the hfc constants together with the absolute yields of the cyclohexadienyl radicals (h_R) and of the diamagnetic species (h_D). The observed polarisations are strongly affected by the limited time resolution of the experiment, which leads to a correction of the measured h values of exp $[-(\pi\nu_0\Delta t)^2/(4 \ln 2)]$, in which ν_0 is the measured frequency (GHz) and Δt the time resolution (ns).[161] In Table XVII the results are given for a series of liquid halobenzenes.[149,155] In Figure 5 a Fourier-transformed spectrum of the three radicals observed with *m*-difluorobenzene is given. A discussion on the data assembled with ten different fluorobenzenes was to a great extent based on information gained with recoil tritium and thermal hydrogen atoms in the same

TABLE XVII. Results for the Reactions of Muonium Atoms with Halobenzenes[149,155]

compound	radical hf constants, MHz	radical yield, h_R[a]	diam. yield, h_D	total yield, h_T
C_6H_6	514.4	0.49	0.21	0.70
C_6H_5F	486.0	0.26	0.24	0.69
	512.0	0.19		
C_6H_5Cl	487.8	0.19	0.34	0.70
	510.3	0.17		
C_6H_5Br	490.8	0.20	0.47	0.84
	509.0	0.17		
C_6H_5I	508.5	0.12	0.55	0.67
o-$C_6H_4F_2$	491.0	0.17	0.32	0.68
	501.2	0.19		
o-$C_6H_4Cl_2$	480.0	0.15	0.42	0.65
	484.6	0.08		
m-$C_6H_4F_2$	477.7	0.16	0.26	0.74
	487.1	0.17		
	514.3	0.15		
m-$C_6H_4Cl_2$	459.4	0.15	0.39	0.62
	481.5	0.08		
1,2,3,4-$C_6H_2F_4$	471.3	0.21	0.30	0.50
1,2,3,5-$C_6H_2F_4$	465.7	0.19	0.28	0.49
1,2,4,5-$C_6H_2F_4$	468.4	0.15	0.28	0.62
	235.2	0.17		
C_6F_6	200.7	0.15	0.23	0.38

[a] The measured yields are corrected by using the formula given in ref 161, with Δt = 1.5 ns.

system:[149] (a) In the case of recoil tritium atoms a very low inorganic T^+ fraction of about 3% was measured in benzene. A much higher fraction of 45% was found in perfluorobenzene, but this yield was thought to be formed through TF elimination from cyclohexadienyl radicals. It was therefore supposed that the almost constant value of the diamagnetic yield of $h_D \simeq 0.25$ for all the fluorobenzenes was mainly derived by hot abstraction and/or substitution reactions. (b) The addition of muonium to aromatic compounds seems to be a thermal process, because only two isomers, probably the ortho and para products, were observed in monofluorobenzene. (Roduner found two muonic radicals in toluene.[158]) (c) A puzzling problem is the large amount of about 30% of a "missing" fraction, for which no good explanation could be given. (d) Radicals that were formed through ipso addition at C–F bonds were observed in 1,2,4,5-$C_6H_2F_4$ and C_6F_6. Thermal addition of hydrogen atoms to the C–F sites in solid perfluorobenzene was already found by Yim and Wood.[100]

In some substituted benzenes addition does not proceed on the aromatic ring, but rather at the substituent; this effect is easily detected by deviations in the hyperfine coupling constants (460–520 MHz for aromatic addition), e.g., for nitrobenzene (36 MHz), styrene (214 MHz), phenylacetylene (421 MHz).[162] A particular problem is the identification of isomeric muonic cyclohexadienyl radicals, such as the ortho, meta, and para addition products from monosubstituted benzenes. In the case of fluorobenzenes information was obtained through relative hfc constant frequency shifts for hydrocyclohexadienyl radicals.[99,100] An overwhelming addition at the ortho site is in agreement with addition of hydrogen atoms at solid toluene, cumene, benzyl alcohol,[98] and fluorobenzene-.[99,100] Once more, it must be mentioned that in μSR and ESR spectroscopy the cyclohexadienyl radicals are observed, whereas generally the final substituted arenes are detected.

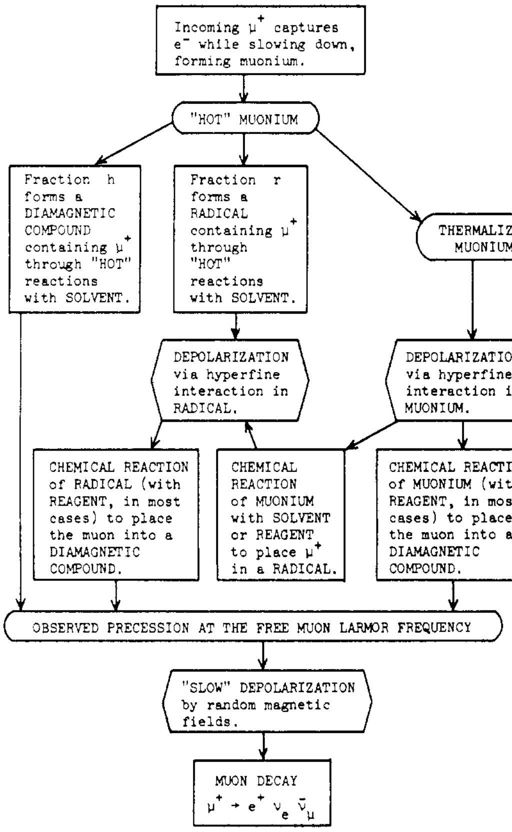


Figure 6. Flow-chart model of depolarization mechanism in liquids.[167] (Reprinted from ref 167 with permission. Copyright 1973, Academic Press.)

3. *Hot Muonium Reactions*

The simplified reaction scheme of Firsov and Byakov[150,151] was unable to describe the dependency of the asymmetry on the concentration of some additives to benzene.[163] The muonium reaction scheme was further developed by the incorporation of hot reactions of muonium atoms and of thermal reactions of muonic radicals with scavengers.[163–169] A flow chart of a proposed depolarisation mechanism is given in Figure 6.[167] According to this scheme the value of h_D = 0.13 in pure benzene was supposed to be achieved by hot reactions, whereas the increase to h_D = 1.0 in the presence of bromine was explained by reactions of muonic cyclohexadienyl radicals:[138,139,163]

$$\cdot C_6H_6Mu + Br \rightarrow c\text{-}C_6H_6MuBr + Br$$

In an expanded discussion on hot muonium reactions Fleming et al. (ref 142, p 322) mentioned the following items: (a) It was doubted that hot reactions are involved in aqueous solutions because observed effects can satisfactorilly be explained by reactions of muons and muonium atoms with radicals that are produced in the terminal spur of the muonium track.[170–173] However, by the addition of scavengers to aqueous solutions it was convincingly shown that (i) muonium is not formed in intraspur reactions, and (ii) diamagnetic compounds are not produced by thermal muonium atoms in the last spur.[173] (b) The linear relationship of h_D as a function of the volume fractions in C_6H_6/CH_3OH mixtures implies the involvement of hot reactions, because otherwise a curved function should have been found as it can be expected that benzene reacts faster than methanol with the thermal muonium atoms.

TABLE XVIII. Absolute Product Yields for the Reactions of Muonium in 1:1 Mixtures of Benzene[a] (B) with Other Compounds (A)[155]

compound	h_D (100% A)	h_R (100% A)	1:1 mixture		
			h_D	h_R(A)	h_R(B)
CCl_4	1.0		0.73		0.12
DMB[b]	nm	nm	0.39	0.11	0.22
C_6F_6	0.23	0.15	0.23	<0.03	0.34

[a] $h_D(B) = 0.21$, $h_R(B) = 0.49$. [b] 2,3-Dimethyl-2-butene.

(c) Bond energy effects are not important, at least when the absolute values of the diamagnetic signals in CCl_4, $SiCl_4$, $SnCl_4$, and $TiCl_4$ are considered. (d) There exists a striking correlation between the value of the diamagnetic yield in the series cyclohexane, cyclohexene, cyclohexadienes, and benzene; this observation may be correlated with the π-bonding behavior toward thermal hydrogen atoms. The ultimate conclusion of Fleming et al. was that hot muonium reactions are assumed to occur, but that there is no overall satisfactory rationalization of all the existing data.

Interesting, but sometimes contradictory, information about hot and/or thermal reactions of muonium with aromatic compounds is obtained from mixtures containing benzene. The linearity between the asymmetry and the molar fraction of methanol in benzene was ascribed to the existence of hot reactions, whereas otherwise benzene should have prevented thermal reactions with methanol. Roduner found a nonlinear relationship of h_D and h_R in mixtures of benzene and methyl iodide, an indication, but not a proof, for thermal reactions.[174]

Values of h_D and h_R measured in a 1:1 C_6H_6/CCl_4 mixture (Table XVIII) fit very well with extrapolated values of the C_6H_6/CH_3I systems, whereas the chemical properties of CH_3I (thermal iodine abstraction and/or substitution by muonium) and of CCl_4 (no neutralization of positive muons) are much more different. In a 1:1 mixture of benzene and 2,3-dimethylbutene the ratio of the radical yields is 2:1. In a 1:1 mixture of benzene and perfluorobenzene only the radical signal of the first compound was observed and not that of the second one, which points toward a discriminating thermal reaction with the preference of addition to benzene.[155] C_6H_6 and C_6F_6 form an addition complex. The 1:1 mixture was irradiated at 300 K, just above the melting point of 297 K of such a composition.[175]

No definite conclusion on hot or thermal reactions can be drawn before the problem of the "missing" fraction—about 30% for the arenes—has been solved. (In the past problems have been raised by speculations about reaction mechanisms of tritium and chlorine recoil atoms as a consequence of the neglect of the polymeric fraction.)

