Laser Isotope Separation. Photochemical Scavenging of Chlorine-37 by Bromobenzene

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Abstract: The photochemical reaction of iodine monochloride with bromobenzene yields chlorobenzene as enriched in either $^{37}$Cl or $^{35}$Cl depending on the excitation wavelength. A gas mixture of ICl and C$_6$H$_5$Br is irradiated by the output of a cw dye laser (0.1 Å bandwidth) tuned to the (18,0) bandhead at 6053 Å of the $^{127}$Cl A $^3$I$^-$X$^1$Σ$^+$ system. At pressures of several Torr, C$_6$H$_5$Cl$^{37}$Cl is formed with a quantum yield of 10% and a maximum enrichment factor of 9 (75% $^{37}$Cl). The extent of enrichment is found to vary with starting conditions, permitting study of the mechanism for isotopically specific reaction and attendant scrambling pathways. Formation of C$_6$H$_5$Cl$^{37}$Cl involves direct reaction of ICl$^*$ with C$_6$H$_5$Br to produce a vibrationally hot radical intermediate, which retains to a high degree its isotopic integrity because of more rapid elimination of Br atom than radical chain propagation. Comparison of iodobenzene with bromobenzene shows that the rate-limiting step must involve a Cl atom migration about the ring which is in competition with loss of Cl atom. While excited ICl transfers Cl to unsaturated halogenated hydrocarbons, no reaction is observed with saturated halogenated hydrocarbons. The general form of this mechanism demonstrates isotopically specific synthesis involving reaction mixtures of natural abundance as starting materials.

Thermolysis is the most common means of activation in chemical synthesis and is a process where energy is supplied statistically. However, photolysis opens the possibility for accomplishing chemical transformations in a selective manner, where energy is provided to the reactant(s) in a localized, specific way. Nevertheless, the criteria for selective photochemistry remain obscure because of inadequate understanding of excited state chemistry, especially intramolecular chemical dynamics following the absorption of a photon. With recent advances in laser technology, physical methods have become available which permit investigation of the parameters involved in selective photochemistry. In particular, laser isotope separation (LIS) represents one aspect of this general area. LIS has the advantage of permitting the observation of a selective phenomenon, isotopic specificity, by following the degree of isotopic labeling in the products (essentially an isotope-tracer technique).

Several laser-isotope-separation schemes have been reported in which selective excitation results in direct photo-dissociation or predissociation of one isotopic species, leaving isotopically enriched starting material and decomposition products. In addition, it has also been possible to effect isotope separation by reacting "scavenger molecules" with selected isotopic species produced in vibrationally or electronically excited states. Previously we found that $^{137}$Cl$^*$ reacts with BrCH$\equiv$CHBr to form $^{37}$Cl-enriched BrCH$\equiv$CHCl and CICH$\equiv$CHCl. This reaction takes advantage of the fact that ICI in its first electronically excited state ($^1$II$_{1}$) has a different reactivity toward halogenated olefins than in its ground state ($^3$Σ$^+$).

We report here that the reaction

$$ICl^* + C_6H_5Br \rightarrow I + C_6H_5Cl + Br$$

is also isotopically specific and present results which reveal some of the mechanistic aspects of this reaction. From these experiments with C$_6$H$_5$Br as a scavenger and data on hot molecule reactions involving chlorine atoms, we have concluded that our observations of isotope enrichments are attributable to two factors. (1) Selective excitation of ICI produces predominantly $^{137}$Cl$^*$ which behaves kinetically like a chlorine atom in reaction with C$_6$H$_5$Br. (2) A radical intermediate having excess vibrational energy is formed from the transfer of $^{37}$Cl from $^{137}$Cl$^*$ to C$_6$H$_5$Br and eliminates a Br atom more rapidly than it suffers collisional deactivation.

The photochemical reaction of $^{137}$Cl$^*$ with C$_6$H$_5$Br illustrates the general scheme for separating isotopes by chemical
scavenging. Selective excitation of I$^{35/37}$Cl produces an excited state. Separation is accomplished because the chemistry of I$^{35/37}$Cl in reaction with C$_6$H$_5$Br is different from that of ground state ICl. Because the photochemical product is stable, preserves its isotopic integrity, and is readily isolable, LIS by photochemical scavenging is of practical importance. Finally, it should be appreciated that this method not only separates isotopes but is capable of allowing the preparation of isotopically labeled compounds of one's own design.

