HALOGEN ATOM REACTIONS ACTIVATED BY NUCLEAR
TRANSFORMATIONS

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PROJECT ABSTRACT

High energy reactions of halogen atoms or ions, activated by nuclear transformations, are being studied in gaseous, high pressure and condensed phase saturated and unsaturated hydrocarbons, halomethanes and other organic systems in order to better understand the reactivity of high energy species. Our experimental and theoretical program consists of six interrelated areas: (1) Systematics of halogen hot atom reactions. The reactions of $^{80}\text{Br}^m$, ^{80}Br , $^{82}\text{Br}^m + ^{82}\text{Br}$, ^{82}Br , ^{128}I , ^{130}I , and $^{130}\text{I}^m + ^{130}\text{I}$ activated by radiative neutron capture or isomeric transition in hydrocarbons and halo-substituted alkanes will be further studied in low pressure and high pressure gaseous systems employing additives and rare gas moderators. (2) The reactions of iodine with olefins and acetylenes activated by radiative neutron capture and isomeric transition will be further studied in low pressure and high pressure gaseous systems employing additives and rare gas moderators. Special attention is given to the reactivity of excited complex formation and structural effects of electrophilic iodine attacks on pi-bond systems. Photochemical addition to gaseous olefins will be further explored. (3) The gas to condensed state transition in halogen hot atom chemistry, involving chlorine, bromine, and iodine activated by the (n, γ) and (I.T.) processes in halomethanes, saturated and unsaturated hydrocarbons will be investigated in more detail. Special attention will be given to defining the nature of the enhancement yields in the condensed phase. (4) Kinetic theory applications of hot atom reactions and mathematical development of caging mechanisms will be continued. (5) The stereochemistry of ^{38}Cl and ^{128}I , $^{130}\text{I}^m + ^{130}\text{I}$ and ^{130}I substitution reactions involving dia-

stereomeric molecules in the gas and condensed phase will be continued.

(6) The applications of hot atom chemistry techniques and theory to neutron activation analysis of biological systems will be explored.

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 Hospital in Omaha, Nebraska. A flux of 1×10^{11} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$ 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. $^{-1} \text{min}^{-1}$ using Fricke dosimetry.

This past year 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, 1974 to September 30, 1975, 302 hours (integrated time in reactor) at 15.5 kilowatts power, making 1,900 irradiations.

B. Radiochemistry Laboratory

All sample preparation and much of the radioassaying 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 two radiogas chromatographs, three single-channel analyzers with several 2" x 2" NaI crystals, four GM counting stations, four gas-flow counters, and a

Nuclear-Data 128-channel analyzer with a 3" x 3" NaI crystal specially housed in a concrete, cadmium, and lead cave.

A small portable radiogas chromatograph has been built and is located in the radiochemistry room of the Omaha V.A. Hospital 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 acetylene and the various isomers of butylene in both the gas and condensed states, precluding the necessity of making corrections for radiation damage and thermal reactions occurring during lengthy neutron irradiations.

For most of our ^{80}Br , ^{38}Cl and ^{128}I total organic product yield experiments, we used the radiochemistry facilities and radioassaying equipment of the Omaha V.A. Hospital. The use of their Nuclear Data ND1024-channel analyzer with 3" x 3" NaI crystals, 3" x 5 mm NaI crystal, and Ge(Li) detectors was most helpful in many of our studies.

SUMMARY OF PRESENT 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 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, hot atom 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 are limited 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 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 molecular environment on the reaction systems from low pressure gas to solid state glasses and crystals is easily studied in bulb experiments. However the multi-collisional processes found in bulb techniques do not permit the study of simple collision reactions or systems with well-defined energy distributions.

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 summary of our main progress during the current contract period:

1. Systematics of Halogen Hot Atom Reactions

Relevance. Systematic studies of high energy reactions activated by various nuclear transformations in gaseous systems are important. From these studies we can generally ascertain the importance of such parameters as steric,¹ bond energy,² translational-inertial³ and energy degradation factors⁴ 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 $^{129}\text{I}(\text{n},\gamma) \text{}^{130\text{m}}\text{I} + \text{}^{130}\text{I}$ and $^{130}\text{I}^{\text{m}}(\text{I.T.}) \text{}^{130}\text{I}$ activations in halomethanes. This data, in conjunction with that of Nicholas, et al.⁵ 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.⁴ The organic yield data appear to be linear with respect to the energy degradation factor (EDF)⁴ and independent of bond energy and steric effects. We have found for $^{129}\text{I}(\text{n},\gamma) \text{}^{130\text{m}}\text{I} + \text{}^{130}\text{I}$ 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 $^{130}\text{I}(\text{I.T.}) \text{}^{130}\text{I}$. 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 $^{130}\text{I}^m + ^{130}\text{I}$ 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.

