

Gas Phase Aromatic Substitution by Positive Bromine and Iodine Ions from $^{80m}\text{Br}(\text{IT})^{80}\text{Br}$ and $^{125}\text{Xe}(\text{EC})^{125}\text{I}$

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Abstract: Gas phase aromatic bromination and iodination by positive bromine or iodine species resulting from the nuclear decay of $^{80m}\text{Br}(\text{IT})^{80}\text{Br}$ and $^{125}\text{Xe}(\text{EC})^{125}\text{I}$, respectively, have been studied in simple aromatic systems of the type $\text{C}_6\text{H}_5\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{CH}_3$). At high Ar- or Xe-moderator concentrations electrophilic substitution reactions of thermal positive halogen ions can be observed. The positional selectivity of the unsolvated Br^+ or I^+ ions is very low by solution chemistry standards; not only hydrogen substitution but also replacement of the substituent X takes place. In the case of Br^+ considerable rearrangement occurs in Br-for-H substitution in fluorobenzene, which increases with increasing concentration of Ar and decreasing total pressure. The results can be rationalized on the basis of excitation isomerization, which competes with collisional stabilization and proton transfer after the formation of an excited arenonium ion. For both bromine and iodine ions the ease of X replacement increases relative to that of hydrogen replacement from fluorobenzene to bromobenzene, and a concomitant increase of the relative amount of ortho substitution is observed. The formation of an aryldihalonium precursor is discussed.

The *in situ* production of nucleogenic species in nuclear transformations can be conveniently used for the study of aromatic substitution. The technique provides a variety of complementary features when compared with classical methods, such as organic solution chemistry, photolysis, radiolysis, and mass spectrometry. The inherently small concentration of the nucleogenic species does not lead to double substitution nor to chain reactions, and experiments can be carried out in the liquid as well as in the gaseous phase over a wide pressure range.¹ Both homolytic substitution (SH_2) and electrophilic substitution (SE_2) can be studied by a suitable selection of the nuclear process and system. We have reported²⁻⁴ on the hot homolytic aromatic substitution (SHH_2) by high kinetic energy halogen atoms produced in (n, γ) and ($n, 2n$) reactions and demonstrated the low intra- and intermolecular selectivity of these species.

The use of labeled gaseous ions from radioactive decay processes provides a unique tool for the study of electrophilic reactions in gaseous systems. This technique fills a gap between solution chemistry and mass spectrometric methods, since it not only allows one to study the substitution reaction at high pressures but also yields information on the structure of the product molecule, *i.e.*, the ortho, meta, and para isomer distribution. Extensive studies have been carried out by Cacace and coworkers⁵⁻⁸ on the gas phase aromatic substitution by $^3\text{HeT}^+$ and R^+ resulting from the nuclear decay of suitable tritiated precursors. Difficulties are encountered when one searches for other decay produced ionic species, such as positive halogen

ions. A number of isomeric transition and electron capture decay processes can, in principle, be applied to create positive halogen ions, particularly those of bromine and iodine.

The chemical consequences of the isomeric transition of ^{80m}Br ($T = 4.4$ hr) are particularly well known and represent a nuclear phenomenon, which is broadly described as "inner shell ionization."⁹ The highly converted isomeric transition of ^{80m}Br gives rise to the Auger process, and vacancy cascades lead to multiply charged daughter ions. In the case of a molecule such as $\text{CH}_3^{80m}\text{Br}$ charge distribution and Coulomb repulsion cause the molecule to explode, thus creating charged fragment ions. Charge spectrometric measurements have shown that in the above mentioned case radioactive ^{80}Br ions with a predominant charge of +7 are created.¹⁰ The Br ions also possess kinetic energies of several electron volts resulting from Coulomb repulsion. Previous work by several investigators has demonstrated that bromine generated by the $^{80m}\text{Br}(\text{IT})^{80}\text{Br}$ can undergo reactions with organic substrate molecules such as methane and methyl bromide in the gas phase as thermal positive bromine ions.¹¹⁻¹⁹

When the decay is allowed to occur in a sufficiently large excess of a rare gas, having an ionization potential intermediate between the first and the second ionization potential of Br, the charge of the Br^{n+} ions is rapidly reduced to +1 by charge-exchange processes and the excess kinetic energy is taken away by moderating colli-

