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THEORETICAL APPROACHES AND MECHANISTIC APPLICATIONS  
IN THE GAS TO CONDENSED PHASE TRANSITION OF  
HIGH ENERGY HEAVY HALOGEN REACTIONS IN  
ORGANIC SYSTEMS

by  
Michael Eric Berg

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In Partial Fulfillment of Requirements  
For the Degree of Doctor of Philosophy  
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Under the Supervision of Edward Paul Rack

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THEORETICAL APPROACHES AND MECHANISTIC APPLICATIONS IN THE GAS  
TO CONDENSED PHASE TRANSITION OR HIGH ENERGY HEAVY HALOGEN  
REACTIONS IN ORGANIC SYSTEMS.

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And especially, my parents for never doubting my abilities.

Michael Eric Berg

Dedicated to my loving family

It is a capital mistake to theorize  
before one has data. Insensibly one  
begins to twist facts to suit theories,  
instead of theories to suit facts.

A. C. Doyle

Against that positivism which stops  
before phenomena, saying "there are  
only facts," I should say: no, it is  
precisely facts that do not exist,  
only interpretations.

F. Nietzsche

## ACKNOWLEDGEMENTS

## LIST OF TABLES

## LIST OF FIGURES

CHAPTER I. Introduction . . . . .	1
A. Hot Atom Chemistry . . . . .	1
B. Characteristics of High Energy Reactions . .	2
C. The Generation and Characterization of Hot Species . . . . .	5
D. The Cage Effect . . . . .	11
E. Characterization of Enhancement Reactions .	13
F. Statement of Problem . . . . .	24
CHAPTER II. Experimental . . . . .	25
A. Materials . . . . .	25
B. Preparation of Reaction Systems . . . . .	25
C. Neutron Irradiation . . . . .	27
D. Total Organic Product Yields . . . . .	28
E. Radio-gas Chromatographic Separations of the Activated Mixtures . . . . .	29
CHAPTER III. The Kinetic Energy Spectra of Heavy Halogens Activated by Isomeric Transition . . . . .	32
A. Introduction . . . . .	32
B. Energetics of Nuclear Transformations . . .	33
C. The Kinetic Energy Spectra of (I.T.)- Activated $^{80}\text{Br}$ and $^{130}\text{I}$ . . . . .	35



	Page
CHAPTER IV. The Gas to Condensed Phase Transition .	59
A. Introduction . . . . .	59
B. Normalized Intermolecular Distance . . . . .	61
C. Product Formation Routes . . . . .	63
CHAPTER V. Systematics of Bromine Reactions Activated by Radiative Neutron Capture and Isomeric Transition with Halomethanes . . . . .	70
A. Introduction . . . . .	70
B. Results and Discussion . . . . .	72
CHAPTER VI. The Suggestion of Multiple Enhancement Reactions in High Energy Iodine-128- Ethane Systems . . . . .	111
A. Introduction . . . . .	111
B. Results and Discussion . . . . .	114
CHAPTER VII. A Computer Simulation Model for Evaluating Kinetic Theory Parameters in Hot Atom Chemistry . . . . .	133
A. Introduction . . . . .	133
B. The System . . . . .	137
C. The Model . . . . .	138
D. Results . . . . .	142
APPENDIX I. Computer Program . . . . .	147
Legend . . . . .	149
Program . . . . .	151

	Page
REFERENCES . . . . .	160
PUBLICATIONS AND PAPERS PRESENTED AT MEETINGS . . . .	169
Publications . . . . .	169
Papers Presented . . . . .	170

PREVIEW

# LIST OF TABLES

Table	Page
1-1 Physical Properties of Nuclear Transformations .	9
1-2 Order of Magnitude Calculations for Kinetic and Collisional Lifetimes . . . . .	20
3-1a Auger Cascade Charge Distribution and Ionization Potentials for $^{80}\text{Br}^m$ . . . . .	36
3-1b Auger Cascade Charge Distribution and Ionization Potentials for $^{130}\text{I}^m$ . . . . .	37
3-1c Ionization Potentials for Carbon and Hydrogen . .	38
3-2 Redistribution Coefficients for Ion of Charge +7 . . . . .	41
3-3a Relative Abundance of Energy Distribution for $^{80}\text{Br}^m\text{-Br}$ (Model II) . . . . .	43
3-3b Relative Abundance of Energy Distribution for $\text{CH}_3\text{-}^{80}\text{Br}^m$ (Model II) . . . . .	45
3-3c Relative Abundance of Energy Distribution for $\text{H-}^{80}\text{Br}^m$ (Model II) . . . . .	47
3-4a Relative Abundance of Energy Distribution for $^{130}\text{I}^m\text{-I}$ (Model II) . . . . .	48
3-4b Relative Abundance of Energy Distribution for $\text{CH}_3\text{-}^{130}\text{I}^m$ (Model II) . . . . .	49
3-4c Relative Abundance of Energy Distribution for $\text{H-}^{130}\text{I}^m$ (Model II) . . . . .	50
3-5a Comparison of Failure to Bond Rupture and Average Kinetic Energy for $^{80m}\text{Br(IT)}^{80}\text{Br}$ in $\text{Br}_2$ . . . . .	51

