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MASTER

HIGH ENERGY HALOGEN ATOM REACTIONS ACTIVATED BY NUCLEAR TRANSFORMATIONS

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NOTICE

PROJECT ABSTRACT

High energy reactions of halogen atoms or ions, activated by nuclear transformations, have been studied in gaseous, high pressure and condensed phase saturated and unsaturated hydrocarbons, halomethanes and other organic systems in order to better understand the mechanisms and dynamics of high energy monovalent species. The experimental and theoretical program consists of six interrelated areas: (1) The reactions of iodine with alkenes and alkynes activated by radiative neutron capture and isomeric transition in low pressure gaseous systems employing additives and rare gas moderators, high pressure and liquid systems. Special attention was given to the reactivity of excited complex formation and structural effects of electrophilic iodine attack on various pi-bond systems. (2) The gas to condensed state transition in halogen high chemistry, involving bromine activated by the (n,γ) and (I.T.) processes in ethane was investigated in more detail. Special attention was given to defining the nature of the enhancement yields in the condensed phase. (3) Systematics of halogen hot atom reactions. The reactions of $^{80}Br^{m}$, ^{80}Br, $^{82}Br^{m} + {}^{82}Br$, ^{82}Br, ^{128}I, ^{130}I, and $^{130}I^{m} + {}^{130}I$ activated by radiative neutron capture or isomeric transition in hydrocarbons and halo-substituted alkanes in low pressure and high pressure gaseous systems employing additives and rare gas moderators. High energy iodine geminate recombination studies with biomolecules suggest efficient caging by the ice lattice. (4) Kinetic theory applications of high energy reactions and mathematical development of caging mechanisms were developed. The kinetic energy spectra of iodine and bromine activated by isomeric transition were calculated. (5) The stereochemistry of ^{38}Cl substitution reactions involving diastereomeric 1,2-dichloro-1,2-difluorethane in liquid mixtures was completed, suggesting that the stereochemical course of the substitution process is controlled by the properties of the solvent molecules.

Evidence for Walden inversion was found in the study of high energy chlorine-forchlorine substitution reactions in gaseous enantiomers of 2-chloropropionyl chloride. (6) The applications of high energy chemistry techniques and theory to neutron activation analysis of biological systems was continued, especially involving aluminum and vanadium trace determinations.

FACILITIES

A. Triga Mark I Reactor

All neutron irradiations were made in the Triga Mark I "swimming pool" nuclear reactor at the Veteran's Administration Medical Center in Omaha, Nebraska. A flux of 1×10^{11} thermal neutrons cm^{-2} sec^{-1} was present at an operating power of 15.5 kilowatts. Various positions in the "lazy susan" sample holder were employed and the assembly was rotated to ensure that all samples received the same neutron flux and radiation dose. For very short irradiations, the assembly was not rotated and samples were irradiated in the same position. The radiation dose was approximately 3×10^{17} e.v.g.$^{-1}$ min^{-1} using Fricke dosimetry.

For the past two years, the nuclear reactor operated routinely for at least four eight-hour days a week at 15.5 kilowatts. The radiochemistry group used for the period from October 1, 1977, to September 30, 1978, 322 hours (integrated time in reactor) at 15.5 kilowatts power, making 1850 irradiations.

B. Radiochemistry Laboratory

All sample preparations were performed in a well-equipped, specially-designed radiochemistry laboratory in the new Hamilton Hall Chemistry building. The two hot laboratories contain four six-foot "Oak Ridge-Type" hoods, several radioactive waste sinks, radiation safety equipment, seven separate vacuum lines for preparing gas, high pressure gas, liquid and solid state systems, and the usual laboratory facilities. The counting room is equipped with one radiogas chromatograph, three single-channel analyzers with several 2"x2" NaI crystals, four GM counting stations, four gas-flow counters, and a Nuclear-Data 128-channel analyzer with a 3"x3" NaI crystal specially housed in a concrete, cadium, and lead cave.

A complete radiogas chromatograph has been built and is located in the radiochemistry room of the reactor facility, allowing us to analyze routinely many more samples containing ^{128}I, ^{80}Br, and ^{38}Cl. This is quite necessary for the study of ^{128}I reactions activated by the (n,γ) process in the acetylenes and the various isomers of butene and pentene in both the gas and condensed states, precluding the necessity of making corrections for radiation damage and thermal reactions occurring during lengthy neutron irradiations. An ISCO Model 1440 High Performance Liquid Chromatograph with sample collector is located at the reactor facility. This location enables us to study efficiently the caging effects of an ice lattice on high energy reactions with organic and biomolecules. We have increased our data-gathering ability by having our equipment located at the reactor site.

SUMMARY OF PRSENT PROGRAM

A. Background of Project

Hot atom, high energy or "hot" chemistry, is an important tool for basic research in areas now considered vital-energy, environment and medical or related technology. "Hot" chemistry is a probe, an interactive science which embraces many fields; from hot atom reactions in simple hydrocarbon systems to theoretical development of high energy particle reactions. Utilizing reactive species possessing non-Boltzmann energy distributions, high energy chemists have discovered and characterized new reaction channels in organic and inorganic systems; contributed to the theories of energetics, dynamics and systematics; developed new techniques of chemical detection and analysis; and aided biological and medical sciences.

High energy distributions of atoms and/or ions can be produced via two classes of activation: chemical accelerators and bulb techniques. Each type of experiment produces reactions that can contribute to the characterization of high energy species. Each experimental class investigates properties unique to its technique.

Chemical accelerators impart kinetic energy to atoms, ions or molecules by use of electromagnetic, pressure differential or ultrasonic gradients. The particles are accelerated in a straight line (linear or tangential, hence the name "beam" experiment) with a resultant kinetic energy distribution of narrow bandwidth (generally a Boltzmann distribution centered about the terminal accelerator energy). The atomic-, ionic- or molecular-beam is produced in a near vacuum and permits the examination of atom-molecule and/or ion-molecule single collision reactions. The data obtained reveals information on intrinsic properties of reactions; e.g., reactive cross sections as functions of scattering angle and energy. However, chemical accelerators <u>are limited</u> in their abilities to measure endoergic reactions, to have (energy) resolution and (product) identification simultaneously, to orient molecules (dynamics), and to study the effect of environment (even 1 torr pressure) and multiple collisions on reactivity.

Bulb techniques are multi-collisionally oriented. The kinetic energy imparted to atoms or ions are the result of nuclear recoil or photochemical recoil activation. While photochemical and some nuclear activation modes produce atoms, ions or radicals within narrow kinetic energy limits, the multi-collisional nature of the technique results in collisional "cooling" of the "hot" entities, producing a broad spectrum of kinetic energies.

Extrinsic properties are readily measured (the hot species or medium taken in bulk) and intrinsic properties are inferred. New reaction channels (both exo- and endoergic) have been observed and characterized. Although molecules cannot be oriented, the ease of product identification (including diastereomers and enantiomers) permit study of reaction dynamics. The effect of the molecular environment on the reaction systems from low pressure gas to solid state glasses and crystals is easily studied in bulb experiments. These studies can significantly contribute to a better understanding of the photocatalytic cage effects or de-excitation processes, an area that may be important in photochemical energy conversion processes.

In our research work, we are interested in the area of monovalent high-energy physical-organic chemistry, concentrating on heavy halogens activated by radiative neutron capture and isomeric transition. We have also used photochemistry, ion cyclotron resonance and mass spectrometry techniques in our work.

B. Summarized below is a report of our main progress during the current contract period:

1. Reactions and Systematics of Iodine Reactions with Alkenes and Alkynes.

Relevance. Olefins, acetylene and acteylenic molecules are unsaturated hydrocarbons which, unlike saturated hydrocarbons and halomethanes, are characterized by an electron-rich pi-bond system. High energy (hot) atoms or ions can undergo substitution and abstraction reactions with saturated hydrocarbons and halocarbons. Similar reactions can occur in hot atom-olefin (or acetylene) systems. Furthermore, unsaturated systems can undergo additional reactions to the pi-bond system by electrophilic attack initiated by high energy, electronically excited, or thermal iodine ions resulting in stable organic products.

Activation of iodine species by radiative neutron capture, isomeric transition and other nuclear transformations (and photochemical irradiation) can provide translationally and electronically excited as well as charged species which in reaction can provide direct information for the development of a kinetic theory of "hot" electrophilic attack and indirect dynamics evidence as functions of multiple bond location and steric (spatial) effects.

Progress.

1) Systematics of Electrophilic High Energy Iodine in Gaseous, High Pressure and Liquid Isomers of Butene. One of our goals of this project was to evaluate all our existing data of iodine reactions with ethene and propene with our newly acquired data on the isomers of butene in order to develop rules for high energy ion electrophilic attack on pi-bond systems and the importance of steric and bond location effects.

Since this study of iodine high energy reactions has recently appeared in the Journal of Physical Chemistry,[1] we will only summarize the major results of this study. One of the interesting aspects of this work is that we employed the density-variation technique as a mechanistic tool in formulating a reaction scheme for the various products.

Reactions of high energy iodine with isomers of butene were studied in gaseous, high pressure, and condensed phase conditions, with rare gas additives and in the presence and absence of radical acavengers (I_2 and O_2). It was found that the trans-butene-2 system behaves as a hot system while cis-butene-2 and methylpropene (isobutylene) are dominated by I_2-dependent ion-molecule reactions. The diverse and complex nature of the reactions cannot be explained by simple chemical and physical parameters. Comparison with other pi-bond systems demonstrates the preferential attack of iodine at the double bond and results in the characterization of general traits common to these systems.

Significance

While reactions of high energy iodine with olefins are complex, the following observations can be made:

1. There is no simple systematic trend with chemical and physical parameters. The impact and inertial molecules are not applicable in these systems.
2. I_2-dependent ion-molecule reactions may show an inverse trend with rare gas additives.
3. Preferential site attack by iodine occurs at the double bond for short chain olefins.
4. Organic products may be formed by diverse reaction channels.
5. For I_2-dependent ion-molecule reactions, the CH_3I yield increases with carbon chain length.
6. Collapsing molecular environment decreases the attack angle on the pi-bond by interposition of bath molecules.
7. When the center of mass is centered on, or along the line bisecting the double bond, attack at the double bond results in bond cleavage and/or molecular translation rather than rotation.

8. The preferential electrophilic attack by iodine on the pi-bond allows the use of bulb techniques as a probe of new high energy reaction channels, not easily observed by other chemical techniques.

2. Systematics of Electrophilic High Energy Iodine in Gaseous, High Pressure and Liquid Alkynes.

In a previous publication,[2] we presented evidence for an excited reaction intermediate in the (n,γ)-activated reactions of iodine with acetylene. In order to determine the effects of structure on the formation of the electronically excited reaction intermediate, we studied, employing the density-variation technique,[2] rare gas additives, oxygen, etc., the reactions of high energy iodine with propyne, 1-butyne and 2-butyne. In addition, our goals in this project are similar to those of our olefin work, to evaluate all our existing data and to attempt to develop rules for high energy ion electrophilic attack on the triple bond systems, and to determine the importance of steric and bond location effects.

