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(9) The numerical expressions of the LCAO coefficients of the χ_i's employed in this paper are *mean values* obtained from a few different molecules. Owing to the remarkable constancy of the localized orbitals (without tails) the choice of the reference molecules is not essential and the mean values do not differ significantly from the value the LCAO coefficients have in the χ_i of a single molecule.
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(11) For a sensible representation of *V*, we mean a representation which gives for points placed outside the van der Waals spheres a mean deviation from the TLO values lower than 0.1 kcal/mol.
(12) The inner shell TLO for the first row atoms can be safely discarded in computing the electrostatic molecular potential, because their effect on *V* is practically only a shielding of the nuclear charge.
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(19) The point-charge representation of H_2O employed in this paper slightly differs from that reported in ref 6 in order to be more consistent with the STO-3G approximation adopted here. The coordinates of the charges are available from the authors on request.
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(21) To give an idea of the reduction of the computation times we report here the time ratio for the calculation of the *V* map of 2-formylaminoacetamide given in Figure 5 according to the three approximations: 100:30:8. If one also considers the time necessary to get the SCF wave function one obtains the following ratio: 100:24:0.7. Such a ratio becomes more and more favorable to the last approximation when the size of the molecule increases.
(22) A recent example of investigations proceeding on the same line is given by a paper by Hayes and Kollman on the electrostatic potential of carboxipeptidase A.[23] These authors use a technique similar to the present one, which relies on the Mulliken populations of some model compounds. This simpler description of the charge distribution could be profitably coupled with the present one for representing groups very far from the region of space where *V* is examined.
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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 ^{35}Cl or ^{37}Cl depending on the excitation wavelength. A gas mixture of ICl and C_6H_5Br 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 $I^{37}Cl$ A $^3\Pi_1$–X $^1\Sigma^+$ system. At pressures of several Torr, $C_6H_5{}^{37}Cl$ 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 $C_6H_5{}^{37}Cl$ involves direct reaction of $I^{37}Cl^*$ with C_6H_5Br 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[2] have been reported in which selective excitation results in direct photodissociation or predissociation of one isotopic species, leaving isotopically enriched starting material and decomposition products.[3] 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.[4] Previously we found that $I^{37}Cl^*$ reacts with BrCH=CHBr to form ^{37}Cl-enriched BrCH=CHCl and ClCH=CHCl.[5] This reaction takes advantage of the fact that ICl in its first electronically excited state (A $^3\Pi_1$) has a different reactivity toward halogenated olefins than in its ground state (X $^1\Sigma^+$).

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_6H_5Br as a scavenger and data on hot molecule reactions involving chlorine atoms,[6] we have concluded that our observations of isotope enrichments are attributable to two factors. (1) Selective excitation of ICl produces predominantly $I^{37}Cl^*$ which behaves kinetically like a chlorine atom in reaction with C_6H_5Br. (2) A radical intermediate having excess vibrational energy is formed from the transfer of ^{37}Cl from $I^{37}Cl^*$ to C_6H_5Br and eliminates a Br atom more rapidly than it suffers collisional deactivation.

The photochemical reaction of $I^{37}Cl^*$ with C_6H_5Br illustrates the general scheme for separating isotopes by chemical scavenging. Selective excitation of $I^{37}Cl$ produces an excited state. Separation is accomplished because the chemistry of $I^{37}Cl^*$ in reaction with C_6H_5Br 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 4W (all line) argon ion laser (Spectra-Physics Model 165). The laser bandwidth is narrowed to ~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.[7] 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 ¾ m spectrometer (SPEX 1702) equipped with scan drive and photomultiplier (Centronic Q4283 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_6H_5Br. 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 $<5 \times 10^{-5}$ 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 (Perkin-Elmer 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_6H_5Br and C_6H_5Cl are 7.27 ± 0.07 and 9.94 ± 0.02, respectively (response factor = [wt. CH_2Br_2] [area C_6H_5X]/[wt. C_6H_5X][area CH_2Br_2]).

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

Materials. Bromobenzene (Mallinckrodt), 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. I_2 (Fisher), Br_2 (Fisher), N_2 (AIRCO), Ar (AIRCO), and C_2H_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).[8] 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_2Br_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 ¾ 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 λ 6053 Å, corresponding to the (18-0) bandhead of the $I^{37}Cl$ A-X system (Figure 2a).

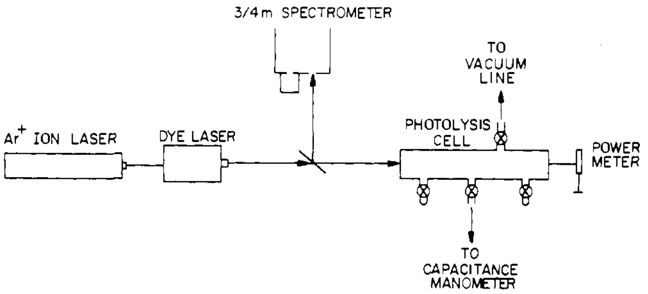


Figure 1. Schematic of apparatus for carrying out the selective reaction of $I^{37}Cl^*$ + C_6H_5Br in the gas phase.