2. Reactions and Systematics of Iodine Reactions with Olefins and Acetylene.

Relevance. Olefins, acetylene and acetylenic 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) Gas Phase Kinetics of Iodine Addition to Pentene Isomers.

We found for the first time the photochemistry-induced addition of iodine to gaseous alkenes. Since Sumrell, *et al.*,⁶ and Skell and Paulis⁷ reported that contrary to information found in the literature⁸⁻¹¹ iodine

readily adds to liquid 1-pentene and C_4 alkenes, several studies¹²⁻¹⁴ suggested possible mechanisms for liquid state addition of iodine. In our previous study of iodine addition to liquid pentene isomers,¹⁵ we suggested that the stereospecific addition is the result of attack of an iodine atom or molecule on a charge transfer complex between the alkene and the corresponding iodine molecule or atom.

In this contract period we found ready addition of iodine, labeled with ^{131}I radioactivity as used previously¹⁵ and ^{128}I by a nuclear reactor irradiation labeling method, with gaseous 2-pentene and 2-methyl-2-butene. Since it was shown by Benson and Amano that iodine can undergo gas phase thermal addition to olefins we restricted our photochemical study to iodine reactions at room temperature; consequently, we were unable to vary the iodine concentration as was possible in our liquid phase study.¹⁵

The addition of iodine to the double bond of the pentenes studied proceeds smoothly when the systems are exposed to light at room temperature, reacting with ^{128}I to form organic yields of 50-80% in 15 minutes. Our previous investigation of liquid phase addition of iodine to pentenes,¹¹ where the initial concentration was varied with the alkene in excess, showed that the reaction was 3/2 order with respect to iodine. Since we were unable¹⁶ to vary the iodine concentration effectly without introducing thermal reactions complications, we observed whether the rates of disappearance of iodine in our gaseous systems were 3/2 order with respect to iodine. If this is the case we would find¹⁵ $1/2 k\tau = (a_0 - x)^{-1/2} - (a_0)^{-1/2}$ where a_0 is the initial concentration of iodine, $(a_0 - x)$ is the concentrations of iodine at time τ .

We intend to complete this phase of our study of kinetics of pentene isomers by determining the quantum yields of the photochemical reactions under controlled irradiation conditions. This will furnish us with data which can serve as a basis for quantitative comparison with related workers.¹⁴ At the completion of this phase a manuscript will be submitted to the Journal of Physical Chemistry for publication.

2) Reactions of Iodine-128 with Isomers of Butene. While studies of iodine reactions in olefins, in general, furnish information on new reaction channels (involving electrophilic attack on pi-bond systems resulting in complex formation that lead to stable addition products), butenes bear special importance since they are the shortest carbon chain system possessing isomeric structures which may display steric (hindrance) and structural (double bond location) effects.

We have determined the total organic product yields for unmoderated samples of gaseous butene isomers: 1-butene, 21.4%; trans-2-butene, 23.8%; cis-2-butene, 53.5%; and 2-methyl-propene 58.5%. We have further determined the identity of (some) individual products (and IOPY values) finding CH_3I the major product in 1-butene (10.2%), trans-2-butene (7.5%) and 2-methyl-propene (13.9%). Vinyl iodide (3.6% and 7.5% respectively) appears to be the second largest product in 1-butene and trans-2-butene. These products are tentively ascribed to decomposition channels of iodine-butene reactions. Also found are stabilization products (butyl-iodides, 3.0 and 4.9% in 1-butene and trans-2-butene respectively). Large decomposition IOPY values are found in 2-methyl-propene (CH_3I , 13.9%; $\text{C}_3\text{H}_7\text{I}$, 11.1%) but are overshadowed by the much larger stabilization product (butyl iodide, 22.2%). The structures

of the butyl iodide products (except n-butyl iodide in the 1-butene system) remain unidentified at this time. We intend to complete our radiogaschromatography on these systems and to identify positively all remaining products in the above systems as well as cis-2-butene.

Gas phase moderator studies of total organic product yields (TOPYs) have been completed on 1-butene and cis- and trans-2-butene. Our data show a reduction in TOPY values for all systems, the magnitudes of which are: 1-butene, unmoderated- 21.4%, He and Kr- 3%, Xe- 20%; cis-2-butene, unmoderated- 53.5%, Xe- 32%, He and Kr 215.5%, trans-2-butene, unmoderated- 23.8%, Xe- 5%, He and Kr 20%. Moderator studies⁴ of ¹²⁸I with hydro- and halocarbon systems generally display TOPY reduction characteristics of He $\approx$ Kr < Xe where helium, krypton and xenon reduce TOPY values as a result of kinetic energy moderation. The additional reduction in TOPY in xenon moderation studies has been explained by Rack and Gordus¹⁷ as near-resonance charge exchange of xenon with iodine ions in the ¹D₂ electronic state. Pettijohn and Rack¹⁸ studied the effects of moderators on the reactions of radiative neutron capture activated iodine-128 with the olefins ethene and propene and found that propene followed the moderator order previously described. Ethene, however, was found to react, in the presenece of moderators, opposite to most halo- and hydrocarbon systems, i.e. Xe < Kr $\approx$ He. Our tentative explanation was that ethene formed complexes with ionic iodine in ion-molecular reaction. We note this moderation order (Xe < Kr $\approx$ He) in cis- and trans-2-butene while 1-butene exhibits the (normal) order of He $\approx$ Kr < Xe found for kinetic energy and electronic excitation of iodine. Although moderator studies have not been completed for 2-methyl-propene,