We have completed about eighty percent of the data gathering in this project. No further report will be made at this time.

2. Gas to Liquid to Solid Transition in High Energy Chemistry.

Relevance. While the gas phase studies of any system may lead to discovery of new high-energy reaction channels, the gas phase quite often does not resemble the final, technological end process to which the system can be applied. The liquid or solid phase system is often ideally suited for chemical, technological or environmental application on an industrial scale. The dilemma lies in the often too complex nature of condensed phase systems. Dynamic, systematic and energetic information is more difficult to extract from high density data than the low pressure gas counterparts. The gas to liquid to solid transition provides a continuity between simple research (gas phase) systems and their applicable end-product (often the condensed phase).

By systematic use of the gas to condensed phase transition, the effects of a collapsing molecular environment on high energy atoms or ions and their reaction chanlels can be observed. The resulting data contribute information as to the nature and importance of various reaction channels; the emergence of new reaction products (channels), unfound in the gas phase; and the relative importance of molecular versus enhancement reactions in the condensed phase.

The nature of condensed phase enhancement reactions has been a controversial subject since the beginning of hot atom chemistry. The interplay of the gas to liquid to solid transition experiments with theoretical chemistry provides a realistic link between observation and postulation. The characterization of phase transitions of any system provides feedback for refinement of enhancement yield theories (see Section 4). However, we realize that care must be employed not to overinterpret gas to condensed phase data. We do not employ the density-variation technique as a kinetics tool to extract quantitative information but a mechanistic probe to develop reaction schemes as seen in the previous section and to observe the effects of a collapsing molecular environment on high energy reaction products.

In the same manner, the gas to condensed phase transition studies on diastereomers and enantiomers provide information for the refinement of current concepts of molecular dynamics of hot atom or ion reactions with organic substrates (see Section 5).

Progress.

1) Effects of a Collapsing Molecular Environment on High Energy Bromine Reactions in Ethane. Since this completed study has recently appeared in Radiochemica Acta,[3] we will only summarize the major results in this Report.

The reactions of (n,γ)- and (I.T.)-activated bromine with ethane were observed throughout the gas to condensed phase transition. The data were examined and a reaction scheme postulated which was found to agree with gas phase moderator studies. A comparison with iodine-ethane and bromine-halomethane gas to condensed phase transition experiments shows a general similarity but emphasizes the diversity of enhancement reactions in various halogen-organic systems.

Significance

Like bromine-halomethane systems, the reactions of (n,γ)- and (I.T.)-activated bromine with ethane proceed via molecular, thermal and enhancement reactions. However, the enhancement reactions in the two carbon system appear to be the result of both caged-ion/caged-radical and caged complex reactions with no emergence of new products as was observed in the bromine-halomethane systems.

2) Caging Effects of an Ice Lattice on High Energy Iodine Geminate Recombination with Biomolecules. In an important preliminary study, Willard et al.[4] found unusually high organic yields of (n,γ)-activated high energy iodine-128 in dilute aqueous solutions of CH_3I. Because of the lack of suitable analytical procedures, no conclusions could be made as to the mechanism of the process. We have reinvestigated the problem by employing dilute aqueous solutions of biomolecules and determining the products by high performance liquid chromatography (HPLC). Biomolecules are ideal for this type of study because of their solubility in water and the ease of their detection by HPLC. In our preliminary studies, we employed dilute aqueous mixtures of monoiodotyrosine (MIT) and diiodotyrosine (DIT).

Polyethylene vials containing 5 mL volumes of dilute aqueous mixtures of MIT or DIT in the liquid and frozen state were irradiated for 15 minutes in the Omaha, Nebraska, V. A. Medical Center TRIGA reactor at a thermal neutron flux of 1.1×10^{11} neutrons $cm^{-2}s^{-1}$. No I^- or I_2 carrier was present, as in the Willard[4] experiment, in order to insure that all ^{128}I labelled products came from the MIT or DIT source molecule and to eliminate possible exchange reactions in the system. Products were identified by HPLC in a manner similar to that performed by others[5,6,7]. We were only interested in determining the absolute yields of $^{128}I^-$ and ^{128}I labelled MIT or DIT. These products were identified by employing carriers. In order to ascertain that the $^{128}I^-$ collection vials indeed were iodide, solvent extraction procedures and silver precipitation techniques were employed.

Presented in Tables I and II are the absolute product yields of high energy ^{128}I in liquid and solid aqueous monoiodotyrosine and diiodotyrosine at several concentrations. The various routes leading to ^{128}I labelled organic products are: (a) geminate retention: failure of ^{128}I to bond rupture after the radiative neutron capture event; (b) geminate recombination: recombination of the high energy ^{128}I with the original radical formed in the radiative neutron capture process; and (c) reassembly of the ^{128}I with some organic fragments in the vicinity of the event. The $^{128}I^-$ can be formed by an abstraction reaction with a water molecule forming $H^{128}I$, which can subsequently ionize to the iodide-128. Based on previous studies, we would not expect a geminate retention of ^{128}I as MIT or DIT greater than 1%. We would expect the extent of geminate recombination or formation of other organic products to decrease with increasing dilution of MIT or DIT in the aqueous medium. On the other hand, the extent of iodide-128 formation should increase with increasing dilution. As can be seen in Tables I and II, with increasing dilution of MIT or DIT in liquid solution, the absolute yields of ^{128}I labelled MIT or DIT decrease to zero while the $^{128}I^-$ yield increases to 100%. We would expect these results in a medium whose "cage walls" are reactive, leading to inorganic iodide formation. Unexpectedly, the results of the frozen MIT and DIT solutions are quite different. The geminate recombination absolute yields of ^{128}I as

MIT and DIT remain constant over the 100-fold concentration range. In addition, for the MIT system, the $^{128}I^-$ yield appears constant at about 75% and in the DIT system increases gradually to 58.2% at the most dilute condition. The iodide-128 yield does not appear to extrapolate to 100% as in the liquid state. We can understand these results by realizing the structure of ice where H_2O molecules are arrayed in a hexagonal pattern by hydrogen bonding with a good deal of empty space between the molecules. We suggest the individual MIT or DIT molecules are trapped in these empty spaces and are exposed to a cage effect not encountered in organic systems. The relative constancy of the absolute values of the ^{128}I leading to geminate recombination does not vary greatly within experimental error over the concentration range. This strongly suggests that the ^{128}I remains quite close to its organic radical by virtue of the efficient caging ability of the ice lattice.

These results suggest that caging effects of high energy reactions with various organic molecules can be studied in ice mixtures.

TABLE I: Absolute Product Yields of High Energy ^{128}I in Liquid and Solid Aqueous Monoiodotyrosine

System	Mole % MIT	Products[a]	Absolute Yield %
Liquid MIT	1.8×10^{-2}	I^-	$\leq 84.7 \pm 1.6$[b]
at 25°C		MIT	8.5 ± 0.4
	1.8×10^{-3}	I^-	$\leq 100 \pm 4.5$
		MIT	5.2 ± 0.4
	1.8×10^{-4}	I^-	$\leq 98.6 \pm 4.3$
		MIT	2.2 ± 0.2
Solid MIT	1.8×10^{-2}	I^-	$\leq 70.0 \pm 5.7$
at -77°C		MIT	10.9 ± 1.1
	1.8×10^{-3}	I^-	$\leq 81.9 \pm 3.7$
		MIT	9.6 ± 0.3
	1.8×10^{-4}	I^-	$\leq 73.6 \pm 4.0$
		MIT	7.2 ± 1.5

[a] ^{128}I labelled product.

[b] Represents a maximum value.

TABLE II: Absolute Product Yields of High Energy ^{128}I in Liquid and Solid Aqueous Diiodotyrosine

System	Mole % MIT	Products[a]	Absolute Yield %
Liquid DIT	8.2×10^{-3}	I$^-$	$\leq 55.6 \pm 4.0$
at 25°C		DIT	9.9 ± 1.8
	8.2×10^{-4}	I$^-$	$\leq 85.1 \pm 3.7$
		DIT	2.3 ± 0.1
	8.2×10^{-5}	I$^-$	$\leq 100 \pm 2.1$
		DIT	0 ± 0.1
Solid DIT	8.2×10^{-3}	I$^-$	$\leq 43.4 \pm 2.1$
at -77°C		DIT	9.6 ± 1.7
	8.2×10^{-4}	I$^-$	$\leq 48.3 \pm 3.1$
		DIT	6.9 ± 0.3
	8.2×10^{-5}	I$^-$	$\leq 58.2 \pm 4.6$
		DIT	8.6 ± 2.5

[a] ^{128}I labelled product.

[b] Represents a maximum value.

3. Systematics of High Energy Halogen Reactions

Relevance. Systematic studies of high energy reactions activated by nuclear transformations in gaseous systems are important. From these studies, we can generally ascertain the importance of such parameters as steric,[9] bond energy,[10] translational-inertial[11] and energy degradation factors[12] on gas-phase hot atom reactions. Moderator studies involving the effect of rare gas additives on the total and individual organic product yields indicate the importance of hot, electronically excited ion, thermal-molecule and thermal-ion reactions. These data characterize the nature of the reactant hot atom and provide data for development of kinetic theories of high energy reactions.

Progress. We are currently studying the systematics of ^{129}I (n,γ) ^{130}I^{m} + ^{130}I and ^{130}I^{m} (I.T.) ^{130}I activations in halomethanes. This data, in conjunction with that of Nicholas et al.[13] for (n,γ)- and (I.T.)-activated ^{130}I in CH_4 and CD_4, show trends similar to that reported by Yoong et al.[12] The organic yield data appear to be linear with respect to the energy degradation factor (EDF)[12] and independent of bond energy and steric effects. We have found for ^{129}I (n,γ) ^{130}I + ^{130}I yields of 4.52%, 5.76% and 8.96% for CH_3I, CH_3Cl and CH_3F respectively. Yields of 1.75% for CH_3I and 4.16% for CH_3F have been found for ^{130}I (I.T.) ^{130}I. These data have not been corrected for possible "thermal" hot-atom reaction. Moderator studies currently in progress for these systems will indicate the importance of hot and thermal reactions.

These studies involving ^{130}I^{m} + ^{130}I activated by radiative neutron capture and ^{130}I activated by isomeric transition in gaseous halomethanes suggest the continuing importance of the energy degradation factor in low-kinetic energy systems.

4. Kinetic Theory Applications of High Energy Reactions and the Mathematical Development of Caging Reactions.

Relevance. A unified kinetic theory of high energy reactions would provide a framework for detailing those characteristics (energetics, kinetics, dynamics and systematics) of reaction found by experimentation and for predicting data trends necessary for application of hot atom systems to high energy chemical technological and environmental problems. A general theory of this kind has yet to be developed. The establishment of a theoretical framework for reactions of heavy monovalent species often possessing positive charge, and easily polarizable, and the characterization of enhancement reactions would benefit our work and that of others, clarify the current controversy of enhancement reactions and detail specifics in energy, environmental and technological disciplines which at this time cannot be deduced.