Experimental Section

Apparatus. Selective excitation of ICl is accomplished with a cw tunable dye laser (Spectra-Physics Model 375) pumped by a 4 W (all line) argon ion laser (Spectra-Physics Model 165). The laser bandwidth is narrowed to about 0.1 Å by using a tuning wedge and a Fabry-Perot etalon (FSR 30 cm$^{-1}$). An intracavity absorption cell (Control Laser) containing I$^{35}$Cl is also placed inside the laser cavity. Power measurements are made with a power meter (Spectra-Physics Model 404) and with a calibrated, air-cooled laser thermopile (Eppley, precision ± 3%). Absorption spectra of ICl are obtained in the standard way: 1000 W Hg-Xe lamp (Hanovia), 1 m long, 5 cm diameter pyrex absorption cell, and 3/4 m spectrometer (SPEX 1702) equipped with scan drive and photomultiplier (Centronic 4283 SA25).

The photolysis cell (1 m long, 5 cm diameter), constructed from Pyrex, is treated with dimethyldichlorosilane and aged with a mixture of ICl and C$_6$H$_5$Br. Pressure is monitored continuously with a capacitance manometer (Datametrics Model 570A transducer and Model 1173 analogue meter). The cell is attached to a standard greaseless, gas handling vacuum line having a pressure < 5 x 10$^{-5}$ Torr.

Analysis. Photolysis products are separated and analyzed by capillary chromatography on a Carbowax 20 M open tubular column (150 ft) in a gas chromatograph with flame ionization detector (PerkinElmer Model 3920). Peak areas are measured by digital integration (Spectra-Physics Autolab Minigrator). Response factors of bromobenzene and chlorobenzene are determined on standard mixtures with methylene bromide as internal standard. The response factors for C$_6$H$_5$Br and C$_6$H$_5$Cl are 7.27 ± 0.07 and 9.94 ± 0.02, respectively (response factor = [wt. CH$_2$Br$_2$]/[area C$_6$H$_5$X]/[wt. C$_6$H$_5$X]/[area CH$_2$Br$_2$]).

Isotope ratios are measured on a JEOL MS-07 double-focusing mass spectrometer, equipped with a JEOL peak-matching unit and a Vacumetrics ratiometer. The precision of these ratios is better than 1%, while the reproducibility based on four independent measurements is better than 5%.

Materials. Bromobenzene (Mallickrodt), iodobenzene (MCB), 1,2-dibromoethylene (Aldrich), and methylene bromide (J. T. Baker) are purified by gas chromatography (Varian A90-P) on a 10 ft × 0.25 in. column of Apiezon L on Chromosorb P (NABW). Iodine monochloride (ICN Life Sciences) is purified by slow vacuum transfer to a trap cooled to 77 K (Fisher). Br$_2$ (Fisher), N$_2$ (AIRCO), Ar (AIRCO), and C$_2$H$_4$ (Matheson) are used without further purification.

Photolysis. In a typical experiment, a weighed amount of scavenger is degassed by several freeze–thaw cycles and vacuum transferred to a cold finger attached to the photolysis cell (see Figure 1). Internal standard, when employed, is degassed and vacuum transferred simultaneously. The sample is sealed off from the rest of the cell by closing a stopcock, and ICl from a bulb of purified material is then expanded into the cell to a given pressure. The stopcock to the cell is closed, and the scavenger and ICl are allowed to mix by expanding the previously trapped scavenger into the cell. After ~2 min, photolysis is begun. The reaction is quenched by adding ~50 Torr of ethylene to remove the unreacted ICl; the mixture is then pumped into a cold trap and subsequently vacuum transferred to an ampule. When quantitative measurements requiring an external standard are made, a weighed amount of CH$_2$Br$_2$ is also vacuum transferred into the ampule. The procedure for photolyzing ternary gas mixtures is similar to the procedure described above.