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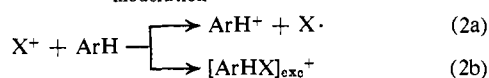
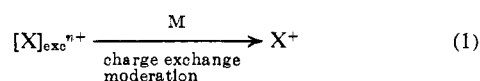
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sion. Cacace and Stöcklin²⁰ have recently used this technique to study the gas phase aromatic substitution by brominium ions, and their results on the intra- and intermolecular selectivity of the Br species from the isomeric transition of ^{80m}Br indeed indicate the behavior of an extremely reactive and unselective electrophile, as expected from Br⁺ ($\Delta H^\circ = 300$ kcal/mol). Their results suggested that the gas phase electrophilic attack involves two kinetically distinct steps, namely the formation of a complex, which determines the intermolecular selectivity, followed by the competition of the individual reaction centers for the electrophile, which regulates the intramolecular selectivity. The suggestion is reminiscent of the π -complex theory of Olah,²¹ an extension of which to the gas phase has been actually proposed in recent mass spectrometric²² and radiolytic²³ studies.

Positive iodine ions can be conveniently prepared via the electron capture decay of ¹²⁵Xe(EC)¹²⁵I ($T = 60$ days). Like internal conversion, EC decay gives rise to an inner shell vacancy, followed by Auger charging, thus leading to ¹²⁵Iⁿ⁺ ions. Schroth and Adloff,²⁴ in a study of the reactions of the ¹²⁵I ions in gaseous methane, estimated the mean primary charge to be about +8 to +9. This is in agreement with direct charge spectroscopic measurements²⁵ on ¹²⁵Te ions from the EC decay of ¹²⁵I. The ¹²⁵I ions from the EC decay of ¹²⁵Xe also possess excess kinetic energies up to 4.4 eV, resulting from neutrino recoil. Like ⁸⁰Br generated in IT, thermal halogen ions should eventually undergo reactions with the aromatic substrate molecules, when the decay is allowed to take place in an excess of Ar or Xe. The method can be summarized by the following scheme:



Both charge exchange with the aromatic molecule (eq 2a) and formation of the arenonium ion (eq 2b) are exothermic in systems such as benzene and halobenzenes. However, the formation of the arenonium ion should predominate,²⁰ and, even if a fraction of halogen ions is neutralized, the resulting thermal halogen atoms will be scavenged by the aromatic substrate without leading to substitution.

The goal of this work was to extend this type of study in order to obtain further mechanistic information on electrophilic aromatic substitution by unsolvated positive halogen ions.

Experimental Section

Materials. Benzene, toluene, fluorobenzene, *p*-difluorobenzene, chlorobenzene, and bromobenzene were obtained from Schuchardt GmbH, München, with a purity >99%. They were further purified by preparative glc.²⁶ Argon and xenon with a stated purity

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level of 99.997 and 99.997%, respectively, were purchased from l'Air Liquide. Methyl bromide with a purity of 99.5%, obtained from J. T. Baker Chemical Co, Phillipsburg, N. J., was used without further purification, since it was purified after labeling (see below).

Preparation of ^{80m}Br Source. ^{80m}Br-labeled methyl bromide, as the source of ⁸⁰Br ions, was prepared by direct recoil labeling of methyl bromide. CH₃Br (1 ml) was sealed in a quartz ampoule and irradiated in the FRJ-2 reactor at a thermal neutron flux density of 10¹⁴ cm⁻² sec⁻¹ for 10 sec. One hour after the irradiation the methyl bromide was purified by gas chromatography on a 2.4-m Polypak 2 (40-70 mesh) column (18-mm i.d.) at 105° and a helium flow of 300 ml/min. The CH₃Br fraction, containing ^{80m}Br-, ⁸⁰Br-, and ⁸²Br-labeled methyl bromide, was trapped in an acetone/CO₂ mixture and transferred into the reaction vessel (see below). The other radioisotopes formed during the irradiation (⁸²Br, ⁸⁰Br, ^{82m}Br) do not disturb, since they either decay out before the beginning of the reaction (^{82m}Br) or lead to stable daughters (⁸⁰Br, ⁸²Br), so that eventually only the reactions of the radioactive ⁸⁰Br daughter ions from the isomeric transition of ^{80m}Br can be observed.

Preparation of ¹²⁵Xe. About 20 ml of Xe at 5 atm was irradiated in a quartz ampoule at the FRJ-1 reactor at a neutron flux density of 8 × 10¹² cm⁻² sec⁻¹ for a period of 75 min. Aliquots were taken from the ampoule and transferred into the reaction vessel. The other radioisotopes of Xe do not cause any problems, since they decay either to stable ¹²⁷I or to Cs isotopes.