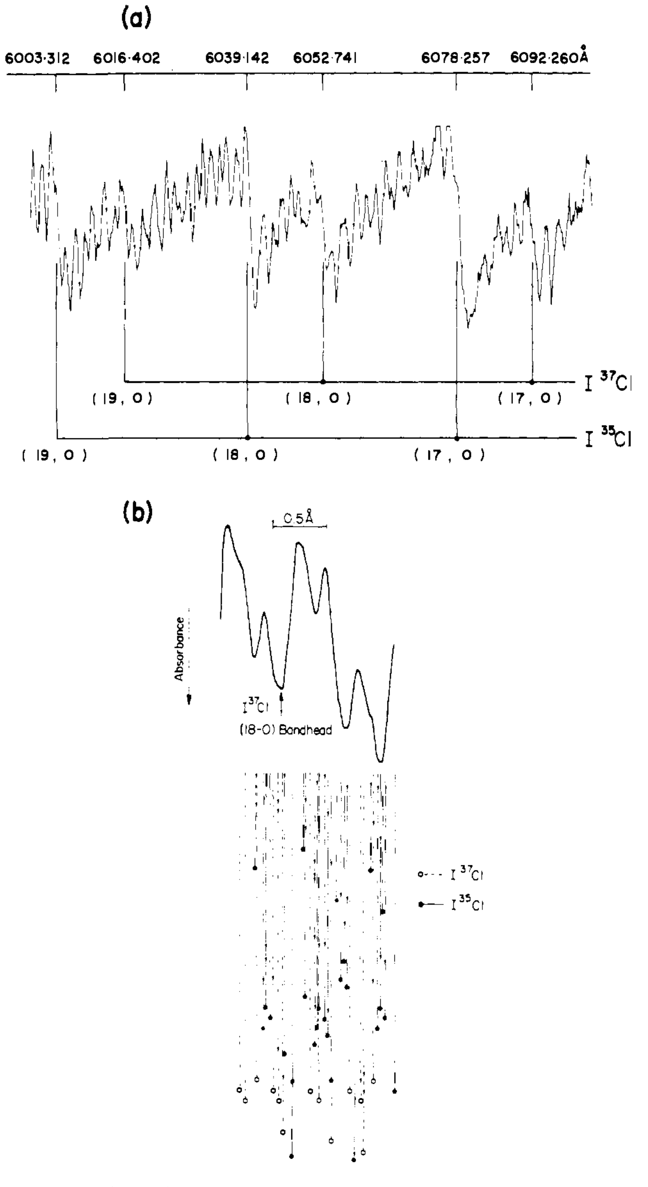


Figure 2. Absorption spectrum of ICl: (a) low resolution spectrum (6000–6100 Å); (b) second-order spectrum of (18,0) bandhead (resolution 0.05 Å). Assignments of bandheads and rotational lines are made using the molecular constants given in ref 10.

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

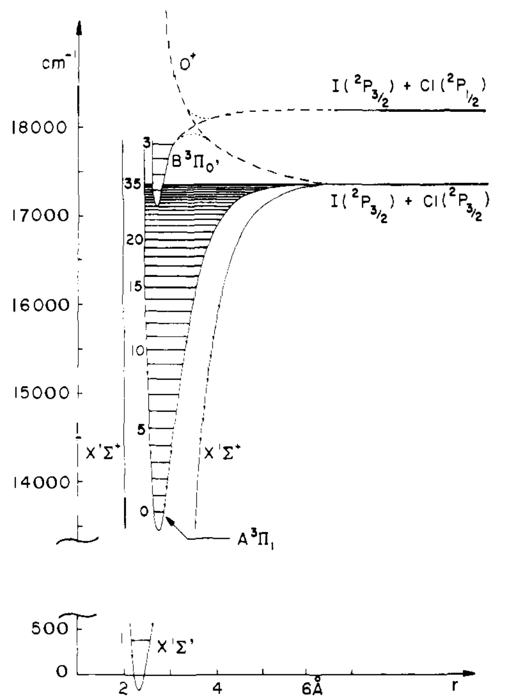


Figure 3. Potential curves of X, A, and B states of ICl, taken from ref 10b.

multiple reflections from the cell windows is included.[8] The number of photons absorbed, n_q, during t seconds of irradiation is given by

$$n_q = \frac{E_{tot}Q_m\lambda}{hc} \times 10^7$$

where E_{tot} is the total energy in joules entering the cell, λ is the wavelength in centimeters, and Q_m is the fraction of energy absorbed by ICl.[9] By measuring the yield of photochemical product, the quantum yield for its formation is calculated as

$$\Phi_p = n_p/n_q$$

where n_p is the number of product molecules of chlorobenzene.

The intensity dependence of the reaction is measured at fixed ICl (0.5 Torr) and C_6H_5Br (~3.3 Torr) pressures by determining the yield of C_6H_5Cl for several incident-light intensities, varying from 15 to 100 mW. The yield of C_6H_5Cl is found to be linear with incident intensity. Hence the quantum yield refers to a single-photon process.

Dark Reactions. The procedure for measuring the extent of dark reaction of ICl with C_6H_5Br involves the same vacuum transfer techniques as described for the photolysis. Quantitative analysis is accomplished by analytical gas chromatography with methylene bromide as an internal standard. No differences are noted when CH_2Br_2 is used instead as an external standard.

