emission intensities were measured at 450 and 480 mm with readings being taken directly off the microphotometer. Tubes were then opened and aerated; the residual signal was measured and subtracted from that of the unopened tube. Emission spectra recorded on a Houston X-Y recorder were identical with those reported for benzophenone in other solvents.[31]

EPR spectra of the biphenyls were obtained in both ethanol and methylcyclohexane glasses at 77 °K on a Varian E-4 EPR spectrometer. The light from a 1 kW high-pressure mercury-xenon arc, filtered only through water, was focused directly onto the cavity.

Phosphorescence spectra of the biphenyls were obtained at 77 °K on the Aminco with the phosphoroscope attachment. Excitation was at 254 mm. Biphenyl concentrations were approximately 10^{-2} M. Absorption spectra were obtained on a Cary 14.

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Selectivity and Reactivity of Hot Homolytic Aromatic Substitution by Recoil Chlorine Atoms

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Abstract: Hot homolytic aromatic chlorination has been studied in simple monosubstituted benzenes C_6H_5X (X = F, Cl, Br, I, NH_2, OCH_3, NO_2) using recoil chlorine atoms produced via the $^{37}Cl(n,\gamma)^{38}Cl$ reaction. In the gas phase, Cl-for-H substitution is a minor process, proceeding exclusively via hot direct replacement with little selectivity. In the liquid phase, dilution experiments reveal that two processes contribute to hydrogen substitution: a one-step reaction being first order with respect to the concentration of the aromatic substrate and a multistep process involving at least two substrate molecules. In either case the Cl atoms exhibit slight electrophilic features. Application of the Hammett correlation reveals a higher selectivity ($\rho^+ = -1.43$) for the multistep than for the one step process ($\rho^+ = -0.56$). Both chlorination reactions seem to proceed via complex formation. In the case of Cl-for-X substitution, thermoneutral or exothermic processes (X = Cl, Br, I, NO_2) can be attributed to thermal σ-complex formation, while endothermic processes (X = F, OCH_3, NH_2) are typically low yield, direct hot replacement reactions being first order with respect to the substrate concentration.

Introduction

In contrast to photolytically or radiolytically produced thermal halogen atoms, hot recoil halogen generated via nuclear reactions can undergo one-step substitution. The reactions of hot tritium and halogen recoil atoms with simple aliphatic and aromatic compounds have been studied extensively in recent years (for review cf. ref 1 and 2). Even though the major process is hydrogen abstraction, substitution of hydrogen and halogen atoms is also observed. The radiochemical yields of such substitution processes are often small but the nuclear recoil technique so far provides the only possibility to study endothermic one-step substitution of halogen atoms. We were interested in hot homolytic aromatic substitution. Although a number of studies have been carried out in aromatic systems both with recoil tritium and recoil chlorine (for a recent review, cf. ref 2), the mechanistic question of how aromatic substitution by recoil atoms proceeds remains unanswered. Of particular interest is the question of selectivity and reactivity. Early work on aromatic recoil tritiation by Ache et al.[3] and on aromatic recoil bromination by willard and collaborators[4] revealed a rather unselective behavior. Among the recoil

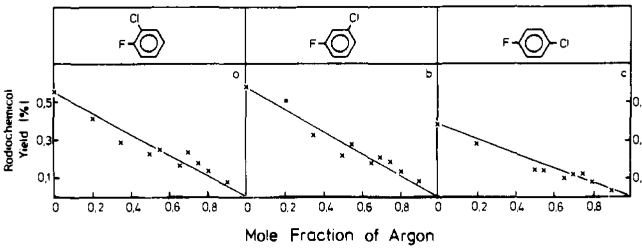


Figure 1. Argon moderator effect on Cl-for-H substitution yield (% of total ^{38}Cl activity) in the fluorobenzene system (17 mol % CCl_4, 70 Torr, 22 °C).

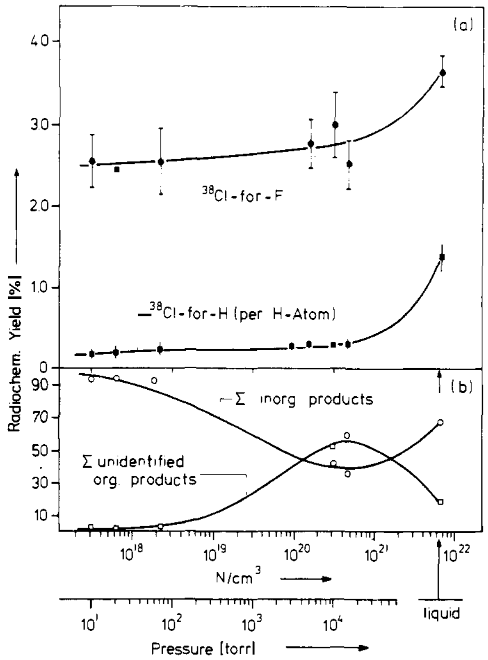


Figure 2. Density effect on the radiochemical yields of ^{38}Cl-for-F, ^{38}Cl-for-H substitution, total inorganic and missing products in the fluorobenzene system (9.5 mol % CCl_4, 0.5 mol % I_2, 22 to 200 °C).

halogens, nucleogenic chlorine is particularly well suited for such studies since it reacts as a neutral ground-state atom in the organic systems of interest.[2] Following the previous systematic studies by Stöcklin and collaborators on selectivity and reactivity in recoil halogenation,[5-7] it was the goal of this work to further elucidate the question of complex formation vs. direct reaction by assessing pressure, phase and solvent effects.