As mentioned before, an increase of the measured diamagnetic yield on addition of Br_2 to C_6H_6 was dedicated to reactions of Br_2 with the muonic cyclohexadienyl radicals. A more convincing experiment was performed by Roduner,[174] who studied the effect of the addition of benzoquinone to benzene on the radical signal. The value of h_R did not change—the initial radical concentration was unaffected—but the relaxation rate (calculated from the width of the radical frequency peaks) increased linearly with the benzoquinone concentration. The height of the radical signal became in the order of the background at about 15 mmol of benzoquinone. The slope of the curve is directly the rate constant (pseudo-first-order reaction), which was found to be $k = (2.6 \pm 0.4) \times 10^8\ mol^{-1}\ s^{-1}$.

TABLE XIX. Absolute Product Yields (%) and Relative Isomer Distribution for the Reactions of ^{76}Br and ^{77}Br with Gaseous (8 kPa, 296 K) and Liquid (296 K) Arenes[178]

C_6H_5F	halogen substitution	hydrogen substitution	inorg yield	relative *o:m:p* distribution
gas, ^{76}Kr	0.98	0.65	86.6	29:39:28
gas, ^{77}Kr	2.11	0.83	85.6	30:54:36
liquid, $^{76,77}Kr$	1.97	5.09	74.4	34:32:34
liquid, $^{76,77}Kr$				
C_6H_6		6.9	71	
C_6H_5Cl	10.8	4.5	57	36:32:32
C_6H_5Br	11.9	3.4	72	38:35:27
$C_6H_5CH_3$	0.19	5.0	80	40:34:26
C_6H_5OH	0.4	9.6	85	53:10:37
$C_6H_5NH_2$	0.05	9.7	83	46:7:47
$C_6H_5OCH_3$	0.51	4.3	57	39:15:47

E. Other Halogens

The chemical research on the fate of recoil bromine, iodine, and astatine is complicated as a consequence of the involvement of reactions of hot and thermal positive and negative ions and of electronically excited neutral and charged particles. Fortunately, at least for bromine and iodine, a choice can be made out of a large variety of nuclear reactions leading to radioisotopes with large differences in recoil energy and initial charges that can have values between −1 in the case of β^- decay and about +10 in the case of decay via isomeric transitions or electron capture (the highly positively charged particles are supposed to react as monovalent ions or as neutral atoms). Early research on the reactions of recoil halogen atoms in organic halides was reviewed by Willard at two I.A.E.A. conferences on hot atom chemistry.[176]

1. Bromine

Five bromine isotopes, with mass numbers of 76, 77, 80, 82, and 83, and two long-lived isomeric states, ^{80m}Br and ^{82m}Br, have been used in recoil studies. Some of the isotopes are directly produced via thermal (n,γ) reactions in bromine containing compounds or mixtures, whereas the nuclear decay of ^{80m}Br, ^{82m}Br, ^{76}Kr, ^{77}Kr, and ^{83}Se isotopes offer a special production route to the formation of charged and excited bromine isotopes.

Decay studies with the krypton isotopes and with compounds such as $CH_3{}^{80m}Br$, $CF_3{}^{80m}Br$, and $H_2{}^{83}Se$[177] have initiated research in gaseous mixtures. The reactions of $^{76,77}Br$ isotopes, from decay of krypton, with gaseous fluorobenzene and toluene were intensively investigated.[178] The results obtained with fluorobenzene are presented in Table XIX. The differences observed in yields between both isotopes are due to a higher average recoil energy of the ^{77}Br isotope. On dilution with krypton the radiochemical yield is reduced to 0, which means that thermal reactions of atoms or ions can be excluded. The ortho:meta:para ratio changes on dilution with krypton for both isotopes to about 16:27:57. Gas-phase experiments were also per-

TABLE XX. Absolute Product Yields (%) and Relative Isomer Distribution for the Reactions of Thermal $^{80}Br^+$ Ions with Gaseous Benzenes (C_6H_5X)

compound	X substitution	hydrogen substitution	relative o:m:p distribution
C_6H_6		3.0	
C_6H_5F	0.43	3.3	32:34:34
C_6H_5Cl	2.16	2.5	34:32:34
C_6H_5Br	18.1	0.9	40:30:30
$C_6H_5CH_3$	1.25	4.6	42:32:26
$C_6H_5CF_3$	0.05	1.0	8:67:25
$C_6H_5OCH_3$	1.17	5.1	29:12:59

TABLE XXI. Absolute Product Yields (%) and Relative Isomer Distribution for the Reactions of Recoil ^{82}Br Atoms with Liquid Halobenzenes[4]

compound	halogen substitution	hydrogen substitution	polymers	inorganic fraction	relative o:m:p distribution
C_6H_5F	1.4	8.6	16.3	73.7	36:27:36
C_6H_5Cl	8.5	6.4	19.7	65.4	40:25:35
C_6H_5Br	18.5	4.5	21.3	55.7	

formed with ^{80}Br recoil particles from decay of CH_3 ^{80m}Br. The experiments were carried out in an excess of argon gas, which ensured that $^{80}Br^+$ ions were the reacting species. The results are given in Table XX.[178–181] The large differences observed in the ortho:meta:para distribution for fluorobenzene compared with the moderated $^{76,77}Br$ experiments were explained by reactions of highly excited Br^+ ions that can more easily survive in argon than in krypton.[178] A Hammett plot for the ^{80}Br experiments resulted in a straight line with slope $\rho^+ = 0.9$, indicating the strong electrophilic character of the hydrogen substitution.

The effect of transitions from the gas phase to the liquid phase for $^{76,77}Br$ can be seen in Table XIX. The Hammett plot gave a ρ^+ value of -0.45.[178] Organic yields as measured in six laboratories for liquid bromobenzene differed, due to the purification methods used, from 54% (simple distillation) to 90% (ozonization). The addition of small amounts of Br_2 decreased the organic yield in all cases to about 30%.[176] Table XXI gives absolute product yields and relative isomer distributions for the reactions of recoil ^{82}Br isotopes with liquid halobenzenes.[4] The formation of the ^{82}Br-for-halogen (X) substitution products was explained by the hot displacement of the halogen atom, followed by a caged recombination reaction:

$$^{82}Br^* + C_6H_5\,X \rightarrow C_6H_5\cdot + {}^{82}Br + X\cdot$$

$$C_6H_5\cdot + {}^{82}Br \rightarrow C_6H_5\,{}^{82}Br$$

The halogen substitution yields were found to be a linear function of a molecular parameter defined by $\sigma_X\alpha_{XBr}/E_{C\text{-}X}$ in which σ_X is the relative geometrical cross section of the C_6H_5X molecule, α_{XBr} the average logarithmic energy loss for a hard-sphere collision of the recoil bromine atom with the halobenzene, and $E_{C\text{-}X}$ the aromatic carbon–halogen bond energy. (Halogen substitution yields by recoil iodine atoms were also described by the same equation.) As is common in liquid-phase experiments, reaction mechanisms of recoil bromine isotopes were evaluated through measurements of organic yields in mixtures. By applying the kinetic theory as developed by Estrup and Wolfgang for gas-phase reactions of hot recoil atoms,[182] Milman concluded that the transfer of energy in collisions of hot bromine isotopes with benzene included the whole molecule and not only one particular atom.[183] Reaction models for binary and ternary mixtures were developed by Kontis et al.[184] and Katsanos et al.[185] The nonstatistical formation of the ortho, meta, and para isomers of halobenzenes in mixtures with bromobenzene and toluene – was correlated with polarization and polarizability effects.[186] Annealing studies of liquid bromobenzene, bromoxylene, and benzyl bromide at 313 K showed an enhancement in the organic yields, in the case of the latter compounds from 67% to 99%.[187]

The transition from liquid to solid *p*-bromochlorobenzene results in a decrease of the inorganic yield from 52% (unscavenged system) to 15% and in an increase in the yield of polymers from 21% to 65%.[188] The polymer yield in solid bromobenzene of about 50% was composed of a hydrolyzable and a nonhydrolyzable fraction.[189] The organic yield in solid benzene was 41% for the $^{82m}Br(IT)$ ^{82}Br decay and 30% for the $^{79}Br(n,\gamma)$ ^{80m}Br reaction, whereas these yields decreased to 31% and 20% on the addition of small amounts of bromine.[190] Annealing studies of di- and tribromobenzenes and of bromoanilines showed also large increases in the organic yields, mainly due to enhanced bromine for bromine exchange.[191–193] No dose or dose rate effects were observed in liquid benzene (Br_2 scavenged) and in several solid bromobenzenes.[188,193,194]

2. *Iodine*

The iodine isotopes that are easily available for recoil studies are those with mass numbers 123, 125, 126, 128, 131, and 132. Nuclear decay studies were performed with xenon (123, 125) and tellurium (131, 132) isotopes. Investigations were described for recoil iodine particles (131, 133, 135) that were produduced by spallation of uranium, but no aromatic compounds were involved.