Preparation of Reaction Mixture. The reaction was carried out in a spherical Pyrex glass vessel with a volume between 350 and 1000 ml furnished with greaseless high-vacuum valves. The vessel was filled with the desired amounts of ⁸⁰Br source or ¹²⁵Xe, the substrate, and additives, using standard vacuum line techniques. The activity levels of ^{80m}Br and ¹²⁵Xe were of the order of 0.5 M Ci, so that radiation damage was negligible. The decay time, *i.e.*, the reaction period, was 30 min for ^{80m}Br and 5 days for ¹²⁵Xe ($T = 16.8$ hr). During this time the reaction vessel was kept in the dark at 23 or 70°.

Sample Analysis. The labeled reaction products were collected in a trap cooled with liquid nitrogen and an appropriate amount of carriers dissolved in CCl₄ was added. The mixture was then washed with a dilute aqueous Na₂CO₃-Na₂SO₃-NaBr(NaI) solution to separate the inorganic products (HX* and XX*). The walls of the reaction vessel were also rinsed with the extractants. The organic phase was washed with distilled water and dried. Aliquots were then submitted to radio gas chromatography and determination of the total radiohalogen activity. A discontinuous radio gas chromatographic technique was used, adsorbing the individual organic fractions on charcoal.² The following columns were used (4-m glass column, 3.5-mm i.d., 100 ml/min He flow): (1) 25% β '-oxydipropionitrile on Celite 545 (60-100 mesh) at 95° (separation of bromofluorobenzenes and bromobenzene); (2) 20% Igepal CO-880 on Chromosorb W-AW-DMCS (60-80 mesh) at temperatures between 70 and 150° (separation of bromochlorobenzenes, dibromobenzenes, bromobenzene, chloriodobenzenes, bromiodobenzenes, and iodobenzene, respectively); (3) 6% Bentone 34 and 20% Silicone oil DC 200 on Chromosorb W at 135° (separation of fluoroiodobenzenes and iodobenzene); (4) 20% 4,4'-azoxydianisole on Chromosorb W-A-W-DMCS (60-80 mesh) at 80° (separation of bromotoluenes, bromobenzene, and benzyl bromide).

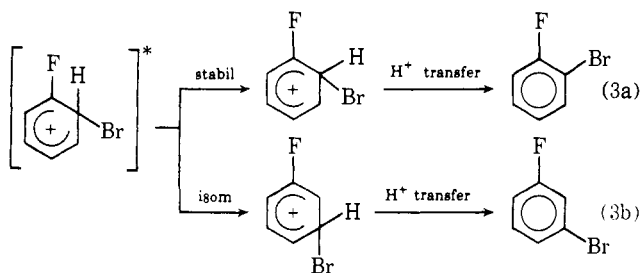
Radioactivity Determination. The individual gas chromatographic fractions adsorbed on charcoal were counted with a well-type scintillation counter. In the case of ⁸⁰Br ($T = 18$ min) the samples were also measured in a well-type Ge(Li) detector, using the 666 keV γ -ray line for purity control and calibration. The absolute radiochemical yields (in per cent of the total radioactive daughter ions formed during the reaction time) were calculated from the radioactive decay and growth laws for the ^{80m}Br-⁸⁰Br system after comparing the activity of an aliquot of the CH₃^{80m}Br source and that of a ⁸⁰Br-labeled product under identical conditions. In the simple case of ¹²⁵I ($T = 60$ days), the ¹²⁵I activity of the individual products was directly compared with that of the total ¹²⁵I activity found in aliquots of the inorganic and organic phases.

Results and Discussion

Aromatic Substitution via ^{80m}Br(IT)⁸⁰Br. Isomerization in Br-for-H and Br-for-F Substitution. In Figure 1 the absolute radiochemical yields of the ⁸⁰Br-for-H and ⁸⁰Br-for-F substitution products in fluorobenzene have

been plotted as a function of Ar concentration. It can be seen that the curves show no resemblance with classical moderator curves obtained in corresponding aliphatic systems.¹¹⁻¹⁹ On the whole, the yields of the substitution products do not change drastically over the entire concentration range. The initial small increase in yields at Ar concentration up to about 50 mol is understandable in terms of charge and kinetic energy removal. Multiply positive charged Br ions will not lead to stable products unless neutralized to the +1 state. Even with a thermal Br⁺ ion ($\Delta H^\circ = 300$ kcal/mol), the formation of the haloarenonium ion is strongly exothermic,²⁰ and a considerable fraction will most likely undergo unimolecular decomposition. Removal of charge and kinetic energy from the Br species will therefore increase the yields of substitution products. Despite the possible neutralization of a small fraction of Br⁺ ions in collisions with methyl bromide or fluorobenzene molecules, which would depend on the reaction cross sections for charge exchange *vs.* those for chemical reaction, the saturation behavior of the moderator curves just below 90 mol % of Ar indicates that in the highly moderated system substitution occurs *via* thermal ionic species. Thermal bromine atoms will be scavenged by the aromatic molecules, leading to addition but not to substitution products.