we predict the order $\text{He} \approx \text{Kr} < \text{Xe}$ will be found. For the olefins reported above we see a pattern emerging. Moderation order is a function of bond location (structure). Double bonds located asymmetrically within the molecule (propene, 1-butene) display normal moderation order ($\text{He} \approx \text{Kr} < \text{Xe}$) indicating the importance of kinetic energy and electronic excitation ($\text{I}^+(\text{}^1\text{O}_2)$) in reactions. Molecules with higher symmetry double bonds (ethene, cis- and trans-2-butene) show opposite moderation order ($\text{Xe} < \text{Kr} \approx \text{He}$) suggesting the importance of ion-molecule reactions and complex formation.

The results of Pettijohn and Rack¹⁸ and our current work with butenes suggest that reactivities of ^{128}I with olefins are functions of carbon chain length (TOPY values increase) and steric effects around the double bond. The mode of reaction (hot, electronic excitation and/or ion-molecule) varies with molecular symmetry. Upon completion of individual product identification and moderator studies a manuscript will be submitted to the Journal of Physical Chemistry. Butene studies will be continued in the gas to condensed phase and studies of pentene isomers will be initiated to provide further tests for the concepts presented above.

3) Radiative Neutron Capture Activated Reactions of Iodine with Acetylene: We have found (n, γ)-activated ^{128}I adds to acetylene in the gas phase. The extent of organic retention is $14.9 \pm 0.6\%$. Individual product analysis (Table I) reveals the existence of seven products in the gas phase ranging in complexity from CH_3I (0.49%) to $\text{CH}_3\text{CH}_2\text{CHICH}_3$ (1.10%) and abundance from $\text{C}_2\text{H}_5\text{I}$ (9.30%) to $\text{CH}_3(\text{CH}_2)_3\text{I}$ (0.20%).

Moderator studies of the gaseous iodine-acetylene system show a reduction in TOPY values from (unmoderated) 14.9% to 12.9% in helium and

krypton and 8.8% in xenon. Utilizing radiogas chromatography we studied IOPY values as a function of mole fraction helium, krypton and xenon. Minor product did not produce definitive trends due to the large relative error magnitude associated with small measured values and CH_3I and CH_2I_2 was treated as a single entity ($\Sigma \text{C}_1 \text{ COPY}$). This channel ($\text{CH}_3\text{I} + \text{CH}_2\text{I}_2$) was found to be insensitive to the mole fraction of all moderators, indicating complete thermal character. The major product, ethyl iodide, shows a decrease in IOPY from $9.3 \pm 0.5\%$ to $5.7 \pm 0.5\%$ in krypton ($6.1 \pm 0.5\%$ in helium). This 4% drop is the result of kinetic energy dependent (hot) reactions. We suggest that the additional 4.1% drop of ethyl iodide (to 1.6%) is due to $\text{I}^+ (^1\text{D}_2)$ reactions. Since ethyl iodide is the only product which is sensitive to kinetic energy moderators and electronically deexcited by xenon we may ascribe a 3.6% "hot" IOPY and 4.1% $\text{I}^+ (^1\text{D}_2)$ IOPY to ethyl iodide. The secondary addition products, 2-iodopropane and 2-iodobutane increase with increasing mole fraction of moderators; the magnitude of the 2-iodopropane product being in the order $\text{He} < \text{Kr} < \text{Xe}$. As discussed in subsection 2 of this section, this trend is indicative of molecular-ion-complex or ion-molecule reactions. The increase of these products partially shadows the effect of kinetic energy moderations in the TOPY data.

We studied the effect of 30 mol % O_2 on TOPY and IOPY values and found a reduction but not a total quenching of reaction products. The TOPY value is reduced from 14.9% to 7.0%. The $\text{C}_2\text{H}_5\text{I}$ TOPY values dropped to 4.8% from 9.3% the minor products vinyl iodide and isopropyl iodide were reduced to 0.36% and 1.83% respectively and no other products were observed. The observance of only three of seven products, with reduction

in two, suggests the presence of some radical reactions, but that the pathways are not solely radical in nature. This has been independently demonstrated in that, unlike olefins (subsection 1, this section), no photochemical addition of iodine to acetylene has been found by us.