Experimental Section

Chemicals. Aniline, anisol, bromobenzene, and nitrobenzene obtained from Schuchardt with 99% purity were subjected to additional purification by fractional distillation. Benzene (>99.7%, Uvasol, Merck), fluorobenzene, chlorobenzene, iodobenzene (all >99.5% from Fluka), pentane (>99.7%, Uvasol, Merck), iodine (>99.99% Merck), and tetrachlorocarbon (>99.7%, Uvasol, Merck) were used without purification after a gas chromatographic analysis.

Sample Preparation and Irradiation. Our basic experimental procedure has been described in detail in a previous paper.[6] In all cases the $^{37}Cl(n,\gamma)^{38}Cl$ process was used for the in situ production of recoil ^{38}Cl ($T_{1/2}$ = 37.3 min). Neutron irradiations were carried out in the FRJ-1 at a thermal neutron flux density of $1.9 \times 10^{10}\ cm^{-2}\ s^{-1}$ for a period of about 90 min. The irradiation temperature was adjusted with a heating cartridge as required. The accompanying γ-exposure rate was about 10^4 R/h.

For irradiations in the gaseous state, weighed amounts (corresponding to the vapor pressure required during irradiation) of the aromatic compound together with 9.5 mol % CCl_4 as chlorine source and 0.5 mol % I_2 as scavenger were placed in quartz ampules of about 1 to 200 mL volume, 0.5-5 cm i.d., depending on pressure. They were outgassed on a vacuum line by freezing and melting cycles and then sealed. In several cases (moderator experiments) increasing amounts of Ar were added but no iodine scavenger. Experiments in the liquid phase were carried out in micro quartz ampules of about 100 to 200 μL, containing the aromatic substrate and the Cl source CCl_4 at a molar ratio of 3:1 and increasing amounts of *n*-pentane in the case of the dilution experiments. No iodine scavenger was added. After neutron irradiation, 2.5 mL of a 1:1 mixture of aqueous Na_2SO_3–Na_2CO_3 solution (10%) was added. The organic products were extracted with 2 mL of carrier containing pentane. The small liquid samples were crushed directly under the surface of the extraction mixture. After washing, centrifugation, and drying, aliquots of the phases were submitted to radioactivity determination and, in the case of the organic phase, to a radio gas chromatographic analysis. The relatively low ^{38}Cl activity made it necessary to use a discontinuous technique,[5,6] individually absorbing the eluted products on charcoal contained in tubes, which then were submitted to radioactivity measurement in a well type scintillation counter. In the presence of iodine or bromine, γ-ray spectroscopy, using a Ge(Li) detector in conjunction with a 4000 channel analyzer, had to be applied for the determination of the total ^{38}Cl activity.

Gas chromatographic separation of the aromatic compounds, in particular of the ortho, meta, and para isomers was achieved by using 4-m glass columns (3.5 mm i.d.) filled with 20% Igepal CO-880 on Chromosorb W-AW-DMCS (60-80 mesh) or 6% Bentone 38 and 20% Silicon oil DC 200 on Chromosorb W-AW-DMCS (60-80 mesh).[8,9]

Results and Discussion

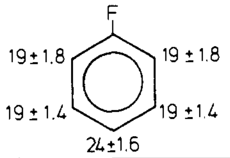
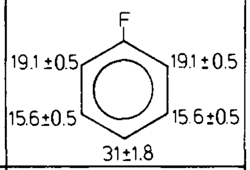
Moderator Experiments in the C_6H_5F System. In order to obtain information on a possible contribution of thermal chlorine atoms to the ^{38}Cl-for-H substitution we first carried out a moderator experiment in the fluorobenzene system. It can be seen from Figure 1 that the absolute radiochemical yields of the *o*-, *m*-, and *p*-chlorofluorobenzene decrease almost linearly and can be extrapolated to zero at 100 mol % Ar. The isomer distribution remains constant over the entire moderator concentration range. The results clearly indicate that thermal reactions do not contribute to ^{38}Cl-for-H substitution and that in the gas phase at a total pressure of 70 Torr, only a single reaction channel leads to hydrogen substitution.

Density Dependence in the C_6H_5F System. In view of the dramatic pressure and density effects observed in aliphatic systems for recoil fluorine[10] and chlorine,[11] it was interesting to look for the effect of density in an aromatic system. The results obtained in the fluorobenzene system are shown in Figure 2. It can be seen (Figure 2a) that both ^{38}Cl-for-H and ^{38}Cl-for-F substitution remains practically constant within the experimental error over the entire pressure range studied, i.e. from about 10 to 10^4 Torr. It should also be noted that Cl-for-F substitution in the gas phase is 10 to 15 times more effective than Cl-for-H substitution per H atom. An increase of these substitution products is only observed when going from the gaseous to the liquid phase; here the Cl-for-H substitution increases by about a factor of 5 and that of the Cl-for-F substitution by a factor of only 1.3. The inorganic yields ($H^{38}Cl$, ^{38}ClF, $^{38}ClCl$) decrease with increasing pressure from about 95 to 40% (Figure 2b), while the missing organic activity (unidentified high-boiling products and "polymers") shows a concomitant increase. When going to the liquid phase, however, this trend is reversed.