Results

Selective Excitation. The visible absorption spectrum of $I^{35}Cl$ and $I^{37}Cl$ has been studied extensively.[10] Figure 3 shows the known low-lying electronic states of ICl. The first excited state, A $^3\Pi_1$, lies ~13 000 cm^{-1} above the ground state, X $^1\Sigma^+$, and is bound by over ~3500 cm^{-1}. A portion of the visible absorption spectrum is shown in Figure 2a. Assignments of rotational lines to $I^{35}Cl$ and $I^{37}Cl$ are based on the work of Hulthén, Järlsäter, and Koffman.[10b]

Figure 2b shows that selective excitation of $I^{37}Cl$ or $I^{35}Cl$ can be achieved only if a light source of narrow bandwidth is used. Moreover, the large number of overlapping $I^{35}Cl$ and $I^{37}Cl$ lines also requires that careful attention be paid to the choice of excitation wavelength.

In a previous communication,[5b] the use of an intracavity $I^{35}Cl$ filter for obtaining selective excitation of $I^{37}Cl$ was reported. The laser bandwidth (~2 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 $I^{35}Cl$ absorption frequencies, however, decreases with the number of modes and is dependent on the threshold characteristics of the laser.[11] Under present experimental conditions, we have observed no differences in enrichment for irradiations performed at λ 6053 Å with and without the $I^{35}Cl$ filter when the bandwidth is 0.1 Å.[12] Therefore, the results reported here, at λ 6053 Å, are effectively obtained with an etalon and tuning wedge only, even though an $I^{35}Cl$ intracavity cell has been used in all of these experiments.

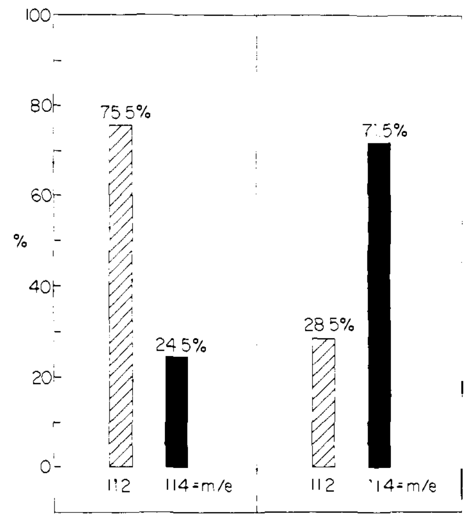


Figure 4. Percent abundance of parent ions from $C_6H_5{}^{35}Cl$(112) and $C_6H_5{}^{37}Cl$(114): (a) natural abundance; (b) from reaction of ICl (11.6 μmol) + C_6H_5Br (306 μmol) irradiated at λ 6053 Å for 1 h.

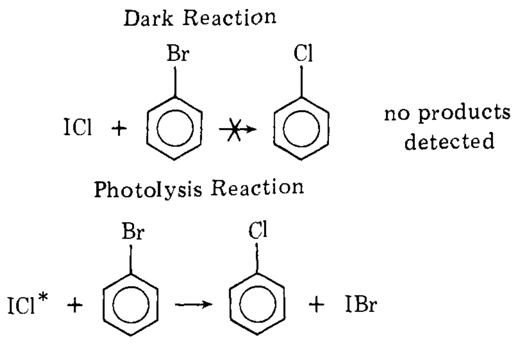
Scavenging of Selectively Excited Isotopes. Figure 4 shows the maximum $C_6H_5{}^{37}Cl$ enrichment obtained at λ 6053 Å from the reaction

$$ICl^* + C_6H_5Br \rightarrow I + C_6H_5Cl + Br \qquad (1)$$

Concurrently, the enrichment in $I^{35}Cl$ starting material is measured by scavenging unreacted ICl with ethylene to form the addition product ICH_2CH_2Cl. The ratio of ^{35}Cl:^{37}Cl (natural abundance, 1.00:0.33) is determined from the abundance of ions with m/e equal to 63 and 65 (CH_2CH_2Cl). Thus, for example, irradiation of ICl + C_6H_5Br (p_{ICl} = 0.5 Torr; $[ICl]/[C_6H_5Br]$ = 0.016) results in enriched ICl starting material with a ^{35}Cl:^{37}Cl ratio of 1.00:0.26 and enriched C_6H_5Cl product with a ^{35}Cl:^{37}Cl ratio of 1.00:1.20.

The quantum yield for formation of isotopically enriched C_6H_5Cl 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 C_6H_5Cl changes linearly with variations in laser intensity.

Irradiation at 6053 Å of gas mixtures containing ICl and saturated halogenated hydrocarbons, e.g., $BrCH_2CH_2Br$, CH_3Br, or CH_2Br_2, does not yield any detectable photochemical products. Mixtures of ICl and olefins, however, react rapidly in the dark, presumably 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:



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 C_6H_5Br are left in the dark for 1 h.

