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HALOGEN ATOM REACTIONS ACTIVATED BY NUCLEAR
TRANSFORMATIONS

Progress Report No. 9

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PROJECT ABSTRACT

By employing radiogas chromatography, solvent extraction, the freeze-thaw method and other techniques for determining total organic and individual product yields induced by radiative neutron capture (n,γ), isomeric transition (IT), and other nuclear processes, "hot atom" reactions of chlorine, bromine and iodine are being studied extensively in various gaseous, liquid, and solid halomethanes, hydrocarbons and other organic systems. The study of the systematics of hot atom reactions in the gaseous state will be continued. The reactions of ^{38}Cl , $^{80}\text{Br}^m$, ^{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 halo-substituted alkanes will be further studied. Of importance will be calculations of kinetic energy spectra of hot atoms activated by radiative neutron capture and isomeric transition, where possible, using various computer techniques. The gas to liquid to solid transitions in halogen hot atom chemistry, involving isotopes of chlorine, bromine and iodine activated by the (n,γ) and (IT) processes will be investigated in more detail. Attention will be given to the high pressure gaseous reactions and those occurring near the critical temperature region. The reactions of iodine with olefins and acetylene will be continued. Reactions of ^{123}I , ^{128}I , ^{130}I , and $^{130}\text{I}^m + ^{130}\text{I}$ with various gaseous, liquid and solid olefins and acetylene (in the gas to condensed state transition) will be studied employing iodine, rare-gas moderators or molecular additives in an attempt to learn more about the systematics and mechanisms of complex iodine hot and thermal reactions. The stereochemistry of energetic

$^{34}\text{Cl}^m$, ^{38}Cl , ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br substitution reactions involving organic molecules containing one asymmetric carbon as well as the diastereomers 2,3-dichlorobutane and $(\text{CHFCl})_2$ will be continued. The general applicability of kinetic theories to heavy halogen gaseous systems will be studied. The application of hot atom chemistry techniques and theory to chemical problems ranging from neutron activation analysis to iodine addition to olefins will be continued.

PREFACE AND LEGAL NOTICE

The following is a report of the work completed during the period February 15, 1974 to February 14, 1975. These studies were supported by the U.S. Atomic Energy Commission, Division of Research, Contract No. AT(11-1)-1617, the Department of Chemistry of the University of Nebraska, and the University Research Council. Most of the material for this report had been submitted, or accepted for journal publication.

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FACILITIES

A. Triga Mark II Reactor

All neutron irradiations were made in the Triga Mark II "swimming pool" nuclear reactor at the Veteran's Administration Hospital at 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 min.⁻¹ using Fricke dosimetry.

The Brookhaven National Laboratory 60" cyclotron was used for production of $^{34}\text{Cl}^{\text{m}}$ and the epithermal patient facility at the Brookhaven Research Reactor was used for the production of ^{38}Cl , whose hot atom chemistry and retention of optical configuration studies were performed in the laboratory of Dr. A. P. Wolf.

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 August 1, 1973 to July 31, 1974, 285 hours (integrated time in reactor) at 15.5 kilowatts power, making 1,800 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}~~cadmium~~, and lead cave.

A small portable radiogas chromatograph is presently being built to be located in the radiochemistry room of the Omaha V.A. Hospital reactor, allowing us to analyze routinely many more samples containing ^{128}I and ^{80}Br . 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 VA Hospital. The use of their RIDL 400-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

Since the discovery of chemical effects of nuclear transformations or hot atom chemistry in 1934 by Szilard and Chalmers,¹ the field has dramatically expanded from studies of simple liquid organic halides to seven well-defined areas, as outlined at the 7th International Hot Atom Chemistry Symposium at Jülich. These are as follows:

1. Theoretical Aspect of Hot Atom Reactions
2. Chemical Dynamics of Hot Atoms Reactions; Beam Studies
3. Gas and Liquid Phase Hot Atom Chemistry
4. Solid State Reactions of Recoil Atoms and Implanted Ions
5. Chemical Effects of Radioactive Decay
6. Consequences of Nuclear Transformations in Biomolecules
7. Applied Hot Atom Chemistry

Of these areas our interest and progress have been made in areas (3) and (7).

Since the discovery of the short-lived isomers $^{82}\text{Br}^m$ and $^{130}\text{I}^m$ it is now possible to do extensive studies of radiative neutron capture and isomeric transition activated reactions of bromine and iodine in gaseous and condensed state organic media.²⁻⁴ Willard in a review⁵ stated that dominant among the questions to which answers are being sought are: (1) the relative importance of kinetic energy and of charge in determining the chemical fate of the atoms studied, and (2) the effect of phase on mechanisms which lead to chemical stabilization.