In the gaseous phase, the isomer distribution is practically statistical (cf. Table I) with slight enhancement in the para position. In the liquid phase the orientation effect expected from the fluorine substituent is slightly reflected; i.e., substitution in the meta position decreases on account of the para position.

In agreement with the moderator experiment, the results again clearly indicate a single substitution mechanism for the gas phase. This is reflected by the unchanged isomer distribution. Excitation decomposition or collisional stabilization

Table I. Isomer Distribution of Cl-for-H Substitution in the Fluorobenzene System. Comparison of Liquid Phase and Gas Phase (25 Mol % CCl_4)

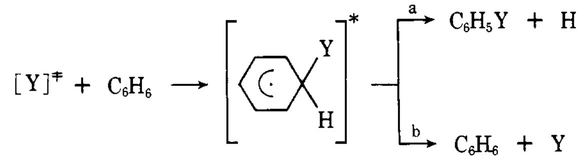
	
Gas Phase 10–15000 Torr 22–200°C	Liquid Phase 22°C

seems to play a minor role in these aromatic systems in the entire pressure range studied. In the gas phase Cl-for-H substitution seems to proceed entirely via a direct replacement process which does not involve any third molecule. As expected, such direct replacement processes are relatively rare events. Cl-for-H substitution occurs with only 0.2 to 0.3% (per H atom) of the total ^{38}Cl produced. As has been pointed out by Urch,[2] these results are consistent with hot collision of rather long duration, i.e., a few bond vibrations, which enable the molecule to adjust to the impact of the incoming atom. Since the excess energy of the recoil atom is absorbed by the molecule the chance of breaking particular bonds is reduced, hence the low vapor-phase yields. The fact that the yield of the Cl-for-F substitution is 10 to 15 times higher than that of the Cl-for-H substitution cannot simply be explained on the basis of a direct replacement process. With increasing pressure, large amounts of unidentified higher boiling products and polymers seem to form. This was to be expected since addition reactions may lead to a σ complex or chlorocyclohexadienyl radical which will undergo further addition reactions with surrounding substrate molecules thus leading eventually to a variety of polynuclear products.

The observed phase effect is considerably less pronounced in the aromatic system than in aliphatic systems,[11] particularly in the case of the Cl-for-F substitution. Obviously, in the gas phase Cl-for-F substitution is much more effective in aromatic systems, and it seems reasonable to assume that this is due to complex formation, which does not occur in gaseous aliphatic systems.

The further increase of substitution product yields after gas-to-liquid phase transition, particularly in the case of ^{38}Cl-for-H substitution, seems to indicate a contribution from an additional substitution process. This is also reflected by the small but significant change in isomer distribution (cf. Table I). The fact that selectivity slightly increases may be explained by assuming an intermediate chlorinating agent, e.g., a ^{38}Cl-substrate complex, which, in a second step, will be reacting with another substrate molecule, leading to a less energetic and consequently more selective chlorination. A similar explanation could, of course, also be given by assuming a contribution from caged radical-radical combination when going to the liquid phase.

Solvent Effects. Dilution experiments were carried out by Kontis and Urch,[12] who had studied the ^{38}Cl-chlorobenzene yield in chlorobenzene-alcohol mixtures, which decreased from 61 to a limit of 10% upon dilution with aliphatic alcohol. The authors proposed intermediate π-complex formation of rather long half-life, from which a scavenger could extract ^{38}Cl or which might eventually undergo chlorine exchange to yield labeled chlorobenzene. We have used as diluent an alkane which is much more effective as a scavenger than benzene itself, due to the great ease of hydrogen abstraction. The activation energy for H abstraction from gaseous pentane by thermal chlorine atoms is only about 0.5 kcal/mol.[13] Dilution with an alkane has also been carried out by Avdonina[14] in the recoil tritium-benzene system. In Figure 3 we compare our results obtained for the recoil ^{38}Cl-benzene system with those of the recoil ^{3}H-benzene system.[14] It is interesting to note that the T-for-H substitution yields were considerably higher than those of ^{38}Cl-for-H substitution. This can hardly be explained on the basis of purely mechanical consideration concerning mass difference, but rather by assuming the formation of an intermediate σ complex; i.e. the incoming energetic recoil atom $[Y]^{\ddagger}$ directly forms a carbon halogen bond, i.e., an excited σ complex



(1)