Progress.

1) Computer Simulation Evaluating Kinetic Theory Parameters in Hot Atom Chemistry. Since this study recently appeared in Radiochimica Acta,[14] we will only summarize the major results of this study. A computer model using simple kinetic theory parameters has been used to simulate the (n,γ)-activated iodine-128-acetylene system throughout the gas to condensed phase transition. The model was found to be sensitive to molecular size and also to reaction probability functions suggesting the importance of chemical parameters. General agreement was found with experiment and the non-inclusion of an enhancement reaction expression in the model suggests that caged complex reactions may be an extension of simple molecular processes.

Significance

(1) The fact that good agreement was obtained with experiment even though

no separate expression was included for enhancement reactions suggest that caged complex reactions may be an extension of molecular reactions.

(2) The general agreement found suggests that it is possible to use kinetic theory parameters throughout the gas to condensed phase transition but kinetic theory is not directly applicable without modifications including the use of chemical parameters.

2) Determination of the Kinetic Energy Spectra of Iodine and Bromine Activated by Isomeric Transition.

Estrup and Wolfgang[15,16] developed a kinetic theory for the reactions of hot atoms based upon observation of recoil tritium in organic systems and modeled after neutron "cooling-down" theory.[17] This theory has been tested for validity[18-20] under a variety of conditions in order to determine the predictive ability of the theory. Urch has found[18] that use of the Estrup-Wolfgang theory often leads to the predicted results even though all criteria of the theory have not been met.

The major criteria of the Estrup-Wolfgang kinetic theory are:[16]

Assumption I: The number of collisions between energies E and E + dE of a hot atom, not undergoing hot combination reaction, is inversely proportional to the energy.

Assumption Ia: The initial energy E_0 of the hot atom is sufficiently high so that the atom has made a number of collisions above the energy E_2, thus making it possible to obtain a distribution of energies in the reactive zone, $E_2 - E_1$. (The reactive zone is the energy region in which high energy reactions occur. It is bounded by upper and lower limits, E_2 and E_1 respectively.

Assumption Ib: The region of interest is well above the thermal region, i.e., the threshold energy E_1 is much greater than thermal energies.

Assumption Ic: The ratio of energies of a hot atom before and after a non-reactive collision is treated as a constant and not a function of energy.

Assumption II: The number of reactive collisions occurring in the energy range E to E + dE is an intrinsic function of energy being proportional to the number of hot atoms in the range, the probability of collision and the probability of reaction per collision.

Assumption III: Over the energy range of interest, the relative probability of collision with a specific system component is not a function of energy, but is proportional to the mole fraction of the component and its reactive cross-section.

A. Energetics of Nuclear Transformations

In view of the difficulties experienced[18-20] with the Estrup-Wolfgang kinetic theory, it becomes important to test all systems before the theory can be applied. Of major importance is Assumption Ia in which the energy with which the hot atom is born, E_0, is sufficiently high to assure a distribution of energies within the reactive zone, $E_2 - E_1$.

Tritium ($^3He(n,p)^3H$) and fluorine-18 ($^{19}F(n,2n)^{18}F$) are born with energies near the MeV range. These are essentially mono-energetic activations, as are all activations involving the ejection of 1 or 2 nucleons, with initial energies much greater than the reactive zone. Collisional cooling permits a distribution of energies as the hot atom initially recoils through the system experiencing only non-reactive collisions.

Halogens heavier than fluorine are often activated by radiative neutron capture. Since several gamma rays may be emitted isotropically (the sum of energies being equal to the neutron binding energy) the energy imparted may fall within a range of energies from zero (total cancellation of gamma ray momenta) to a maximum value (single gamma emission).

We[21] calculated the kinetic energy spectra of the reaction $^{127}I(n,\gamma)^{128}I$ utilizing a three-dimensional random walk in space process reported by

Hsiung and Gordus.[22] Based upon the gamma ray spectrum,[23] we were able to computer-simulate the kinetic energy spectrum of ^{128}I. We found that the kinetic energy spectrum was a continuous function from 0 to 194 eV with a maximum probable energy of 152 eV. Aside from this maximum, the spectrum showed that a substantial fraction of the ^{128}I atoms or ions were born in or near the reactive zone[16] (roughly estimated to be 80-10 eV for iodine reactions).

There are insufficient gamma-ray spectral data for the $^{79}Br(n,\gamma)\ ^{80}Br^m$, $^{79}Br(n,\gamma)^{80}Br$ and $^{81}Br(n,\gamma)^{82}Br^m + {}^{82}Br$ activation to permit similar calculations of probability distribution versus recoil energy. However, it is known from neutron binding energy data[24] that the kinetic energy spectra for ^{80}Br and $^{82}Br^m + {}^{82}Br$ range from 0- to 417-eV and 0- to 378-eV respectively. This is similar to (n,γ)-activated ^{38}Cl which ranges from 0- to 530-eV, with an average kinetic energy of about 300 eV.

B. <u>The Kinetic Energy Spectra of (I.T.)-Activated ^{80}Br and ^{130}I.</u>

It is generally recognized that, as a result of the isomeric transition reaction, halogen atoms can acquire a high positive charge as a result of Auger and secondary electron radiolysis. In the gaseous state, the high positive charge can induce intramolecular electron transfer resulting in two positive centers within the molecule. The ions can then acquire a spectrum of kinetic energies as a consequence of the intramolecular coulombic explosion.

A probability distribution of energies for bromine and iodine ions can be calculated. The probability distributions of bromine[25] and iodine[26] ion's charge states created by internal conversion is known. Also known (or estimatable) are the ionization energies associated with these charged states.[27] These distributions are summarized in Tables III, IV and V. However, the intramolecular redistribution of charge cannot be determined experimentally since a highly charged ion will rapidly charge transfer with its medium.

TABLE III: Auger Cascade Charge Distribution and Ionization Potentials for $^{80}Br^{m}$. Adapted from Wexler and Anderson[25] and Kiser[27]

Charge State	Relative Abundance(%)	Ionization Potential (eV)
+1	5.7	11.8
+2	6.9	21.6
+3	5.7	35.9
+4	5.4	47.3
+5	10.5	59.7
+6	14.0	88.6
+7	15.4	103
+8	14.2	193
+9	10.0	207
+10	7.4	217
+11	3.3	229
+12	0.9	241
+13	0.6	253
		266

TABLE IV: Auger Cascade Charge Distribution and Ionization Potentials for $^{130}\mathrm{I}^{m}$. Adapted from Carlson and White[26] and Kiser[27]

Charge State	Relative Abundance(%)	Ionization Potential (eV)
+1	5.1	10.5
+2	9.3	19.1
+3	13.2	32.5
+4	17.8	43.0
+5	22.0	54.5
+6	13.7	78.0
+7	10.8	92.3
+8	5.1	170
+9	2.2	181
+10	0.7	192
+11	0.1	203
		214

TABLE V: Ionization Potentials for Carbon and Hydrogen. Adapted from Kiser[27].

Atom	Charge State	Ionization Potential (eV)
H	+1	13.6
C	+1	11.3
	+2	24.4
	+3	47.9
	+4	64.5
	+5	392
		490

Conservation of momentum requirements dictate that the bromine recoil energy be dependent on the molecule in which it is born. Three molecules of interest as sources of activated halogen are: the hydrogen halide, HX; the methyl halide, CH_3X; and the dihalide, X_2.

Recoil momentum imparted by Auger and secondary electron cascades impart minor energies to the product ion as is evidenced by the low energies in studies of (E.C./β^+)-activated ^{123}I.[28] Of more importance in isomeric transition activation is the electrostatic repulsion arising from two positively charged centers within the molecule following charge redistribution.

Electrostatic repulsion may be calculated from Coulomb's Law:

$$E_{coul} = kq_1q_2/r$$

where E_{coul} is the repulsion energy, k is Coulomb's constant, q_1 and q_2 are the charges of the two centers and r is the internuclear separation. Using r = 2.28 Å for dibromine and r = 2.67 Å for diiodine,[78] E_{coul} = 6.295 eV/(unit charge)^2 and 5.375 eV/(unit charge)^2 respectively. For a halogen, X, bound in a molecule, RX the net energy, E_{net}, available as kinetic energy is:

$$E_{net} = E_{coul} - E_{RX}$$

where E_{RX} is the bond energy of the halogen molecular bond. Conservation of momentum dictates the apportionment of the net energy between the halogen and the molecular moiety. The breaking of the R-X bond is an importnat consideration since experimental evidence shows very low percentages of hot atoms failing to bond rupture (FBR).

Because there are no quantitative data on the redistribution of intramolecular charge, the kinetic energy spectra of (I.T.)-activated $^{80}Br^m$ and $^{130}I^m$ were calculated by a coulombic repulsion model under several assumed charge redistributions.

Assumption I: Equal Probability. Consider an ion of charge +7 (Table VI). The molecule RX may retain this distribution 7-0 or redistribute charges as 6-1, 5-2 or 4-3. As a first approximation all (re)distributions of charge are taken as equally probable. The distributions of charged ions[25,26] can then be partitioned into charge redistributions and the repulsive energies calculated. The equal weighting of all redistributions yields the range of energies attainable from the isomeric transition process.

Assumption II: Equilibrium Model. This model is skewed toward higher energies in order to obtain an "upper-limit" case for comparison with kinetic theory.[15,16] Since electronic motions are orders of magnitude faster than nuclear motion, charges may redistribute faster than the charge centers can translate from each other. In the extreme, the two charge centers may obtain equal or near equal charge before the nuclear separation may occur. Binomial expansion coefficients (Table VI) are used as weighting coefficients.

Presented in Tables VII, VIII and IX are the energy distributions for $^{80}Br^{m}(I.T.)^{80}Br$ in Br_2, CH_3Br and HBr as calculated by this model. The data for the corresponding systems of $^{130}I^{m}(I.T.)^{130}I$ are presented in Tables X, XI and XII.

Assumption III: Rapid Explosion Model. At the other extreme, the repulsion generated by the transfer of the first electron may be sufficient to separate the two charge centers and prevent further redistribution. To reflect this repulsion, the weighting coefficients were based on the ratio of the ionization potential of the donor to the electron affinity of the receptor.

Assumption IIIa: Selective Electron Collapse. A deficiency of previous models is their inability to predict low values for Failure to Bond Rupture (Tables XIII and XIV). Within the large percentage of molecules that fail to rupture the halogen bond (no redistribution of charge) an unstable electronic

TABLE VI: Redistribution Coefficients for Ion of Charge +7

Charge Distribution	Coefficient			
	I	II	III	IV
7-0	1	1	1	1
6-1	1	6	6	6•E
5-2	1	15	3.6	3.6•E
4-3	1	20	3.0	3.0•E

E = the energy released by the ion from the collapse of a valence electron to fill a K, L or M shell vacancy. It is approximated as I.P.(n^+) - I P.(1^+) where I.P.(n^+) is the n^{th} ionization potential of the atom and I.P.(1^+) is the first ionization potential.