Before irradiation, a portion of the ICl absorption spectrum is recorded with a Hg-Xe lamp source and a 3/4 m grating monochromator operated in second order (resolution 0.05 Å). Then the laser output is tuned to the spectroscopic feature of interest (λ 6053 Å, see Figure 2) by passing part of the beam through the spectrometer (see Figure 1). Unless otherwise stated, all of the experiments are carried out at the same laser intensity, 25 mW (±5%) and at 6053 Å, corresponding to the (18–0) bandhead of the I$^{35}$Cl A-X system (Figure 2a).

Quantum Yields and Absorbance Measurements. Absorbance measurements are made by measuring the laser intensity with an Eppley thermopile in the usual manner; the standard correction for

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The laser bandwidth (-2 Å) and cavity configuration are used. Moreover, the large number of overlapping ICl and CH2Br2 is used instead as an external standard.

Results

Selective Excitation. The visible absorption spectrum of 13Cl has been studied extensively. Figure 3 shows the known low-lying electronic states of ICl. The first excited state, \( \Lambda^3 \Pi_v \) lies \( \sim 13,000 \text{ cm}^{-1} \) above the ground state, \( X^1 \Sigma^+ \), and is bound by over \( \sim 3500 \text{ cm}^{-1} \). A portion of the visible absorption spectrum is shown in Figure 2a. Assignments of rotational lines to 13Cl and 37Cl are based on the work of Hultén, Järlsäter, and Koffman.

Figure 2b shows that selective excitation of 13Cl or 37Cl can be achieved only if a light source of narrow bandwidth is used. Moreover, the large number of overlapping 13Cl and 37Cl lines also requires that careful attention be paid to the choice of excitation wavelength.

In a previous communication, the use of an intracavity ICl* filter for obtaining selective excitation of 37Cl was reported. The laser bandwidth (\( \sim 2 \text{ Å} \)) and cavity configuration in those experiments differed from those in the present work. Here, we have used a Spectra Physics cw dye laser with an etalon and tuning wedge to obtain a bandwidth of 0.1 Å. Using an analyzing etalon, we estimate that within this bandwidth there are no more than five longitudinal modes at 6053 Å. The effectiveness of intracavity absorption in quenching laser action at 13Cl absorption frequencies, however, decreases with the number of modes and is dependent on the threshold characteristics of the laser.

Dark Reactions. The procedure for measuring the extent of dark reaction of ICl with C6H5Br involves the same vacuum transfer technique as described for the photolysis. Quantitative analysis is accomplished by analytical gas chromatography with methylene bromide as an internal standard.

Concurrently, the enrichment in 13Cl starting material is measured by scavenging unreacted ICl with ethylene to form the addition product ICH2CH2Cl. The ratio of 35Cl:37Cl (natural abundance, 1.00:0.33) is determined from the abundance of ions with \( m/e \) equal to 63 and 65 (CH2CH2Cl). Thus, for example, irradiation of ICl + CH3Br (pICl = 0.5 Torr: [ICl]/[CH3Br] = 0.016) results in enriched ICl starting material with a 35Cl:37Cl ratio of 1.00:0.26 and enriched C6H5Cl product with a 35Cl:37Cl ratio of 1.00:1.20.

The quantum yield for formation of isotopically enriched C6H5Cl is 0.096 ± 0.05 and is the result of a single photon process. The latter is based on the observation that the yield of C6H5Cl changes linearly with variations in laser intensity.

Irradiation at 6053 Å of gas mixtures containing ICl and saturated halogenated hydrocarbons, e.g., BrCH2CH2Br, CH2Br, or CH2Br2, does not yield any detectable photochemical products. Mixtures of ICl and olefins, however, react rapidly in the dark, presumable by a heterogeneous reaction at the cell walls. This high reactivity is reduced by adding substituents such as halogen atoms to the double bond or by using aromatic halides. Thus, for example, bromobenzene reacts slowly with ICl in the dark and yields a product different from that formed during photolysis:

**Figure 4.** Percent abundance of parent ions from C6H535Cl(112) and C6H537Cl(114): (a) natural abundance; (b) from reaction of ICl (11.6 μmol) + C6H5Br (306 μmol) irradiated at λ 6053 Å for 1 h.
Within the limits of flame ionization detection, no chlorobenzene or dichlorobenzenes are formed in the dark reaction, under any of the conditions used for laser isotope separation. Evidence for a dark reaction is loss of 8% bromobenzene when mixtures of ICl and C₆H₅Br are left in the dark for 1 h.