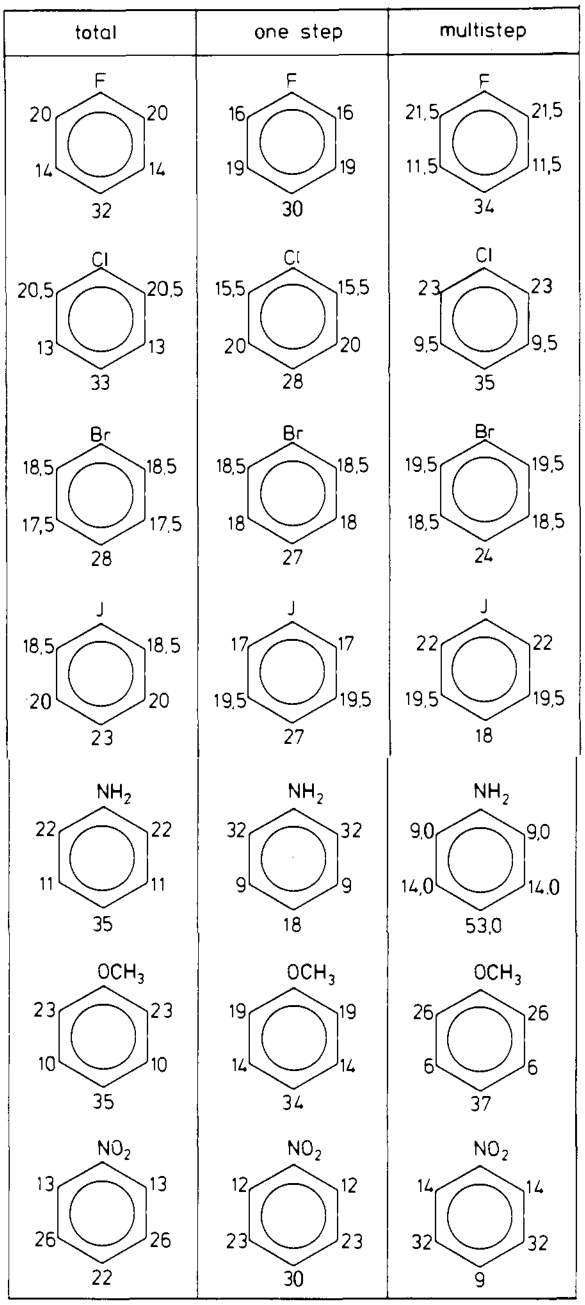
Since the resulting X-for-H yield in halobenzenes is below 10%, obviously a significant fraction undergoes the reverse reaction, i.e., the loss of the incoming atom Y. The most favorable case is T-for-H substitution (Y = T), where the almost symmetrical σ complex can undergo reactions 1a and 1b with almost equal probability, neglecting the presumably large isotope effect. The considerably higher yields observed in T-for-H substitution when compared with Cl-for-H substitution also provide good evidence against a major contribution from caged radical reactions in the chlorine case, e.g.

$$\cdot {}^{38}Cl + \cdot C_6H_4X \rightarrow C_6H_4X^{38}Cl \qquad (2)$$

Caging, if any, should only occur in recoil chlorine systems. In general, no caging is found in recoil tritium substitution reactions, due to the great ease of out of cage diffusion for the smaller tritium atoms. Yet, the T-for-H yields are considerably higher than those of Cl-for-H substitution.

If we deal with a simple bimolecular process which is first order with respect to the concentration of the aromatic compound, a linear dilution curve is to be expected. Any process involving more than one aromatic molecule should give rise to a stronger decrease. When correcting for the dilution to zero mole fraction of n-pentane by multiplying the radiochemical yield A_n at a mole fraction X_n with $(1 - X_n)^{-1}$, one obtains $A_0 = A_n(1 - X_n)^{-1}$ for $X_n \neq 1$, i.e., the corrected yields. In Figure 4 we have plotted the uncorrected (above) and the corrected substitution yields (below) in the benzene and fluorobenzene systems. The curves indicate that ^{38}Cl-for-H substitution consists of two different channels, a multistep and a single-step process. The multistep process is eliminated by the solvent above about 50 to 60 mol % n-pentane and only the one step process remains (cf. Figure 4; corrected yields remain constant above about 0.6 mole fraction, lower curves). In contrast, the ^{38}Cl-for-F substitution in fluorobenzene remains practically unaffected by the dilution (constant corrected yields), thus indicating only a simple bimolecular reaction, being first order with respect to the concentration of the aromatic substrate. In ^{38}Cl-for-H substitution dilution with n-pentane obviously provides an easy possibility to discriminate between at least two product forming processes, one of them being a simple one-step reaction. For instance, Figure 4 indicates that in pure liquid benzene about a 3.5% yield may be attributed to a one-step process and a 5.3% yield to at least one additional multistep reaction; in fluorobenzene the corresponding values are 2.5 and 5.0%, respectively. Hence, only about 40 and 32%, respectively, of ^{38}Cl-for-H substitution occurs via a one-step process, while ^{38}Cl-for-F substitution in fluorobenzene proceeds exclusively through a one-step process being first order with respect to the concentration of the aromatic compound.

Table II. Isomer Distribution of Cl-for-H Substitution in Liquid Monosubstituted Benzenes (25 Mol % CCl_4, 22 °C) for Different Chlorinating Processes (Total = Undiluted System, One-Step = >60 Mol % *n*-Pentane, Multistep = Total Minus One Step)



total	one step	multistep
F 20 20 14 14 32	F 16 16 19 19 30	F 21,5 21,5 11,5 11,5 34
Cl 20,5 20,5 13 13 33	Cl 15,5 15,5 20 20 28	Cl 23 23 9,5 9,5 35
Br 18,5 18.5 17,5 17.5 28	Br 18,5 18,5 18 18 27	Br 19,5 19,5 18,5 18,5 24
J 18,5 18.5 20 20 23	J 17 17 19,5 19,5 27	J 22 22 19,5 19,5 18
NH_2 22 22 11 11 35	NH_2 32 32 9 9 18	NH_2 9,0 9,0 14,0 14.0 53,0
OCH_3 23 23 10 10 35	OCH_3 19 19 14 14 34	OCH_3 26 26 6 6 37
NO_2 13 13 26 26 22	NO_2 12 12 23 23 30	NO_2 14 14 32 32 9

The isomer distribution also changes with increasing dilution (cf. Table II). As the contribution from the multistep process is removed with increasing dilution the relative yield of the meta position increases on account of the other positions; i.e., the selectivity is decreasing.