3-5b	Comparison of Failure to Bond Rupture and Average Kinetic Energy for $^{130m}\text{I}(\text{IT})^{130}\text{I}$ in $\text{I}_2$ . . . . .	52
4-1	Product Ratios for 1-iodobutane to 1-iodobutene in $^{128}\text{I}$ -butene-1 moderated system . . . . .	66
4-2	Product Ratios for 1-iodobutane to 1-iodobutene in the $^{128}\text{I}$ -butene-1 system . . . . .	67
5-1	Systematics of Bromine Halomethane Systems . . . . .	73
5-2	Approximate Maximum Kinetic Energies (eV) after 0, 1 or 2 collisions . . . . .	79
5-3	Effect of Mole Fraction $\text{Br}_2$ on Product Yields of $^{80}\text{Br}(\text{n},\gamma)$ in Liquid $\text{CH}_3\text{F}(23^\circ\text{C})$ . . . . .	84
5-4	Effect of Mole Fraction $\text{Br}_2$ on Product Yields of $^{82}\text{Br}(\text{I.T.})$ in Liquid $\text{CH}_3\text{F}(23^\circ\text{C})$ . . . . .	85
5-5	Effect of Density Variation on the $\text{Br}-\text{CH}_3\text{F}$ System Total Organic Product Yield Under Various Activations . . . . .	91
5-6	Total and Individual Organic Product Yields for the $^{82}\text{Br}(\text{I.T.})-\text{CH}_3\text{Br}$ System . . . . .	98
5-7	Total and Individual Organic Product Yields for the $\text{Br}(\text{n},\gamma)-\text{CH}_3\text{Br}$ System . . . . .	99
6-1	Total and Individual Organic Product Yields for the $^{128}\text{I}$ -ethane system . . . . .	120
6-2	Reactions of $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ with $\text{C}_2$ Hydrocarbons . . . . .	130

Table	Page
7-1 Dependence of Computer Model on Various Parameters . . . . .	143
7-2 Comparison of Experimental and Simulation Data for Iodine-128-Acetylene . . . . .	144

PREVIEW

# LIST OF FIGURES

Figure		Page
1-1	Hypothetical collision yield dependence on kinetic energy, for reaction of atomic halogen (X) with arbitrary compound RH . . . . .	3
1-2	Kinetic and collisional lifetimes for $\text{CH}_3\text{F}$ with $^{80}\text{Br}(n,\gamma)$ , $^{82}\text{Br}^m + ^{82}\text{Br}(n,\gamma)$ and $^{82}\text{Br}(\text{I.T.})$ . . . . .	22
1-3	Kinetic and collisional lifetimes for $\text{CH}_3\text{I}$ with $^{128}\text{I}(n,\gamma)$ and $^{130}\text{I}(\text{I.T.})$ . . . . .	23
3-1	Probability distribution of bromine ions <u>vs</u> recoil energy . . . . .	54
3-2	Probability distribution of iodine ions <u>vs</u> recoil energy . . . . .	55
3-3	Kinetic energy spectrum for $^{80}\text{Br}^m$ in $\text{Br}_2$ . . . . .	56
3-4	Kinetic energy spectrum for $^{130}\text{I}^m$ in $\text{I}_2$ . . . . .	57
5-1	Total organic product yield vs. energy degradation factor for halomethanes . . . . .	76
5-2	Effect of mole fraction $\text{Br}_2$ on total and individual organic product yields of $^{80}\text{Br}(n,\gamma)$ in liquid $\text{CH}_3\text{F}$ at room temperature . . . . .	86
5-3	Effect of mole fraction $\text{Br}_2$ on total and organic product yields of $^{82}\text{Br}(\text{I.T.})$ in liquid $\text{CH}_3\text{F}$ at room temperature . . . . .	87