Thermal gas-phase iodination by $^{125}I^+$ ions formed by the decay of ^{125}Xe in an excess of xenon gas gave organic yields between 3 and 18% for pressures ranging between 10 and 100 kPa. The ortho:meta:para ratios in these experiments were 14:20:66 (C_6H_5F), 48:22:30 (C_6H_5Cl), and 80:12:8 (C_6H_5Br). The drastic increase in the relative amount of ortho substitution in this series was explained by enhanced attack at the site of the halo substituent, followed by transfer to the ortho position.[179] The total organic ^{128}I yield in gaseous benzene was only 0.19%, indicating the almost total absence of hot reactions.[195]

Higher organic yields were measured in liquid (12%) and solid (24%) benzene, which behavior is a consequence of reactions of ^{131}I atoms with radicals produced by autoradiolysis.[195] Organic yields of about 20% were measured in benzene for iodine isotopes with mass numbers of 123, 125, 126, 128, 130, and 131[196–199] (Table I in ref 197 reviews all the available information). A large isotope effect was observed for ^{125}I recoiling in either C_6H_6 or C_6D_6; the organic yields were 40 and 30%, which values decreased to 13 and 7% on the addition of I_2. This effect was also explained by the formation of labeled products through reactions with radicals.[197] Addition of iodine to liquid iodobenzene and iodotoluene decreases the ^{128}I–organic yield from about 60% to 30%[200] and the ^{131}I–organic yield from 25 to

TABLE XXII. Absolute Product Yield (%) and Relative Isomer Distribution for the Reactions of Recoil ^{211}At from Decay of ^{211}Rn with Benzene and Halobenzenes[206,a]

compound	halogen substitution	hydrogen substitution	inorg yield	relative o:m:p distribution
C_6H_6, gas		2.6 (1.1)	54 (81)	
liquid		23 (12)	20 (75)	
solid		12 (3)	31 (90)	
C_6H_5F, gas	3.1 (0.4)	2.4 (0.9)	46 (93)	44 (36):36 (40):20 (24)
liquid	4.9 (3.6)	14 (9)	27 (65)	38 (40):40 (40):22 (20)
solid	2.7 (2.3)	9 (7)	40 (65)	38 (40):40 (40):22 (20)
C_6H_5Cl, gas	3.7 (1.5)	1.1 (0.3)	51 (97)	50 (30):34 (48):16 (22)
liquid	35 (19)	11 (8)	18 (55)	40 (40):40 (40):20 (20)
solid	10 (7)	3.7 (2.5)	32 (29)	36 (34):34 (34):30 (32)
C_6H_5Br, gas	(2.4)	(0.2)	(96)	- (44):- (26):- (30)
liquid	41 (28)	7.8 (6.2)	22 (41)	56 (48):30 (34):14 (18)
solid	17 (12)	3.7 (3.4)	48 (57)	50 (48):32 (32):18 (20)
C_6H_5I, liquid	44 (33)	3.7 (4.8)	20 (30)	48 (48):36 (34):16 (18)
solid	18 (14)	3.0 (5.5)	42 (55)	48 (48):36 (34):16 (18)

[a] Values in parentheses for I_2 scavenged experiments.

11%, whereas iodopropene enhances the organic yield to 90%.[201] The ortho:meta:para ratios in liquid fluorobenzene are not much different for several isotopes, 38:37:25 (^{128}I),[4] 38:38:24 (^{125}I),[202a] and 30:36:34 (^{123}I).[202b] Production yields of C_6H_5I from I^+ beams on solid benzene increase from 1.1% (10 eV) to 4.9% (2 keV).[203]

3. *Astatine*

Only three papers have been published on the reactions of recoil astatine with aromatic compounds. Samson and Aten reported on the formation of astatobenzene formed by the reaction of ^{211}At, produced by the ^{209}Bi(α,2n) ^{211}At nuclear reaction, with triphenylbismuth.[204] The nuclear decay of ^{211}Rn(EC) ^{211}At was used by Berei et al. as another source of ^{211}At recoil particles in investigations with liquid chlorobenzenes.[205] The Cl substitution yields of 14.7% in chlorobenzene fitted the correlation found between the yields for recoil halogen-for-Cl substitution and a parameter $[M_{C_6H_5X}/(m_y + M_{C_6H_5X}](1/E_{C-X})$ in which m_y and $M_{C_6H_5X}$ represent the mass of the colliding hot atom and the aromatic molecule and E_{C-X} is the bond energy of the halogen to be replaced. An extensive study was made by Vasáros et al. for the reactions with gaseous, liquid, and solid benzene and halobenzenes,[206] with and without iodine (Table XXII).

The most important conclusions are the following: (a) A significant scavenger effect on the ^{211}At-for-halogen substitution yields and on the missing fraction (polymers) indicates that an appreciable amount of organic products is formed via thermal reactions. (b) The almost statistical ortho:meta:para distribution is characteristic of a hot homolytic halogenation process, which means that the positively charged astatine ions, formed by the electron capture of ^{211}Rn, are neutralized before they react through hydrogen substitution. (c) The similar trends in product yield and isomer distribution for the liquid and the gaseous systems indicate that thermal radical recombination reactions in the liquid cage do not contribute significantly to product formation.

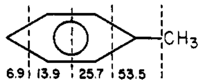
F. Carbon

Two carbon isotopes are readily available for organic recoil research. In the early experiments use was mainly made of ^{14}C atoms, because they can easily be produced in a nuclear reactor by the ^{14}N(n,p) ^{14}C reaction. In later research attention was focused more on ^{11}C atoms, for which production high energy accelerators are needed for (γ,n), (n,2n), and (p,pn) reactions on ^{12}C atoms.

1. *Carbon-14*

Several problems are involved in the research with ^{14}C recoil atoms: (a) The long half-life of 5730 years of ^{14}C necessitates long irradiation times, e.g., for some days in a thermal neutron flux of about 10^{13} n s^{-1} cm^{-2}. Such irradiations are accompanied by high radiation doses in the order of 1–10 MGy, giving rise to a high degree of radiation damage in the sample and to decomposition of already labeled products. (b) Nitrogen-containing compounds are needed for the production of the ^{14}C atoms. (c) The nuclear decay of ^{14}C proceeds through the emission of β^- particles with maximal energies of 0.16 MeV. This radiation introduces problems in the determination of the relative yields of labeled compounds, in particular in early investigations when only Geiger–Müller counters were available.

Wolf has reviewed the ^{14}C results in 1960[207,208] and in 1964,[209] whereas Urch reviewed the subject shortly in 1975.[12] The main research was focussed on the reactions with liquid benzene and toluene. In the case of benzene the most intriguing observation was the formation of 2–4% labeled benzene: the aromatic compounds survives the replacement of a ^{12}C atom by a ^{14}C atom. Another product, which was also found with a small yield of about 2%, is toluene. Degradation studies by Visser et al. proved that in toluene 14% of the ^{14}C atoms were in ring positions, but they were not statistically distributed:[210]



These results excluded all reaction mechanisms in which a symmetrical intermediate plays the only part. The majority of the ^{14}C recoil atoms is recovered in high-boiling dimeric and poly-

2. *Carbon-11*

The use of ^{11}C recoil atoms reveals also several disadvantages; however, they are different from the problems mentioned for ^{14}C: (a) The short half-life of 20 min limits the possibility of applying extensive degradation techniques for the determination of the ^{11}C atom positions. (b) Most of the common substituents such as nitrogen, oxygen, fluorine, and chlorine atoms interfere in the radioassay through the formation of ^{13}N, ^{15}O, ^{18}F, and ^{34m}Cl isotopes. In general, the cross sections for these nuclear reactions are higher than for ^{11}C. Furthermore, these isotopes have comparable half-lives (2 min–2 h) and emit, just as ^{11}C, β^+ particles in their decay.

In liquid benzene the yield of [^{11}C]benzene varied between 2.0 and 4.9% whereas the yield of [^{11}C]toluene was more consistent: 2.3–2.6%.[211-214a] Besides the recognition of these two compounds 16 more labeled products were observed in ^{11}C recoil-benzene chemistry, among them methane (0.2%), acetylene (4.7%), vinylacetylene (0.6%), diacetylene (1.6%), cycloheptatriene (3.2%), xylenes (0.8%), styrene (0.5%), and phenylacetylene (1.9%).[213] About 80% of the ^{11}C recoil atoms are incorporated in higher boiling species; a Sephadex LH20 radiochromatogram is not much different from a chromatogram obtained for tritium recoiling in benzene.[214b] The yields of benzene and toluene are not much different in solid benzene, but in moderated gas-phase systems all product yields are lowered, whereas the polymer yield becomes 93%.[212] The observations are a proof of the extreme reactivity of atomic carbon toward benzene. In liquid toluene 25 compounds with a total yield of 26% were observed,[213] among them the isomeric xylenes, methylcycloheptatrienes, and methylstyrenes. The yields of the three xylenes are, within experimental error, statistical, as was also found with ^{14}C recoil atoms, but in the irradiation of *m*-xylene no 1,2,3-trimethylbenzene was detected.[214a] Complicated product compositions were furthermore observed for the xylenes and ethylbenzene as the target compounds.[213,214a]