Substituent Effects. Distinction between one-step and multistep ^{38}Cl-for-H substitution was carried out by means of the dilution technique for a variety of monosubstituted benzenes in order to obtain further information on intramolecular selectivity of individual processes. Analyses, however, were carried out only for the undiluted and the 60 mol % *n*-pentane containing system, since Figure 4 shows that the corrected substitution yields are constant above about 50 to 60 mol % *n*-pentane in the case of benzene and fluorobenzene.

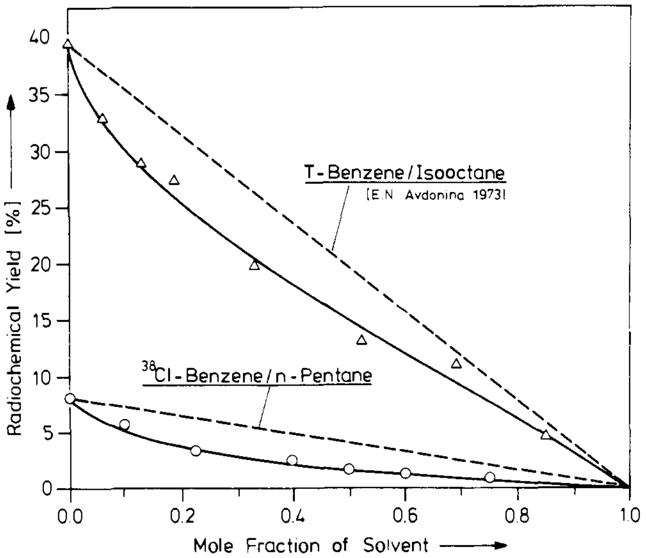


Figure 3. Solvent effect on the radiochemical yields of T-for-H[14] and on ^{38}Cl-for-H substitution in liquid benzene (25 mol % CCl_4, no scavenger, 22 °C).

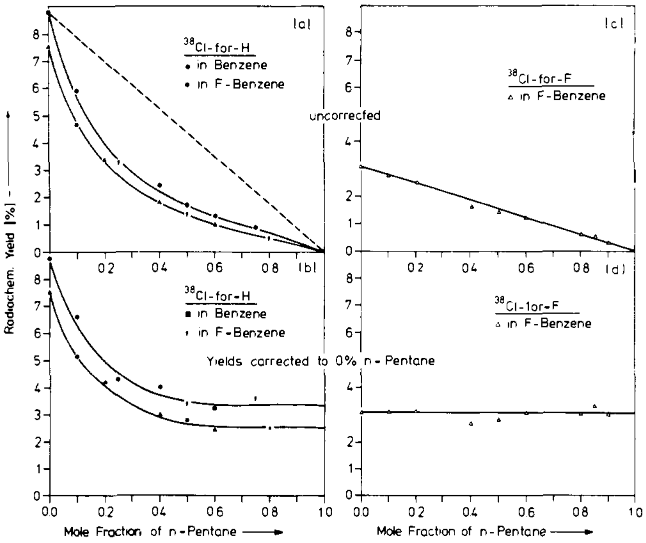


Figure 4. *n*-Pentane solvent effect on the radiochemical yields of ^{38}Cl-for-H and ^{38}Cl-for-F substitution, respectively, in the liquid benzene and fluorobenzene system (25 mol % CCl_4, no scavenger, 22 °C). Uncorrected radiochemical yields (a and c); corrected to zero % *n*-pentane (b and d).

By subtracting this remaining constant yield (one-step process) from the total yield in the undiluted aromatic compound the yield of the multistep process was obtained. In Table II the relative isomer distribution is shown for a variety of monosubstituted benzenes with activating and deactivating groups for the undiluted system (total substitution), the 60 mol % *n*-pentane containing system (one-step substitution) and the difference between both (multistep substitution). It can be seen that multistep substitution exhibits intramolecular selectivity higher than that of the one-step process. In general the features of isomer distribution reflect the features of an electrophilic substitution with low positional selectivity. Although this cannot be expected a priori for homolytic substitution,[15] electrophilic properties can be expected for chlorine atoms due to their high electronegativity.[16] It is interesting to note that the isomer distribution resembles very much the one observed in photocyanation by Spagnolo et al.[17] In fact, the distribution for the total chlorination process in anisole is practically identical with that observed for thermal cyanation. A ρ^+ value

Table III. *n*-Pentane Solvent Effect on Major Product Distribution in C_6H_5X/CCl_4 System (Molar Ratio $C_6H_5X{:}CCl_4$ = 3:1); No Scavenger