The IOPY data summarized in Table I when compared to higher density IOPYs (discussed in section 3 - Gas to Condensed Phase Transition) reveal a pattern emerging from groupings of individual organic product yields. These groupings will be referred to as Channels of Organic Product Yields or COPYs. These COPYs are similar, but not equivalent, to the concept of reaction channels as the term is used in chemical kinetics. A kinetic channel describes a particular mechanistic route resulting in product formation. We grouped individual products into three reaction classes: (1) decomposition (ΣC_1 COPY), (2) stabilization (ΣC_2 COPY) and (3) further addition ($\Sigma C_3 + \Sigma C_4$ COPY). The product analysis suggests the formation of an iodine-acetylene reaction complex as the first step in stable product formation. Our proposed reaction scheme is:

where reaction (A) is the activation of ^{128}I resulting in excess kinetic energy, positive charge and/or electronic excitation energy, (1) is the creation of the iodine-acetylene complex, (2) the decomposition of the complex to form CH_3I or CH_2I_2 by hydrogen abstraction or iodine scavenging (ΣC_1 COPY), (3) the addition of a second acetylene to form butyl iodides (ΣC_4 COPY, 3') or expulsion of a C_1 unit to propyl iodide (3a), (3b possible expulsion of a C_2 unit), (4) the formation of a vinyl iodide secondary intermediate which may stabilize (5) or abstract $\text{H}\cdot$ (6) to form ethyl iodide. It also appears that addition to the iodo side of the $[\text{C}_2\text{H}_2\text{I}^+]_{\text{exc}}$ complex is preferred as evidenced by (see Table I) the small yield of n-butyl iodide and the absence of n-propyl iodide.

Due to the paucity of thermodynamic data concerning iodine containing compounds, we report no probable heats of reaction. We are undertaking an ion cyclotron resonance study in an attempt to obtain suitable thermodynamic information.

Significance:

1) We have evidence for photochemical addition of iodine to olefins but not acetylene systems. This addition displays 3/2 order kinetic behavior suggesting the importance of I_2 in the reaction scheme.

2) A new reaction channel was found for the iodine-acetylene system which involves a reaction intermediate that forms primarily addition products.

3) Evidence of reactions in butenes and acetylene are resulting in the development of dynamical and energetic concepts for a concise theory of electrophilic attack of heavy halogen "hot" ions in ground and excited electronic states. This theory will specifically detail the importance of pi-bond electronic density, bond location and steric effects.

3. Gas to Liquid to Solid Transition in Hot Atom 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 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 effect of collapsing molecular environment on high energy atoms or ions and their reaction channels 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 5).

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 4).

Progress. We studied¹⁹ the effect of the gas to condensed phase transition on radiative neutron capture activated ^{128}I in acetylene. The gas phase study provided a possible reaction scheme which would be interesting to observe in the gas to condensed phase transition. The iodine and acetylene system also provides an opportunity to test methods and concepts developed in our work²⁰ with bromine-80 activated by radiative neutron capture and bromine-82 activated by isomeric transition reacting with various halomethanes. These methods and concepts include the use of normalized intermolecular distance (λ/σ) to predict the onset of caging and the degradation effect and packing effect parameters.

Other workers have studied the gas to condensed phase transition in nuclear transformation reaction of halogens with halomethanes,²¹ diastereomers²² and saturated fluoroethanes.²³ Radiative neutron capture activated ^{128}I in reaction with acetylene is the first gas to condensed phase system studied which reacts solely through pi-bond addition leading to complex formation. The iodine-acetylene system provides an environment for the direct study of enhancement yields resulting from a reaction complex.

Presented in Table II is a summary of COPY, TOPY and selected IOPY values for various experimental conditions ranging from atmospheric gas to low temperature liquid. It was not possible to study a solid state system because of fractional crystallization of the sample. Samples

with experimental conditions between 30 atm gas and room temperature liquid were not attempted as a result of explosive hazards in the reactor caused by the low critical temperature (35.5°C) and high critical pressure (61.6 atm) of acetylene.

Three characteristics of Table II are noteworthy: 1) the TOPY remains approximately constant from 1 to 30 atm., 2) the ΣC_2 COPY (stabilization channels) increase at the expense of the secondary addition ($\Sigma C_3 + \Sigma C_4$ COPYs) and decomposition (ΣC_1 COPY) until IOPY increases to a maximum and then decreases until it disappears. At high pressures and liquid state conditions the IOPY, COPY and TOPY values are experimentally identical. The sole product observed is ethyl iodide, $C_2H_5^{128}I$.

Root has suggested²³ that an approximately constant total yield with redistributing yields of individual reaction channels is an indication of an RRKM reaction mechanism. We observe a constant TOPY value in the range 1-30 atm. but the existence of C_3 - and C_4 -iodides implies the iodine-acetylene reaction complex is not wholly unimolecular in nature, since a second acetylene must add to the complex (in bimolecular combination) to form carbon chains of the observed length. However, the disappearance of further addition products ($\Sigma C_3 + \Sigma C_4$ COPYs) suggest the dominance of unimolecular over bimolecular pathways and the depletion of decomposition products (ΣC_1 COPY) is consistent with RRKM theory,²⁴ showing increasing stabilization (ΣC_2 COPY) with increasing density.