Having established that the reactivity of $X\,{}^1\Sigma^+$ and $A\,{}^3\Pi_1$ states of ICl toward bromobenzene is different, we next establish that $I^{37}Cl^*$ is the reactive species involved in the isotopically specific reaction and not ${}^{37}Cl$ atoms. (1) It is well known that Cl atoms react with saturated hydrocarbons and halogenated hydrocarbons by hydrogen abstraction.[13] Photodissociation of ICl at 5145 Å (19 436 cm^{-1}, see Figure 3) in the presence of CH_2Br_2 results in the disappearance of starting material from the reaction

$$Cl + CH_2Br_2 \rightarrow HCl + \cdot CHBr_2$$

Irradiation of ICl at 6053 Å, where the $A\,{}^3\Pi_1$ state is 2786 cm^{-1} below the dissociation limit, however, does not lead to photochemical reaction, i.e., the concentration of CH_2Br_2 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 C_6H_5Cl from reaction of C_6H_5Br with Cl atoms or ICl*, produced at λ 6053 Å, appears to be nearly the same; $\Phi_{5145 Å}(C_6H_5Cl) = 0.12 \pm 0.01$; $\Phi_{6053 Å}(C_6H_5Cl) = 0.096 \pm 0.003$. Although it is not possible to rule out an ICl-addition product as an intermediate in the photochemical reaction,[14] 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 $I^{37}Cl^*$ with the scavenger. However, electronically excited ICl differs from a Cl atom in reactions involving hydrogen abstraction.

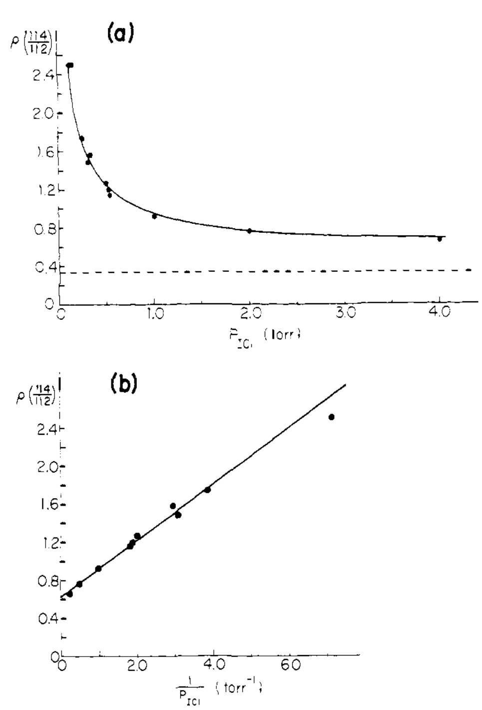
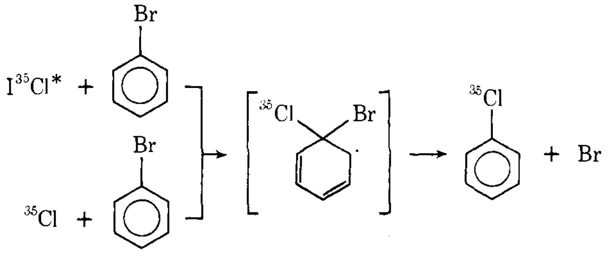


Figure 5. (a) ICl pressure dependence of $C_6H_5{}^{37}Cl$ enrichment, measured as the ratio of $\rho = m_{114}/m_{112}$, at constant C_6H_5Br pressure (~3.3 Torr = 306 μmol). For natural abundance, $\rho(114/112) = 0.33$. (b) Plot of $\rho(114/112)$ vs. $[p_{ICl}]^{-1}$ from data in (a) (correlation coefficient, $r^2 = 0.999$).

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 $I^{37}Cl$. This implies that competitive reactions exist which cause isotopic scrambling.

Loss of isotopic specificity can occur by two different reactions



(2)

(3)

where $I^{35}Cl^*$ is produced by energy transfer

$$I^{37}Cl^* + I^{35}Cl \rightarrow I^{37}Cl + I^{35}Cl^* \qquad (4)$$

and the ${}^{35}Cl$ atom is formed during the exchange reaction

$$I^{35}Cl + {}^{37}Cl \rightarrow I^{37}Cl + {}^{35}Cl \qquad (5)$$

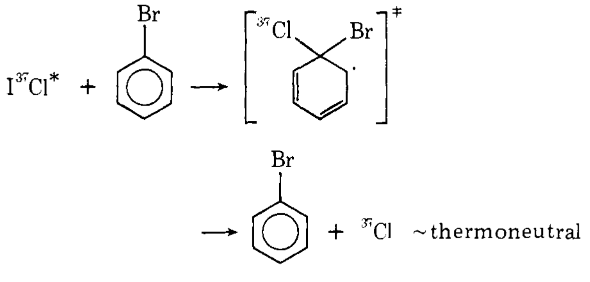
This reaction is in competition with the reaction

$$ICl + {}^{37}Cl \rightarrow Cl_2 + I$$

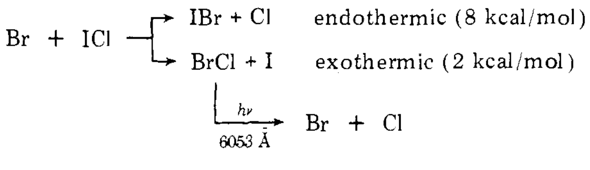
which has the effect of removing Cl atoms from the reaction. Several potential sources of Cl atoms are postulated:

$$I^{37}Cl^* + M \rightarrow I + {}^{37}Cl + M$$

endothermic (2.6 kcal/mol) (6)