System[a]	Radiochemical yield %						
	Org. products	Inorg. products	Missing org, activity	Cl-for-H total	Cl-for-H per H atom	Cl-for-X total	X subst. / H subst.
$C_6H_5NH_2$ 1	7.8 ± 0.8	92.2 ± 0.8	4.6 ± 1.3	1.82 ± 0.48	0,36 ± 0.10	0.92 ± 0.27	2.6
2	11.5 ± 0.9	88.5 ± 0.9	8.2 ± 1.1	0.91 ± 0.25	0.18 ± 0.05	1.18 ± 0.29	6.7
3				0.91	0.18		
$C_6H_5CH_3$ 1	29.7 ± 1.8	70.3 ± 1.8	21.6 ± 4.5	3.69 ± 0.75	0.74 ± 0.15	1.70 ± 0.11	2.3
2	19.8 ± 2.7	80.3 ± 2.7	9.1 ± 3.6	1.95 ± 0.23	0.40 ± 0.05	1.65 ± 0,18	4.1
3				1.74	0.34	0.05	0.15
C_6H_5F 1	40.2 ± 2.0	59.8 ± 2.0	25.3 ± 2.6	7.52 ± 0.38	1.50 ± 0.09	3.06 ± 0.33	2.0
2	38.8 ± 5.5	61.2 ± 5.5	31.0 ± 3.5	2.45 ± 0.30	0.50 ± 0.05	2.33 ± 0.20	4.7
3				5.07	1.00	0.73	0.73
C_6H_5Cl 1	65.7 ± 1.8	34.3 ± 1.8	25.5 ± 3.6	6.99 ± 1.01	1.40 ± 0.20	29.3 ± 2.51	21
2	53.8 ± 5.3	46.2 ± 5.3	41.8 ± 8.8	2.28 ± 0.23	0.45 ± 0.05	4.60 ± 0.88	10
3				4.71	0.95	24.7	26
C_6H_5Br 1	64.7 ± 3.3	35.3 ± 3.3	45.8 ± 9.5	3.25 ± 1.5	0.65 ± 0.30	13.82 ± 4.71	21
2	47.6 ± 7.2	52.4 ± 7.2	40.4 ± 9.4	1.28 ± 0.55	0.26 ± 0.11	1.88 ± 0.46	8
3				1.97	0.39	11.94	31
C_6H_5I 1	37.9 ± 4.2	62.1 ± 4.2	20.0 ± 5.0	1.88 ± 0.35	0.38 ± 0.07	9.93 ± 0.58	26
2	56.8 ± 8.8	43.2 ± 8.8	46.8 ± 10.0	1.03 ± 0.15	0.20 ± 0.02	3.60 ± 0.68	18
3				0.85	0.18	6.33	35
$C_6H_5NO_2$ 1	37.6 ± 4.5	62.4 ± 4.5	22.9 ± 9.2	1.56 ± 0.35	0.31 ± 0.07	13.1 ± 4.4	42
2	36.8	63.2	19.8	0.65	0.13	3.10	24
3				0.91	0.18	10.0	56

[a] 1 = total yield in undiluted aromatic system; 2 = yields at ≥60 mol % *n*-pentane corrected to zero dilution (one-step process); 3 = difference between 1 and 2 (multistep process).

of −0.42 was found by the authors, thus supporting their view regarding electrophilicity associated with the cyano radical.

However, a drastic difference exists when comparing our results with those obtained in high-temperature chlorination,[13] where a strong preference of the meta position is observed, while in recoil chlorination, substitution predominantly occurs at the para position. Since high-temperature chlorination is supposed to proceed via a chain reaction induced by thermal chlorine atoms, the significant difference in selectivity observed provides additional evidence against any major contribution from thermal caged radical reactions in recoil chlorination.

We also applied the linear free energy relationship. Even though its application should not strictly be valid for nonequilibrium hot processes, we feel that the high-energy step is involved only in the non-rate-determining formation of a complex. Final product formation and positional selectivity essentially seem to be a thermal process. If this is the case, a Hammett correlation should be found. In the present instance the radiochemical yield ratios (A) can be used instead of the partial rate constants; i.e., the relative reactivities of the para and meta position p_f and m_f, respectively, are given by

$$p_f = k_p/k_0 = \frac{k_{para}}{k_{C_6H_6}/6} = \frac{A_{p\text{-}C_6H_4XCl}\cdot 6}{A_{C_6H_5Cl}} \tag{3}$$

and

$$m_f = k_m/k_0 = \frac{k_{meta}/2}{k_{C_6H_6}/6} = \frac{A_{m\text{-}C_6H_4Cl}\cdot 3}{A_{C_6H_5Cl}} \tag{4}$$

However, proportionality between relative rate constants and relative yields is only fulfilled when the reactivity of recoil chlorine toward other competing processes such as hydrogen abstraction remains practically unchanged in the different systems. In a first approximation this is probably true for the series of halobenzenes and nitrobenzene; however, it will be changing drastically when going to compounds such as anisole or aniline. In the latter case, hydrogen abstraction from aliphatic C-H or N-H bonds will be enhanced. This is also obvious from individual product yields (cf. Table III). In the case of anisole and aniline, the inorganic yields are considerably higher than those of other systems. Despite the general difficulties obviously arising when the Hammett correlation is applied to multi-channel hot atom reactions, we have attempted to do so for the Cl-for-H substitution in fluoro-, chloro-, bromo- and nitrobenzene, using Brown's σ^+ constants.[18] The data are given in Table IV for the total chlorination, the one-step, and the multistep process. Figures 5a, b, and c show the Hammett plot, for which the best fit was determined by means of linear regression calculation, for the two different contributions to substitution (b and c) and for the total chlorination process. Despite the relatively large errors expected, a reasonable correlation of the normalized partial rate factors p_f and m_f with the σ^+ parameters according to the Hammett relationship is obtained, giving a slope of $\rho^+ = -0.95$ for the total process of $\rho^+ = -0.56$ for the one-step and $\rho^+ = -1.43$ for the multistep process. The negative sign indicates the electrophilic character of the processes. The absolute values of the reaction constants reflect the above-mentioned isomer distribution. The smallest value, i.e., the highest reactivity and lowest selectivity, is obtained for the one-step process, the multistep chlorination having a considerably higher absolute value, which is again in agreement with what one would expect if an intermediate chlorinating complex is formed.