In our attempt to answer these questions in chlorine, bromine and iodine hot atoms chemistry we are concentrating our efforts in five areas:

- (1) Systematics of halogen hot atom reactions.
- (2) Gas to liquid to solid transitions in halogen hot atom chemistry.
- (3) Reactions of iodine with olefins.
- (4) Stereochemistry of chlorine, bromine and iodine atoms with molecules containing an asymmetric carbon.
- (5) General applicability of kinetic theories to heavy halogen gaseous systems.

These areas of research in which we are stressing can provide answers to such general questions of chemical kinetic as what are the mechanisms for chemical reactions which occur with kinetic energies well above the thermal region? What is the stereochemistry of these high energy reactions? How fast are they? and what are the energy ranges involved?

B. Summarized below is an overview of our main progress during the whole contract period:

1. Systematics of Halogen Hot Atom Reactions

Systematic studies of halogen reactions activated by radiative neutron capture and isomeric transition in gaseous hydrocarbons and halomethanes are important for several reasons. From these studies we can generally ascertain the importance of such parameters⁶ as steric, bond energy, translational-inertial and energy-degradation factors on gas phase halogen hot atom reactions. The moderator studies⁷⁻¹³ involving the effects of rare gas additives on the total and individual organic product yields allow us to determine the importance of hot (kinetic-energy dependent) and thermal (mainly ion-molecule in ground or excited ionic states) halogen hot atom reactions. Unlike hot tritium, fluorine

and chlorine, there is a thermal character to bromine reactions activated by isomeric transition and iodine reactions activated by both radiative neutron capture and isomeric transition. As a first step to understanding the dynamics of the halogen hot atom reactions it is important to know whether the reactive species are hot atoms or thermal ions. These systematic studies especially involving ^{80}Br and $^{82\text{m}+82}\text{Br}$ isotope separations,¹⁰ and (n,γ) $^{130\text{m}+130}\text{I}$ and (I.T.) ^{130}I isotope separations, coupled with determinations of kinetic energy spectra of ^{128}I by the (n,γ) process⁶ and ^{82}Br and ^{130}I by the (I.T.) process,¹⁴ allow us to evaluate the general applicability of existing kinetic theories to (n,γ) and (I.T.) activated bromine and iodine reactions. These are really first steps which are necessary to take for the formation of kinetic theory expressions for heavy halogen hot atom reactions with organic molecules in the gas phase.

Our progress in the area of systematics is presented in our manuscript submitted for publication.¹⁴ Briefly, we find as we did for ^{128}I reactions⁶ in halomethanes that a prime factor for bromine reactions activated by radiative neutron capture and isomeric transition in gaseous halomethanes is the system's energy degradation factor. The importance of these result is that like iodine, a significant fractions of the bromine are born in the reactive energy zone, E_2-E_1 ; therefore the conditions of Wolfgang's assumption are not met. This is consistent with the finding of an isotope effect¹⁰ in the reaction of bromine with CH_3F and CD_3F .

2. Gas to Liquid to Solid Transition in Hot Atom Chemistry.

A fundamental question in condensed phase hot atom chemistry is whether reactions activated by nuclear transformations in organic media proceed by caging or molecular mechanisms or both. Since Franck and Rabinowitsch¹⁵ postulated the cage event there have been many studies⁵ directed at characterization of radical reactions in the cage; yet no direct evidence of the caging process has been presented. In the condensed phase the concept of the caging process suggests complex and diverse kinetic events for both hot atom¹⁶⁻¹⁸ and photochemistry.¹⁹⁻²¹

Recent analytic studies^{20,21} and computer simulations^{19,22} have cast doubt upon the adequacy of bulk properties like viscosity to describe the caging process. Bunker and Jacobson¹⁹ have suggested that recoil energy, molecular size and intermolecular forces play a most important role in the determination of cage recombination reactions. It is unfortunate that those experimental techniques most sensitive to molecular properties, e.g. molecular beam and ion cyclotron resonance studies, are ill-suited to high density or pressure regions where the caging event occurs. Photochemical studies have provided a wealth of information on reactions within the cage but cannot provide simultaneous data on cage and molecular reactions since, in the majority of events, the reactant species is born within the cage.