TABLE VII: Relative Abundance of Energy Distribution for $^{80}Br^{m}$ - Br (Model II).

Kinetic Energy(eV)	Coulombic Energy(eV)	Abundance (%)	Kinetic Energy(eV)	Coulombic Energy(eV)	Abundance (%)
0	0	11.06	55.66	113.3	3.11
2.15	6.30	4.48	61.95	125.9	5.74
5.30	12.59	4.27	65.10	132.2	1.11
8.44	18.89	1.84	74.54	151.1	2.69
11.59	25.18	6.16	77.69	157.4	3.60
14.74	31.48	1.86	83.98	169.9	0.03
17.89	37.77	8.07	87.13	176.3	1.08
21.03	44.07	1.27	93.43	188.9	1.87
24.18	50.36	5.26	99.72	201.4	0.12
27.33	56.66	6.78	109.2	220.3	0.36
30.48	62.95	5.24	112.3	226.6	0.48
36.77	75.54	10.79	124.9	251.8	0.02
43.07	88.13	1.07	131.2	264.4	0.39
46.21	94.43	5.16	140.6	283.3	0.04
49.36	100.7	6.70	150.1	302.2	0.11
			153.2	308.5	0.19

TABLE VIII: Relative Abundance of Energy Distribution for CH_3 - $^{80}Br^m$ (Model II)

Kinetic Energy(eV)	Coulombic Energy(eV)	Abundance (%)	Kinetic Energy(eV	Coulombic Energy(eV)	Abundance (%)
0	0	11.03	22.91	148.0	4.77
0.72	7.40	4.56	24.08	155.4	2.27
1.88	14.80	4.32	25.25	162.8	0.02
3.05	22.19	1.98	27.58	177.6	4.16
4.22	29.59	6.29	28.75	185.0	0.82
5.39	36.99	2.34	31.09	199.7	0.15
6.56	44.39	8.18	32.25	207.1	2.07
7.72	51.79	0.70	34.59	221.9	0.63
8.89	59.18	5.91	36.93	236.7	0.48
10.06	66.58	5.73	38.09	244.1	0.05
11.23	73.98	6.03	40.43	258.9	0.23
13.56	88.77	10.46	41.60	266.3	0.35
15.90	103.6	1.60	46.27	295.9	0.33
17.07	111.0	5.45	48.61	310.7	0.06
18.24	118.4	5.63	52.11	332.9	0.09
20.57	133.2	3.57	55.62	355.1	0.04

TABLE IX: Relative Abundance of Energy Distribution for H - $^{80}Br^{m}$ (Model II)

Kinetic Energy (eV)	Coulombic Energy (eV)	Abundance (%)
0	0	18.99
0.08	10.18	4.26
0.20	20.36	4.12
0.33	30.54	4.16
0.46	40.72	8.56
0.58	50.90	12.14
0.71	61.07	13.56
0.83	71.25	13.27
0.96	81.43	9.38
1.08	91.61	6.93
1.15	101.8	3.08
1.34	112.0	0.89
1.46	122.1	0.60

TABLE X: Relative Abundance of Energy Distribution for $^{130}I^{m}$ - I (Model II)

Kinetic Energy (eV)	Coulombic Energy (eV)	Abundance (%)
0	0	14.67
1.91	5.38	5.96
4.59	10.75	9.98
7.28	16.13	6.05
9.97	21.50	16.71
12.66	26.88	1.77
15.34	32.25	15.32
18.03	37.63	0.16
20.72	43.00	5.06
23.41	48.38	6.65
26.09	53.75	3.66
31.47	64.50	6.90
36.84	75.25	0.24
39.53	80.63	1.82
42.22	86.00	2.32
47.59	96.75	0.69
52.97	107.5	1.24
55.66	112.9	0.10
63.72	129.0	0.23
66.41	134.4	0.32
74.47	150.5	0.05
79.84	161.3	0.09

TABLE XI: Relative Abundance of Energy Distribution for $CH_3{}^{130}I^m$ (Model II)

Kinetic Energy (eV)	Coulombic Energy (eV)	Abundance (%)
0	0	15.81
0.45	6.71	5.82
1.15	13.41	9.82
1.84	20.12	6.87
2.53	26.82	16.59
3.23	33.53	2.54
3.92	40.24	14.45
4.62	46.94	0.31
5.31	53.65	5.75
6.00	60.36	5.11
6.70	67.06	4.34
8.09	80.47	6.13
9.48	93.88	0.41
10.17	100.6	1.92
10.86	107.3	1.68
12.25	120.7	0.79
13.64	134.1	0.95
14.33	140.8	0.22
16.42	160.9	0.34
17.11	167.7	0.06
19.19	187.8	0.09
20.58	201.2	0.02

TABLE XII: Relative Abundance of Energy Distribution for H - $^{130}I^{m}$ (Model II)

Kinetic Energy (eV)	Coulombic Energy (eV)	Abundance (%)
0	0	25.48
0.04	8.91	5.41
0.11	17.83	9.32
0.18	26.74	13.57
0.24	35.66	17.64
0.31	44.57	11.66
0.38	53.48	9.42
0.45	62.40	4.68
0.52	71.31	2.05
0.58	80.23	0.62
0.65	89.14	0.14

TABLE XIII: Comparison of Failure to Bond Rupture and Average Kinetic Energy for $^{80m}Br(I.T.)^{80}Br$ in Br_2

	Failure to Bond Rupture	Average Kinetic Energy
I	31.50%	22.0 eV
II	11.06%	35.6 eV
III	8.25%	24.0 eV
IIIA	1.22%	24.0 eV

TABLE XIV: Comparison of Failure to Bond Rupture and Average Kinetic Energy for $^{130m}I(I.T.)^{130}I$ in I_2

	Failure to Bond Rupture	Average Kinetic Energy
I	37.3 %	9.56 eV
II	14.7 %	14.22 eV
III	9.32%	12.10 eV
IIIA	1.22%	12.10 eV

configuration remains from the emission of K, L or M shell electrons during Auger and secondary electron radiolysis. The "collapse" of an outer shell electron releases energy in an amount equal to the difference between the respective electron energies. This has been approximated by differences in ionization potentials.

The electron densities in molecules are highest in the vicinities of chemical bonds implying that this is the most probable region for electron collapse, especially in highly charged molecules. The selected collapse of a bonding electron serves a dual purpose. First, bond rupture occurs as a result of electron collapse, and secondly, the energy released imparts translational motion to the halogen ion. Figure 1 shows spectra for sources molecules Br_2, CH_3Br and HBr calculated from model IIIA for the reaction $^{80}Br^{m}(I.T.)^{80}Br$, and Figure 2 for the analogous $^{130}I^{m}(I.T.)^{130}I$ system. Although these are not in absolute agreement with models I and II, they are qualitatively similar and disagree by no more than 10%. The spectra appear discontinuous, going through many maxima and exhibiting zero probability at several points. This is the result of discrete energies generated by the transfer of unit electrical charges (electrons). It is important to note that collisional cooling of the halogen ions with system molecules will rapidly redistribute the kinetic energies and "smooth" the distribution.

The spectra for each model in the dihalogen molecule are shown in Figure 3 for Br_2 and 4 for I_2. Average kinetic energy and failure to bond rupture calculations are listed in Tables XIII and XIV. Model IIIa exhibits a low failure to bond rupture while maintaining a consistency within the average kinetic energies. Comparison of the data shows that although no one model may be correct, the method is consistent within itself. Furthermore, the correct orders of reactivity of bromine and iodine are predicted and the lower energies associated with the isomeric transition process are demonstrated.

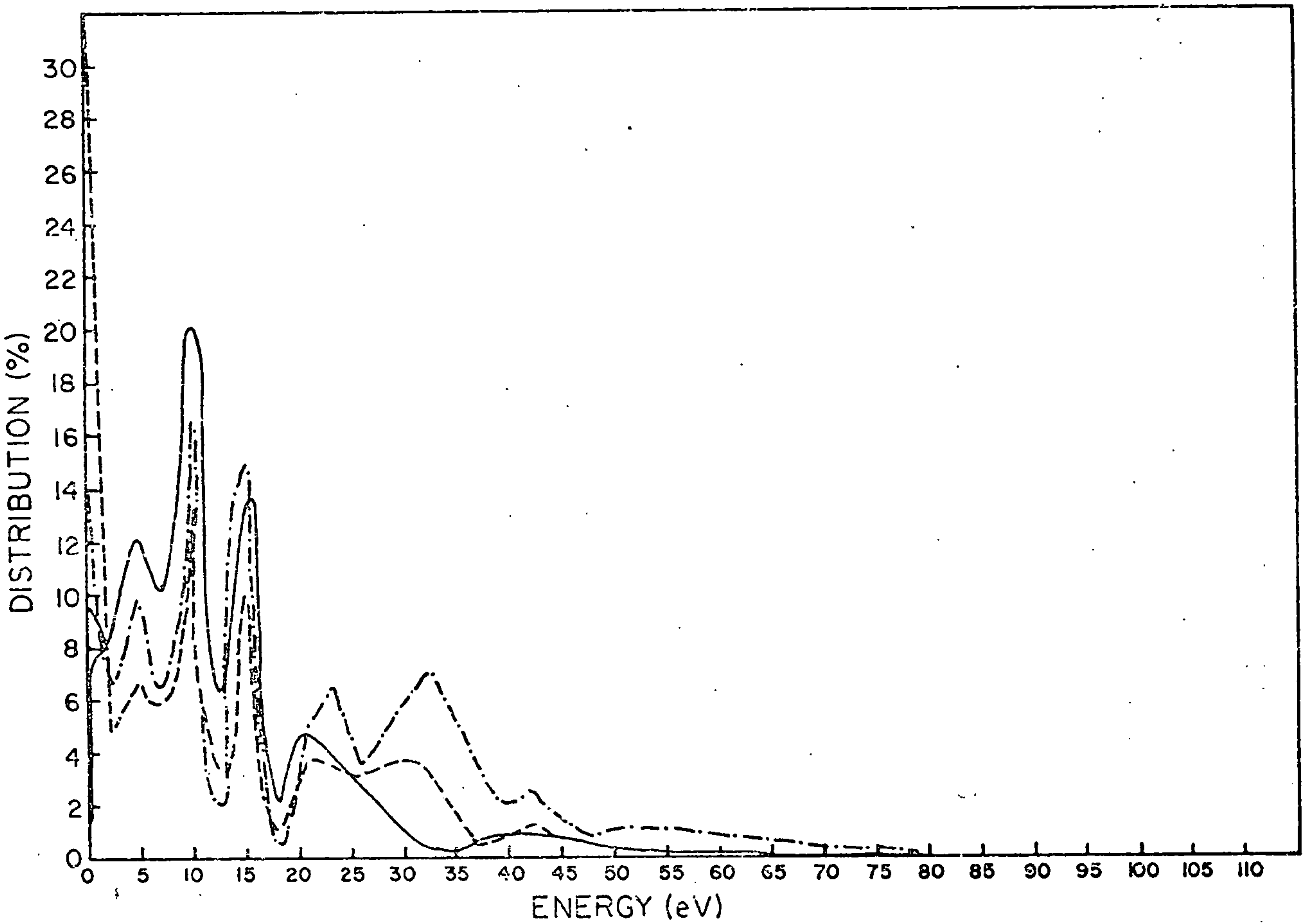

Figure 4. Kinetic energy spectrum for $^{130}I^{m}$ in I_2. Assumption I (---); Assumption II (-·---); Assumption III (——).