Having established that the reactivity of X°⁺ and A³π⁺ states of ICl toward bromobenzene is different, we next establish that Cl atoms react with saturated hydrocarbons and halogenated hydrocarbons by hydrogen abstraction. Photodissociation of ICl at 5145 Å (19 436 cm⁻¹, see Figure 3) results in the disappearance of starting material from the reaction:

\[
\text{Cl} + \text{CH}_2\text{Br}_2 \rightarrow \text{HCl} + \text{CHBr}_2
\]

Irradiation of ICl at 6053 Å, where the A³π⁺ state is 2786 cm⁻¹ below the dissociation limit, does not lead to photochemical reaction, i.e., the concentration of CH₂Br₂ remains unchanged. (2) The products of photolysis of mixtures of ICl and BrCH=CHBr are the same at 5145 and 6053 Å. (3) The quantum yield for the formation of C₆H₅Cl from reaction of C₆H₅Br with Cl atoms or ICl°⁺, produced at 6053 Å, appears to be nearly the same: \( \phi_{5145 Å} = 0.12 \pm 0.01; \phi_{6053 Å} = 0.096 \pm 0.003 \). Although it is not possible to rule out an ICl-addition product as an intermediate in the photochemical reaction, it is highly improbable that such an intermediate intervenes when bromobenzene is the scavenger.

From these considerations we conclude that ICl°⁺ behaves kinetically as a Cl atom in addition to double bonds and that isotopic specificity is the result of a direct reaction of ICl°⁺ with the scavenger. However, electronically excited ICl differs from a Cl atom in reactions involving hydrogen abstraction.

Competing Reactions and Isotope Scrambling. We have observed that it is possible to vary the degree of isotopic specificity by changes in reaction conditions which do not affect the selective excitation of I³⁷Cl. This implies that competitive reactions exist which cause isotopic scrambling.

Loss of isotopic specificity can occur by two different reactions:

\[
\begin{align*}
\text{I}^\text{35} \text{Cl}^\ast + \text{M} \rightarrow \text{I}^\text{37} \text{Cl}^\ast + \text{I}^\text{35} \text{Cl} \\
\text{Br} + \text{ICl} \rightarrow \text{BrCl} \rightarrow \text{Br} + \text{Cl}
\end{align*}
\]

where \( \text{I}^\text{35} \text{Cl}^\ast \) is produced by energy transfer:

\[
\text{I}^\text{37} \text{Cl}^\ast + \text{I}^\text{35} \text{Cl} \rightarrow \text{I}^\text{37} \text{Cl} + \text{I}^\text{35} \text{Cl}^\ast
\]

and the \( \text{I}^\text{35} \text{Cl} \) atom is formed during the exchange reaction:

\[
\begin{align*}
\text{I}^\text{35} \text{Cl}^\ast + \text{M} \rightarrow \text{I}^\text{37} \text{Cl}^\ast + \text{I}^\text{35} \text{Cl}
\end{align*}
\]
of IC1 pressure at constant CHBr pressure (306 pmol shown in Figure 6a. The higher 3CI enrichment demonstrates presence of 12. For 0.3 Torr worker~ found in using IC1 as a source of CI atoms that the bling.

Since 12 also absorbs at 6053 

Figure 6. Effect of added gases on the C6H537Cl enrichment from the reaction of IC1 (47.8 pmol) + C6H5Br (306 pmol), irradiated at \( \lambda = 6053 \) Å for 1 h: (a) I2 (28.9 pmol); (b) Br2 (28.9 pmol); (c) Cl2 (28.9 pmol).

Figure 7. Effect of 0.21 Torr of I2 on C6H537Cl enrichment as a function of IC1 pressure at constant C6H5Br pressure (306 pmol \( \sim 3.3 \) Torr).

4] and 35Cl [reaction 5 together with reactions 6, 7, or 8] are both second order in IC1 pressure and account for variations in enrichment with IC1 pressure if reactions 2 and 3 are pseudo-first-order in 35Cl* or 35Cl, respectively (excess bromobenzene), and reactions 4–8 are all rate limiting. A distinction between free radical [reactions 5–8] and energy transfer [reaction 4] scrambling can be made by addition of a chlorine-atom scavenger to the reaction. Benson and co-workers\(^{15}\) found in using IC1 as a source of CI atoms that the presence of I2 reduced the concentration of CI to negligible amounts. This observation is attributed to the reaction

\[
I2 + CI \rightarrow IC1 + I
\]  
(9)

The effect of I2 (0.3 Torr) on the C6H537Cl enrichment is shown in Figure 6a. The higher 37Cl enrichment demonstrates that chlorine atom reactions contribute to isotopic scrambling.