The most interesting feature is the splitting of the isomer distribution above about 50 mol % of Ar: the para- and ortho-isomer yields are seen to decrease while the yield of the meta product increases. These results seem to indicate a rearrangement of the intermediate arenonium ion. It is known from nmr studies on the protonation of xylenes that even in solution ortho and para forms of the arenonium ion have a tendency to rearrange to the thermodynamically most stable meta isomer.²⁷ The observed change of the isomer distribution with increasing Ar concentration is then a consequence of two competing processes, namely unimolecular isomerization (eq 3b) and bimolecular proton transfer, possibly after collisional stabilization (eq 3a).



At high Ar concentration the arenonium ion has enough time to undergo intramolecular isomerization before it encounters a substrate molecule; thus the ortho- and para-product yields will decrease on account of the meta-product yield. Eventually an isomer distribution is reached, which possibly corresponds to the thermodynamic equilibrium. Therefore, the apparent isomer distribution does not necessarily indicate the original selectivity, since it essentially depends on the environment of the first formed arenonium ion. This includes the total pressure of the system. With increasing pressure the rate of the bimolecular stabilization and

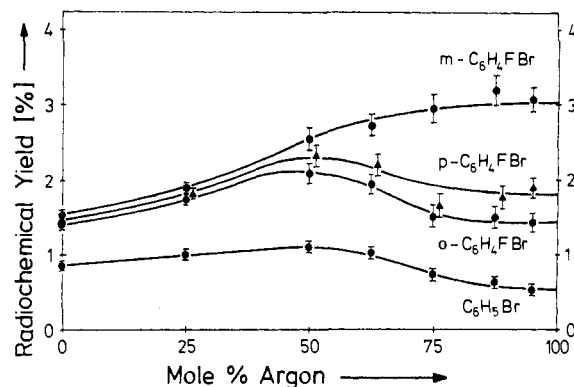


Figure 1. Effect of Ar additive on absolute radiochemical ⁸⁰Br-for-H and ⁸⁰Br-for-F substitution yields in the fluorobenzene system: total pressure, 120 Torr; temperature, 23 °; equimolar ratio of C₆H₅F and CH₃⁸⁰mBr.

proton transfer by substrate molecules will increase, and the relative amount of the meta isomer is expected to decrease. Table I shows the relative isomer distribu-

Table I. Pressure Dependence of Isomer Distribution in Br-for-H Substitution in Fluorobenzene

Total pressure ^a	<i>o</i> -C ₆ H ₄ FBr	% relative yield <i>m</i> -C ₆ H ₄ FBr	<i>p</i> -C ₆ H ₄ FBr
120	22 ± 1.6	48 ± 2.4	30 ± 2.1
500	27 ± 1.4	43 ± 2.3	30 ± 2.5
760	30 ± 1.4	38 ± 2.0	32 ± 1.6

^a System composition: 2.5 mol % of C₆H₅F, 2.5 mol % of ⁸⁰mBr-labeled CH₃Br, 95 mol % of Ar; temp 23 °.

tion (*o* + *m* + *p* = 100%) in the highly moderated system (95 mol % of Ar) for the pressure range from 120 to 760 Torr. The isomer distribution shows the expected trend. The relative yield of *m*-C₆H₄FBr decreases with increasing pressure, while the yield of *o*-C₆H₄FBr increases.

It is interesting to note that not only hydrogen but also fluorine is replaced by bromine (*cf.* bromobenzene yield in Figure 1). The Br-for-F replacement cannot be due to high kinetic energy processes, since the yields are very little affected by the moderator concentration. Further information concerning Br-for-F substitution was obtained from the highly moderated *p*-difluorobenzene system at 760 Torr. Table II clearly demonstrates that considerable isomerization also occurs in Br-for-F substitution. Only 55% of the total F substitution yield appears at the original location of the replaced fluorine, while 30.6% is found next to the original site, *i.e.*, in the meta position to the remaining fluorine, and 14.4% appears in the next position beyond, *i.e.*, in the ortho position to the remaining fluorine. The primary attack of the unsolvated Br⁺ probably not only occurs at the π -electron system of the aromatic ring but also at the fluorine substituent, the location of the highest electron density. In any case, F⁺ transfer to an aromatic substrate molecule seems to compete with proton transfer.