The low positional selectivity and the fact that the one-step process is indeed first order with respect to the aromatic substrate seem to indicate that this reaction proceeds via direct addition, i.e., the formation of a σ complex (eq 1). It is interesting to note that the primary formation of a σ complex was demonstrated for homolytic arylation by DeTar.[19]

The multistep process, on the other hand, may involve a π- to σ-complex reaction sequence. The formation of an intermediate excited Cl-solvent complex between aromatic substrate and chlorine atom similar to charge transfer complexes might explain a two or more step mechanism. The existence of charge transfer complexes in aromatic solvents has been demonstrated by Bühler and Ebert[20] by pulse radiolytic techniques. It has also been found by Russel[21,22] that in the

Table IV. Brown's Substituent Constants and Relative Reactivities in Hot Homolytic Chlorination by Recoil Chlorine in Liquid Monosubstituted Benzenes

X	σ^+	Total k/k_0	Total Log k/k_0	"One-step" k/k_0	"One-step" Log k/k_0	"Multistep" k/k_0	"Multistep" Log k/k_0
p-F	−0.07	1.683	0.226	1.270	0.104	1.951	0.290
m-F	0.35	0.725	−0.140	0.826	−0.083	0.660	−0.181
p-Cl	0.11	1.574	0.197	1.130	0.053	1.861	0.270
m-Cl	0.40	0.626	−0.203	0.809	−0.092	0.508	−0.294
p-Br	0.15	0.547	−0.262	0.574	−0.241	0.530	−0.276
m-Br	0.40	0.380	−0.421	0.330	−0.481	0.412	−0.385
p-NO_2	0.79	0.200	−0.633	0.487	−0.313	0.068	−1.170
m-NO_2	0.67	0.277	−0.557	0.348	−0.459	0.231	−0.636
		ρ^+	−0.947		−0.556		−1.428

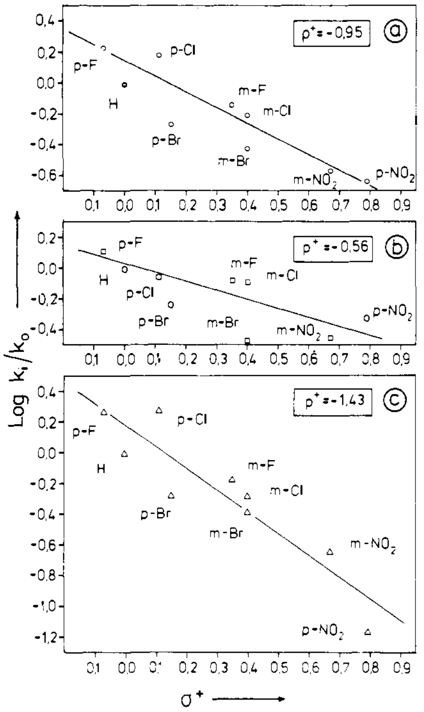


Figure 5. Hammett plot for recoil chlorination of monosubstituted liquid benzenes (a = total substitution; b = one-step substitution; c = multistep substitution).

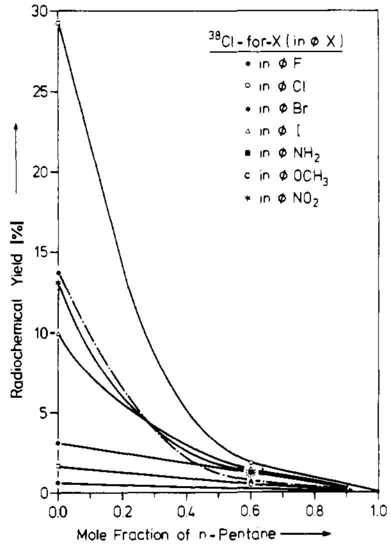
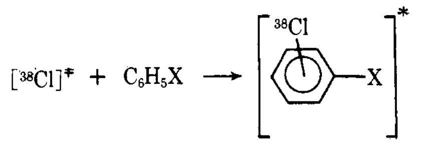
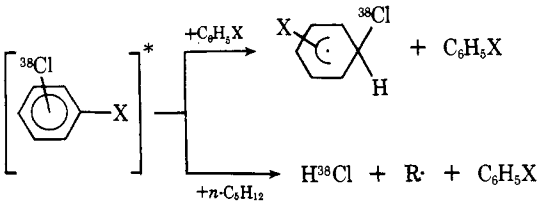


Figure 6. Solvent effect on the radiochemical yields of ^{38}Cl-for-X substitution (X = F, Cl, Br, I, NH_2, OCH_3, NO_2) in monosubstituted liquid benzenes C_6H_5X (25 mol % CCl_4, no scavenger, 22 °C).

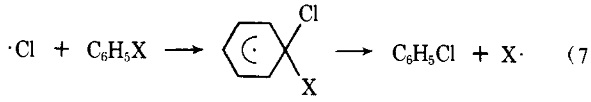
chlorination of alkanes aromatic solvents increase the selectivity, an effect which was attributed to the intermediate formation of a π complex. In our case such an intermediate π complex, probably excited due to the high kinetic energy of the incoming chlorine atom, can either undergo intra- or intermolecular rearrangement to form a σ complex or in a competing process react with *n*-pentane by hydrogen abstraction (eq 5 and 6). In the high-density liquid phase, π complex formation seems to be favored, while in the gas phase even at high pressure the excited complex rather collapses, releasing a thermal chlorine atom, which then can only undergo abstraction and addition reactions. This is also in agreement with the observed phase effect (see below).