To optimize the enrichment in C6H5Cl, the effect of changes in IC1 pressure with fixed concentration of I2 and C6H5Br was studied (Figure 7). These results indicate that there are at least two additional competing reactions that are related to the presence of I2. For 0.3 Torr \( p_{IC1} \leq 0.8 \) Torr, the higher enrichment (Figure 7) reflects CI-atom scavenging by reaction 9 or perhaps by halogen trimmer formations.\(^{16}\) At higher IC1 pressures, where I2 has no effect, chlorine exchange [reaction 5] must necessarily be occurring faster than CI-atom scavenging. Since I2 also absorbs at 6053 Å (\( \epsilon_{I2} \sim 50 \) IC1), energy transfer

\[
I2^* + IC1 \rightarrow I2 + IC1^*
\]  
(10)

is very likely and would result in lower isotopic specificity. It appears from Figure 7 that at \( p_{IC1} < 0.3 \) Torr, reaction 10 predominates over (9), reflecting a change in the ratio \( [^{37}Cl^*]/[I2^*] \). and therefore a change in the ratio of rates for the various competing reactions. As a consequence, it is anticipated that higher enrichments should be possible with a different CI-atom scavenger.

Further confirmation of the presence of CI atoms comes from irradiation of mixtures of IC1, Cl2, and C6H5Br. As shown in Figure 6c, the C6H537Cl enrichment decreases due to the additional CI-atom exchange reaction

\[
^{37}Cl + Cl2 \rightarrow ^{37}ClCI + CI
\]  
(11)

which leads to isotopic scrambling. No other sources of CI atoms are introduced since Cl is transparent to light at \( \lambda = 6053 \) Å. Although there is no experimental evidence to exclude the four-center reaction

\[
^{137}Cl^* + CI2 \rightarrow ^{135}Cl^* + ^{37}ClCI
\]

preliminary work of Engelke, Whitehead, and Zare\(^{18}\) suggests that this is unlikely.

Chlorine atoms can be produced from several competing reactions 6–8. Since Br2 photodissociates at \( \lambda = 6053 \) Å, it should be possible to evaluate the effect of Br atoms on the enrichment [reaction 8] by addition of Br2. It was found, however, that two competing processes are involved. CI-atom scavenging and scrambling. For low Br2 pressure (0.3 Torr, \( p_{Br2}/p_{IC1} = 0.6 \)), the enrichment increases to 59% C6H537Cl (Figure 6b), whereas for higher pressure (0.6 Torr, \( p_{Br2}/p_{IC1} = 1.2 \)) the enrichment decreases to 42% C6H537Cl. These results do not elucidate the scrambling effect of Br atoms produced in reaction 1. However, when C6H5I was substituted in place of C6H5Br (see Table 1), no change in the C6H537Cl enrichment was observed, implying that the concentration of Br atom formed in reaction 1 is not significant in causing a decrease in isotopic specificity.

Distinctions experimentally between reactions 6 and 7 as sources of CI atoms in the course of reaction 1 are not possible in the present study. However, Figure 8 shows that additions of inert gases causes the enrichment in C6H537Cl to decrease as would be expected if CI-atom reactions were more important under these reaction conditions. Irradiation at 6053 Å promotes \( ^{13}Cl^* \) to \( \epsilon_{IC1} = 18 \) of the A 3nl state, \( \sim 2.6 \) kcal/mol below the dissociation limit. Addition of inert gases increases the number of nonreactive collisions which can result in the transfer of kinetic energy to \( ^{13}Cl^* \) promoting dissociation or changing deactivation. Collisional deactivation is reflected in a decreased quantum yield up to a total pressure of 50 Torr (0.064 compared to 0.096 in the absence of N2) and collisional dissociation is reflected in a lower C6H537Cl enrichment [reaction 5]. Moreover, dilution of the reaction mixture virtually eliminates energy transfer [reaction 4].