3. Reaction Mechanisms

The large variety of products that is observed indicates already that the reactions of recoil carbon atoms with arenes are not consistent with the acceptance of a simple reaction mechanism. The situation is further complicated by the possible involvement of reactions of bare carbon atoms (in the ^3P ground state or in the ^1D excited state[215]), methylene, carbene (singlet or triplet), and methyl radicals, which species can be formed by subsequent hydrogen abstraction. It must be admitted that most of the mechanistic interpretations of the behavior of recoil carbon atoms is obtained from detailed studies of the reactions of beams of energetic $^{14}C^+$ ions with solid benzene. Lemmon et al. found in 1956 that 45 keV $^{14}C^+$ ions resulted in the production of 2% [^{14}C]benzene and of 1% [^{14}C]toluene, yields that are not significantly different from results obtained with ^{11}C atoms recoiling in solid benzene.[212,216] Even the distribution of the ^{14}C atoms in the toluene ring is exactly the same for 5 keV $^{14}C^+$ ions as for ^{14}C recoil atoms as mentioned before: C1 (50%), C2,6 (32%), C3,5 (12%), C4 (6%).[210,217] It seems that the energetic $^{14}C^+$ ions are neutralized before they react, because no differences in product yields were observed between the reactions of $^{14}C^+$ ions (0.1–15 keV) and neutralized ^{14}C particles (0.5–5 keV) that were formed by neutralization of a charged ion beam.[218] The major information about the specific reaction mechanisms was obtained through degradation studies on the most abundant products and by varying the energy of the $^{14}C^+$ beams between 15 keV and 2 eV.[219-221] The main results and conclusions are reviewed by Lemmon.[25]

TABLE XXIII. Absolute Yields (in Parentheses) and Activity Distributions (%) Obtained with $^{14}C^+$ Beams on Solid C_6H_6

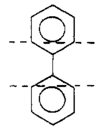
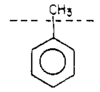
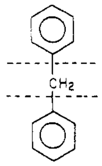
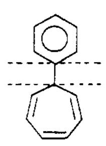
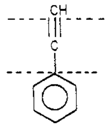
	5 keV	5 eV	2 eV
	(3.4)	(3.9)	(3.5)
	9 (1.3) 81 9	8 (1.7) 84 8	0 (5.5) 100 0
	85 (1.0) 13	63 (0.2) 41	94 (0.2) 6
	5 (1.5) 91 5	9 (2.6) 76 9	6 (2.9) 87 (3 eV) 6
	55 (2.5) 45	66 (0.5) 34	(0.9)
	16 (5.3) 52 30	22 (10.8) 57 19	9 (13.0) 85 (3 eV) 6
	30 (1.6) 66 4	33 (0.3) 62 4	30 (0.2) 63 6

Table XXIII shows some of the results. From the discussion as carried on by Lemmon three main reaction channels that lead to the major fraction of identified products with yields >1% can be distinguished:

(a) Acetylene and Phenylacetylene. The first compound can be formed by the decomposition of an excited C_7 intermediate or by a pickup of a ^{12}C atom to give a reactive C_2H_x fragment. The second pathway seems more plausible for the formation of phenylacetylene when the unequal distribution of the ^{12}C and ^{14}C atoms in the acetylene group is considered. This behavior can only be explained by an asymmetrical distribution of energy in the C_2H_x fragment, favoring the ^{14}C atom site to react with a benzene molecule.

(b) Toluene, Cycloheptatriene, Diphenylmethane, and Phenylcycloheptatriene. The activity distribution in the ring of toluene measured with 5 keV $^{14}C^+$ ions is exactly the same as found by Visser et al. with ^{14}C recoil atoms.[210] It is supposed that above 5 eV the precursor is $^{14}CH_2$ that inserts into a C–H bond. However, a mechanism through a cycloheptatriene intermediate formed by $^{14}CH_2$ insertion into a C–C bond followed by isomerization reactions can explain the ring distribution that diminishes when moving farther away from the methyl group. The sudden change observed at 5 eV in the ring/side chain ratio and in the total [^{14}C]toluene yield was connected to reactions of bare ^{14}C atoms. The routes to the formation of toluene and cycloheptatriene must be closely related. It appears that cycloheptatriene is formed at all eneriges from interactions of $^{14}CH_2$ because no changes in the activity distribution were observed at 5 eV. Diphenylmethane has also a maximum activity in the benzene ring at 5 eV and is therefore supposed to be formed by a similar phenylcarbene (C_6H_5CH) intermediate. This carbene can lead either to diphenylmethane by C–H insertion or to phenylcycloheptatriene by C–C insertion. The increase in the yield of both compounds at low $^{14}C^+$ energies is not well understood.

(c) Benzene and Biphenyl. A direct ^{14}C-for-^{12}C substitution is not considered as a serious reaction mechanism. The high yields of acetylene and phenylacetylene suggested the formation of a bicyclo-C_8 intermediate that could lead to benzene by splitting off two carbon species, but such a mechanism was rejected because no [^{14}C]benzene was formed in case of irradiations of *o*-xylene, whereas it was similarly expected that from a bridged C_{10} intermediate a C_4 group could also be emitted. Another possible route that can lead to labeled benzene is the formation of a bridged C_7 compound. The observation that similar yields of [^{14}C]benzene are formed in irradiations of solid benzene with 5 and 10 eV $^{14}CH_2^+$ ions as with $^{14}C^+$ ions further complicates the proposed mechanism.[222] The almost 100% labeling of the C1 position in biphenyl indicates that the new labeled phenyl ring reacts with another benzene molecule before the excess of energy is transferred to another carbon atom.

G. Other Recoil Atoms

1. Nitrogen

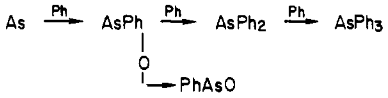
The only useful nitrogen isotope for recoil studies is ^{13}N ($t_{1/2}$ = 10 min), which was produced by the ^{12}C(d,n) ^{13}N, ^{13}C(p,n) ^{13}N, ^{12}C(p,γ) ^{13}N reactions.[223-225] The products that were identified in reactions with benzene are NH_3, HCN (or CN^-), and also small traces of benzonitrile. Their summed yield accounts only for about 30% of the total activity, and the remaining ^{13}N atoms are incorporated in other organic compounds. With ^{14}C recoil atoms [^{14}C]benzene was found in the irradiations of pyridine and [^{14}C]toluene from aniline. Conversely no [^{13}N]pyridine or [^{13}N]aniline was observed in the reactions of recoil ^{13}N atoms with benzene.[208,223] Temperature and dose effects are important factors for the activity distribution over the several products.

2. Phosphorus

The only isotope involved in aromatic studies is ^{32}P ($t_{1/2}$ = 14.3 d), which is produced in a nuclear reactor by either the ^{31}P(n,γ) ^{32}P or the ^{32}S(n,p) ^{32}P process.[226-229] During irradiation of a solution of phosphorus trichloride in benzene, labeled products were formed that upon hydrolysis yielded 18% phenylphosphoric acid. The same compound and also phenylphosphinic acid were obtained in irradiations of diphenyl sulfoxide and diphenyl sulfone. Four aromatic esters with P–O–C bounds and three aromatic phosphorus compounds with C–P bounds were identified in irradiated solid triphenyl phosphate[229] whereas solutions of aromatic phosphorus compounds in benzene resulted likewise in a variety of labeled species.[230] At the moment not much is known about the reaction mechanism of recoil phosphorus atoms.

3. Arsenic

The main isotope in use is ^{76}As ($t_{1/2}$ = 26.3 h), produced by thermal neutron irradiation of arsenic, whereas the reactions of ^{77}As ($t_{1/2}$ = 38.8 h) can be studied through the decay of ^{77}Ge ($t_{1/2}$ = 11.3 h). The studies of the reactions of recoil arsene with aromatic compounds are recently reviewed by Wiles and Baumgärtner.[231] These studies deal in general with the irradiations of solid phenylarsenic compounds (Ph_3As, Ph_3AsO, $Ph_3As(OH)_2$) or of solutions (Ph_3As, $AsCl_3$) in benzene. The ^{76}As products formed are mono-, di- and triphenylarsine compounds and their formation appears to be a stepwise process in which the first step is probably a hot reaction that can be interrupted at certain stages, e.g., by reactions with oxygen



$$\begin{tikzcd} As \arrow[r, "Ph"] & AsPh \arrow[r, "Ph"] \arrow[d, dash] & AsPh_2 \arrow[r, "Ph"] & AsPh_3 \\ & O \arrow[r] & PhAsO & \end{tikzcd}$$

4. Sulfur

^{35}S ($t_{1/2}$ = 87 d) is the only sulfur isotope whose reactions have been studied with aromatic systems. It can be produced with thermal neutrons by the ^{34}S(n,γ) ^{35}S and ^{35}Cl(n,p) ^{35}S reactions. Panek found 18% thiophenol and 80% polymeric species in chlorobenzene/benzene mixtures.[232] High yields of polymers were also found in carbon tetrachloride/benzene mixtures.[233] Benzenesulfinic and -sulfonic acids were found after irradiation of diphenyl sulfoxide and sulfone.[229] Insertion of ^{35}S recoil atoms into C–H and C–C bonds of benzothiazoles was reported.[234]

5. Other Elements

Wiles and Baumgärtner have also reviewed the reactions of many other radioactive recoil atoms with aromatic compounds (Ge, Sb, Tc, Te, Hg, Tl, Bi, Pb).[231] Due to identification problems no definite conclusions about reaction mechanisms could be drawn from the experiments.