(5)


(6)

Replacement of Substituent Groups. Recoil atoms are also able to replace halogen atoms or other substituent groups such as NO_2 in aromatic molecules. It was demonstrated by White and Rowland[23] that the replacement yields for heavy atoms and groups by recoil tritium in monosubstituted benzoic acids increase with decreasing energy of theC–X bond. This was also shown by Pozdeev et al.[24] in T-for-X replacement in monohalobenzenes. For recoil halogens, however, the yield-determining factors of heavy atom replacement are more complex as has been pointed out by Berei and Stöcklin.[7] The present results confirm the Cl-for-X substitution yields at different solvent (*n*-pentane) concentrations as shown in Figure 6. While the yields follow the sequence Cl ≫ Br > NO_2 > I > F > OCH_3 > NH_2 in the undiluted system, the order changed in the presence of 60% mol % *n*-pentane to Cl > I > NO_2 ≃ F > Br > OCH_3 > NH_2. Both sequences do not reflect any simple relationship to chemical effects such as bond energy, where the yields would follow I > Br > Cl ≃ NO ≃ OCH_3 ≃ NH_2 > F. Figure 6 also shows that a linear dilution curve is only obtained for the replacement of F (cf. also Figure 4), OCH_3, and NH_2. Obviously the replacement here is first order with respect to C_6H_5X and in agreement with the small phase effect (cf. Figure 2) for the ^{38}Cl-for-F substitution. The major process seems to be a hot one-step substitution for both the gaseous and the liquid phase. The somewhat lower yields in ^{38}Cl-for-OCH$_3$ and ^{38}Cl-for-NH$_2$ substitution are most likely due to the presence of H atoms at the substituent X, thus giving rise to competing H abstraction.

Substitution of Cl, Br, I, and NO$_2$, on the other hand, shows a strongly overproportional decrease in yield with increasing *n*-pentane concentration, particularly in the case of the ^{38}Cl-for-Cl exchange. As was demonstrated previously by Berei and Stöcklin[7] by means of iodine scavenger experiments, these substitution processes exhibit considerable contribution from thermal processes, a fact which is particularly true for the ^{38}Cl-for-Cl exchange. This is apparently the case whenever the substitution process is thermoneutral or exothermic (X = Cl, Br, NO$_2$, 1). The yield for these thermal and/or multistep processes decreases in the order of Cl > Br ≃ NO$_2$ > I; i.e., with the exception of NO$_2$, the yields decrease with decreasing C–X bond energy of the leaving group X. Exothermic and thermoneutral homolytic replacement of substituents such as 1, Br, Cl, NO$_2$ by Cl atoms is well known,[25,26] and it is assumed that these replacement reactions proceed via σ-complex formation:[27]


(7)

The fact that yields decrease with decreasing C–X bond energy does not, however, follow from reaction 7, in which case the reverse effect would be expected. An explanation can be provided by assuming a major competition from X abstraction

$$\cdot\mathrm{Cl} + \mathrm{C_6H_5X} \rightarrow \mathrm{C_6H_5}\cdots\mathrm{X}\cdots\mathrm{Cl} \rightarrow \mathrm{XCl} + \mathrm{C_6H_5}\cdot \quad (8)$$

which might overcompensate the replacement reaction when going from Cl to Br to I substituents. This is also reflected by the concomitant increase in corresponding inorganic yields (cf. Table III).

That the chlorine atom preferentially attacks the region of the maximum electron density distribution, viz. the halogen substituent, is also reflected by the relatively high yield of Cl-for-F substitution as compared to Cl-for-H substitution in fluorobenzene. It can be seen from Figure 4 that the one-step Cl-for-H substitution yield is almost identical with the Cl-for-F substitution yield, despite the fact that there are 5 times as many H atoms available per molecule as F-atoms. This result cannot possibly be explained by the small difference between the bond energies.

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Heat Capacities of Ureas and Water in Water and Dimethylformamide

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Abstract: Apparent molal heat capacities are reported for eight ureas and substituted ureas and for water in *N,N*-dimethylformamide as a solvent. Data for four substituted ureas are reported in water as a solvent. Excess apparent molal heat capacities are calculated and group contributions to the excess heat capacities are calculated in aqueous solutions. It is found that the relative hydrogen bonding strengths of protons to the peptide carbonyl oxygen are NH$_2$ > OH$_2$ > NH. Denaturation of proteins is postulated to be caused either by interaction of the urea NH$_2$ protons with the peptide carbonyl or by a hydrophobic interaction when alkyl-substituted ureas are most effective.

Although aqueous solutions of urea, substituted ureas, and guanidinum salts are found to be effective denaturants of proteins, the mechanism of the denaturation process is incompletely understood. On the one hand there is evidence for direct "binding" of denaturants to proteins.[1,2] Alternatively, it has been proposed that changing of the water structure by the denaturant plays a role in the denaturation process. Unfortunately, in spite of the many data that are too numerous to reference there is no unanimity of opinion as to the exact effect of urea, for example, on the solvent structure.[3] Perhaps a portion of the problem is in the semantics involved when one speaks of "structure making" or "structure breaking" solutes. Heat capacity measurements have proven useful in elucidating solute-solvent interactions,[4-8] but one limitation in the cal-