The behavior of vinyl iodide IOPY values is unusual in that the values increase to a maximum ($28 \times 10^{-3} \text{ g cm}^{-3}$), followed by depletion until C_2H_3I disappears. The vinyl iodide product is the result of collisional stabilization of the secondary reaction intermediate, $[C_2H_3I^+]_{exc}$.

An alternate to stabilization of the second reaction intermediate is hydrogen abstraction followed by stabilization. Hydrogen abstraction is an endoergic process which provides non-radiative deexcitation (by reaction) in addition to collisional deexcitation.

The ethyl iodide product ($C_2H_5^{128}I$) is formed by a pathway allowing for greater deexcitation than vinyl iodide ($C_2H_3^{128}I$) and results in a thermodynamically more stable product.

Our COPY vs. density studies of ^{128}I with acetylene show typical characteristics of the Richardson-Wolfgang type,²¹ but display a stronger similarity to the isomeric transition activated $^{82}Br + CH_3Br$ system than the (n, γ)-activated $^{80}Br + CH_3Br$ system. Iodide-128 activated by radiative neutron capture and bromine-82 activated by isomeric transition compare favorably with each other when contrasted with (n, γ)-activated ^{80}Br since the former displays lower kinetic energy and higher charge populations than ^{80}Br .

The COPY data as a function of normalized intermolecular distance (λ/σ) display similar behavior to that of bromine-halomethane systems previously reported. Normalized intermolecular distance (λ represents the intermolecular distance; σ the solvent molecule diameter) provides a method of direct comparison among different systems. The data appear as two approximately linear segments intersecting at a value of $\lambda/\sigma = 1.42$. At $\lambda/\sigma > 1.42$ the segment is almost horizontal and has been ascribed²⁰ to molecular reactions while at closer intermolecular distance ($\lambda/\sigma < 1.42$) the segment is diagonal and ascribed to enhancement reactions.

The packing effect and degradation effect parameters previously developed in our halogen-halomethane work²⁰ were not directly applicable

in this system. The energy degradation factor (fraction of translational energy lost by a high energy atom or ion in collision with a solvent molecule) is much lower in $^{128}\text{I} + \text{C}_2\text{H}_2$ than $^{80}\text{Br} + \text{CH}_3\text{Br}$ but C_2H_2 , unlike CH_3Br , acts as a reactive cage wall; i.e., in addition to collisional energy degradation, endoergic hydrogen abstraction provides a non-radiative deexcitation pathway. The packing effect correlates molecular diameter with "holes" in the cage wall. While acetylenes molecular diameter (4.2 Å) compares favorably with that of CH_3Br (4.13 Å) two important differences are present. First, CH_3Br has a much larger EDF resulting in CH_3Br being more difficult to dislocate, which would result in a "hole" in the cage wall. Secondly, C_2H_2 is spheroidal only when molecular rotations are excited. When molecular rotations are not excited, as near the freezing point (-80.8°C), the molecules more closely resemble an ellipsoid, possessing both a long and short axis. As these molecules attempt to orient in crystalline configuration, "holes" open along crystal orientations.

Significance.

- 1) A new reaction channel has been observed in the (n, γ)-activated $^{128}\text{I} + \text{C}_2\text{H}_2$ system resulting in complex formation from electrophilic attack of a positively charged heavy halogen on a dense pi-bond system.
- 2) The $\text{I} + \text{C}_2\text{H}_2$ system is the first direct study of the enhancement reactions of a reaction complex and provides a test system for theories of enhancement yields and molecular reactions.
- 3) A framework for the development of rules of reactivity for high energy monovalent electrophilic attack on pi-bond systems is provided by the iodine-acetylene system.

4. Kinetic Theory Applications of Hot Atom 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. No significant progress in gas phase kinetic theory development of heavy halogen hot atom reactions was done during this contract period.

Three general schools of thought apply to the nature of enhancement yields in high-density halogen hot atom chemistry; radical cage reactions,^{20,25} unimolecular decay theory applications,²³ and caged complexes.²² While these theories have emerged from diverse hot atom reaction studies; they try to explain the general nature of enhancement product yields found in high pressure gas and condensed phase systems.

In their work with $^{18}\text{F} + \text{CH}_3\text{F}$, Richardson and Wolfgang²¹ suggested that the enhanced product yields of CH_3^{18}F and CH_2^{18}F were the result of radical cage reactions. They felt that in systems with small inter-

molecular distances any reaction complex would have to be stabilized within a period of vibration and therefore could not have previously existed (as a chemically bound entity). This does not invalidate the concept of collisional stabilization; rather prevents its invocation to explain the appearance of new products in the condensed phase. One of the strong points of the radical cage reaction concept is its ability to explain the emergence of new products in the condensed phase that cannot be the result of simple molecular reaction. The new products are the results of the hot atom being "trapped" within the confines of a cage cell with radicals of its own creation. The hot atom after cooling can combine with these radicals to form products.