Acknowledgments. This article would never have been written if Dr. F. M. Kaspersen (Organon, Oss) had not put pressure on me. The enthusiasm, interest, and comments of Dr. Kaspersen are gratefully acknowledged. I am also very grateful to Dr. E. Roduner and Professor Dr. H. Fischer (University of Zürich) for an introduction into muonium chemistry and collaboration with experiments at the Swiss Institute of Nuclear Research (SIN). This work was made possible by financial support from the Foundation for Fundamental Research on Matter (FOM) and the Netherlands Organisation for the Advancement of Pure Research (ZWO).

V. References and Notes

(1) Traynham, J. G. *Chem. Rev.* **1979**, *79*, 323–330.
(2) Tiecco, M. *Acc. Chem. Res.* **1980**, *13*, 51–57.
(3) Milligan, B.; Bradow, R. L.; Rose, J. E.; Hubbert, H. E.; Roe, A. J. *J. Am. Chem. Soc.* **1962**, *84*, 158–162.
(4) Berei, K.; Stöcklin, G. *Radiochim. Acta* **1971**, *15*, 39–46.
(5) Coenen, H. H.; Machulla, H. J.; Stöcklin, G. *J. Am. Chem. Soc.* **1977**, *99*, 2892–2898.
(6) Brinkman, G. A.; Veenboer, J. Th.; Visser, J.; Kaspersen, F. M.; Lindner, L. *Radiochim. Acta* **1979**, *26*, 85–91.
(7) Brinkman, G. A.; Kaspersen, F. M.; Visser, J. *Radiochim. Acta* **1980**, *27*, 7–10.

(8) Brinkman, G. A.; Veenboer, J. Th. *Radiochim. Acta*, in press.

(9) Everly, C. R.; Traynham, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 4316–4317; *J. Org. Chem.* **1979**, *44*, 1784–1787.

(10) Gandour, D. R. *Tetrahadron* **1980**, *36*, 1001–1009.

(11) Stöcklin, G. "Chemie Heiszer Atome"; Verlag Chemie: Berlin 1969.

(12) Urch, D. S. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1975**, *8*, 49–104.

(13) Dorrepaal, W.; Louw, R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1815–1818.

(14) Dorrepaal, W.; Louw, R. *Int. J. Chem. Kinet.* **1978**, *10*, 249–275.

(15) Moehlmann, J. G.; MacDonald, J. D. *J. Chem. Phys.* **1975**, *62*, 3061–3065.

(16) Cramer, J. A.; Rowland, F. S. *J. Am. Chem. Soc.* **1974**, *96*, 6579–6584.

(17) Cipollini, R.; Lilla, G.; Pepe, N.; Speranza, M. *J. Phys. Chem.* **1978**, *82*, 1207–1212.

(18) Benson, S. N.; Shaw, R. *J. Am. Chem. Soc.* **1967**, *89*, 5351–5354.

(19) Kim, P.; Lee, J. H.; Bonnans, R. J.; Timmons, R. B. *J. Chem. Phys.* **1973**, *59*, 4593–4601.

(20) Wolfgang, R. *Prog. Reaction Kinet.* **1965**, *3*, 97–169.

(21) Neutralization depends on the medium. In the case of tritium recoiling in liquid CCl_4, 99.5% of the activity is T^+ (Brinkman, G. A., Veenboer, J. Th., unpublished results). This may be due to nonneutralization of T^+, to thermal Cl abstraction, or to reaction of T with radiolytically produced Cl_2.

(22) Können, G. P.; Grosser, J.; Haring, A.; Eerkens, F.; Vries, A. E. de; Kistemaker, J. *Chem. Phys.* **1974**, *6*, 205–216.

(23) Parson, J. M., Shobatake, K.; Lee, Y. T.; Rice, S. A. *J. Chem. Phys.* **1973**, *59*, 1402–1415.

(24) Ascoli, S.; Cacace, F.; Giacomello, G.; Possagno, E. *J. Phys. Chem.* **1967**, *71*, 427–430.

(25) Lemmon, R. M. *Acc. Chem. Res.* **1973**, *6*, 65–73.

(26) Wolfgang, R. *Sci. Am.* **1968**, *219(4)*, 44–52.

(27) There is no good definition of a "hot" displacement or abstraction reaction, but in general it means a fast direct reaction in which the lifetime of the transition state is shorter than or comparable with molecular vibration times, which means that reaction occurs before the excitation energy is spread out over the whole molecule.

(28) Radiochlorine atoms recoiling in liquid CCl_4 provide a typical example of cage reactions. CCl_4 is inert toward thermal reactions of Cl atoms, but a yield of 35% $CCl_3{}^{38}Cl$ has been measured. This yield decreases to about 5% on the addition of several additives (Brinkman, G. A.; Gerritsen, G. A. V.; Visser, J. *Radiochim. Acta* **1979**, *26*, 153–161).

(29) Jones, W. E. Skolnik, G. E. *Chem. Rev.* **1976**, *76*, 563–592.

(30) (a) Smith, D. J.; Setser, D. W.; Kim, K. C.; Bogan, D. J. *J. Phys. Chem.* **1977**, *81*, 898–905. (b) Bogan, D. J.; Setser, D. W. *J. Chem. Phys.* **1976**, *64*, 586–601.

(31) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Phys. Chem.* **1970**, *74*, 2083–2090.

(32) (a) Shobatake, K.; Parson, J. M.; Lee, Y. T.; Rice, S. A. *J. Chem. Phys.* **1973**, *59*, 1427–1434. (b) Shobatake, K.; Lee, Y. T.; Rice, S. A. *Ibid.* **1973**, *59*, 1435–1448.

(33) Moehlmann, J. G., McDonald, J. C. *J. Chem. Phys.* **1975**, *62*, 3052–3060.

(34) Moss, M. G.; Ensminger, M. D.; Stewart, G. M.; Mardaunt, M.; McDonald, J. D. *J. Chem. Phys.* **1980**, *73*, 1256–1264.

(35) Vasek, A. H.; Sams, L. C. *J. Fluorine Chem.* **1972/3**, *2*, 257–262.

(36) Vasek, A. H.; Sams, L. C. *J. Fluorine Chem.* **1973/4**, *3*, 397–401.

(37) Jeffrey, C. L.; Sams, L. C. *J. Org. Chem.* **1977**, *42*, 863–865.

(38) Aten, A. H. W., Jr.; Koch, B.; Kommandeur, J. *J. Am. Chem. Soc.* **1955**, *77*, 5498.

(39) Li Wang Chang; Wang Tung; Fu Ke-Chien; Lin Yuang Fang. *Acta Chim. Sinica* **1965**, *5*, 369 (Abstract).

(40) Ledrut, J. H. T.; Point, J. J. *Radiochim. Acta* **1968**, *9*, 113–115.

(41) Anbar, M.; Neta, P. *J. Chem. Phys.* **1962**, *37*, 2757–2763.

(42) The production of the recoil ^{18}F atoms was performed in a nuclear reactor by a sequence of two nuclear reactions: $^6Li(n,\alpha)T$, followed by $^{16}O(T,n)\,^{18}F$.

(43) (a) Van Dulmen, A., Ph.D. Thesis, University of Amsterdam, 1968. (b) Van Dulmen, A.; Aten, A. H. W. Jr. *Radiochim. Acta* **1971**, *15*, 34–39.

(44) Berei, K.; Vasâros, L. *Radiochim. Acta* **1974**, *21*, 75–80.

(45) Brinkman, G. A.; Veenboer, J. Th.; Visser, J.; Lindner, L. *Radiochim. Acta* **1977**, *24*, 161–166.

(46) Brinkman, G. A.; Visser, J.; Lindner, L. *Radiochim. Acta* **1979**, *26*, 77–83.

(47) Brinkman, G. A.; Kaspersen, F. M.; Visser, J. *Radiochim. Acta* **1980**, *27*, 7–10.

(48) Bakker, C. N. M.; Brinkman, G. A.; Kaspersen, F. M. *Radiochim. Acta* **1979**, *26*, 163–170.

(49) Cacace, F.; Giacomello, P.; Wolf, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 3511–3515.

(50) For the gas-phase experiments the recoil ^{18}F atoms were produced by high-energy protons with an average intensity of 50 nA through the $^{19}F(p,pn)\,^{18}F$ nuclear reaction. The total organic yield depends on the average beam intensity, and considerable radiation effects seem to be involved. However, it is not known to which extent the ^{18}F-for-F substitution yield is influenced by the beam intensity. (Brinkman, G. A.; Visser, J. *Radiochem. Radioanal. Lett.* **1980**, *44*, 29–36.)

(51) Molecular fluorination, at almost finite F_2 dilution, of liquid toluene at 273 K delivers equal amounts of benzyl fluoride and the combined yields of fluorotoluenes.[49] The substitution mechanism must be quite different from that by recoil ^{18}F atoms.

(52) Kazmina, N. B.; German, L. S.; Rubin, I. D.; Knunyants, I. L. *Dokl. Akad. Nauk SSSR* **1970**, *194*, 1329–1331.

(53) Grakauskas, V. *J. Org. Chem.* **1970**, *35*, 723–728.

(54) Fragmentation products are unidentified compounds that elute from the GLC before biphenyls.

(55) Stöcklin, G.; Tornau, W. *Radiochim. Acta* **1968**, *9*, 95–105.