(7)



$$Br + ICl \rightarrow IBr + Cl \quad \text{endothermic (8 kcal/mol)}$$
$$Br + ICl \rightarrow BrCl + I \quad \text{exothermic (2 kcal/mol)} \qquad (8)$$
$$BrCl \xrightarrow[6053\ Å]{h\nu} Br + Cl$$

Figure 5a shows the dependence of ${}^{37}Cl$ enrichment (m_{114}:m_{112} ratio) on the ICl pressure at a fixed concentration of C_6H_5Br. Linear regression analysis of the enrichment vs. $1/p$ shows that the data fit a straight line (see Figure 5b) with a correlation coefficient, 0.999. The minimum expected enrichment, ρ_0 (y intercept), in C_6H_5Cl for high ICl pressure is $0.62 = m_{114}/m_{112}$. This has been observed up to an ICl pressure of 10 Torr. The data imply that loss of isotopic specificity is due to second-order scrambling reactions, i.e., the enrichment is proportional to $[P_{ICl}]^{-2}$. Formation of $I^{35}Cl^*$ [reaction

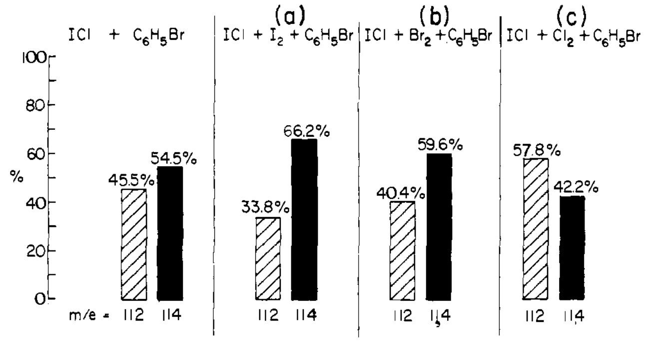


Figure 6. Effect of added gases on the $C_6H_5{}^{37}Cl$ enrichment from the reaction of ICl (47.8 μmol) + C_6H_5Br (306 μmol), irradiated at λ 6053 Å for 1 h: (a) I_2 (28.9 μmol); (b) Br_2 (28.9 μmol); (c) Cl_2 (28.9 μmol).

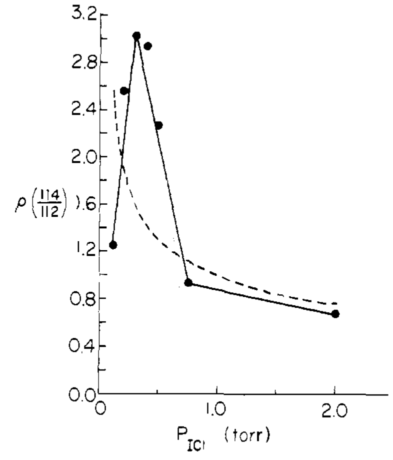


Figure 7. Effect of 0.21 Torr of I_2 on $C_6H_5{}^{37}Cl$ enrichment as a function of ICl pressure at constant C_6H_5Br pressure (306 μmol ~ 3.3 Torr).

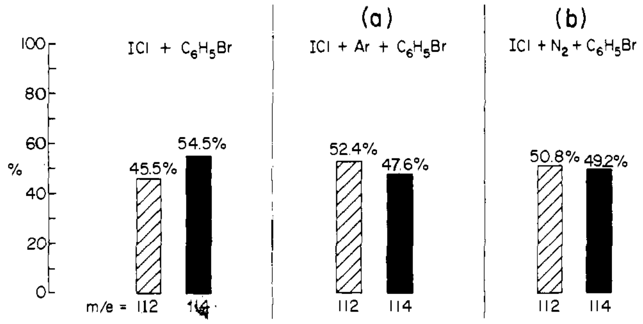


Figure 8. Effect of added gases on the $C_6H_5{}^{37}Cl$ enrichment from reaction of ICl (47.8 μmol) + C_6H_5Br (306 μmol), irradiated at λ 6053 Å for 1 h: (a) Ar (2.07 mmol = 21.5 Torr); (b) N_2 (1.94 mmol = 20.1 Torr).

4] and ^{35}Cl [reaction 5 together with reactions 6, 7, or 8] are both second order in ICl pressure and account for variations in enrichment with ICl pressure if reactions 2 and 3 are pseudo-first-order in $I^{35}Cl^*$ or ^{35}Cl, 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 coworkers[15] found in using ICl as a source of Cl atoms that the presence of I_2 reduced the concentration of Cl_2 to negligible amounts. This observation is attributed to the reaction

$$I_2 + Cl \rightarrow ICl + I \qquad (9)$$

The effect of I_2 (0.3 Torr) on the $C_6H_5{}^{37}Cl$ enrichment is shown in Figure 6a. The higher ^{37}Cl enrichment demonstrates that chlorine atom reactions contribute to isotopic scrambling.

