LASER ISOTOPE SEPARATION
BY
SELECTIVE EXCITED STATE PHOTOCHEMISTRY

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R. N. Zare

Department of Chemistry
Columbia University
New York, New York 10027

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Previously, we demonstrated¹ that it was possible to separate chlorine isotopes photochemically by selective excitation of ICl in the presence of halogenated olefins. The present report summarizes our recent experimental results which have provided reasonable insight into the mechanism of this chemical process. Moreover, this study reveals the type of scrambling reactions that can be expected to occur when the scavenging technique is used for isotope separation and suggests strategies for minimizing those reactions.

Below, we have briefly outlined experimental results and conclusions. The full account is given in the paper (accepted for publication in J. Amer. Chem. Soc.) which will be sent to you shortly.

(1) The reaction

occurs in an isotopically specific manner ($\beta \sim 9$) with

$\epsilon_{\text{C}_6\text{H}_5\text{Cl}}^{6053\text{\AA}} = 0.096$ (single photon absorption). The ground state of ICl ($\chi^1\Sigma^+$) is essentially unreactive towards bromobenzene.

(2) The reaction (1) involves a bound electronic state of ICl which behaves kinetically like a chlorine atom in addition to double bonds. Evidence is taken from the observations that

- (a) $\text{ICl}^* + \text{CH}_2\text{Br}_2 \rightarrow \text{no reaction}$, whereas $\text{Cl} + \text{CH}_2\text{Br}_2 \rightarrow \text{HCl} + \text{CHBr}_2$;
- (b) the quantum yield for reaction (1) is virtually the same as that for the reaction occurring with Cl atoms ($\phi = 0.12$).
- (3) The ^{37}Cl enrichment in chlorobenzene is proportional to $\frac{1}{(P_{\text{ICl}})^2}$, as evidenced by a linear relationship between the enrichment, ρ , and $\frac{1}{P_{\text{ICl}}}$. This implies that scrambling is due to a second order reaction. Both energy transfer and Cl atom reactions are consistent with this observation.
- (4) The enrichment increases upon addition of I_2 to the reaction for $0.3 \text{ torr} \leq P(\text{ICl}) \leq 0.8 \text{ torr}$. This is attributed to the scavenging of Cl atoms by I_2 . Consistent with this interpretation is the observation that addition of Cl_2 causes a decrease in the enrichment.
- (5) Chlorine atoms are thought to arise from the reversible addition of ^{37}Cl (from I^{37}Cl^*) to bromobenzene. Collisionally induced dissociation of ICl^* is expected to be inefficient² and reactions involving Br atoms are excluded based upon the observation that iodobenzene gives the same enrichments as bromobenzene.

The general mechanism which we have proposed can be represented as follows:

The initial transfer reaction involving ICl^* and bromobenzene can either be viewed as a Cl-atom, electrophilic-like addition³ to the aromatic ring

or as proceeding through a charge-transfer complex

The involvement of a vibrationally hot intermediate is based on evidence in the literature.⁴ The most stable radical intermediate(s) is that derived from attack by Cl at the

p (or o) and predominates over that derived from attack at the ipso position. Loss of chlorine competes with Cl migration about the benzene ring. This is based on (a) the fact that iodobenzene as scavenger gives the same enrichments in chlorobenzene as bromobenzene and (b) evidence from arrested relaxation studies⁵ that the excess energy of the radical is statistically distributed. If attack at the ipso position were predominant, one would expect iodobenzene to have given higher enrichments than bromobenzene.

References:

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Personnel:

D. M. Brenner	(NSF Postdoctoral Fellow; will be joining the Department of Chemistry, Brookhaven National Laboratory in June, 1977)
Z. Karny	(postdoctoral)
S. Datta	(4th year graduate student)
R. N. Zare	(principal investigator)

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