Unimolecular decay theory has been employed recently to investigate the nature of enhancement yields.^{23,26} In low to moderate density systems it has proved valuable in explaining the yields and variety of products in hot atom chemistry. Root and co-workers²³ have extended the unimolecular complex concept to condensed phase systems of ^{18}F with CF_3CH_3 and CH_2FCF_3 . The activated complex is envisioned as an energy sink of loosely coupled oscillators which interchange energy. Although molecular rotations and reorientations are allowed in RRKM theory, unimolecular decay cannot explain products indicative of extensive scavenger reaction. Recently,²⁷⁻²⁹ non-RRKM kinetic behavior has been found in several systems which indicate the failure of the random lifetime distribution. If, as Richardson and Wolfgang suggest,²¹ high density systems imply stabilization within a vibrational period then RRKM theory should be inapplicable due to non-randomization of energy.

Halogen hot atom for halogen substitution reaction studies²² of diastereomeric molecules as functions of phase and solvent have led to

the suggestion of a "caged" complex. In this hypothesis an electronically excited intermediate is held together by the solvent for a time sufficient for reaction. The adduct formed from the hot atom and substrate constitute the sole occupants of the cage cell, thus bridging the idea of a complex with caging reactions. The complex, however, need not be chemically bound as no interchange of internal energy is necessary.

To overview the controversy it is necessary to examine the reaction channels observed in each type of experiment. Our work in halomethanes with hot bromine atoms²⁰ has contributed to the radical cage reaction hypothesis, but has been limited to substitution and combined substitution-abstraction reactions. Abstraction reactions are not observed because of experimental difficulties (rapid thermal exchange of HBr with Br₂). The importance of the degradation and packing effects and the emergence of new products in the condensed phase, e.g. CHBr₃ and CBr₄ in CH₃Br + Br₂ systems can only be explained by cage radical reactions. In order to utilize RRKM theory,²⁴ all reaction channels must be quantitatively observed; however, new products in condensed phase^{20,25} and some critical applications^{25,26} have been found inconsistent with RRKM behavior. The caged complex hypothesis is based on substitution reactions on diastereomers in various phases. The caged complex requires no internal energy redistribution and no external source of atoms, radicals or molecules for reaction. It is for the latter reason that a caged complex cannot account for products formed by heavily scavenged systems.

The iodine-acetylene system is unlike any other hot halogen system in that the number of observed products decrease rather than increase in the gas to condensed phase transition. In the high pressure region and

liquid state, only one product, $C_2H_5^{128}I$, was observed. Our proposed reaction scheme suggests the formation of an electronically excited reactive intermediate, $[C_2H_2I^+]_{exc}$. The gas to condensed phase transition data do not indicate any evidence for cage radical reactions. Therefore, the gas to condensed phase study should suggest whether a complex can cage and have behavior similar to that predicted for radical reactions.

While it would be desirable to characterize the nature and lifetimes of reaction complexes on a rigid mathematical basis employing the arguments presented by Richardson and Wolfgang²¹ it is virtually impossible for the following reasons: (1) the distribution of the hot atom's translational energy into internal and translational modes of the complex is not known; (2) the intermolecular distance required in the collisional lifetime calculations is dependent on the microscopic density which cannot be assumed identical to the macroscopic density because of local perturbations and possible radical formation; (3) the unimolecular rate constants for RRKM kinetic lifetimes is experimentally unobtainable; and (4) the energy distribution function is non-Boltzmann in nature as a result of incomplete thermalization.

A "true" unimolecular complex requires $\geq 10^{-12}$ sec to completely randomize internal energy.³⁰ Lifetimes of this magnitude require low internal energies and small collision numbers. These conditions require thermal or near-thermal systems at low to moderate pressures. An order of magnitude calculation of the collisional lifetime in comparison with simple RRK kinetic lifetimes³⁰ indicates that the condensed phase iodine-acetylene reaction complex is collisionally limited and of the order of a vibrational period or less ($\sim 10^{-14}$ sec). We must conclude

that an insufficient time is available to the complex for energy redistribution and concede the possibility that the complex might not be chemically bound as a result of lack of vibrational modes. Although gas phase calculations appear to be of the same order of magnitude (10^{-13} to 10^{-12} sec) or greater than RRK calculations, the lifetime cannot be ascribed to collisional or kinetic limitation because of large uncertainties in the calculations. In either case, it is only possible to obtain sufficient time for energy redistribution at low pressures and low internal energies.

We must conclude that except at low energies and pressures, unimolecular decay complexes do not play a significant role in product formation.