Figure		Page
5-4	Total organic product yields as a function of density in the $\text{CH}_3\text{F} - \text{Br}_2$ system. . . . .	92
5-5	Total and individual organic product yields as a function of density in the $^{82}\text{Br}(\text{I.T.}) - \text{CH}_3\text{Br}$ system . . . . .	100
5-6	Total and individual organic product yields as a function of density in the $^{80}\text{Br}(\text{n},\gamma) - \text{CH}_3\text{Br}$ system . . . . .	101
5-7	Effect of normalized intermolecular distance on the total organic product yields of $(\text{n},\gamma)$ -activated Br in halomethanes . . . . .	104
5-8	Effect of normalized intermolecular distance on the total organic product yields of $^{82}\text{Br}(\text{I.T.})$ in halomethanes . . . . .	105
5-9	Effect of normalized intermolecular distance on the total organic product yield of halogen-halomethane systems . . . . .	109
6-1	Organic yields vs. density for $^{128}\text{I} + \text{C}_2\text{H}_6$ . . . . .	121
6-2	Total and individual organic product yields vs. normalized intermolecular distance . . . . .	123

## CHAPTER I

### INTRODUCTION

#### A. Hot Atom Chemistry

Hot atom or high energy chemistry is the study of translationally excited species (atoms, radicals, ions, and neutral molecules) in reaction with a thermal chemical environment. The "hot" species may be generated by photochemical, beam acceleration, nuclear transformation or other means, and generally possess energies in the eV up to the MeV range. This is in sharp contrast to thermal equilibrium chemical studies where Maxwell-Boltzmann statistics predict energies less than a few tenths of an electron volt.

The first reported study of hot atom chemistry was in 1934 by Szilard and Chalmers.<sup>1</sup> They found that after irradiation of ethyl iodide followed by extraction, iodine-128 was found in the aqueous phase. They hypothesized that the momentum of the captured thermal neutron was sufficient to rupture the C-I bond and that recombination did not have to occur. The following year Amaldi and co-workers<sup>2</sup> proposed that the bond rupture was due to a cascade of gamma rays resulting from the de-excitation of a compound nucleus. Glueckauf and Fay<sup>3</sup> reported that irradiated halogens could react with alkyl halides to form new carbon-halogen bonds.

From these beginnings the field has grown to embrace all halogens, tritium and other atoms. Several review articles



have appeared concerning the reactions of high energy species with organic compounds: Willard,<sup>4-6</sup> Wolfgang,<sup>7-9</sup> Wolf,<sup>10</sup> Urch<sup>11</sup> and Rowland.<sup>12</sup> A complete bibliography of all publications in hot atom chemistry through 1962 has been collected by Suida.<sup>13</sup> Through the efforts of J. P. Adloff<sup>14</sup> an annual listing was made available through 1975.

#### B. Characteristics of High Energy Reactions.

The chemical effects of nuclear transformations and other activations methods that produce translationally excited species show a diversity of reaction products and product formation routes not normally associated with thermal chemistry. By virtue of its activation the hot species is not in thermal equilibrium with its environment. Collision with its environment may result in three possible events: (1) collisional cooling, i.e. the (partial) de-activation of the hot species by collision with a thermal molecule. This is governed in the highest energy regions by kinetic energy and momentum conservation ("hard" collision) and by general energy transfer to all available degrees of freedom ("soft" collision) at lower energies; (2) thermal reaction where the translational energy of the hot species permits an ease of access across the energy barrier (activation energy) not usually found in thermal equilibrium systems; or (3) the formation of a product or products not available to thermal species. See Figure 1-1. These products are formed via reaction paths which have finite (non-zero) reaction cross