Figure 9 shows the relationship between the enrichment and changes in the total pressure, adjusted by adding N2. The ob-
ogenated olefins are not likely unless the elimination [reaction
of these pathways is affected by addition of inert gases.6c
and isotopically specific pathways obtains. Scrambling under
surprising conclusion that an equilibrium between scrambling
and becomes constant for large nitrogen pressures implies the
observation that ρ does not decrease to 0.33 (natural abundance)
and becomes constant for large nitrogen pressures implies the
surprising conclusion that an equilibrium between scrambling
and isotopically specific pathways obtains. Scrambling under
these reaction conditions is attributed exclusively to chlorine
atom reactions, since energy-transfer scrambling is unimportant
with nitrogen dilution. If a steady state between reactions
5 and 12 is reached in which (12) predominates, ρ would be

\[ \text{I}^* + \text{C}_6 \text{H}_5 \text{Br} \rightarrow \text{C}_6 \text{H}_5 \text{Cl} + \text{Br} \]  

(12)

>0.33. The possibility also exists that \(^{137}\text{Cl}^*\) reacts with
\( \text{C}_6 \text{H}_5 \text{Br} \), contributing to the observed isotopic preference. The
latter reaction, however, should become less important as the
N\(_2\) pressure increases because \(^{137}\text{Cl}^*\) is quenched to lower
vibrational levels, thereby becoming less reactive. Unless col-
lossional quenching of \(^{137}\text{Cl}^*\) is very insensitive, requiring a very
large number of collisions, the observed limiting value of ρ in
Figure 9 for \( p_{\text{N}_2} > 50 \text{Torr} \) is more readily explained by a
preference of reaction 12 over 5.19

Discussion

The photolysis of halogenated olefins is a well-known
reaction20 which proceeds through a free-radical chain
mechanism. From studies of Ayscough and co-workers20 it has
been demonstrated that these reactions involve vibrationally
hot radical intermediates; for example,

\[
\begin{align*}
\text{CH}_2\text{=CHBr} + \text{Cl} &\rightarrow \text{CH}_2\text{=CHCl} + \text{Br} \\
\text{Cl}_{2} + \text{Br} &\rightarrow \text{ClBr} + \text{Cl}
\end{align*}
\]

that are converted into products by several channels; the ratio
of these pathways is affected by addition of inert gases.6c

Because chain propagation occurs at random, isotopically
specific scavenging reactions of chlorine atoms involving hal-
genated olefins are not likely unless the elimination [reaction
\( \text{ICl}^* + \text{C}_6 \text{H}_5 \text{Br} \rightarrow \text{ICl}^* + \text{C}_6 \text{H}_5 \text{Cl} \) is fast relative to subsequent chlorination. Thus we have
observed in the presence of excess N\(_2\) that part of the formation of \( \text{C}_6 \text{H}_5 \text{Cl} \) may be attributed to reaction of \(^{37}\text{Cl}^\text{at}\)oms and subsequenl collisonally induced dissociation. This is the result
of a competition between reaction 5 and 12 although the pos-
sibility cannot be excluded that the enrichment involves re-
action of \(^{137}\text{Cl}^*\). This is to be contrasted with the absence of
isotope separation in the reaction of selectively excited Br\(_2\) with
perfluorobutene-2.21 Photolysis of Br\(_2\) at 6940 Å causes preferential excitation of \(^{79}\text{Br}^*\) which subsequently undergoes
rapid collisional dissociation (calculated to be 99% efficient)
to \(^{79}\text{Br}\) atoms. Reaction of Br\(_2\) with (CF\(_3\))\(_2\text{C} = \text{C}((\text{CF}_3))\) pro-
duces the radical (CF\(_3\))\(_2\)BrC - ((CF\(_3\)))\(_2\) which is calculated
to have ~12 kcal/mol excess energy and which is stabilized by
 trifluoromethyl substituents. This radical can only eliminate
or add Br. As a consequence of faster isotope exchange22

\[ ^{79}\text{Br} + \text{Br}_2 \rightarrow ^{79}\text{BrBr} + \text{Br} \]

relative to formation of dibrominated product, isotopic speci-
licity is not preserved.