Analysis of our product yields as functions of density (pressure), intermolecular distance and phase shows that a collapsing molecular environment decreases the decomposition and secondary addition modes by increasing stabilization as we would expect. In contrast to our halo-methane study²⁰ the number of products has decreased in the gas (7) to condensed (1) phase transition. Caging radical reactions suggest the opposite trend with an increase in the number of observed products with increasing density.

Our data suggest that in the iodine-acetylene system the enhancement yield increase is due to the caging of the electronically excited complex. It is our contention that unless systematic studies and consideration of all reaction channels that can be observed involved in the hot atom reactions, we cannot on an a priori basis conclude that enhancement yields are primarily the result of a cage radical or caged complex reaction.

We feel that kinetic energy, positive charge, and electronic excitation energy of ^{128}I with subsequent electrophilic attack on the acetylene bond system result in an excited complex with unimolecular (low pressure) and caged complex (high pressure) characteristics.

The foregoing argument for the iodine-acetylene system suggests that further studies of the gas to condensed phase transition and computer simulations will yield a definitive set of rules for the prediction of the onset of enhancement reaction and characterization of molecular, complex, ion-molecule and enhancement reactions.

The iodine-acetylene work described in the olefin, gas to condensed phase and kinetic theory sections of this report have been prepared in manuscript form (U.S. E.R.D.A. document No. C00-1617-42) and submitted to the Journal of Physical Chemistry for publication.

Significance:

1) A lower limit of lifetimes for unimolecular complexes in relation to collisional lifetimes can be made. This evidence suggests the limited importance of unimolecular decay theory in explaining enhancement yields.

2) The available facts establish that more than one type of reaction can contribute to enhancement yields. These reactions do not appear to be molecular in nature.

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, $\text{X}_i^* + \text{RX}_j \xrightarrow{\text{Xi-for Xj}} \text{RX}_i^* + \text{X}_j$, 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. The progress in this contract period has been a collaboration effort with Dr. H. J. Ache of Virginia Polytechnic Institute and State University.

In a very important experiment Machulla and Stöcklin²² demonstrated the importance of rotational conformation on the stereochemical course of hot halogen for halogen substitution in liquid 2,3-dichlorobutane. Briefly what they found was that in the non-polar solvents the most predominant conformers were those where inverted attack from the opposite side of the halogen to be replaced can occur. In a joint project utilizing the facilities of both this laboratory and those of Prof. Ache we studied the solvent dependence of the stereochemistry of the ³⁸Cl for Cl substitution following ³⁷Cl (n,γ) ³⁸Cl in liquid meso and dl-(CHFC1)₂. The main purpose of these experiments are to serve as a test for the general applicability of the Stöcklin approach using solvents to determine the influence of rotational conformation on the nature of the liquid phase substitution process. We have completed the hot atom experimental phase of our study. Briefly what we found is that for both meso- and dl-(CHFC1)₂, increasing mole fractions of Br₂ or CH₃OH increased the retention/inversion ratio. The effect of bromine is greater than that of the CH₃OH solvent. Increasing mole fractions of the non-polar solvents cyclohexane or n-pentane decrease the retention/inversion ratio. The results are remarkably similar to those of Machulla and Stöcklin for

2,3-dichlorobutane. While it is tempting to make the obvious conclusions, we are awaiting the results of the conformational analysis employing nmr spectroscopy.

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. Hospital Staff has resulted in a waving of the reactor-irradiation fee and, generally, unrestricted use of the reactor and laboratory facility for our hot atom chemistry studies.

Progress. Aluminum is the third most abundant element in the earth's crust. It is not considered an essential trace element for animal life. However, it is an important element in that a large number of artifacts to which humans are exposed are made of aluminum metal and great quantities of aluminum compounds are consumed by the population for various clinical purposes. There has been raised, in recent medical literature,³¹⁻³⁷ the question of whether aluminum is retained in the body in significant amounts to result in toxicity. It has generally been assumed that aluminum is not harmful because it is an abundant element, but this reasoning is not necessarily true since silicon is also an abundant element and silicosis is a serious disease.³⁸ It has also been suggested that aluminum in blood tissue affects the activity of some physiological enzymes.³⁹

At the present time there is no good analytical procedure for the determination of aluminum in all biological matrices. As a result there is no definite idea as to what quantities of aluminum are considered normal in tissue, serum, bone, urine and feces. Considering the various complications³⁹ that exist in other techniques such as colorimetry and atomic absorption, the potentially most suitable technique is neutron activation analysis. Because of the low levels of aluminum found in biological matrices, except faeces, and complications due to the presence of sodium, chlorine, and phosphorous [$^{31}\text{P}(\text{n},\alpha)^{28}\text{Al}$], nondestructive neutron activation cannot be employed. A pre-irradiation wet chemical procedure is required because of the short half life of ^{28}Al ($T_{1/2} = 2.3$ min).