One of the most significant studies was the "Richardson-Wolfgang" effect.²³ In their study of ^{18}F reactions activated by the (n,2n) process in CH_3F , they found an increase in product yields with increasing density in the gas to liquid to solid transition. Above a density of

0.1 g cm^{-3} the product yields were essentially constant, giving a continuous plateau through the critical density region, before rising again, above a density of 0.5 g cm^{-3} , where mean intermolecular distances shrink to about half the diameter of the fluorine atom. If the plateau that Richardson and Wolfgang observe is due to collisional stabilization of molecular products, then the subsequent increase in product yields with increasing density must be the result of caging reactions involving the hot atom and organic radicals it has produced in the medium.

In this contract period we studied¹⁴ the effects of bromine concentration, density, phase and intermolecular distance on bromine reactions activated by radiative neutron capture and isomeric transition on halomethane systems in an attempt to learn more about the characteristics and systematics of molecular and radical cage reactions.

As demonstrated by mole fraction studies, the condensed phase is a viable although complex source of information. In conjunction with density we observed changes in product production both in mode and in yield during the gas to condensed phase transition. Although no specific information on the relative contributions of molecular versus radical reactions could be obtained from these studies, we observed continuities both within a system and among the various halomethane systems; e.g. the duplication of the "Richardson-Wolfgang",²³ effect and the characteristic concavity/convexity of $(n, \gamma)/(I.T.)$ -activated density plots. These density studies, viewed with the gas phase systematics, demonstrate the importance of mode of activation in molecular reaction and in the caging event. The normalized intermolecular distance (λ/σ) studies provide a method for the direct comparison of systems, hot atoms and modes of

activation and the means to separate cage and molecular events. The λ/σ work also suggests the importance of molecular parameters on caging events and demonstrates the importance of the degradation effect (EDF) in both gas and condensed state systematic studies. In our opinion these studies are not only of interest to other hot atom chemists but kineticists in general because of the preceeding statements we can make regarding caging effects.

3. Reactions of Iodine with Olefins

At the present time, there is sufficient data in the literature²⁴⁻²⁸ to indicate that the reactions of iodine, activated by various nuclear processes, in gaseous alkanes, and halomethanes, are exceedingly complex. One of the goals of our study of the reactions of ^{128}I and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ activated by radiative neutron capture and ^{130}I activated by isomeric transition, is to shed more light on the understanding of these reactions.

Pettijohn and Rack¹² studied the reactions of (n, γ)-activated ^{128}I in gaseous ethylene and propylene. By determining the individual product yields at varying mole fractions of several additives, they were able to determine the reaction mechanisms of ^{128}I and its product intermediates.

We are presently studying the reactions of ^{128}I with acetylene and the butene isomers; 1-butene, cis-2-butene, trans-2-butene, and 1,3-butadiene in the gaseous state. In addition, since these gases are relatively easily compressed, we will extend this investigation into the higher pressure gas and the condensed states. Specific progress in this area was reported in the previous progress report. Our chromatographic analyses have not yet been completed. Two separate studies are in progress; one is the acetylene system and the other is gas and condensed state butenes should be completed sometime in the next year and submitted

to the Journal of Physical Chemistry. Not only will these studies define to a better extent the nature of iodine hot atom reactions but also suggest possible theories for iodine reactions in the condensed state.

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

This is a collaboration effort with Dr. Wolf at Brookhaven National Laboratory.

The fundamental question of whether high-energy halogen atoms replace another halogen by retention or inversion of configuration at asymmetric carbon atoms, $X^* + RX_j \xrightarrow{X_i\text{-for } X_j} RX_i^* + X_j$, has been investigated²⁹⁻³³ in order to provide insight to the dynamics of hot-atom reactions. Heretofore these studies have been restricted to diastereomeric compounds, such as rac- and meso-(CHCl)₂ and rac- and meso-2,3-dichlorobutane (DCB), because of the opinion³¹ that chemical resolution of enantiomeric molecules would not be possible because of the relatively short half-lives of the chlorine isotopes. In the first halogen hot-atom stereochemistry experiment Rowland et al.²⁹ showed racemization effects in liquid and solid rac- and meso-DCB suggesting the importance of cage effects in the condensed state. In their study of gaseous rac- and meso-DCB Rowland et al.³¹ found $\geq 93\%$ retention of configuration at the asymmetric centers and $> 97\%$ retention of configuration during gas phase substitution³⁴ of ¹⁸F-for-F at asymmetric carbon atoms in rac- and meso-(CHCl)₂. In a recent interesting experiment Stöcklin et al.³² found substitution of chlorine in liquid rac- and meso-DCB by recoil ³⁸Cl can lead to both retention and inversion depending on the con-

formation of the molecule by varying the solvent. These results suggest that strong conformational steric effects may overshadow the primary substitution event when diastereomers are used. In their study of ^{38}Cl substitution in gaseous, high pressure, and liquid rac- and meso- $(\text{CHFCl})_2$, Stöcklin et al.³³ found > 93% retention in the entire gaseous range with decreasing stereospecificity-but mainly retention-in the liquid phase.

