LASER ISOTOPE SEPARATION
BY
SELECTIVE EXCITED STATE PHOTOCHEMISTRY

Progress Report
for Period June 1, 1975 - February 29, 1976

R. N. Zare

Department of Chemistry
Columbia University
New York, New York 10027

NOTICE
This report was prepared as an account of work
sponsored by the United States Government. Neither
the United States nor the United States Energy
Research and Development Administration, nor any of
their employees, nor any of their contractors,
subcontractors, or their employees makes any
warranty, express or implied, or assumes any legal
liability or responsibility for the accuracy, completeness
or usefulness of any information, apparatus, product or
process disclosed, or represents that its use would not
infringe privately owned rights.

February, 1976

Prepared For

THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT E(11-1)-2724

MASTER

427 attached

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal responsibility or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

ABSTRACT

Progress has been made on the development of a low-temperature source for the generation of uranium atoms, and the use of laser-induced predissociation in Rb_2^* for isotope separation. However, our main efforts have concentrated on understanding and improving the laser isotope separation of ^{35}Cl and ^{37}Cl by photochemical means. The gas-phase reaction ICl^* with 1,2-dibromoethylene produces both cis-1-bromo-2-chloroethylene and cis-1,2-dichloroethylene stereospecifically. Selective excitation of I^{37}Cl with a tunable cw dye laser causes identical degrees of isotope enrichment in both products. By the use of an I^{35}Cl cell placed inside the cavity of the dye laser, the $^{35}\text{Cl}:^{37}\text{Cl}$ ratio may be changed from 3:1 (natural abundance) to $> 1:15$. A competing pathway, cis-trans isomerization of starting material, also occurs and is the fastest reaction. The stereospecificity of the reaction and the relative rate of geometrical isomerization to substitution are the same when chlorine atoms, formed by the photodissociation of ICl or Cl_2 , are scavenged by dibromoethylene. We conclude that, kinetically, ICl^* acts as a free chlorine atom. That isotope separation is achieved by a free-radical scavenging mechanism is indeed remarkable and owes its success to the structure of the scavenger and the choice of initial conditions.

PROGRESS REPORT: E(11-1)-2724; 6/1/75 - 2/29/76

Advances in laser technology have made practicable the study of selective photochemical reactions, the most notable of which is laser isotope separation. Recent experiments in this field have demonstrated that there are several necessary conditions for achieving isotopic selectivity. Given a molecule I-X, where I exists either as isotope I_1 or I_2 , selective excitation of I_1X or I_2X may be accomplished if (1) IX has a well characterized absorption spectrum in which there are non-overlapping absorption lines of the individual isotopic species and (2) a laser of suitable frequency exists the output of which is sufficiently monochromatic and intense to excite selectively I_1X or I_2X . These two requirements for photoselectivity are common to every laser isotope separation scheme, but the actual separation has been engineered by two different methods. The more prevalent scheme has involved photopredissociation and/or collisional photodissociation in which isotopically enriched photofragment and starting material are produced. At Columbia, we have been investigating an alternative method, scavenging of selectively excited isotopes or their photofragments. In this method, the excited electronic state of the isotope-containing molecule, for example, reacts irreversibly

with a second molecule S to form a chemically distinguishable molecule I_1S or I_2S . This technique appears to be chemically efficient and generalizable, and we report here our results on the study of chlorine laser isotope separation.

The overall scheme for separating chlorine isotopes involves reaction of selectively excited $I^{37}Cl^*$ with a scavenger, 1,2-dibromoethylene (DBE). The absorption spectrum of ICl has been well characterized,¹ a portion of which is shown in Fig. 1. Selective excitation of either $I^{35}Cl$ or $I^{37}Cl$ ($A^3\Pi_1$) is accomplished with a tunable cw dye laser (purchased from this grant). Irradiation of the 18-0 bandhead of $I^{37}Cl$ ($\lambda=6054\text{\AA}$) leads to an excited bound state which does not predissociate (see Fig. 2). Photoexcitation is carried out in the presence of the scavenger in a static reactor at pressures of 20 torr or less. The course of the reaction is followed continuously by gas-liquid phase chromatography (purchased from this grant), and the isotope enrichment measured on a Nier-type mass spectrometer (circa 1955).