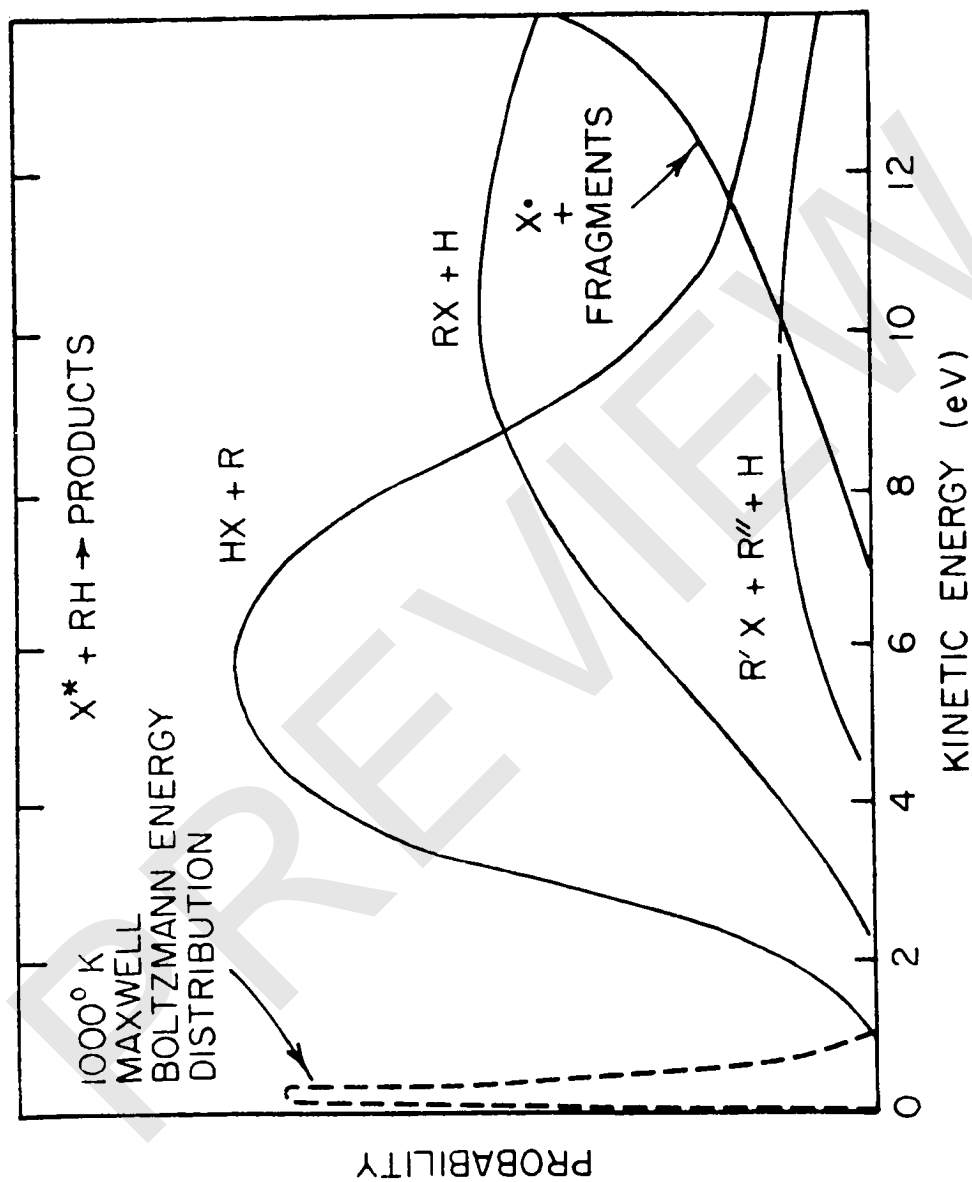


Figure 1-1. Hypothetical collision yield dependence on kinetic energy, for reaction of atomic halogen (X) with arbitrary compound RH.

sections only at high energies.

High energy reaction systems may display the following attributes:

a. If a particular product yield shows no temperature and little or no pressure dependence at low to moderate pressures (1-10 atm.) then this is evidence for a hot reaction mechanism. However, pressure and phase dependence do not constitute sufficient criteria to reject a hot reaction.

b. A product formed via a high energy mechanism will display a decrease in yield with the addition of rare gas moderators due to collisional deexcitation of translational energy.

c. High energy product formation routes often lead to stabilized products which are energetically inaccessible to a chemically equivalent thermal system.

d. Reaction yields due directly to primary events (substitution, abstraction) are not changed by the addition of small amounts of radical scavengers. Secondary products formed by multiple step processes (stabilization reactions or enhancement reactions) may be strongly affected by added scavengers.

The study of high energy chemistry provides a method to investigate the entire non-thermal range of chemical reactions and their mechanisms as well as thermal reactions which normally require the input of large amounts of energy

to initiate product formation. Thus high energy chemistry may be a useful tool in the investigation of chemical kinetics, systematics and dynamics.

### C. The Generation and Characterization of Hot Species

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 reveal information or 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.