In order to minimize conformational effects, we employed in halogen hot-atom chemistry enantiomers for the first time, 2(S)-chloropropionyl chloride and 2(R)-chloropropionyl chloride, which offer little hindrance to a back-side substitution attack, and the back-side sterically hindered enantiomer 2(S)-chloro-4-methylvaleryl chloride. In the gas phase where mechanistically complicating cage effects are not present, the surprising results of $81 \pm 8\%$ and $80 \pm 2\%$ inversion of configuration have been observed 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-chloropropionyl chloride. This is the first report where net inversion has been observed in any gas tritium or halogen hot atom reaction.

Fukushima³⁵ found the gauche prime conformation of 2-chloropropionyl chloride significantly more abundant in the gas than in the liquid phase. It is this configuration which provides a relatively unhindered approach to attack on the asymmetric carbon from the back side (with respect to the alpha chlorine). In addition, trajectories for chlorine attack leading to Walden inversion may approach within a wide range of angles. Back-side approach to 2-chloropropionyl chloride in gauche conformations is less hindered than for any rotational conformation of

(CHFC1)₂ or DCB, which are relatively hindered in all conformations. If the open conformation explains why gas phase Cl-for-Cl substitution proceeds with such a high degree of inversion with enantiomeric 2-chloropropionyl chloride, then blocking back-side attack with large substituents should hinder the inversion mode. To test this hypothesis the extent of inversion was measured at the alpha chlorine position 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±0.3%. This drastic increase in retention compared to 2-chloropropionyl chloride is indicative that the degree of retention (or inversion) is severely affected by steric hindrance.

The results indicate that not all hot-atom substitution reactions are fast and direct involving a front-angle attack³⁶⁻⁴² (retention of configuration) but can occur from the opposite side of the molecule involving Walden inversion,⁴³ in a collision time sufficiently long to allow movements of the substituents. Apparently objections voiced by Rowland³¹ and Stöcklin³² that hot substitution with inversion may involve so much vibrational excitation energy that the molecules formed will undergo secondary decomposition is not entirely valid.

From the experimental results of ³⁸Cl and ^{34m}Cl-for-Cl substitution at the asymmetric carbon of 2(S)-(+)- and 2(R)-(-)-chloropropionyl chloride in the condensed phases it is obvious that (1) the absolute substitution yields are similar for both ³⁸Cl and ^{34m}Cl indicating that the initial kinetic energies are not a factor; (2) there is an increase in the percent yield from the gas to the liquid to the solid phases (increasing density) similar to the trends found for recoil fluorine,²³

chlorine,³³ and bromine,⁴⁴ and (3) Cl-for-Cl substitution is mainly by inversion in the gas phase but produces racemic mixture in the condensed phases. Because this condensed state data is preliminary no attempt is made to propose possible condensed state mechanisms at this time.

5. Kinetic Theory Applications to Hot Halogen Atom Reactions Activated by Radiative Neutron Capture and Isomeric Transition.

We are interested in considering the relevance of kinetic theories to heavy halogen (bromine and iodine) hot atom reactions activated by radiative neutron capture and isomeric transition in gaseous alkanes and halomethanes. As part of this program we determined⁶ the kinetic energy spectrum of (n, γ) activated Iodine-128 using computer techniques. In addition, we are in the process of simulating possible kinetic energy spectra for (n, γ)-activated bromine isotopes. Also of interest is the determination of the kinetic energy spectra of Iodine-130 and Bromine-80¹⁴ activated by isomeric transition.

6. Applied Hot Atom Chemistry

Applied hot atom chemistry is mainly the utilization of hot atom reactions to prepare labelled biomolecules directly and simple inorganic compounds or other precursors for the described labelled compound. Our interests in applied hot atom chemistry has been in the application of hot atom chemistry theory and techniques to physical organic chemistry⁴⁵ and analyses either involving neutron activation⁴⁶⁻⁴⁸ or radiometric techniques.^{49,50} It is our contention that it is easier for a hot atom chemist to demonstrate the applicability of his theory and techniques to various chemical problems rather than another chemist not familiar with

the field to apply them. Applications of hot atom chemistry are obviously of immediate interest and benefit to other scientific interests and the U.S.A.E.C.