Intramolecular Selectivity in Hydrogen and Halogen Substitution. Br-for-H and Br-for-X substitution have been studied in simple monosubstituted benzenes of the type C₆H₅X (X = F, Cl, Br, CH₃), again using highly moderated (95% Ar) gas phase systems containing

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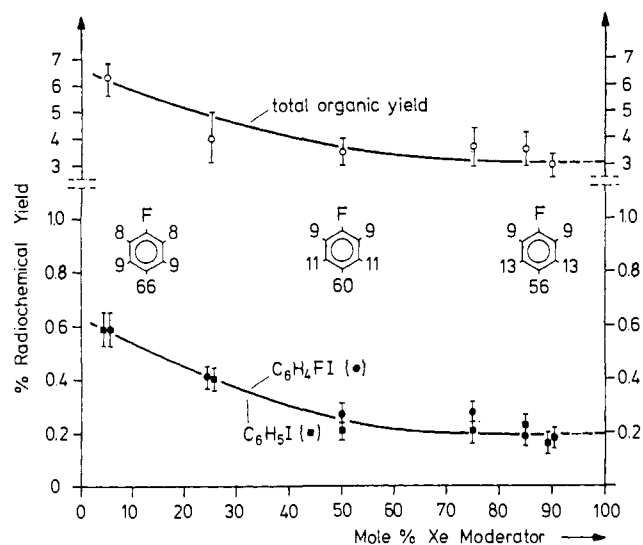
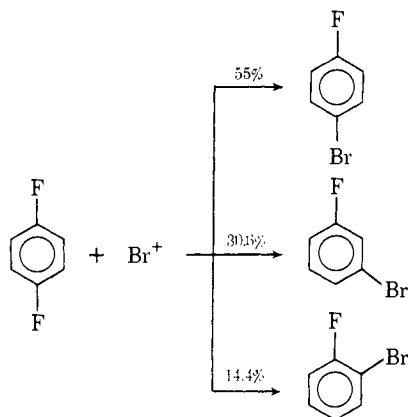


Figure 2. Effect of Xe additive on absolute radiochemical ^{125}I -for-H and ^{125}I -for-F substitution yields and total organic yield in the fluorobenzene system: total pressure, 60 Torr; temperature, 23° .

Table II. Isomerization in Br-for-F Substitution^a



^a Experimental conditions: 95 mol % of Ar, 2.5 mol % of $p\text{-C}_6\text{H}_4\text{F}_2$, 2.5 mol % of $^{80\text{m}}\text{Br}$ labeled CH_3Br ; 760 Torr; 23° . Isomer distribution in per cent; average of at least three individual runs; standard deviation about 10%.

CH_3 $^{80\text{m}}\text{Br}$ as $^{80}\text{Br}^+$ source. Experiments were carried out at 70° in order to obtain suitable substrate vapor pressures. The substitution yields in per cent of the total ^{80}Br daughter ions formed during the reaction time are given in Table III. It can be seen that (i) the positional selectivity is very low by solution chemistry standards and (ii) the $1/2$ ortho:para ratio decreases in the order $\text{F} < \text{Cl} < \text{Br} < \text{CH}_3$, despite the increasing bulk of the substituent X, in agreement with the trend observed in classical solution chemistry. The ratio of Br-for-X to Br-for-H substitution increases in the order $\text{F} < \text{CH}_3 < \text{Cl} < \text{Br}$. This is in agreement with the assumption that the attack at the substituent competes with the attack at the π -electron system. As the electron density distribution of the substituent increases, attack at this site is favored and the Br-for-X substitution increases relative to the Br-for-H substitution. Furthermore, X^+ transfer is also facilitated and can more effectively compete with H^+ transfer when going from fluorine to bromine.

Aromatic Substitution via $^{125}\text{Xe}(\text{EC})^{125}\text{I}$. Moderator

Table III. Absolute Radiochemical Yields^a from Gas Phase^b ^{80}Br -for-H and ^{80}Br -for-X Substitution

Product	Substrate				
	C_6H_6	$\text{C}_6\text{H}_5\text{F}$	$\text{C}_6\text{H}_5\text{Cl}$	$\text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{CH}_3$
<i>o</i> - $\text{C}_6\text{H}_4\text{XBr}$		1.02	0.84	0.36	1.90
<i>m</i> - $\text{C}_6\text{H}_4\text{XBr}$		1.10	0.79	0.27	1.45
<i>p</i> - $\text{C}_6\text{H}_4\text{XBr}$		1.11	0.85	0.28	1.19
$\text{C}_6\text{H}_5\text{Br}$	3.00	0.43	2.16	18.06	1.25
Br-for-X: Σ Br-for-H		0.13	0.87	19.80	0.27
$1/2$ ortho:para		0.46	0.49	0.64	0.80
$1/2$ meta:para		0.50	0.46	0.48	0.61

^a In per cent of total ^{80}Br daughter ions formed; average of at least three individual runs, whose standard deviation is about 10%.