(56) Krasnyanskii, A. V.; Lisin, S. K.; Nesmeyanov, An. N.; Firsova, L. P. *Bull. Moscow Univ., Chem. Ser.* **1978**, *19*, 340–342.

(57) (a) Srpek, O. *Monatsh. Chem.* **1980**, *11*, 429 (b) Eibner, A. *Ber.* **1903**, *36*, 1229. (c) Olivier, S. C. J. *Recl. Trav. Chim. Pay-Bas* **1926**, *45*, 296. (d) Ansinger, F. *Monatsh. Chem.* **1934**, *64*, 153. (e) Goerner, G. L.; Nanertz, R. C. *J. Am. Chem. Soc.* **1951**, *73*, 2940–2941. (f) Voegtli, W.; Muhr, H.; Langer, P. *Helv. Chim. Acta* **1954**, *37*, 1627–1634.

(58) Bühler, R. E.; Ebert, H. *Nature (London)* **1967**, *214*, 1220–1221.

(59) Miller, B.; Walling, C. M. *J. Am. Chem. Soc.* **1957**, *79*, 4187–4191.

(60) Milligan, B.; Bradow, R. L. *J. Phys. Chem.* **1962**, *66*, 2118–2121.

(61) Lu, C. S.; Sugden, S. *J. Chem. Soc.* **1939**, *7*, 1273–1279.

(62) Miller, J. M.; Dodson, R. W. *J. Chem. Phys.* **1950**, *18*, 865–875.

(63) Kim, Y. S. *J. Korean Nucl. Soc.* **1973**, *5*, 44–54.

(64) Brinkman, G. A.; Veenboer, J. Th. *Radiochem. Radioanal. Lett.* **1979**, *41*, 307–316.

(65) (a) Kontis, S. S.; Urch, D. S. *Radiochim. Acta* **1971**, *15*, 21–26; (b) *Ibid.* **1973**, *19*, 13–16; (c) *Ibid.* **1973**, *20*, 39–47.

(66) Kontis, S. S.; Malcolme-Lawes, D. J.; Urch, D. S. *Radiochim. Acta* **1977**, *24*, 87–90.

(67) Bhave, R. H.; Rao, B. S. M. *Radiochim. Acta*, in press.

(68) Stöcklin, G.; Tornau, W. *Radiochim. Acta* **1966**, *6*, 86–93.

(69) Stöcklin, G.; Tornau, W. *Radiochim. Acta* **1968**, *9*, 95–105.

(70) Berei, K.; Vasâros, L. *Isotopenpraxis* **1968**, *4*, 19–23.

(71) Kardos, Zs.; Berei, K.; Vasâros, L. *Radiochem. Radioanal. Lett.* **1974**, *17*, 233–238.

(72) Brinkman, G. A.; Gerritsen, G. A. V.; Visser, J. *Radiochim. Acta* **1980**, *27*, 85–90.

(73) (a) Berei, K.; Ache, H. J. *J. Phys. Chem.* **1980**, *84*, 687–691. (b) Berei, K.; Vasâros, L.; Ache, H. J. *Ibid.* **1980**, *84*, 1063–1064.

(74) Echols, J. T.; Chuang V. T.-C.; Parrish, C. S.; Rose, J. E.; Milligan, B. *J. Am. Chem. Soc.* **1967**, *89*, 4081–4088.

(75) Wendenburg, C. J. Von; Henglein, A. *Z. Naturforsch.* **1962**, *176*, 590–597.

(76) Louwrier, P. W. F.; Bakker, C. N. M. (NIKHEF-K, Amsterdam), private communication.

(77) Stöcklin, G. "Hot Atom Chemistry Status Report"; IAEA: Vienna, 1975; pp 171–174.

(78) Jones, W. E.; MacKnight, S. D.; Teng, L. *Chem. Rev.* **1973**, *73*, 407–440.

(79) Yang, K. *J. Am. Chem. Soc.* **1962**, *84*, 3795–3799.

(80) Sauer, M. C., Jr.; Ward, B. *J. Phys. Chem.* **1967**, *71*, 3971–3983.

(81) Sauer, M. C., Jr.; Mani, J. *J. Phys. Chem.* **1970**, *74*, 59–63.

(82) Kim, P.; Lee, J. H.; Bonanno, R. J.; Timmons, R. B. *J. Chem. Phys.* **1973**, *59*, 4593–4601.

(83) Hoyermann, K.; Preuss, A. W.; Wagner, H. Gg. *Ber. Bunsenges. Phys. Chem.* **1975**, *79*, 156–165.

(84) Knutti, R.; Bühler, R. E. *Chem. Phys.* **1975**, *7*, 229–243.

(85) Sloane, T. M.; Brudzynski, R. J. *J. Chem. Phys.* **1980**, *72*, 4394–4400.

(86) Benson, S. W.; Shaw, R. *J. Am. Chem. Soc.* **1967**, *89*, 5351–5354.

(87) Benson, S. W.; Shaw, R. *J. Chem. Phys.* **1967**, *47*, 4052–4055.

(88) Pryor, W. A.; Lin, T. H.; Stanley, J. P.; Henderson, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 6993–6998.

(89) Henderson, R. W.; Pryor, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 7437–7441.

(90) (a) Neta, P.; Dorfman, L. M. *J. Phys. Chem.* **1969**, *73*, 413–417. (b) Neta, P.; Schuler, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 1056–1059.

(91) Neta, P. *Chem. Rev.* **1972**, *72*, 533–543.

(92) Michael, B. D.; Hark, E. J. *J. Phys. Chem.* **1970**, *74*, 2878–2884.

(93) Lichtscheidt, J.; Getoff, N. *Monatsh. Chem.* **1979**, *110*, 1377–1386.

(94) Calvert, J. G.; Pitts, J. N. Jr. "Photochemistry"; Wiley: New York, 1966; p 627.

(95) Brett, C. L.; Gold, V. *J. Chem. Soc., Perkins, Trans. 2* **1973**, *2*, 1437–1450.

(96) Brett, C. L.; Gold, V.; Perezo, G. *J. Chem. Soc., Perkin Trans. 2* **1973**, *2*, 1450–1453.

(97) Brett, C. L.; Gold, V. *J. Chem. Soc., Perkin Trans.* 2 **1973**, *2*, 1453–1456.

(98) Bennet, J. E.; Mile, B. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1398–1414.

(99) DiGregorio, S.; Yim, M. B.; Wood, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 8455–8458.

(100) Yim, M. B.; Wood, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 1004–1010.

(101) Tang, Y. N. *Isot. Org. Chem.* **1978**, *4*, 85–176.

(102) Zifferero, M. *Ener. Nucl.* (*Paris*) **1957**, *4*, 479.

(103) Brown, W. G.; Garnett, J. L. *Int. J. Appl. Radiat. Isot.* **1959**, *5*, 114–120.

(104) White, R. M.; Rowland, F. S. *J. Am. Chem. Soc.* **1960**, *82*, 4713–4717.

(105) Nesmeyanov, An. N.; Dzantiev, B. G.; Pozdeev, V. V.; Simonov, E. F. *Radiokhimiya* **1962**, *4*, 116–122.

(106) Pozdeev, V. V.; Nesmeyanov, An. N.; Dzantiev, B. G. *Radiokhimiya* **1962**, *4*, 398–404.

(107) Pozdeev, V. V.; Nesmeyanov, An. N.; Dzantiev, B. G. *Radiokhimiya* **1962**, *4*, 404–410.

(108) (a) Avdonina, E. N. *Radiokhimiya* **1962**, *4*, 617–619. (b) Avdonina, E. N.; Nesmeyanov, An. N.; Hao-Ming, W. *Radiokhimiya* **1964**, *6*, 323–329.

(109) Pozdeev, V. V.; Nesmeyanov, An. N.; Dzantiev, B. G. *Radiokhimiya* **1963**, *5*, 395–397.

(110) Garland, J. K.; Rowland, F. S. *Radiochim. Acta* **1965**, *4*, 115–116.

(111) Garland, J. K.; Rowland, F. S. *J. Phys. Chem.* **1966**, *70*, 735–743.

(112) Schroeder, J. W.; Monroe, N. M.; Garland, J. K. *J. Phys. Chem.* **1969**, *73*, 1252–1256.

(113) Brinkman, G. A.; Cecchi, A.; Hulsinga, E.; Visser, J. *Radiochim. Acta* **1980**, *27*, 197–202.

(114) Brinkman, G. A.; Veenboer, J. Th. *Radiochim. Acta*, in press.

(115) Wolfgang, R. *Prog. Reaction Kinet.* **1965** *3*, 97–160 (Table 5).

(116) Avdonina, E. N. *Radiokhimiya* **1967**, *9*, 741–742.

(117) Avdonina, E. N.; Minkovskii, E. B. *Radiokhimiya* **1968**, *10*, 51–58.

(118) Ivanov, Yu. A.; Kukin, P. P.; Filatov, E. S. *Radiokhimiya* **1973**, *15*, 893–895.

(119) Filatov, E. S.; Kukin, P. P.; Ivanov, Yu. A. *Radiochem. Radioanal. Lett.* **1973**, *15*, 157–165.

(120) Avdonina, E. N.; Nesmeyanov, An. N. *Radiokhimiya* **1968**, *10*, 568–574.