In developing an optimum procedure for urine which can have applicability to all biological matrices, we first evaluated the pre-irradiation procedures of Fritze and Robertson⁴⁰ who employed cation exchange chromatography with subsequent elution of the aluminum thru the resin employing hydrofluoric acid solution. One major drawback to their procedure - not indicated in their paper - is that commercial reagent grade hydrofluoric acid solutions contain large quantities of aluminum; in many instances larger than that in the biological sample to be analyzed. We found that the method of Gilmore and Goodwin⁴¹ which was applied for aluminum determinations in bone samples was not applicable to urine specimens which contain appreciable amounts of sodium. Irradiating the resin containing the aluminum as well as sodium and other cations not only increases the dead time of the Ge(Li) detection system, but also has the added complication of a large Compton contribution (mainly due to sodium)

in the aluminum area. For urine samples containing small aluminum concentrations, this complication renders the analytical results statistically meaningless.

Girardi et al⁴² suggested the use of hydrated antimony pentoxide (HAP) as a cation-exchanger for the removal of sodium ions. We have evaluated the use of both an anion exchange resin and HAP under various experimental conditions for the removal of sodium, chloride and phosphate ions and find that while the process may have further applicability, it is not suitable for urine specimens at this time.

Our procedure which gives us the best results involves the following operations. 1) Digestion of the urine with nitric acid by the Hahn, et al method.⁴³ 2) Treatment of the digested urine with 1 M HNO₃. 3) Elution of the nitric acid solution thru a Dowex AG 50 WX-8, 200-400 mesh cation resin which retained all of the sodium and aluminum ions. The phosphate and chloride ions passed thru the resin. 4) The sodium ions were removed by the passage of concentrated nitric acid thru the resin leaving the aluminum retained on the column. 5) The aluminum containing resin was radioassayed for the aluminum activity using a Ge(Li) detection system.

Significance

Normal and disease-stable aluminum levels in all biological matrices can now be readily determined. The role of aluminum levels in the environment and human welfare can be studied by using the developed procedure. This procedure can be used to concentrate the long-lived isotope ²⁶Al (half-life = 7.4×10^4 years) from biological specimens. ²⁶Al may be produced in the thermonuclear reactor if tritium breeding in LiAl is adopted (BNL-18636, 1973).

TABLE I

TOPY, COPY and IOPY Values of the Reaction of $^{127}\text{I}(n,\gamma)$
 $^{128}\text{I} + \text{C}_2\text{H}_2$ in the Gas Phase Without Additives

<u>Product</u>	<u>IOPY</u>	<u>Carbon Length</u> <u>COPY</u>	
CH_3I	0.49 ± 0.02		
CH_2I_2	0.70 ± 0.05		
		1.19 ± 0.07	ΣC_1
$\text{C}_2\text{H}_3\text{I}$	0.40 ± 0.05		
$\text{C}_2\text{H}_5\text{I}$	9.30 ± 0.46		
		9.70 ± 0.51	ΣC_2
$i\text{-C}_3\text{H}_7\text{I}$	2.71 ± 0.43	2.71 ± 0.43	ΣC_3
$\text{CH}_3\text{CH}_2\text{CHICH}_3$	1.10 ± 0.20		
$\text{CH}_3(\text{CH}_2)_3\text{I}$	0.20 ± 0.03		
		1.30 ± 0.23	ΣC_4

TOPY = $14.9 \pm 0.6\%$

Table II

TOPY, COPY and Selected IOPY Values in the Gas to
Condensed Phase Transition

<u>$\rho(\text{g cm}^{-3})$</u>	<u>λ/σ</u>	COPY					IOPY	
		<u>TOPY</u>	<u>ΣC_1</u>	<u>ΣC_2</u>	<u>ΣC_3</u>	<u>ΣC_4</u>	<u>C_2H_5I</u>	<u>C_2H_3I</u>
0.001 (1 atm)	8.35	14.9 $\pm$ 0.6	1.19	9.70	2.71	1.30	9.30	0.40
0.004	5.26	15.2 $\pm$ 0.7	0.22	12.4	1.88	0.70	11.4	0.76
0.008	4.18	15.4 $\pm$ 0.6	0.14	14.0	0.40	0.80	12.4	1.59
0.010	3.88	15.4 $\pm$ 0.4	0.14	15.3	--	--	14.4	0.85
0.032 (30 atm)	2.62	16.2 $\pm$ 1.3	--	16.2	--	--	16.2	--
0.388 (liq, 23°)	1.15	41.0 $\pm$ 1.3	--	41.0	--	--	41.0	--
0.465 (liq 0°)	1.08	49.0 $\pm$ 1.6	--	49.0	--	--	49.0	--
0.615 (liq, -78°)	0.98	56.3 $\pm$ 7.7	--	56.3	--	--	56.3	--

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Reprints
Removed*

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1. Frank J. Bryant, "The Radiolysis of Cyclopentace-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.
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