^b The gaseous system was kept at 760 Torr at 70° ; composition: 95 mol % of Ar, 2.5 mol % of $\text{C}_6\text{H}_5\text{X}$, and 2.5 mol % of $^{80\text{m}}\text{Br}$ -labeled CH_3Br as $^{80}\text{Br}^+$ source.

and Pressure Effect. In Figure 2 the absolute yields of the individual I-for-H and I-for-F substitution products as well as the total organic yield are plotted as a function of Xe concentration in the fluorobenzene system at 60 Torr and 23° . The relative ortho-, meta-, and para-isomer distribution is also listed for 10, 50, and 90 mol % of Xe, respectively.

It can be seen that the I-for-H and I-for-F substitution yields exhibit an almost identical trend, *i.e.*, a slow decrease with increasing moderator concentration, eventually leveling off at about 0.2% each above some 70 mol % of Xe. The absolute yields are considerably smaller than those observed in substitution by $^{80}\text{Br}^+$. Within the experimental error the isomer distribution is almost independent of the moderator concentration. In contrast to bromination, intramolecular rearrangement is negligible, as expected for the heavier iodine. This finding is in agreement with the considerably greater intramolecular selectivity observed in iodination. Besides the lower reactivity of I^+ ($\Delta H^\circ = 267$ kcal/mol) as compared to Br^+ ($\Delta H^\circ = 300$ kcal/mol), the main reason for the greater apparent selectivity of positive iodine is the almost complete lack of intramolecular isomerization. The lack of significant changes in the isomer distribution also indicates that the nature of the substituting species (charge and energy state of those species which really undergo substitution) should not change significantly.

The total organic yield also decreases with the Xe moderator concentration. This comprises also unidentified organic products which could not be eluted from the glc columns. These products probably arise from further reactions of iodinated aromatic intermediates with the substrate, thus leading eventually to polynuclear products. With increasing Xe concentration these intermediates reach the wall of the bulb before encountering a substrate molecule. The high inorganic yield ($100 - \%$ organic), which includes the wall activity, arises most likely from unreacted iodine and iodinated intermediates as well as from abstraction and decomposition products (HI, FI), which also end up at the wall of the reaction vessel.

The pressure dependence of the organic product yields is shown in Figure 3 for the range of 60 to 760 Torr in the highly moderated (90 mol % of Xe) fluoro benzene system at 23° . Except for the I-for-F substitution yield, which remains practically constant, the yields are seen to increase. The ortho-, meta-, and

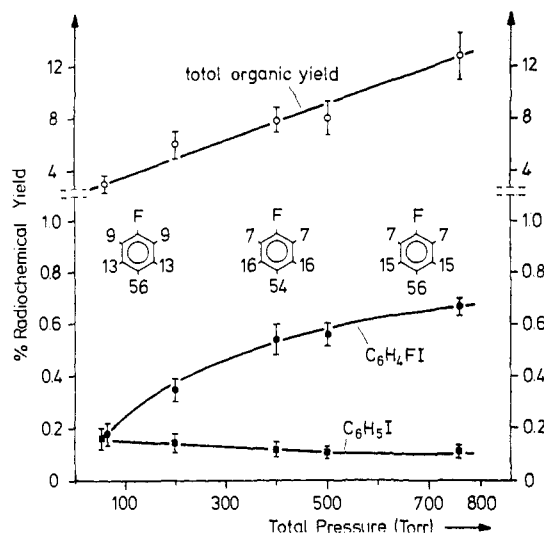


Figure 3. Pressure effect on absolute radiochemical ^{125}I -for-H and ^{125}I -for-F substitution yields and total organic yield: 90 mol % of Xe moderator; temperature, 23° .

para-isomer distribution again remains practically unaffected, in agreement with the above mentioned lack of rearrangement. The different pressure dependence of I-for-H and I-for-F substitution can be interpreted in terms of collisional stabilization which favors I-for-H but not I-for-F substitution. It can be tentatively assumed that the exothermic formation of the haloarenonium ion leads to considerable excitation decomposition and hence increasing pressure stabilizes hydrogen substitution. Replacement of fluorine, on the other hand, is energetically much more difficult and any excitation energy available should favor I-for-F substitution.