(121) (a) Fosche, E.; Hahn, W.; Stroh, R. Houben-Weyl, "Methoden der Organische Chemie", 4th ed.; 1962; Band V/3, p 79. (b) Shteingarts, V. D.; Oksenenko, B. G. *Zh. Org. Khim.* **1970**, *6*, 1611. (c) Bastock, J. W.; Harely, M. E.; Pedler, A. E.; Tatlow, J. C. *J. Fluorine Chem.* **1975**, *6*, 331–355. (d) Shtark, A. A.; Shteingarts, V. D. *Izv. Sib. Otd. Akad. Nauk SSSR* **1976**, 123. (e) Shtark, A. A.; Shteingarts, V. D. *Zh. Org. Khim.* **1976**, *12*, 1499.

(122) Sokolowska, A. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1965; Vol. I, pp 255–264.

(123) Sokolowska, A. *Radiochim. Acta* **1968**, *10*, 44–49.

(124) Ache, H. J.; Herr, W.; Thiemann, A. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1961; Vol. II, pp 111–121.

(125) Ciranni, E.; Ciranni, G.; Guarino, A. *Gazz. Chim. Ital.* **1965**, *95*, 52–60.

(126) Elutrask, A. M.; Johnsen, R. H. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1961; Vol. II, pp 123–132.

(127) Krasnyanskii, A. V.; Lisin, S. K.; Nesmeyanov, An. N.; Firsova, L. P. *Bull. Moscow Univ., Chem. Ser.* **1978**, *19*, 340–342.

(128) Simirskii, Yu. N.; Firsova, L. P. *Radiokhimiya* **1978**, *20*, 300–304.

(129) Firsova, L. P.; Do Kim Tyung. *Radiokhimiya* **1967**, *9*, 681–687.

(130) Firsova, L. P.; Muravêv, V. V.; Kapitanchuk, V. A. *Radiokhimiya* **1969**, *11*, 711–754.

(131) Muravêv, V. V.; Firsova, L. P. *Radiokhimiya* **1969**, *11*, 730–732.

(132) Gershtein, S. S.; Petrukhin, V. I.; Ponomarev, L. I.; Prokoshkin, Yu. D. *Sov. Phys. Usp.* **1969**, *97*, 3–36.

(133) Souder, P. A.; Casperson, D. E.; Crange, T. W.; Hughes, V. W.; Lu, D. C.; Orth, H.; Reist, H. W.; Yam, M. H. *Phys. Rev. Lett.* **1975**, *34*, 1417–1420.

(134) Varlamov, V. G.; Dolgashein, B. A.; Dobretsov, Yu. P.; Kirillov-Ugryumov, V. G.; Nevoky, P. L.; Rogozhin, A. M.; Smilga, V. P. *Yad. Fiz.* **1975**, *21*, 120–132; *Sov. J. Nucl. Phys. Engl. Transl.* **1975**, *21*, 61–68.

(135) Hughes, V. W.; McColm, D. W.; Ziock, K.; Prepast, R. *Phys. Rev. Lett.* **1960**, *5*, 63–65.

(136) Goldanski, V. J.; Firsov, F. G. *Annu. Rev. Phys. Chem.* **1971**, *22*, 209–258.

(137) Virsov, V. G.; Goldanski, V. J. *Int. Rev. Sci. Inorg. Chem., Ser. Two* **1975**, *8*, 1–48.

(138) Brewer, J. H.; Crowe, K. M.; Gygax, F. N.; Schenck, A. "Muon Physics III"; 1975; Chapter VII, Section 1.

(139) Schenck, A. "Exotic Atoms"; International School of Physics and Exotic Atoms: Erice, 1977; pp 355–458.

(140) "Positronium and Muonium Chemistry"; Adv. *Chem. Ser.* **1979**, No. 175.

(141) Brewer, J. H.; Crowe, K. M. *Annu. Rev. Nucl. Part. Sci.* **1978**, *28*, 239–326.

(142) "Exotic Atoms 79"; Crowe, K., Duclos, J., Fiorentine, G., Tozelli, G., Eds.; Plenum Press: New York and London, 1980.

(143) Percival, P. W. *Radiochim. Acta* **1979**, *26*, 1–14.

(144) Brodskii, A. M. *Zh. Eksp. Teor. Fiz.* **1963**, *44*, 1612–1617; *Sov. Phys.—JETP* (*Engl. Transl.*) **1863**, *17*, 1085–1088.

(145) Fleming, D. G.; Garner, D. M.; Vaz, L. C.; Walker, D. C.; Brewer, J. H.; Crowe, K. M. In ref 140, p 309.

(146) Roduner, E.; Fischer, H. *Hyperfine Interact.* **1979**, *6*, 413–417.

(147) Swanson, R. A. *Phys. Rev.* **1958**, *112*, 580–586.

(148) Reference 140, Table IV, p 325.

(149) Roduner, E.; Brinkman, G. A.; Burkhard, P.; Louwrier, P. W. F.; Fischer, H. *Radiochim. Acta*, submitted.

(150) Firsov, V. G.; Byakov, V. M. *Zh. Eksp. Teor. Fiz.* **1964**, *47*, 1074–1083; *Sov. Phys.*—JETP (*Engl. Transl.*) **1965**, *20*, 719–725.

(151) Firsov, V. G. *Zh. Eksp. Teor. Fiz.* **1965**, *48*, 1179–1183; *Sov. Phys.—JETP* (*Engl. Transl.*) **1965**, *21*, 786–789.

(152) Babaev, A. I.; Balats, M. Ya.; Myasishcheva, G. G.; Obokhov, Yu. V.; Roganov, V. S.; Firsov, V. G. *Zh. Eksp. Teor. Fiz.* **1966**, *50*, 877–889; *Sov. Phys.—JETP* (*Engl. Transl.*) **1966**, *23*, 583–591.

(153) Myasishcheva, G. G.; Obukhov, Yu. V.; Roganov, V. S.; Firsov, V. G. *Khim. Vys. Energ.* **1967**, *1*, 390–393; *High Energy Chem.* (*Engl. Transl.*) **1967**, *1*; 340–342.

(154) Myasishcheva, G. G.; Obukhov, Yu. V.; Roganov, V. S.; Firsov, V. G. *Khimiya Vysokikh Energii* **1969**, *3*, 510–514; *High Energy Chem.* (*Engl. Transl.*) **1969**, *3*, 463–466.

(155) Roduner, E.; Brinkman, G. A.; Burkhard, P.; Strub, W.; Fischer, H. Unpublished SIN results.

(156) Brinkman, G. A., Veenboer, J. Th. Unpublished results.

(157) Roduner, E.; Percival, P. W.; Fleming, D. G.; Hochmann, J.; Fischer, H. *Chem. Phys. Lett.* **1978**, *57*, 37–40.

(158) Roduner, E., Thesis, University of Zürich, 1979.

(159) (a) Roduner, E.; Fischer, H. *Chem. Phys. Lett.* **1979**, *65*, 582–586. (b) Roduner, E., ref 142, pp 379–397.

(160) Roduner, E.; Fischer, H. *Chem. Phys.* **1981**, *54*, 261–276.

(161) Holzschuh, E.; Kündig, W.; Patterson, B. D. *Proc. 2nd Int. Conf. Muon Spin Rotation, Hyperfine Interact.*, in press.

(162) Roduner, E.; Strub, W.; Burkhard, P.; Hochmann, J.; Percival, P. W.; Fischer, H. *Chem. Phys.*, to be submitted.

(163) Brewer, J. H.; Crowe, K. M.; Gygax, F. N.; Johnson, R. F.; Fleming, D. G.; Schenck, A. *Phys. Rev. A* **1974**, *9*, 495–507.

(164) Ivanter, I. G.; Smilga, V. P. *Zh. Eksp. Teor. Fiz.* **1968**, *54*, 559–570; *Sov. Phys.—JETP* (*Engl. Transl.*) **1968**, *27*, 301–306.

(165) Ivanter, I. G.; Smilga, V. P. *Zh. Eksp. Teor. Fiz.* **1968**, *55*, 1521–1531; *Sov. Phys.—JETP* (*Engl. Transl.*) **1969**, *28*, 796–801.

(166) Ivanter, I. G.; Smilga, V. P. *Zh. Eksp. Teor. Fiz* **1971** *60*, 1985–2000; *Sov. Phys.—JETP* (*Engl. Transl.*) **1971**, *33*, 1070–1077.

(167) Brewer, J. H.; Gygax, F. N.; Fleming, D. G. *Phys. Rev. A* **1973**, *8*, 77–86; ref 138, p 55.

(168) Fischer, W. E. *Helv. Phys. Acta* **1976**, *49*, 629–643.

(169) Percival, P. W.; Fischer, H. *Chem. Phys.* **1976**, *16*, 89–99.

(170) Gygax, F. N.; Schenck, A. *Chem. Phys. Lett.* **1977**, *47*, 11–14.

(171) Roduner, E.; Percival, P. W.; Fischer, H. "Meson Chemistry and Mesomolecular Processes in Matter"; Dubna, 1977; pp 326–347.

(172) (a) Percival, P. W.; Roduner, E.; Fischer, H. *Chem. Phys.* **1978**, *32*, 353–367. (b) Percival, P. W.; Roduner, E.; Fischer, H. Reference 140, pp 333–355.

(173) Walker, D. C.; Jean, Y. C.; Fleming, D. G. *J. Chem. Phys.* **1979**, *70*, 4534–4541.