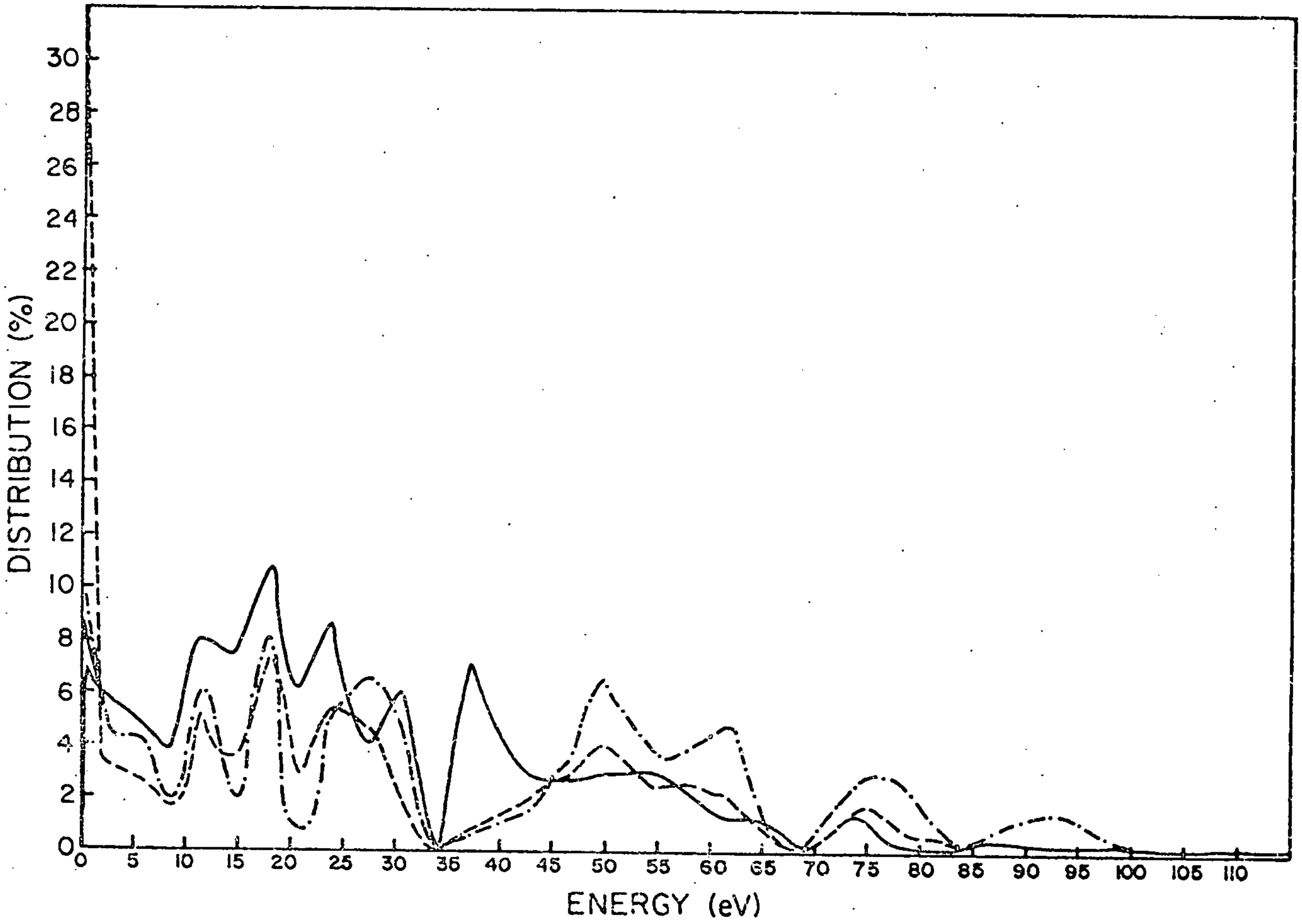

Figure 3. Kinetic energy spectrum for $^{80}Br^m$ in Br_2. Assumption I (---); Assumption II (-•-•-); Assumption III (——).

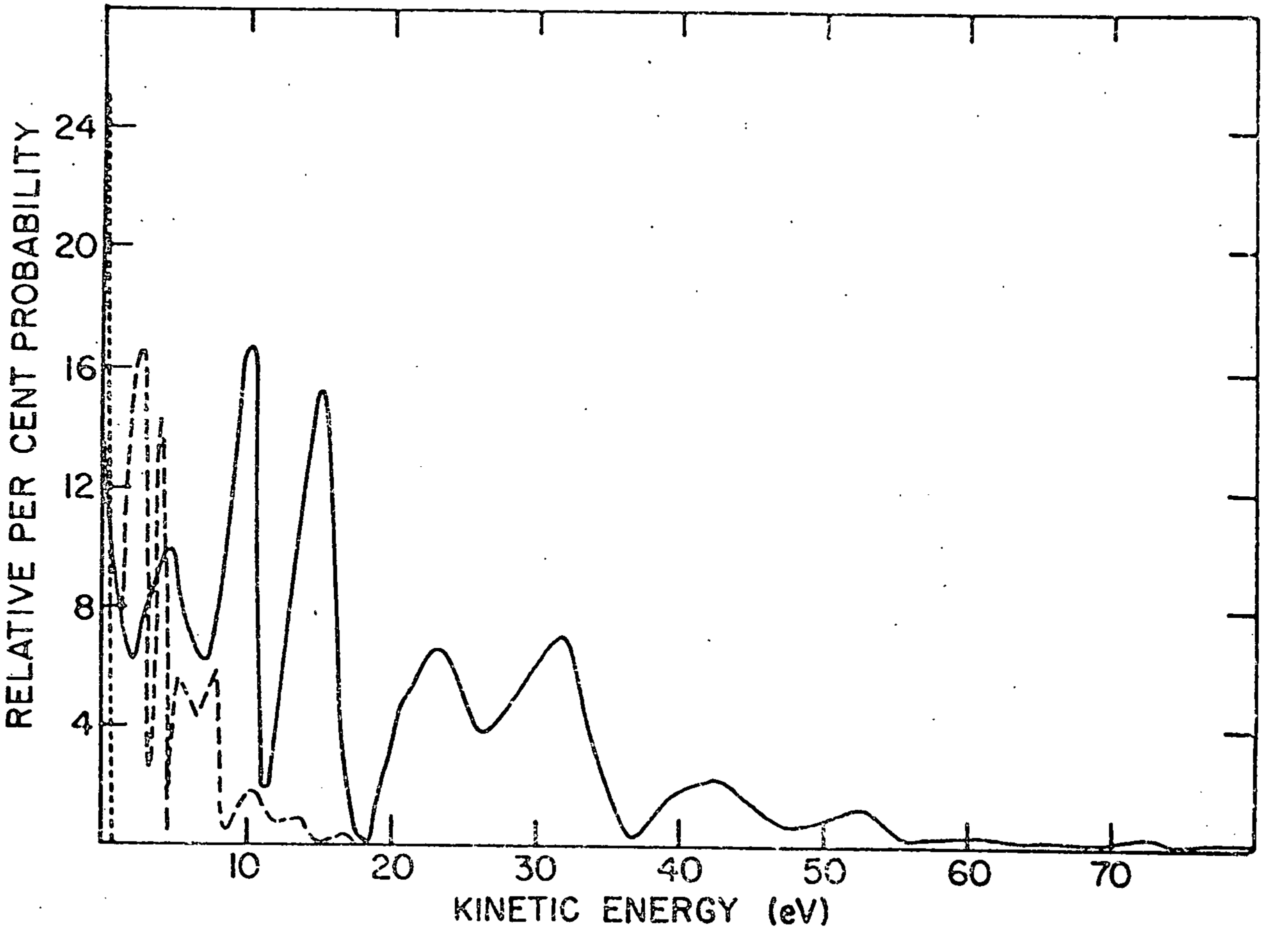

Figure 2. Probability distribution of iodine ions vs recoil energy.

I_2(——); CH_3I(---); HI(---).