Comparison of Gas Phase Bromination and Iodination of Halobenzenes. The intramolecular reactivity of gas phase iodination has also been determined within the series fluorobenzene, chlorobenzene, and iodobenzene.

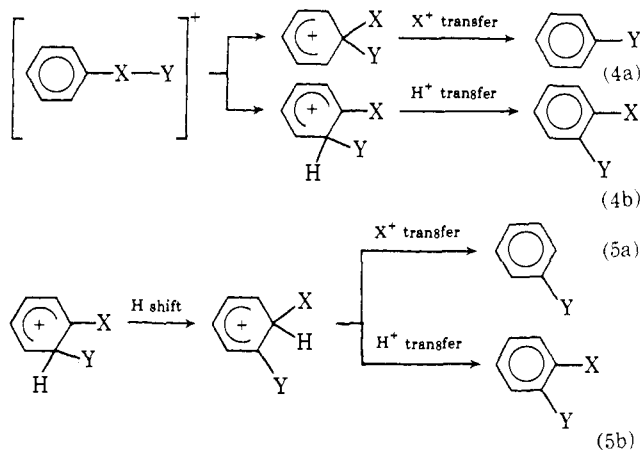
Table IV. Comparison of Gas Phase Bromination^a and Iodination^b of Halobenzenes

	Br^+ from $^{80\text{m}}\text{Br}(\text{IT})^{80}\text{Br}$		
$\frac{\Sigma\text{H subst}}{\text{X subst}}$	7.5	1.2	0.05
	I^+ from $^{125}\text{Xe}(\text{EC})^{125}\text{I}$		
$\frac{\Sigma\text{H subst}}{\text{X subst}}$	4.5	1.1	0.5

^a Experimental conditions: 2.5 mol % of $\text{C}_6\text{H}_5\text{X}$, 2.5 mol % of $^{80\text{m}}\text{Br}$ labeled CH_3Br , 95 mol % of Ar; temp 70° ; reaction time 30 min; standard deviation $\pm 10\%$. ^b Experimental conditions: 2.5 mol % of $\text{C}_6\text{H}_5\text{X}$, 0.5 mol % of ^{125}Xe labeled Xe, 97 mol % of Xe; temp 70° ; reaction time 5 days; standard deviation $\pm 20\%$.

The isomer distribution and the ratios (Σ H-substitution yield):(X-substitution yield) are given in Table IV and are compared with the corresponding data for bromination taken from Table III. The results can be summarized as follows. (1) For both bromination and iodination, replacement of the halogen substituent increases relative to hydrogen substitution, when going from fluorobenzene to bromobenzene. (2) The relative amount of ortho substitution increases in the same direction. This effect is much more pronounced for iodination than for bromination. (3) The apparent intramolecular selectivity in hydrogen substitution is considerably greater in iodination than in bromination.

The isomer distribution obtained in Br-for-H substitution can only be considered as an apparent distribution not reflecting the structure of the initially formed arenonium ion, due to substantial intramolecular isomerization. This is different in I-for-H substitution. However, the drastic increase in the relative amount of the ortho isomer for I-for-H substitution, when going from fluorobenzene to bromobenzene, cannot be explained only by classical inductive and mesomeric factors. With increasing electron density distribution of the halogen substituent, the positive I^+ ion will predominantly attack the halogen instead of the π -electron system. Electrophilic attack at halogen substituents and the formation of alkylarylhalonium ions has recently been demonstrated by Olah and Melby²⁸ for bromo- and iodobenzene. While in our specific case the corresponding intermediates would be quite different in charge delocalization and stability, their transient formation seems likely. After the attack at the halogen substituent, the electrophile can either be transferred to the substituted carbon (eq 4a) or, with greater probability, to the carbon atom in the ortho position (eq 4b). X^+ transfer and H^+ transfer will eventually lead to halogen or hydrogen replacement, respectively.



In addition, H shift after rearrangement (eq 5) of the halogen would also explain the observed isomerization in Br-for-F substitution. Again, X^+ transfer (eq 5a) will compete with H^+ transfer and thus lead to the ortho isomer of either X or H substitution. Transfer of radioactive Y^+ should of course also occur but will not be observed.