The success of \(^{37}\text{Cl}^\text{at}\)-atom scavenging in the reaction of
\(^{137}\text{Cl}^*\) with \( \text{C}_6 \text{H}_5 \text{Br} \) is thus attributed to the rapid elimination of
Br atom from a chemically activated radical.23 This reaction
occurs more rapidly than scrambling from energy transfer or
Cl-atom reactions. The latter originate primarily from reaction
7 since reaction 8 was shown to be unimportant; reaction 6 may
also be important, although it is endothermic relative to re-
anction 7.

Another contributing factor to the high degree of isotopic
selectivity is inferred from the absence of a change in product
composition when high pressures of nitrogen are employed.
Under these conditions, in the photochlorination of cfs-di-
chloroethylene, the formation of tetrachloroethane (13b) is
expected to predominate over isomerization to trans (13a).6c
Since the formation of chlorobenzene is not quenched and no
dichlorinated product is formed under these conditions, the
lifetime of the radical, I, or its precursors must be less than that
of the radical in reaction 13 (10\(^{-7}\) s).6c This is perhaps ra-
ionalized from the thermochemistry.

Reactions of the type

\[ \text{CH}_2\text{=CHBr} + \text{Cl} \rightarrow \text{CH}_2\text{=CHCl} + \text{Br} \]

are exothermic by ~13 kcal/mol \([D^0(C-Cl) = \text{energy of } \pi\]

bonds).6a

\[ \text{CH}_2\text{=CHBr} \sim 25 \text{kcal/mol} \]

\[ \text{CH}_2\text{=CHCl} \sim 12 \text{kcal/mol} \]

\[ \text{Cl} \text{CH}_2\text{=CHBr} \]

Elimination of Br from this radical will be more facile com-
pared to elimination of Cl. For reaction 1, the radical in-
mediate \( I \) will have less excess energy because of the higher
stabilization energy of benzene resonance compared to pen-
tadienyl resonance. However, the activation energy for loss of
Br, \( I \rightarrow \text{C}_6 \text{H}_5 \text{Cl} \), will also be smaller and may be zero or neg-
ative.24

Although reaction 1 must eventually proceed through the
radical of structure I, thermochemical considerations indicate
that addition of ICl\(^*\) to \( \text{C}_6 \text{H}_5 \text{Br} \) at the ortho or para positions
should be more favorable than addition at C\(_1\).24

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**Table I. Comparison of Enrichment from Reaction of \(^{137}\text{Cl}^*\) with \( \text{C}_6 \text{H}_5 \text{Br} \) and \( \text{C}_6 \text{H}_5 \text{I} \)**

<table>
<thead>
<tr>
<th>( p_{\text{N}_2} ) Torr</th>
<th>( \rho(114/112) )</th>
<th>( \rho(114/112) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.84</td>
<td>0.79</td>
</tr>
<tr>
<td>0.52</td>
<td>0.70</td>
<td>0.75</td>
</tr>
<tr>
<td>0.22</td>
<td>1.39</td>
<td>1.43</td>
</tr>
</tbody>
</table>

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* Because \( \text{C}_6 \text{H}_5 \text{Br} \) and \( \text{C}_6 \text{H}_5 \text{I} \) have different vapor pressures, the
comparison was made with identical molar quantities of scavenger
(306 pmol) and with the pressure of \( \text{C}_6 \text{H}_5 \text{Br} \) adjusted by cooling a cold
finger with ice water to equal that of \( \text{C}_6 \text{H}_5 \text{I} \). The results reported here
for a given pressure were obtained on the same day at a constant
wavelength. Slight inaccuracy in adjusting the wavelength on a day
to day basis is likely to be the reason for the slightly lower enrichment
at 0.52 Torr compared to 1.0 Torr. * Accuracy in \( \rho(114/112) \) is ±5%,
based on several repetitions of experiments with both scavengers.

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The occurrence of a Cl-atom migration in 2 and 3 as a mechanism which permits $^{37}\text{Cl}$ enrichment is therefore plausible only if the rate of migration compared to loss of Cl is the same for reactions involving both C$_6$H$_5$Cl and C$_6$H$_5$Br. This requires that migration be rate limiting compared with loss of Br or I. Moreover, since it is observed that Cl-atom scrambling is involved as a competitive pathway, direct reaction at the ipso position is excluded as a dominant pathway; were this not the case, the equilibrated energy distribution in 1 would require according to RRKM theory that the C$_6$H$_5$Cl scavenger yields higher enrichments than C$_6$H$_5$Br.