(174) Roduner, E., Proc. 2nd Int. Conf. on Muon Spin Rotation, *Hyperfine Interact.*, in press.

(175) (a) Patrick, R.; Prosser, G. S. *Nature* (*London*) **1960**, *187*, 1021. (b) Boeyens, J. C. A.; Herbstein, F. H. *J. Phys. Chem.* **1965**, *69*, 2153–2159. (c) Duncan, W. A.; Swinton, F. L. *Trans. Faraday Soc.* **1966**, *62*, 1082–1089. (d) Duncan, W. A.; Sheridan, J. P.; Swinton, F. L. *Trans. Faraday Soc.* **1966**, *62*, 1090–1096. (e) Fenley, D. V.; Scott, R. L. *J. Phys. Chem.* **1967**, *71*, 4103–4110.

(176) Willard, J. E. "Chemical Effects of Nuclear

Transformations"; IAEA: (a) Vienna, 1960; Vol. I, pp 215–227; (b) Vienna, 1964; Vol. I, pp 221–238.
(177) de Jong, D.; van Halteren, B. (NIKHEF-Amsterdam), private communication.
(178) Coenen, H. H. Thesis, University of Köln, 1979.
(179) Cacace, F.; Stöcklin, G. *J. Am. Chem. Soc.* **1972**, *94*, 2518–2520.
(180) Knust, E. J.; Halpern, A.; Stöcklin, G. *J. Am. Chem. Soc.* **1974**, *96*, 3733–3738.
(181) Knust, E. J. *J. Am. Chem. Soc.* **1977**, *99*, 3037–3041.
(182) Estrup, P. J., Wolfgang, R. *J. Am. Chem. Soc.* **1960**, *82*, 2661–2665, 2665–2669.
(183) Milman, M. *Radiochim. Acta* **1964**, *2*, 180–188.
(184) Kontis, S. S.; Santiwongs, P.; Weston, M. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1964; Vol. I, pp 311–331.
(185) (a) Katsanos, N. A.; Stamouli, M. I. *Radiochim. Acta* **1967**, *7*, 126–130. (b) Katsanos, N. A.; Leontiadis, J. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 295–305.
(186) Laser, M.; Merz., E. *Radiochim. Acta* **1966**, *5*, 65–70.
(187) (a) Katsanos, N. A.; Varvoglis, A. G. *J. Chem. Soc.* **1964**, 5935–5942. (b) Katsanos, N. A. *Ibid.* **1965**, 4751–4757.
(188) Halpern, A. *Radiochim. Acta* **1971**, *15*, 83–88.
(189) Siekierska, K. E.; Milman, M.; Fenger, J. *Radiochem. Radioanal. Lett.* **1970**, *4*, 251–256.
(190) Kemnitz, E. J.; Hahn, H. K. J.; Rack, E. P. *Radiochim. Acta* **1970**, *13*, 112–114.
(191) Narbutt, J.; Danzewics, D.; Halpern, A. *Radiochim. Acta* **1967**, *7*, 55–57.
(192) Arnikar, H. J.; Patnaik, S. K.; Pathak, T. P. S. *Radiochim. Acta* **1976**, *23*, 167–169.
(193) Siekierska, K. E.; Halpern, A.; Maddock, A. G. *J. Chem. Soc. A* **1968**, 1645–1651.
(194) Llabador, Y.; Halter, M. E. *Radiochem. Radioanal. Lett.* **1975**, *20*, 241–249.
(195) Ünak, T.; Llabador, Y. *Radiochim. Acta* **1972**, *18*, 5–11.
(196) (a) Macrae, J. E. C.; Shaw, P. D. F. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1327–1336; (b) *Ibid.* **1962**, *24*, 1337–1350.
(197) Vernois, J.; Arapaki-Strapêlias, H.; Muxart, R. *Radiochem. Radioanal. Lett.* **1974**, *17*, 145–154.
(198) Zaitsev, V. M.; Alekseev, E. G. *Radiokhimiya* **1974**, *17*, 132–136.
(199) Muxart, R.; Vernois, J.; Strapêlias, H. *Radiochim. Acta* **1974**, *21*, 88–89.
(200) (a) Macrae, J. E. C.; Shaw, P. F. D. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1327–1336; (b) *Ibid.* **1962**, *24*, 1337–1350.
(201) (a) Halpern, A. *J. Inorg. Nucl. Chem.* **1963**, *25*, 619–625. (b) Halpern, A.; Sokolwska, A. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1893–1903.
(202) (a) Vernois, J.; Abdel Ghani, A. H.; Muxart, M. *Radiochem. Radioanal. Lett.* **1972**, *12*, 7–14. (b) Abdel Ghani, A. H.; Vernois, J.; Muxart, M. *Radiochem. Radioanal. Lett.* **1974**, *18*, 359–364.
(203) Akcay, H.; Cailleret, J.; Abbé, J. C., Paulus, J. M.; Llabador, Y. *J. Chim. Phys. Physicochim. Biol.* **1973**, *70*, 970–972.
(204) Samson, G.; Aten, A. H. W., Jr. *Radiochim. Acta* **1970**, *13*, 220–221.
(205) Berei, K.; Vasâros, L.; Norseyev, Yu. V.; Khalkin, V. A. *Radiochem. Radioanal. Lett.* **1976**, *26*, 177–184.
(206) Vasâros, L.; Norseyev, Yu. V.; Meyer, G. J.; Berei, K.; Khalkin, V. A. *Radiochim. Acta* **1979**, *26*, 171–176.
(207) Wolf, A. P. *Annu. Rev. Nucl. Sci.* **1960**, *10*, 259–280.
(208) Wolf, A. P. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1960; Vol. II, pp 4–15.
(209) Wolf, A. P. *Adv. Phys. Org. Chem.* **1964**, *2*, 201–277.
(210) Visser, R.; Redvanly, C. R.; Sixma, F. L. J.; Wolf, A. P. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 533–536.
(211) Suryanarayana, B.; Wolf, A. P. *J. Phys. Chem.* **1958**, *62*, 1369–1373.
(212) Rose, T.; Mackay, C.; Wolfgang, R. *J. Am. Chem. Soc.* **1967**, *89*, 1529–1530.
(213) Williams, R. L.; Voigt, A. F. *J. Phys. Chem.* **1969**, *73*, 2538–2544.
(214) (a) Brinkman, G. A.; Gerritsen, G. A. V.; Visser, J. *Radiochem. Radioanal. Lett.* **1979**, *41*, 383–392. (b) Brinkman, G. A.; Veenboer, J. Th. Unpublished results.
(215) Taylor, K. K.; Ache, H. J.; Wolf, A. P. *J. Am. Chem. Soc.* **1976**, *98*, 7176–7178.
(216) Lemmon, R. M.; Mazetti, F.; Reynolds, F. L.; Calvin, M. *J. Am. Chem. Soc.* **1956**, *78*, 6414–6415.
(217) Lin, Hz-Hong; Lemmon, R. M. *J. Phys. Chem.* **1971**, *71*, 3524–3525.
(218) Pohlit, H. M.; Lin, Hz-Hong; Erwin, W.; Lemmon, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 5421–5424.
(219) Pohlit, H. M.; Lin, Hz-Hong; Lemmon, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 5425–5429.
(220) (a) Pohlit, H. M.; Erwin, W.; Lin, Hz-Hong; Lemmon, R. M. *J. Phys. Chem.* **1971**, *75*, 2555–2557. (b) Pohlit, H. M.; Lemmon, R. M. *J. Phys. Chem.* **1971**, *75*, 2558–2560.
(221) Lintermans, J.; Erwin, W.; Lemmon, R. M. *J. Phys. Chem.* **1972**, *76*, 2521–2524.
(222) Erwin, W. R.; Gordin, B. E.; Lemmon, R. M. *J. Phys. Chem.* **1976**, *80*, 1852–1853.
(223) Koski, W. S.; Malimin, D.; Berta, M. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1964; Vol. I, 177–184.
(224) Welch, M. J.; Straatmann, M. G. *Radiochim. Acta* **1973**, *20*, 124–129.
(225) Sensui, Y.; Tamura, K.; Fukuda, Y.; Iwai, H. *Radiochim. Acta* **1976**, *23*, 12–15.
(226) Halmann, M. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1960; Vol. I, pp 195–202.
(227) Siuda, A. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1964; Vol. I, pp 265–272.
(228) Kiso, Y.; Kobayashi, M.; Kitaoka, Y.; Kawamoto, K.; Takada, J. *Radiochim. Acta* **1969**, *11*, 65–71.
(229) Wheeles, O. H.; Gonzales, C. L.; Facetti, J. F. *Radiochim. Acta* **1969**, *12*, 79–82.
(230) Jovanović, O., in a discussion on ref 227, pp 272–275.
(231) Wiles, D. R.; Baumgärtner, F. "Chemical Effects of Nuclear Transformations in Inorganic Systems"; North-Holland: Amsterdam, 1979; pp 261–273.
(232) Panek, K.; Sloma, L. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1960; Vol. II, pp 209–211.
(233) Dzantiev, B. G.; Stukan, R. A.; Shvedchikov, A. P.; Shukhov, A. V. "Chemical Effects of Nuclear Transformations"; IAEA: Vienna, 1964; Vol. I, pp 399–407.
(234) Niisawa, K.; Taki, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 57–59.