The hypothetical reaction scheme outlined above (eq

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4 and 5) is in agreement with our findings. Both attack at the halogen and subsequent X^+ transfer will increase when going from fluoro- to chloro- to bromobenzene; thus replacement of the halogen substituent and of

the ortho hydrogen will also increase in the same direction.

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Reaction of Oxygen Atoms, $O(^3P)$, with Olefins in Liquid Nitrogen Solution at 77°K¹

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Abstract: The reaction of ground state oxygen atoms, $O(^3P)$, with propylene, 1-butene, and isobutene in liquid nitrogen solution at 77°K has been studied. The major and perhaps the exclusive addition products are: propylene oxide, propanal, and acetone for propylene; α -butene oxide, *n*-butanal, and methyl ethyl ketone for 1-butene; and isobutene oxide, isobutanal, and methyl ethyl ketone for isobutene. The ratios of the yields of these products have been determined. The type of products formed is discussed in terms of the general mechanism of addition of $O(^3P)$ atoms to olefins. The effect of concentration of propylene and 1-butene on the quantum yield of addition products was measured. The quantum yield of oxygen atoms scavenged by propylene and 1-butene to form the addition products was 0.29 and 0.27, respectively. The quantum yields lower than unity suggest an appreciable cage recombination and scavenging of the ground state oxygen atoms with the trace amounts of molecular oxygen formed in the reaction and present as an impurity. Relative rates of addition of $O(^3P)$ atoms to ethylene, propylene, 1-butene, and isobutene in liquid nitrogen solution at 77°K have been determined. The effect of the concentration of added oxygen on the product yields and the relative rate constants for addition of $O(^3P)$ to molecular oxygen, to propylene, and to 1-butene have been investigated. The rates of addition of $O(^3P)$ atoms to propylene, 1-butene, isobutene, and molecular oxygen in liquid nitrogen solution at 77°K are approximately the same, suggesting that these reactions are probably diffusion controlled.

In a previous publication the results of a detailed study of the reaction of oxygen atoms, $O(^3P)$, with ethylene in liquid nitrogen solution have been reported.² The present work is an extension of this study to the reactions of oxygen atoms with three other olefins dissolved in liquid nitrogen at 77°K. This investigation has two distinct objectives: (1) to establish the reaction mechanism and the type of products formed and (2) to obtain information on the relative rates of these reactions in liquid nitrogen solution at 77°K.

The reaction of oxygen atoms, $O(^3P)$, with simple olefins in the gas phase was studied extensively in this laboratory using several different sources of $O(^3P)$ atoms, such as the mercury-photosensitized decomposition of N_2O and the photolysis of NO_2 , and a general reaction mechanism has been established.³⁻⁵

Studies of the liquid phase $O(^3P)$ atom reactions with olefins at low temperature should provide interesting additional information about the type of products formed because energy-rich intermediates may be expected to be rapidly stabilized by transfer of excess energy to the solvent molecules. Relative rate measurements for the $O(^3P)$ addition to olefins in liquid nitrogen solution at 77°K may also complement the observations made in gas phase investigations because at low

temperatures the competing reactions of higher activation energy tend to be suppressed and the reaction rate is very sensitive to small activation energy differences.^{2,3,6,7}

Reaction of $O(^3P)$ atoms with simple olefins in liquid argon solution at 87.5°K has been recently studied by DeMore.⁸

Experimental Section

Oxygen atoms were generated by photolyzing ozone, using the 253.7-nm line from a low-pressure mercury lamp. The initially formed excited oxygen atoms, $O(^1D_2)$, are rapidly deactivated to the ground state, $O(^3P)$, by collisions with the excess nitrogen molecules present.

Matheson research grade nitrogen was used after it was passed through two spiral traps cooled with liquid oxygen. Matheson research grade ethylene, propylene, 1-butene, and isobutene were used after thorough degassing and distillation. The samples of the dissolved reactants were prepared and irradiated in the same manner as previously described.²

The products were analyzed at room temperature on a 3.6-m cyanosilicone-packed column with a thermistor detector and a 3.4 m long 20% w/w β,β' -thiodipropionitrile column in series with a 25-cm column of 20% w/w dinonyl phthalate, provided with flame ionization detector.

The following flame ionization detector molar responses relative to benzene taken as unity were used: ethylene oxide 0.159; acetaldehyde 0.161; propylene oxide 0.326; propanal 0.321; acetone 0.322; α -butene oxide 0.533; *n*-butanal 0.489; isobutene oxide 0.466; isobutanal 0.463; methyl ethyl ketone 0.500. The molar responses for ozonides were approximately obtained by extrapolation.

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