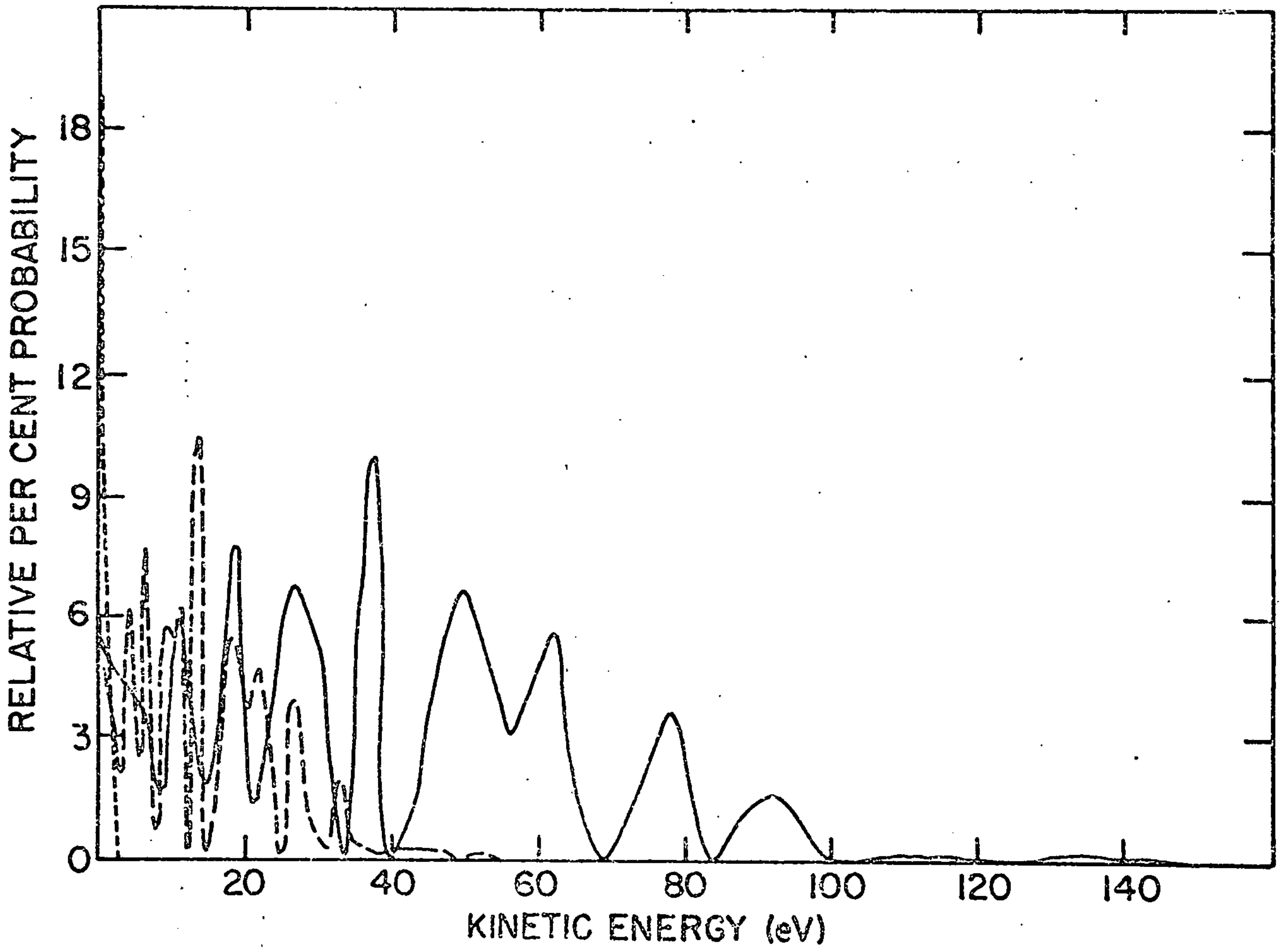

Figure 1. Probability distribution of bromine ions vs recoil energy.

Br_2(——); CH_3Br(---); HBr(---).

Significance. In terms of energy, the I.T. process is inefficient in the production of hot atoms as a result of bond energy requirements and the apportionment of the remaining energy between the created ions. Momentum restrictions suggest the highest energies obtained are in molecular RX where the masses or R and X are equal. Therefore, (I.T.)-activated processes produce large portions of the ions within or below the reactive zone rendering kinetic theory inapplicable. This study is being prepared for publication.

5. The Stereochemistry of Energetic Halogen Substitution Reactions at Asymmetric Carbon Atoms.

Relevance. The fundamental question of whether high-energy halogen atoms replace another halogen by retention or inversion of configuration at asymmetric carbon atoms, $X_i^* + RX_j \xrightarrow{Xi\text{-for }Xj} RX_i^* + X_j$, is important to investigate since it can provide insight into the dynamics of hot-atom reactions. The continuing role of simple physical models for hot atoms with molecules such as the "Impact Model" and the "Inertial Model" can be evaluated and refined.

Progress.

1) Effects of Solvent-Solute Interactions on the Stereochemical Course in High Energy Chlorine-38-for-Chlorine Substitution in meso- and rac-1,2-Dichloro-1,2-difluoroethane in Solution. This project was a collaboration effort with Dr. H. J. Ache of Virginia Polytechnic Institute and State University. Since this study recently appeared in the Journal of Physical Chemistry,[28] we will only summarize the major results of this study.

The stereochemistry of the chlorine-38-for-chlorine substitution was sutdied in diastereomeric 1,3-dichloro-1,2-difluoroethanes in solutions. The experimental results are very similar to those previously observed in meso- and d,ℓ-2,4-dichloropentane solutions which by analogy suggest tha the stereochemical course of the substitution process is in the present system also predominantly and directly controlled by the properties of the solvent molecules, most likely by the factors which govern the magnitude of intermolecular interaction between reactants and solvents. It appears that strong intermolecular interaction favors substitution via retention of confirguration, whereas in solvents having a low dielectric constant the retention/inversion ratio decreases. These results seem further to suggest that if the reaction occurs via a caged complex or excited intermediate that the primary attack by the energetic ^{38}Cl proceeds via both front and backside replacement.

Significance.

(1) No evidence for conformational effects on the stereochemical course of the reaction was observed, suggesting that the electronically excited intermediate is formed by both direct and backside replacement.

(2) The experimental results indicate that the stereochemical course of the substitution process is predominantly and directly controlled by the properties of the solvent molecules, most likely by the factors which govern the magnitude of intermolecular interaction between reactants and solvents. It appears that strong intermolecular interaction favors substitution via retention of configuration, whereas in solvents having a low dielectric constant the retention/inversion ratio decreases.

2) Evidence for Walden Inversion in High Energy Chlorine-for-Chlorine Substitution Reactions. This project was a collaborated effort with Dr. A. P. Wolf of Brookhaven National Laboratory. Dr. K.-C. To, our research associate, completed this phase of our project in Dr. Wolf's laboratory. This phase of our work has been accepted for publication by the Journal of Physical Chemistry.

Rowland[29-31] and Stocklin[32,33] have investigated the stereochemical course of halogen-for-halogen substitution reactions in halocarbon molecules with multiple asymmetric centers. These studies have been restricted to diastereomeric compounds such as rac- and meso-$(CHFCl)_2$ and rac- and meso-2,3-dichlorobutane because of experimental difficulties in resolving chiral molecules with a single chiral center. In their study of the hot-atom stereochemistry of rac- and meso-2,3-dichlorobutane, Rowland and co-workers[29-31] found greater than 93% retention of configuration at the asymmetric centers in gas reaction phase while racemization occurred in the liquid and solid phase systems. Their results suggested cage radical reactions in the condensed state. In an important study, Stöcklin et al.[32] found the substitution of chlorine in liquid rac- and meso-2,3-dichlorobutane by recoil ^{38}Cl can lead to both retention and inversition depending on conformational change due to solvent interactions. In a subsequent study of ^{38}Cl-for-Cl substitution in meso- and rac-$(CHFCl)_2$, Machulla and Stöcklin[33] postulated that hot substitution can proceed via two channels: (1) a direct replacement with retention of configuration in accordance with an impact model,[34-37] (2) a backside attack leading to the formation of a highly excited complex with lifetimes long enough to allow inversion of configuration to occur. However, recent studies by Ache, Rack et al.[28,38] observed no conformational effects in the stereochemical course of ^{38}Cl-for-Cl substitution in various dichloroalkanes and $(CHFCl)_2$. The stereochemical course of substitution process is controlled by the properties of the solvent molecules, most likely intermolecular interaction between reactants and solvents. Their results[28] also suggest that the excited complex is formed by both direct and backside attack in ^{38}Cl-for-Cl substitution reactions in $(CHFCl)_2$.

In this study, we report for the first time the studies of high energy Cl-for-Cl substitution in the gaseous and condensed phases at the asymmetric carbon atom of the enantiomers 2(S)-(+)- and 2(R)-(-)-chloropropionyl chlorides in which steric effects are significantly minimized and the backside sterically hindered enantiomer 2(S)-chloro-4-methyl-valeryl chloride. In addition, attack in the gas phase on this molecule with a single chiral center minimizes or obviates the influence of conformational effects on the substitution reaction (vide infra).

2(S)-(-)- and 2(R)-(+)-chloropropionic acids were prepared from optically pure R- and S-alanine according to the method of Fu _et al_.[39] 2(S)-(+)- and 2(R)-(-)-chloropropionyl chlorides were prepared by the method described by Lucas and co-workers.[40] Polarimetric analysis of the R- and S- acid chlorides showed a specific rotation $[\alpha]_0^{25}$ of -4.38 ± 0.01 and $[\alpha]_0^{25}$ of +4.38 ± 0.01, respectively. S-(+)-valine methyl ester was prepared by passing anhydrous hydrogen chloride gas into a slurry of S-valine in anhydrous methanol at 0°C for 1.5 hours. After re-crystallization, the optical purity of the ester was found to be greater than 98%.

Fifty to 100 μl of the acid chlorides were used for the study. An aliquot of either S- or R-acid chlroide was transferred to a quartz irradiation vessel. To minimize the possibility of hydrolysis of the acid chlorides the storage container and the sample vessel were purged with dry nitrogen before use. After transfer, the samples were outgassed on a vacuum line by freeze-thaw cycles until gas evolution was no longer visible. The cyclotron vessels were closed off by turning the teflon stopcock while the reactor vessels were sealed off quickly using a gas-oxygen flame while the sample was frozen in the far end.

The ^{34m}Cl studies were carried out at the Brookhaven National Laboratory 60-inch cyclotron. A 20 MeV proton beam was used to produce ^{34m}Cl from ^{35}Cl which has a natural abundance of 75.53%. By using 20 MeV protons for the in-situ production of ^{34m}Cl, ^{11}C isotope production can be suppressed to acceptable levels without seriously decreasing chlorine ^{34m}Cl production. Nitrogen-13 yields at EOB are comparable to ^{34m}Cl yield.

In order to irradiate an adequate gas phase concentration, sample holders were heated during irradiation by an aluminum target holder. The irradiation vessel was inserted into the holder and allowed to come to equilibrium ($\sim$30 minutes) before irradiation was begun. A temperature of 110° was used. The samples received an average irradiation of 50 μA sec. The 10 mil quartz window of the irradiation vessel degraded the 20 MeV proton beam from 20 to 18.5 MeV. The beam was further degraded to 18.15 MeV in the target gas. Thus, the energy deposited during a proton irradiation of 2-chloropropionyl chloride at a pressure of 380 torr was 0137 eV per molecule at 50 μA sec.

The ^{38}Cl samples were irradiated at the epithermal patient facility at the Brookhaven Research Reactor at a thermal neutron flux of 3×10^{10} n-cm^{-2} sec^{-1}. The in-situ production of ^{38}Cl was effected by the ^{37}Cl(n,γ)^{38}Cl reaction. The gas phase samples were heated in an aluminum block which was surrounded by quartz thermal insulation. Heating was controlled by a heating tape. Temperature was measured on a calibrated iron-constantan thermocouple. Low temperature studies were carried out by irradiating the sample in an unsilvered quartz dewar containing either liquid nitrogen or dry ice. Dose rates to the sample were of the order of 60 R/min. The neutron dose to gaseous sample was approximately 10^{-7} eV/molecule for a one minute irradiation. The samples were usually irradiated for a period of 5 to 15 minutes.

The stereochemistry of the replacement of chlorine atoms in alkyl halides which contain a single chiral center has not been studied partly because of the experimental difficulties in separating the enantiomers within the period of time allowed by the half-life of the nuclide in question. Halpern and Westley[41,42] have shown that the diastereomers of N-chloroacyl amino acid methyl esters can be rapidly separated by gas chromatography. This technique was employed to resolve the enantiomers. A systematic search for the optimum resolving agent for 2-chloropropionyl chloride indicated that the S-valine methyl ester gave the optimum resolution in the shortest time. Two columns were used for the separation of the diastereomers. Column I was 1/8"x12' packed with 10% Carbowax 20M on Chromosorb-W 100/200 HMDS and run at 175°C with a He flow rate of 37 ml/min. Column II was 1/4"x20' of glass construction filled with 17% Carbowax 20M on Anakrom 80/90 HMDS with a He flow rate of 100 ml/min. For Column I, the SR and RR diastereomers eluted at 14.9 min and 16.6 min, respectively, after injection; while Column II gave a retention time of 55.5 min and 61 min for the SR and RR diastereomers, respectively. Resolution using Column I was superior to the resolution using Column II but owing to the greater capacity of the latter (hence allowing larger amounts of sample injection) Column II was used for all analytical determinations.