To optimize the enrichment in C_6H_5Cl, the effect of changes in ICl pressure with fixed concentration of I_2 and C_6H_5Br was studied (Figure 7). These results indicate that there are at least two additional competing reactions that are related to the presence of I_2. For 0.3 Torr $\leq p_{ICl} \leq$ 0.8 Torr, the higher enrichment (Figure 7) reflects Cl-atom scavenging by reaction 9 or perhaps by halogen trimer formations.[16] At higher ICl pressures, where I_2 has no effect, chlorine exchange [reaction 5] must necessarily be occurring faster than Cl-atom scavenging. Since I_2 also absorbs at 6053 Å ($\epsilon_{I_2} \sim 50\epsilon_{ICl}$), energy transfer

$$I_2^* + ICl \rightarrow I_2 + ICl^* \qquad (10)$$

is very likely and would result in lower isotopic specificity. It appears from Figure 7 that at $p_{ICl} < 0.3$ Torr, reaction 10 predominates over (9), reflecting a change in the ratio $[I^{37}Cl^*]/[I_2^*]$,[17] 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 Cl-atom scavenger.

Further confirmation of the presence of Cl atoms comes from irradiation of mixtures of ICl, Cl_2, and C_6H_5Br. As shown in Figure 6c, the $C_6H_5{}^{37}Cl$ enrichment decreases due to the additional Cl-atom exchange reaction

$$^{37}Cl + Cl_2 \rightarrow {}^{37}ClCl + Cl \qquad (11)$$

which leads to isotopic scrambling. No other sources of Cl atoms are introduced since Cl_2 is transparent to light at λ 6053 Å. Although there is no experimental evidence to exclude the four-center reaction

$$I^{37}Cl^* + Cl_2 \rightarrow I^{35}Cl^* + {}^{37}ClCl$$

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 Br_2 photodissociates at λ 6053 Å, it should be possible to evaluate the effect of Br atoms on the enrichment [reaction 8] by addition of Br_2. It was found, however, that two competing processes are involved, Cl-atom scavenging and scrambling. For low Br_2 pressure (0.3 Torr, $p_{Br_2}/p_{ICl} = 0.6$), the enrichment increases to 59% $C_6H_5{}^{37}Cl$ (Figure 6b), whereas for higher pressure (0.6 Torr, $p_{Br_2}/p_{ICl} = 1.2$) the enrichment decreases to 42% $C_6H_5{}^{37}Cl$. These results do not elucidate the scrambling effect of Br atoms produced in reaction 1. However, when C_6H_5I was substituted in place of C_6H_5Br (see Table I), no change in the $C_6H_5{}^{37}Cl$ 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 Cl 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 $C_6H_5{}^{37}Cl$ to decrease as would be expected if Cl-atom reactions were more important under these reaction conditions. Irradiation at 6053 Å promotes $I^{37}Cl$ to $v' = 18$ of the A $^3\Pi_1$ state, ~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 $I^{37}Cl^*$ promoting dissociation or causing 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 N_2) and collisional dissociation is reflected in a lower $C_6H_5{}^{37}Cl$ enrichment [reaction 5]. Moreover, dilution of the reaction mixture virtually eliminates energy transfer [reaction 4].

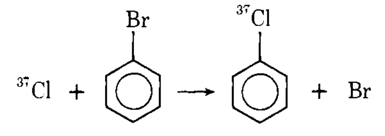
Figure 9 shows the relationship between the enrichment and changes in the total pressure, adjusted by adding N_2. The ob-

Table I. Comparison[a] of Enrichment from Reaction of $I^{37}Cl^*$ with C_6H_5Br and C_6H_5I[b]

p_{ICl}, Torr	$ICl^* + C_6H_5Br$ $\rho(114/112)$	$ICl^* + C_6H_5I$ $\rho(114/112)$
1.0	0.84	0.79
0.52	0.70	0.75
0.22	1.39	1.43

[a] Because C_6H_5Br and C_6H_5I have different vapor pressures, the comparison was made with identical molar quantities of scavenger (306 μmol) and with the pressure of C_6H_5Br adjusted by cooling a cold finger with ice water to equal that of C_6H_5I. 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. [b] Accuracy in $\rho(114/112)$ is ±5%, based on several repetitions of experiments with both scavengers.

servation 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

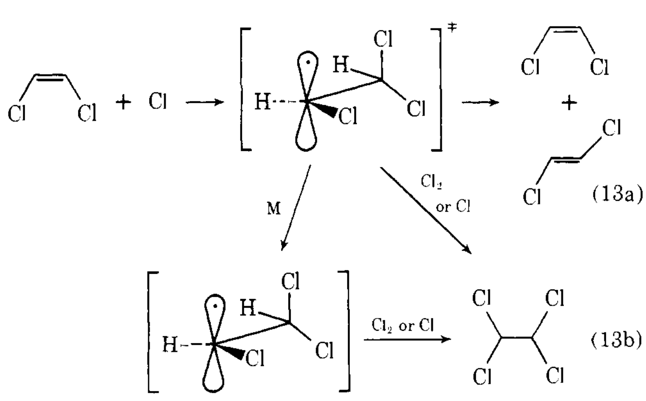


(12)

>0.33. The possibility also exists that $I^{37}Cl^‡$ reacts with C_6H_5Br, contributing to the observed isotopic preference. The latter reaction, however, should become less important as the N_2 pressure increases because $I^{37}Cl^‡$ is quenched to lower vibrational levels, thereby becoming less reactive. Unless collisional quenching of $I^{37}Cl^‡$ is very insensitive, requiring a very large number of collisions, the observed limiting value of ρ in Figure 9 for $p_{N_2} > 50$ Torr is more readily explained by a preference of reaction 12 over 5.[19]