Early experiments² showed that when a 1:1 mixture of ICl and DBE (cis and trans) was irradiated for 3 hr at the 18-0 bandhead of $I^{37}Cl$, trans-1,2-dichloroethylene (DCE) was formed with an isotope ratio $^{35}Cl:^{37}Cl$ of 2:1 compared to the natural abundance 3:1. Enrichment in ^{35}Cl of the starting material ICl

Figure 1. Low-resolution visible absorption spectrum of ICl taken from 6000 to 6100 Å. Note that the separation between the $I^{35}Cl$ and $I^{37}Cl$ bandheads are about 15 Å in this spectral region.

Figure 2. Potential energy curves for the X, A, and B states of ICl, taken from reference 1b with minor modification.

was also observed. The small degree of isotope selectivity was attributed to the broad laser bandwidth of $\sim 2\text{\AA}$.

In subsequent experiments,³ the difficulties arising from low resolution were surmounted by using the intracavity absorption method developed at NBS, Washington.⁴ A cell containing I^{36}Cl is placed in the laser cavity and thereby increases the losses in those modes which are absorbed by I^{36}Cl . The gain curve is thus shifted in favor of frequencies which excite only I^{37}Cl . Using identical conditions as those in the initial experiments, a dramatic increase in enrichment, 1:15, $^{36}\text{Cl}:^{37}\text{Cl}$, was observed in the trans-DCE product.

In order to determine the basic structural requirements for scavenging, several hydrocarbons and saturated halohydrocarbons were tried as scavengers. Bromomethane, dibromomethane, and 1,2-dibromoethane showed no reaction; cyclohexane reacted via a free radical mechanism with electronically excited ICl ; and ethylene formed an addition product, 1-iodo-2-chloroethane, with ground state ICl very rapidly, presumably by a free radical reaction also. These experiments in conjunction with previous results lead to the conclusion that an element of unsaturation is necessary for scavenging ICl^* and that exchange reactions, such as

do not occur with a reasonable rate.

One problem with olefinic scavengers is that a dark reaction takes place when, for example, a 1:1 mixture (total pressure equal to 20 torr) of $\text{ICl}:\text{DBE}$ is allowed to stand in the dark. It has been found that this difficulty is circumvented when the ratio of reactants is changed to 1:12 (13 torr), in favor of the scavenger. The major product of the dark reaction is the addition product 1-iodo-1,2-dibromo-2-chloroethane, which at room temperature slowly decomposes to a cis-trans mixture of 1-bromo-2-chloroethylene (BCE). This decomposition is unaffected by light or added ICl .

Irradiation of the 1:12 mixture ($\text{ICl}:\text{cis}$ and trans-DBE) at the 18-0 bandhead of I^{37}Cl yields, in addition to trans-DCE , cis-DCE and only cis-BCE ; however, the cis:trans DCE ratio is > 300:1. If pure cis or trans-DBE is used as starting material, a second reaction, geometrical isomerization, is also observed, with a rate that is faster than substitution.

A large amount of work has been done on the reaction of chlorine atoms with olefinic halides. If a chlorine atom were involved in the isotope-scavenging reaction, the stereospecificity of the reaction should be maintained irrespective of the source

of chlorine atom. Photodissociation of Cl_2 or ICl in the presence of cis-DBE produced stereospecific-cis, substitution products. Since decomposition of the ICl addition product leads to a cis-trans mixture, these observations are taken as evidence for an isotopically selective free-radical mechanism.

Formation of a free chlorine atom from the bound, A $^3\Pi_1$ electronic state of I^{37}Cl^* may occur only if a second photon is absorbed or if collisional break-up occurs. Although the first possibility has not been ruled out experimentally, under the reaction conditions this seems most unlikely. Tiffany has calculated that photoexcitation of Br_2 at 6940 Å, corresponding to 10 kT below the Br_2 dissociation limit, leads to 99% collisional dissociation. Since ICl^* excited at 6054 Å is only 4 kT away from the dissociation limit where the vibrational levels are closely spaced, the probability of collision-induced transitions is high and a large proportion of the excited ICl molecules should dissociate into atoms.