The gas chromatograph used in this work was a Perkin Elmer 880-FID. The column, injector end, and detector were all heated to 180°C. The exit port of the chromatograph was fitted with a 1/8" swagelock to a 1/4" Ultra Torr fitting and was heated to approximately 200°C. Fractions eluting from the chromatograph were trapped in glass tubes packed with 40/60 mesh activated charcoal with cotton plugs at both ends. The samples trapped in activated charcoal were then placed in vials for static counting in a NaI well counter.

Post-irradiation derivatizations of diastereomers was accomplished by adding a solution of 0.05 gm of S(+)-valine methyl ester in 0.5 ml of chloroform to the irradiated sample. 0.2 ml triethylamine was added slowly and reaction was allowed to proceed for five minutes at 0°C. At the end of five minutes, 0.1 ml of absolute methanol was added to convert the unreacted acid chloride to methyl ester. The organic solution was then washed with distilled water, extracted and dried with $CaSO_4$ and an aliquot of the organic solution was injected into the gas chromatograph. The relative percent retention was determined from the activities found in the diastereomer peaks. The results listed in Table I have been corrected for optical impurities present in the resolving agent and in the acid chloride.

Absolute yields for the Cl-for-Cl substitution were determined by adding 0.5 ml of absolute methanol to the activated sample. The rate of formation of the methyl ester was very fast and was found to proceed to greater than 99% completion within one minute at 25°C. Due to the formation of the radionuclide ^{13}N ($t_{1/2}$ = 10 min) during sample activation the samples were counted about 100 min after the end of the irradiation in order to minimize the ^{13}N contribution. There was no detectable ^{13}N activities in the assayed peaks at EOB + 100 min.

The specific activity of the irradiated sample was determined and an aliquot of the sample was injected into the gas chromatograph. The amount injected was determined gravimetrically. The methyl ester eluted after 13 min at 130°C with a He flow rate of 65 ml/min and was trapped on charcoal and counted (vide infra). The absolute yield after corrections for decay and for split of the effluent to the FID detector was the activity found in the trapped ester peak divided by the total activity injected into the column.

Derivatization of the diastereomers of N-2-chloropropionyl-(S)-valine methyl ester has been described in the previous section. The derivatization takes place in chloroform in the presence of a considerable quantity of chloride ion and triethylamino. Isotopic exchange reactions are therefore a possibility during the derivatization. If exchange reactions occur during the derivatization steps, the experimental results will not be the true percent retention of a Cl-for-Cl substitution.

We have done a series of control experiments in which the derivatization was run in the presence of externally generated ^{34m}Cl in ad mixture with the substrate. $H^{34m}Cl$ was generated by irradiating gaseous sample of methylene chloride with 20 MeV protons at a dose similar to that used for 2-chloropropionyl chloride irradiations. The irradiated methylene chloride samples were washed with methylene chloride and $H^{34m}Cl$ was isolated by gas chromatographic separation, using a 6% Halocarbon grease on Fluropak 80 column. The $H^{34m}Cl$ eluted rapidly (∿1-2 min) at room temperature and was trapped in a solution of S(+)-valine methyl ester and chloroform. Derivatization was performed under conditions identical with those described previously. After gas chromatographic separation, no detectable activity was found in the trapped diastereomers. To check the feasibility of ^{34m}Cl-for-Cl exchange reaction in a more reactive substrate under these conditions, isopropyl tosylate was treated with $H^{34m}Cl$ under the same conditions. Labelled isopropyl chloride was readily isolated. We, therefore, conclude that post-irradiation ^{34m}Cl-for-Cl exchange reaction is not singificant under the conditions employed for the derivatization of the diastereomers.

Wai and Rowland[31] have used 1,3-butadiene as a free radical scavenger for the ^{38}Cl reactions with 2,3-dichlorobutane and have found that the substitution of ^{38}Cl-for-Cl proceeds almost entirely with retention of configuration in the presence of the free radical scavenger. This led to their suggestion that a free radical recombination mechanism is involved in the formation of the inverted product.

We have investigated the effect of 1,3-butadiene on the ^{38}Cl-for-Cl substitution of 2-chloropropionyl chloride. In a study of the effect of concentration of 1,3-butadiene on the percent retention in the gas phase, a slight increase in retention (∿8%) is observed when large amounts of the additives are present. The retentions are 15.2% and 23.5% with 2.89 and 23.5 mole percent of 1,3-butadiene present, respectively. This may be due to the high efficiency of 1,3-butadiene as a chlorine moderator. It is therefore concluded that the free radical combination mechenism described by Wai and Rowland is not operative in this system.

High energy species produced by nuclear transformations are usually ionic. It can be assumed that species with very high recoil energies (in the KeV range) will undergo multiple charge-transfer collisions with the bath molecules before reaching the chemically reactive region and react as energetic atoms. For low energy species ($\sim 10^2$ eV), this may not be the case.

In their study of the reactions of energetic chlorine with gaseous alkyl halides, Wai and Rowland[31] showed that there was no difference in the chemical reaction pattern using chlorine produced by $^{37}Cl(n,\gamma)^{38}Cl$ (E_{max} recoil = 530 eV) and $^{40}Ar(\gamma,p)^{39}Cl$ (E_{max} recoil $\sim 10^3$ eV) as one would expect from theoretical consideration. Additional kinetic moderation studies using argon and zenon as moderators indicated that the reacting chlorine species are not ionic. This is expected since a chlorine ion in a chlorocarbon environment of IP = 10.5 ± 0.5 eV will be neutralized by exothermic charge transfer reactions. Therefore, it is assumed that the energetic ^{34m}Cl (E_{max} recoil = 0.3 MeV) and ^{38}Cl reported in this study react with 2-chloropropionyl chloride as neutral atoms.

Presented in Table XV are the absolute yields, percent retention and ratio of retention to inversion of optical configuration for the gas to condensed phase Cl-for-Cl substitution at the asymmetric carbon atoms of 2(S)-(+)- and 2(R)-(-)-chloroopropionyl chloride. In the gas phase where mechanistically complicating cage effects are probably not present, our results show a surprisingly small degree of retention of configuration at the asymmetric carbon atoms for both ^{38}Cl and ^{34m}Cl substitutions, respectively. The level of inversion has been determined independently for both the R- and S-isomers of 2-chlorooopropionyl chloride and they are identical within experimental error. This is the first report where net inversion has been observed in any gas phase halogen hot atom reaction. While it may be argued that 50% of the apparent inversion is actually due to racemization (the complete retention of configuration in other gas phase studies makes this an implausible consideration), there is the remaining 30% of the substitution reaction that must result from a Walden type inversion.

Fukushima[43] has studied the rotational conformations of 2-chloropropionyl chloride in the gas and liquid state. It was found that in the liquid state, the molecules exist in three rotational conformations--trans, gauche, and gauche prime forms. In non-polar solvents and in the gaseous state, the gauche prime conformation becomes significantly more abundant than in the liquid phase while only the transform persists in the solid state. The gauche prime conformation provides a relatively unhindered approach to attack of the asymmetric carbon from the backside (with respect to the 2-chlorine). In addition, trajectories for chlorine attack leading to Walden inversion involve a wide range of angles. The backside approach to 2-chloropropionyl chloride is less hindered than for any rotational conformation of $(CHFCl)_2$ or 2,3-dichlorobutane, both of which are relatively hindered in all conformations. If it is the open conformation which determines gas phase Cl-for-Cl substitution with such a high degree of inversion, then blocking the backside with large substituent groups should hinder the inversion mode. In addition, the increased inertia of the alkyl group should prohibit extensive motion during a reactive collision.

The data in Table XVI show the percent retention of ^{38}Cl and ^{34m}Cl-for-Cl substitution at the asymmetric carbon of 2(S)-chloro-4-methyl-valeryl chloride. The percent retention of ^{34m}Cl-for-Cl at the asymmetric carbon was found to be 59.3 ± 0.8%. This large increase in retention compared to 2-chloro-propionyl chloride is consistent with the hypothesis that the degree of retention (or inversion) is strongly affected by steric hindrance.

There are several important implications to high energy chemistry. According to the impact model,[34-37] hot atom displacement reactions are fast ($\sim 10^{-14}$ sec) and direct, independent of bond strengths, but dependent primarily on the point and direction of impact (steric factors). The inertial model, an outgrowth of the impact model, places severe restrictions on the hot atom substitution process: Hot atom reactions requiring nuclear motions which are slow relative to the time of collision tend to be forbidden. Specifically, substitution is affected by the presence of substituents other than those being displaced; substitution yields are related to the ability of the target molecule to rotate rapidly; and inertial effects are of greater magnitude than steric effects.

Experimentally, we found Cl-for-Cl substitution leading to preferential inversion of configuration in the gas phase for 2(S)-chloropropionyl chloride and 2(R)-chloropropionyl chloride. However, Cl-for-Cl substitution in gaseous 2(S)-chloro-4-mehtyl-valeryl chloride leads to predominant retention of configuration supportive of a steric factor being in operation. It would appear that in backside attack, either inovlving a multi-centered collision complex or an ineleastic reactive collision, little excitation energy is involved. However, the collision time must be long enough to insure the inversion process (movement of substituent groups during the reactive collision). In propionyl chloride, substitution is not as predicted by the impact model, i.e., direct with retention of configuration nor consistent with an inertial model. The general obvious implication of our experimental results is that both the impact and inertial models in their present forms do not have general validity in halogen hot atom chemistry.

Based on our results, we can suggest the predominant factor controlling the substitution event is not inertial restriction but steric restriction. Not all hot atom substitution reactions are fast and direct involving a front-angle attack, but can be from the backside of the molecule, colinear with the bond being broken, involving Walden inversion; perhaps by an inelestic reactive collision. If there is steric obstruction to Walden inversion, then reactions can occur via other pathways. It is interesting to note that Bunker and Pattengill[44] in their trajectory studies of hot atom reactions of tritium with methane suggested that some substitutions in methane may proceed with Walden inversion.

As can be seen in Table XV, the absolute yields for the ^{38}Cl and ^{34m}Cl-for-Cl substitution display a density dependence with an increase in yield, progressing from low to higher pressure to the condensed phase. This effect is similar to those previously reported for recoil fluorine,[37] chloride,[33] bromine,[45] and iodine.[2,46] With the increase in absolute yield, there is an increase in the retention to inversion ratio, becoming one and remaining constant, within experimental error for the liquid, glass and solid phases. This <u>increase</u> in stereospecificity in the gas to condensed phase transition is in contrast to the previous studies[32-36] on the stereochemistry of substitution to high energy halogen atoms at asymmetric carbon atoms in diastereomers.