Discussion

The photochlorination of halogenated olefins is a well-known reaction[20] which proceeds through a free-radical chain mechanism. From studies of Ayscough and co-workers[6a] it has been demonstrated that these reactions involve vibrationally hot radical intermediates; for example,



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

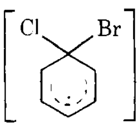
Because chain propagation occurs at random, isotopically specific scavenging reactions of chlorine atoms involving halogenated olefins are not likely unless the elimination [reaction 13a] is fast relative to subsequent chlorination. Thus we have observed in the presence of excess N_2 that part of the formation of $C_6H_5{}^{37}Cl$ may be attributed to reaction of ^{37}Cl atoms and subsequent collisionally induced dissociation. This is the result of a competition between reaction 5 and 12 although the possibility cannot be excluded that the enrichment involves reaction of $I^{37}Cl^‡$. 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 $^{79}Br_2$, which subsequently undergoes rapid collisional dissociation (calculated to be 99% efficient) to ^{79}Br atoms. Reaction of Br with $(CF_3)_2C{=}C(CF_3)_2$ produces the radical $(CF_3)_2BrC\text{-}\dot{C}(CF_3)_2$, 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 exchange[22]

$$^{79}Br + Br_2 \rightarrow {}^{79}BrBr + Br$$

relative to formation of dibrominated product, isotopic specificity is not preserved.

The success of ^{37}Cl-atom scavenging in the reaction of $I^{37}Cl^*$ with C_6H_5Br 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 reaction 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 *cis*-dichloroethylene, 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, **1**, or its precursors must be less than that



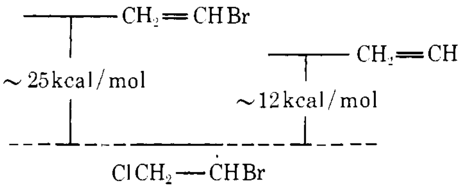
1

of the radical in reaction 13 (10^{-7} s).[6c] This is perhaps rationalized from the thermochemistry.

Reactions of the type

$$CH_2{=}CHBr + Cl \rightarrow CH_2{=}CHCl + Br$$

are exothermic by ~13 kcal/mol [$D°$(C-Cl) − energy of π bond].[6a]



Elimination of Br from this radical will be more facile compared to elimination of Cl. For reaction 1, the radical intermediate **1** will have less excess energy because of the higher stabilization energy of benzene resonance compared to pentadienyl resonance. However, the activation energy for loss of Br, **1** → C_6H_5Cl, will also be smaller and may be zero or negative.[24]

Although reaction 1 must eventually proceed through the radical of structure **1**, thermochemical considerations indicate that addition of ICl^* to C_6H_5Br at the ortho or para positions should be more favorable than addition at C_1.[24]

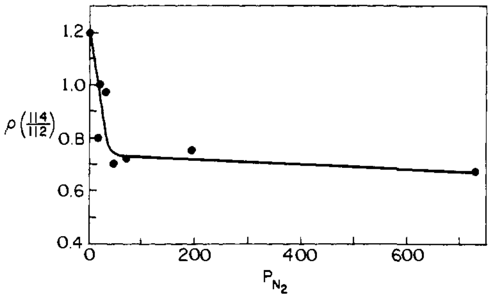
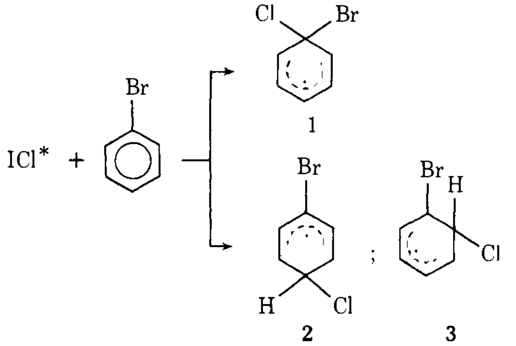


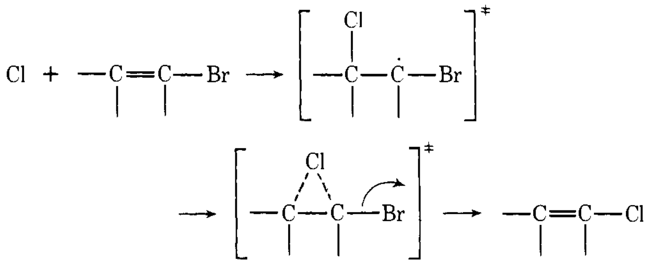
Figure 9. Effect of variation in total pressure, adjusted by adding N_2, on the reaction of ICl (47.8 μmol) + C_6H_5Br (306 μmol), irradiated at λ 6053 Å for 1 h.