Two types of bimolecular reactions are possible for $\text{Cl}^{\cdot}$ atoms,

of which only (1a) leads to scrambling. Reaction (1b) is responsible for lowering the overall yield, whereas (2) produces a chemically activated Cl-isotope-specific radical with ~ 25 kcal of excess energy. As shown in the studies of Herschbach and coworkers, formation of a vibrationally hot radical leads to rapid loss of Br· atom and under our reaction conditions this should proceed faster than bimolecular, free radical chain processes. Isotope enrichment is thus accomplished by choosing the structure of the olefinic scavenger so as to maximize the ratio of (3) over the scrambling reaction (4).

It is anticipated that scavengers such as 1,2-difluoroethylene or perhaps 3-bromo-acrylonitrile should decrease the rate of reaction (3) and cause scrambling (4) to become competitive.⁵

Isotope scrambling in BCE or DCE may occur either from chemical reaction (${}^{37}\text{Cl} \cdot + \text{ICl}$) or from nonselective photoexcitation.

Spectroscopic studies show that the 18-0 bandhead of $I^{37}Cl$ contains several $I^{35}Cl$ rotational lines. Using an etalon to narrow the resolution of the dye laser to $0.1\text{\AA}$, three 1:12 mixtures were each irradiated for 1.5 hr at what appeared to be the maximum absorption of the 18-0 bandhead. Mass spectrometry revealed three different results: enrichments of 3.6:1, 1:1.2, and 3:1 (no enrichment). Furthermore, irradiation in the same region with a bandwidth of $< 1\text{\AA}$, resulted in an enrichment once of 1:30. The irreproducibility of these results implies that with a narrow-band excitation source, isotopic selectivity can be achieved only if a specific $I^{37}Cl$ rotational line alone is excited. This requires detailed information concerning ICl spectroscopy and limits the wavelength which may be used for selective excitation of ICl at room temperature. This problem is eliminated by using the intra-cavity absorption technique. Alternatively, dynamic cooling of the ICl might be employed, but we have not explored this possibility.

In summary, our results in chlorine isotope separation show that chemical separation of isotopes may be effected by taking advantage of the chemistry of the excited state of ICl and by judicious choice of scavenger. Reaction of $^{37}Cl\cdot$, formed from collisional dissociation of $I^{37}Cl^*$, with DBE occurs with

near-zero activation and high efficiency. Rapid unimolecular decay of the chemically activated radical occurs to give a stable compound, containing enriched isotope. The latter step is essential for the success of this scheme. A program is underway for determining the detailed kinetics controlling isotope specificity in this bulk process.

During this grant period studies were also made on the use of uranocene as a low-temperature source of uranium atoms and the possibility of Rb isotope separation from the predissociation of the $\text{Rb}_2 \text{ C } ^1\Pi_u$ state. This has led to two publications:

1. H. U. Lee and R. N. Zare, "A Low-Temperature Source for the Generation of Uranium Vapor," J. Chem. Phys. 64, 431 (1976).
2. D. L. Feldman and R. N. Zare, "Evidence for Predissociation of $\text{Rb}_2^*(\text{C } ^1\Pi_u)$ into $\text{Rb}^*(^3P_{3/2})$ and $\text{Rb}(^2S_{1/2})$," Chemical Physics (submitted for publication).

In addition, a preliminary account of our studies on chlorine laser isotope separation by photochemical means under ERDA sponsorship has appeared in:

3. S. Datta and R. N. Zare, "Laser Separation of Chlorine Isotopes By Photochemical Reactions of Iodine Monochloride," 1975 Electro-Optical Systems Design Conference/International Laser Conference Proceedings (Industrial & Scientific Conference Management, Inc., Chicago, Ill., 1976).

Reprints and preprints of the above have been submitted previously and therefore will not be included in this report.

REFERENCES

1. (a) E. Hulthén, N. Johansson, and U. Pilsäter, Ark. Fys. 14, 31 (1958); (b) E. Hulthén, N. Järlsäter, and L. Koffman, ibid. 18, 479 (1960).
2. D. D.-S. Liu, S. Datta, and R. N. Zare, J. Amer. Chem. Soc. 97, 2557 (1975).
3. S. Datta, R. W. Anderson, and R. N. Zare, J. Chem. Phys. 63, 5503 (1975).
4. S. H. Atkinson, A. H. Laufer, and J. J. Kurylo, J. Chem. Phys. 59, 350 (1973).
5. W. B. Tiffany, J. Chem. Phys. 48, 3019 (1968).