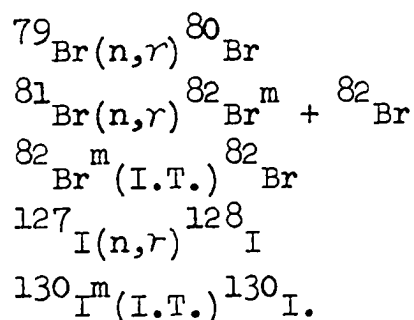
Bulb techniques are multi-collisionally oriented. The kinetic energy imparted to atoms or ions are the result of nuclear recoil or photochemical recoil activation. While photochemical and some nuclear activation modes produce atoms, ions or radicals within narrow kinetic energy limits the multi-collisional 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) may be 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 or 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.

Nuclear transformations may occur when a target nucleus (A) is bombarded by an incident nuclear particle (a). The number of transformations is dependent upon reaction cross

section, intensity of incident particles (a), concentration of target nuclei (A) and duration of irradiation. The reaction is initiated by the formation of a compound nucleus (A+a); the degree of excitation dependent on the energy of (a). The compound nucleus model assumes strong interactions among all nucleons in the compound nucleus, leading to equipartition of the excitation energy and consequent loss of identity of (a). The compound nucleus is thought to have a mean life time of  $10^{-16 \pm 3}$  seconds, after which dissociation occurs. The dissociation may be the emission of one or two particles (e.g.  ${}^3\text{He}(n,p){}^3\text{H}$  or  ${}^{19}\text{F}(n,2n){}^{18}\text{F}$ ) or one or more high energy photons (gamma rays). In the former case, the new nucleus ("hot" atom) is born with energies within a narrow range; the range being determined by the laws of conservation of mass-energy, linear and angular momentum. In the latter case, the hot atom may be born with a spectrum of kinetic energies, each hot atom having its energy determined by the vector sum of kinetic energies imparted by the (isotropic) gamma ray cascade.

This work is concerned with activations of the second kind, viz:



A comparison of these and other nuclear transformations may be found in Table 1-1.

The  $(n,\gamma)$  or radiative neutron capture transformation is initiated by a thermal neutron being captured by the target nucleus. The excitation energy is sufficient to emit a nucleon but is dissipated by the emission of one or more gamma rays. It is the emission of these photons which, due to conservation of momentum, provides the high translational energy of the recoiling species.

The recoil energy spectrum is a continuous function varying from zero to a maximum of  $(537 B^2/M)$  eV in which  $B$  is the neutron binding energy and  $M$  is the atomic mass of the hot atom. Maximum recoil would be obtained when one gamma ray, equivalent to the entire excitation energy, was the sole emission. This has not been experimentally observed. The recoil energy spectrum is obtained since the momenta of several  $\gamma$ -rays emitted in an isotropic cascade may partially or entirely cancel each other.

If the component of recoil energy in the direction of a chemical bond is less than the bond energy it will remain bonded. Although failure to bond rupture is a rare event it has been experimentally measured as 1.1% for  $\text{CH}_3^{128}\text{I}$  and less for other  $(n,\gamma)$  events.<sup>15,16</sup>

Internal conversion can provide an alternate mechanism for nuclear de-excitation. If an emitted photon is captured by an inner (K, L or M) shell electron the electron obtains

TABLE 1-1

## PHYSICAL PROPERTIES OF NUCLEAR TRANSFORMATIONS

Isotope	Reaction	Neutron Energy (MeV)	Recoil Energy	Half-Life
$^3\text{H}$	$^3\text{He}(n,p)$	high	1 MeV	12.26 y
$^{18}\text{F}$	$^{19}\text{F}(\gamma,n)$	--	1 MeV	110 m
$^{18}\text{F}$	$^{19}\text{F}(n,2n)$	15.0	0.7 MeV	110 m
$^{38}\text{Cl}$	$^{37}\text{Cl}(n,\gamma)$	thermal	Max. 530 eV	37.3 m
$^{80}\text{Br}$	$^{79}\text{Br}(n,\gamma)$	thermal	Max. 417 eV	17.6 m
$^{82}\text{Br}$	$^{81}\text{Br}(n,\gamma)$	thermal	Max. 360 eV	35.4 h
$^{82}\text{Br}$	$^{82}\text{Br}^m(\text{I.T.})$	---	Max. 153 eV	35.4 h
$^{128}\text{I}$	$^{127}\text{I}(n,\gamma)$	thermal	Max. 194 eV	25.0 m
$^{130}\text{I}$	$^{130}\text{I}^m(\text{I.T.})$	---	Max. 80 eV	12.5 h