$\Delta H(1) - \Delta H(2,3) \simeq 4$ kcal/mol

This would be especially true if electrophilic substitution were involved.[25] Since the C-H bond strength is considerably larger than C-Cl, radicals **2** and **3** would be expected to lose Cl faster than H, leading to no isotopic specificity, unless a Cl-atom migration were involved.[26]

Durana and McDonald[27] have postulated that Cl migration occurs in reaction of the type



$$\mathrm{Cl} + \mathrm{-C{=}C{-}Br} \longrightarrow \left[\mathrm{-C(Cl){-}\dot{C}{-}Br}\right]^{\ddagger} \longrightarrow \left[\mathrm{-C{-}C{-}Br}\ (\text{Cl bridged})\right]^{\ddagger} \longrightarrow \mathrm{-C{=}C{-}Cl}$$

and may proceed through a bridged-intermediate structure. This hypothesis is based on infrared chemiluminescence using the arrested relaxation technique. It is found that under collisionless conditions, the exothermicity is distributed nonstatistically in the product and that this energy is located preferentially in carbon skeleton vibrations. From the latter, the authors conclude that a C-C bending vibration facilitates the migration of Cl which is accompanied by lengthening of the C-Br bond and subsequent cleavage. In the reaction of Cl with C_6H_5Br, however, the arrested relaxation method shows that the energy in C_6H_5Cl is distributed statistically;[27] hence no insight into the question of Cl migration in the aromatic system is acquired from observation of the infrared chemiluminescence.

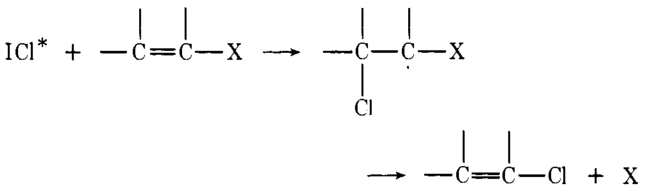
Isotopic specificity in reaction 1 requires that elimination of Br be faster than elimination of ^{37}Cl. However, thermochemistry suggests that **2** and **3** should be formed faster than **1** and that loss of Cl should occur more rapidly than loss of H in the formation of a stable product. Moreover, the ratio of reaction 1 to 7 is the same for iodobenzene as for bromobenzene, despite evidence from arrested relaxation methods that **1** involves an equilibrated energy distribution.

The occurrence of a Cl-atom migration in **2** and **3** as a mechanism which permits ^{37}Cl enrichment is therefore plausible only if the rate of migration compared to loss of Cl is the same for reactions involving both C_6H_5I and C_6H_5Br. 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[28] that the C_6H_5I scavenger yield higher enrichments than C_6H_5Br.

It is well known that I_2* forms charge-transfer complexes with aromatic hydrocarbons.[29] It is therefore possible that the first step of the reaction of ICl* (A $^3\Pi_1$) with C_6H_5Br involves a charge-transfer complex. From the work of Russell,[30] one might also speculate that a π complex is involved, formed from a charge-transfer complex or directly from reaction of ICl in an excited state with C_6H_5Br. 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[31] found that the collisional quenching rate is 7.2 $\mathrm{Torr^{-1}\ \mu s^{-1}}$, 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 $^3\Pi_2$ state[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 $ICl^{\ddagger}$ with C_6H_5Br results in formation of C_6H_5Cl 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 $I^{37}Cl$* with 1,2-dibromoethylene, bromobenzene, and iodobenzene, we believe that the general mechanism for these reactions,



$$\mathrm{ICl^*} + \mathrm{-C{=}C{-}X} \longrightarrow \mathrm{-C(Cl){-}\dot{C}{-}X} \longrightarrow \mathrm{-C{=}C{-}Cl} + \mathrm{X}$$

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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(8) Because the vapor pressure of bromobenzene is low (~4 Torr at room temperature), small changes in the initial weight of bromobenzene result in negligible changes in pressure. Hence initial conditions are expressed in terms of the pressure of ICl and the molar ratio $[ICl]/[C_6H_5Br]$.

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Fluorine-19 NMR Studies of Fluoroaromatic Systems with Complete Proton Decoupling. The Signs and Magnitudes of Certain F···F and ^{13}C···F Spin–Spin Couplings[1a]

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Abstract: Using complete proton decoupling, the fluorine-19 NMR spectra of the ^{13}C satellites of a particular isotopomer of each of the difluorobenzenes and 1,8-difluoronaphthalene and two isotopomers of 2-fluorotrifluoromethylbenzene have been studied in ^{19}F[^{19}F] and ^{19}F[^{13}C] experiments. Based on the sign of the ^{13}C–F spin–spin coupling as negative, the signs and magnitudes of various F···F and ^{13}C···F couplings have been determined. These results are compared with other available pertinent spin–spin coupling information. Also, it was noted that the directly bonded ^{13}C-fluorine isotope chemical shift in the trifluoromethyl group is larger (11.1 Hz upfield) than observed in the case of fluorine bonded to sp^2 carbon (all about 8 Hz upfield). A significant result emerges relative to the sign of ^{13}C–C–C–F coupling, at least for molecular fragments involving sp^2 carbon. The stereochemical disposition of the spin coupled nuclei appears to matter very little and the observed sign must depend in a complicated manner on substituent effects. This conclusion stands in contrast to all previous observations on other types of vicinal couplings where stereochemical orientation has been demonstrated to be much more important than electronic substituent effects and can be determined from the coupling magnitude with some reliability.

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 ^{19}F and ^{1}H spectra. Perhaps another aspect of the problem has been that the observed trends of F···F coupling constants in many cases defy comparison with