It is well known that I$_2^*$ forms charge-transfer complexes with aromatic hydrocarbons.\textsuperscript{29} It is therefore possible that the first step of the reaction of ICl* (A $^3\Pi_1$) with C$_6$H$_5$Br involves a charge-transfer complex. From the work of Russell,\textsuperscript{30} one might also speculate that a σ complex is involved, formed from a charge-transfer complex or directly from reaction of ICl in an excited state with C$_6$H$_5$Br. In the latter case the question arises whether the ICl reactant is in the initial A $^3\Pi_1$ state or has been converted to some other state.

In a study of self-quenching of ICl fluorescence at λ 6068 Å, Holleman and Steinfeld\textsuperscript{31} found that the collisional quenching rate is 7.2 Torr$^{-1}$ μs$^{-1}$, i.e., has a collision number of 1.2. Thus it may be concluded that nearly every collision of ICl* with ICl results in electronic deactivation. The most plausible mechanism for such rapid quenching is intersystem crossing to high vibrational levels of the ground state, although energy transfer to produce the heretofore unobserved $^3\text{I}_2$ state\textsuperscript{32} cannot be excluded. Under the reaction conditions used for producing isotopic specificity, it is likely that this quenching mechanism is also applicable. We therefore speculate that reaction of ICl* with C$_6$H$_5$Br results in formation of C$_6$H$_5$Cl and that vibrational excitation, alone, is sufficient for reaction 1. Since it is now possible to produce molecules in high vibrational levels of the ground state by nonlinear, multiphoton infrared absorption, chemical scavenging may be applied with advantage to this area of selective photochemistry as well.

Based on our observations of the reaction of $^{13}$Cl* with 1,2-dibromomethane, bromobenzene, and iodobenzene, we believe that the general mechanism for these reactions,

$$\text{ICl}^* + \text{C}_6\text{H}_5\text{X} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{X}$$

where X is a leaving group having a weaker C–X bond than C–Cl, can be extended to other scavenger systems. The principal difficulty that will be encountered is competition from dark reactions which present major problems as the degree of substitution is reduced. Ultimately, however, the limiting feature is the ratio of rates for isotopic scavenging compared to isotopic scrambling, and this is determined solely by the structure of the scavenger. The present study illustrates that there are some scavengers for which the degree of isotope enrichment can be varied advantageously depending upon reaction conditions.

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References and Notes
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\textsuperscript{(2)} For a comprehensive review, see J. P. Aldridge, III, J. H. Birely, C. D.
Fluorine-19 NMR Studies of Fluoroaromatic Systems with Complete Proton Decoupling. The Signs and Magnitudes of Certain F–•F and 13C–•F Spin–Spin Couplings

Stanley L. Manatt* and M. Ashley Cooper

Abstract: Using complete proton decoupling, the fluorine-19 NMR spectra of the 13C satellites of a particular isotopomer of each of the difluorobenzences and 1,8-difluorobenzenanthrene and two isotopomers of 1-fluoro-1-fluoromethylbenzene have been studied. Based on the sign of the 13C–•F spin–spin coupling as negative, the signs and magnitudes of the F–•F spin–spin coupling constants have been determined. These results are compared with other available pertinent spin–spin coupling information. Also, it was noted that the directly bonded 13C-fluorine isotope chemical shift in the trifluoromethyl group is larger (11.1 Hz upfield) than observed in the case of fluorine bonded to sp2 carbon (all about 8 Hz upfield). A significant result emerges relative to the sign of 13C–•C–•F coupling, at least for molecular fragments involving sp2 carbon. The stereochemical disposition of the spin coupled nuclei appears to matter very little and the observed sign must de-

Substantial interest in the NMR parameters of fluoroaromatic molecules has persisted for some years as various difficulties have accompanied the unequivocal establishment of the signs of the various F–•F and F–•H coupling constants. Originally this state of affairs no doubt arose because of the complexities of the observed 19F and 1H spectra. Perhaps another aspect of the problem has been that the observed trends of F–•F coupling constants in many cases defy comparison with...