If the Cl-for-Cl substitution in the gas phase were mainly by direct substitution with retention of configuration and produced a racemic mixture in the liquid and solid phase, no conclusions could be made as to whether the substitution event were the result of (a) complex formation in excited states with lifetimes long enough to allow configurational changes[33] (and stabilized by the cage effect to a greater extent in the condensed phase) or (b) cage radical reactions, as both modes are possible.

If the Cl-for-Cl substitution in the gas phase were mainly by "inversion" of configuration and in the liquid and solid phases produced racemic mixtures, we could rule out significant contributions from excited complex formation with subsequent configurational changes, as their yield contributions would increase (increasing "inversion" product yield) with increasing density. Therefore, cage radical effects may be the explanation of the condensed phase experimental results.

Interpretation of condensed phase stereochemical experiments using diastereomers is difficult due to the difference in the thermodynamic stabilities of such compounds as the meso- and racemic isomers of 2,3-dichlorobutane. If cage effects are present in these studies, then the effect of the solvent on the conformation of a chloro-sec-butyl radical must be considered. Furthermore, the difference in energies between the apparent retained product and the apparent inverted product during recombination may give a distorted view of the stereochemical course of the replacement reactions taking place. Enantiomeric molecules provide a means of studying replacement reactions in which both the initial and final energy states of the reaction are thermodynamically identical.

The experimental values of the retention of optical configuration in the condensed phases are 50% (within experimental error) as shown in Table XV. These results could be due to racemization and/or equal rates of retention and inversion reaction channels.

In order to test these possibilities, a condensed phase study was carried out with 2(S)-chloro-4-methyl-valeryl chloride. The properties of this molecule have been previously described. These properties should cause a large increase in the percent retention (>50%) if a direct hot Cl-for-Cl replacement mechanism is involved. The experiment was carried out at 25°C and resulted in 48.6 ± 1.3% retention as shown in Table XVI. This strongly suggests that racemization is occurring through radical-radical recombination in the liquid, glass, and crystalline solid. In addition, the presence of both labelled isomers in equal amounts is evidence that planarity of the $CH_3CHCOCl$ and $(CH_3)_2CH_2CHCOCl$ radicals is established before recombination.

TABLE XV: Yields of ^{38}Cl and ^{34m}Cl-for-Cl substitution at the asymmetric carbon of 2(S)-(+) and 2(R)-(-)-chloropropionyl chloride in the gas (at +110°C) and condensed phases.

Enantiomer	Nuclide	Phase	Absolute Yield %	Retention %	Rate Retention to Inversion
S-(+)	^{34m}Cl	Gas(400 Torr)	1.3 ± 0.1	18.8 ± 2.0	0.23 ± 0.03
R-(-)	^{34m}Cl	Gas(400 Torr)	1.3 ± 0.1	21.3 ± 2.0	0.27 ± 0.03
S-(+)	^{34m}Cl	Gas(590 Torr)	1.0 ± 0.1	17.6 ± 0.9	0.21 ± 0.01
S-(+)	^{38}Cl	Gas(590 Torr)	1.0 ± 0.1	17.7 ± 8.0	0.21 ± 0.13
R-(-)	^{38}Cl	Gas(590 Torr)	1.0 ± 0.1	20.0 ± 7.3	0.25 ± 0.12
S-(+)	^{34m}Cl	Gas(800 Torr)	2.38± 0.9	37.5 ± 7.1	0.60 ± 0.13
S-(+)	^{34m}Cl	Liquid(+25°C)	4.3 ± 0.2	53.0 ± 2.0	1.12 ± 0.10
R-(-)	^{34m}Cl	Liquid(+25°C)	4.5 ± 0.2	53.4 ± 2.0	1.15 ± 0.10
S-(+)	^{38}Cl	Liquid(+25°C)	4.1 ± 0.3	52.7 ± 4.7	1.11 ± 0.24
S-(+)	^{38}Cl	Glass(-78°C)	6.6 ± 0.1	47.5 ± 4.1	0.90 ± 0.17
S-(+)	^{38}Cl	Solid Crystalline (-196°C)	7.8 ± 0.1	49.2 ± 0.4	0.97 ± 0.01

TABLE XVI: Stereochemistry of ^{38}Cl and ^{34m}Cl-for-Cl substitution at the asymmetric carbon of 2(S)-chloro-4-methyl-valeryl chloride.

Enantiomer	Nuclide	Temperature(°C)	Phase	Retention(%)
S	^{38}Cl	25	Liquid	48.6 ± 1.3
S	^{34m}Cl	130	Gas	59.3 ± 0.8

Machulla and Stöcklin[33] have suggested that the inversion reaction channel is made possible by formation of an excited reaction complex with life-time long enough to allow configuration changes, including Walden inversion. Such a complex, they argue, would be stabilized in the condensed phases leading to an apparent decrease in the percent retention. However, our results indicate that the smallest degree of retention (∿20%) occurs in the gas phase where a complex would not be stabilized. This is clearly in disagreement with the complex theory which would predict a higher degree of retention in the gas than liquid phase.

Significance. The experimental results of ^{38}Cl and ^{34m}Cl-for-Cl substitution at the asymmetric carbon of 2(S)-(+)- and 2(R)-(-)-chloropropionyl chloride in the gaseous and condensed phase indicates a high percent inversion of configuration in the gaseous phase and decrease to a retention to inversion ratio of about one. These results, along with the lack of conformational effects in the condensed phases, give additional support for a cage-radical combination mechanism leading to racemization. The almost identical substitution yields for both ^{38}Cl and ^{34m}Cl indicate that the initial kinetic energies are not a factor. The gaseous phase results indicate that not all hot-atom substitution reactions are fast and direct (as predicted by the impact model) involving a front-side approach but can indeed occur from the backside of the molecule resulting in Walden inversion. From the results of 2(S)-chloro-4-methyl-valeryl chloride experiments, we conclude that the predominant factor controlling the substitution event is steric in character.

6. Applied Hot Atom Chemistry

Relevance. While applications of hot atom chemistry techniques or theory may, by themselves, not be energy-related, it is important to realize that the hot-atom chemistry approach may be the most efficient method to assist in a problem solution. Our main applied interests have been in neutron activation analysis of biological specimens. This collaboration with the Omaha V. A. Medical Center staff has resulted in a waving of the reactor-irradiation fee and, generally, unrestricted use of the reactor and laboratory facility for our high energy chemistry studies.

Progress. Our entire progress during the current contract period involved the determination of a neutron activation analysis procedure for trace aluminum in bone,[47] a comparative study[48] between neutron activation analysis and graphite furnace atomic absorption spectrometry in biological materials, and the determination of trace-level vanadium in marine biological samples by chemical neutrons activation analysis.[49]

1) Trace Aluminum Determination and Sampling Problems of Archeological Bone Employing Destructive Neutron Acrivation Analysis. We developed a neutron activation procedure for determining trace aluminum content in bone. We found that soil contamination can influence the aluminum levels in prehistoric bone specimens. These maximum aluminum content values for prehistoric bone are larger than those of modern bone and comparable to aluminum levels present in bone from renal patients. This completed study appeared in the 1978 U.S.A. National issue of the Journal of Radioanalytical Chemistry.[47]

2) Comparison between Neutron Activation Analysis and Graphite Furnace Atomic Absorption Spectrometry for Trace Aluminum Determination in Biological Materials. Currently, there is no biological aluminum assayed Standard Reference Material available, such as bovine liver or orchard leaves, which can be used to test the validity of an analysis. As a result, we felt that an intercomparative study of two different techniques for determining trace aluminum in bone and urine must be carried out before definitive studies on the role of aluminum in metabolisms and disease can be carried out. While neutron activation analysis

gives excellent results, few people have access to a reactor. We developed a method based on furnace atomic absorption which is in much more general use throughout the world. This completed study appeared in the January, 1978, issue of Analytical Chemistry.[48]

3) Determination of Trace-Level Vanadium in Marine Biological Samples by Chemical Neutron Activation Analysis. A pre-irradiation chemistry neutron activation analysis procedure employing cation-exchange chromatography was developed for the determination of trace-level vanadium in marine biological specimens. The limit of detection of the method is 30 ppb. The determination of the vanadium content of NBS Standard Reference Material, 1971, Orchard Leaves resulted in a value of 0.60 ± 0.02 ppm. Determinations of the vanadium content in shrimp, crab and oyster from four sites off and near Galveston Island, Texas, showed that the vanadium content is greater in samples taken in the industrialized areas as compared to a non-industrialized section.

Significance.

(1) We developed both neutron activation analysis and atomic absorption spectrometry procedures for trace aluminum in bone.

(2) These procedures allowed us to give the first evidence for aluminum absorption from the gastrointestinal tract and bone deposition by aluminum carbonate ingestion with normal renal function.

(3) Normal and disease aluminum levels in all biological matrices can now be readily determined.

(4) Vanadium can be determined in the parts per billion concentration range in biological specimens.

Master of Science Dissertations

1. Frank J. Bryant, "The Radiolysis of Cyclopentane-Iodine Using Internally Dissolved Iodine-131 and a Nuclear Reactor", February, 1966.
2. William K. Ellgen, Jr., "The Reactions of Bromine Activated by Radiative Neutron Capture and Isomeric Transition in Carbon Tetrachloride", August, 1966.
3. James B. Nicholas, "Effect of Moderators on the Isomeric Transition Induced Reactions of Bromine-82 with Methane", May, 1967.
4. Myung H. Kim, "Gas Phase Reactions of Iodine with Pentene Isomers Activated by Reactor Radiation and Light". December, 1974.
5. Alex Loventhal, 1. "A Comparison Between Szilard-Chalmers and a Radiometric Labelling Technique in Kinetic Studies of Photochemical Iodine Addition to Gaseous Pentene Isomers" 2. "Gas to Condensed Phase Transistion in Bromine-Ethane Systems. Evidence for Competitive Enhancement Reactions", August, 1977.

Ph.D. Theses Directed

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2. R. M. Lambrecht, "Reactions of Halogen Atoms Activated by Nuclear Processes with Organic Media at 77° and 298°K", 1969.
3. N. J. Parks, "Reactions of Iodine Activated by Radiative Neutron Capture and Isomeric Transition with Gaseous and Condensed State Polyhalomethanes", 1969.
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5. R. L. Ayres, "Reactions of Iodine Activated by the Neutron Capture Process in Liquid and Solid Alkanes and Alkenes", 1970.
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9. R. R. Pettijohn, "Radiative Neutron Capture Induced Reactions of Iodine-128 with Gaseous Ethylene and Propylene. Stereochemistry of the Cl-Cl Substitution Activated by Nuclear Transformations in Enantiomeric Chlorocarbons", 1973.

10. M. E. Berg, "Theoretical Approaches and Mechanistic Applications in the Gas to Condensed Phase Transition of High Energy Heavy Halogen Reactions in Organic System, 1977.

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