Using hot atom separation techniques we studied previously the kinetics⁴⁵ of the addition of iodine to liquid 1-pentene, cis- and trans-2 pentene, 2-methyl-1-butene, and 2-methyl-2-butene employing ¹³¹I-labelled iodine. We extended these liquid state studies to the gaseous state where we are now studying the kinetics of gas phase addition of iodine to the isomers of pentene. Surprisingly, we are finding that I₂ does add to the pentenes in the gaseous phase - the first observed photochemical addition to olefins in the gas phase - with similar kinetics to liquid phase addition. These results will be of importance to physical organic chemists. Our experimental approach to the problem is to irradiate gaseous mixtures of I₂ and the olefin with CH₃I source molecule in the nuclear reactor producing ¹²⁸I-labelled iodine. By keeping the compounds in light varying lengths of time we can study the kinetics by analytical techniques we reported previously.⁴⁵ Comparing the results to those generated using the ¹³¹I labelled method demonstrate the validity of the hot-atom labeling technique.

An interesting applications of hot atom chemistry to trace analysis involving neutron activation was our determination of iodine in urine.⁴⁸ Since this procedure now is in the literature⁴⁸ no attempt will be made to discuss it here.

Important analyses that are necessary in areas having nuclear power reactors is for reactor produced trace elements in test animals around the site to observe if there is any contamination into the environment.

These procedures are of importance not only to the U.S.A.E.C. but other governmental agencies such as E.P.A. One such fission product is Iodine-129. One the of the recent problems now is that there is no good analysis reported in the literature for Iodine-129 in animal tissues such as from the thyroid. We feel that our total iodine procedure in urine can be modified by employing the $^{129}\text{I} (n,\gamma) ^{130m+130}\text{I}$ reaction to enhance the sensitivity of ^{129}I detection with several experimental variations to allow not only total iodine analysis in the thyroid tissue of test animals but an ^{129}I analysis as well. The work we have done in ^{130}I hot atom chemistry as well as the recognition¹¹ of the complicating reactions induced by ^{130m}I isomeric transition during the analysis will allow us to develop an adequate procedure.

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.

Ph.D. Theses Directed

1. J. A. Merrigan, "Reactions of Bromine Activated by (n, γ) and (I.T.) Processes in Carbon Tetrachloride and the C₆-alkanes, 1966.
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", 1969.
4. E. J. Kemnitz, "Reactions of Selected Halogens and Interhalogens Activated by Radiative Capture and Isomeric Transition with Condensed State Cyclopentane and Aromatic Hydrocarbons", 1970.
5. R. L. Ayres, "Reactions of Iodine Activated by the Neutron Capture Process in Liquid and Solid Alkanes and Alkenes", 1970.
6. J. B. Nicholas, "Effect of Moderates on the Isomeric Transition Induced Reactions of Iodine-130 and Bromine-82 with Methane and d-Methane", 1971.
7. M. S. C. Yoong, "Kinetic Theory Applications to Halogen Hot Atoms Activated by Radiative Neutron Capture in Methane, Deuterated Methane, and Polyhalomethanes", 1972.
8. R. W. Helton, "Reactions of Bromine and Chlorine Activated by Radiative Neutron Capture and Isomeric Transition in Gaseous and Condensed Halomethanes", 1972.
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.

PUBLICATIONS OF PRINCIPAL INVESTIGATOR

1. W. W. Miller, E. P. Rack, E. Burrell, and C. N. Trumbore, Organic Radiation Reactions with Dissolved Radioactive Iodine, J. Chem. Phys., 23, 1457 (1955).
2. E. P. Rack and A. A. Gordus, Effect of Moderators on the (n, γ) Activated Reaction of Br-80 with CH₄, J. Chem. Phys., 23, 1457 (1955).
3. E. P. Rack and A. A. Gordus, Effect of Inert-gas Moderators on the (n, γ) Activated Reactions of I-128 with CH₄, J. Chem. Phys., 34, 1855 (1961).
4. E. P. Rack and A. A. Gordus, Reactions of High Energy, Excited I-128 Ions with Gaseous Molecules, J. Chem. Phys., 36, 287 (1962).
5. E. P. Rack and A. F. Voigt, Radiation Dose and Iodine Scavenger Effects on Recoil C¹¹ Reactions in Cyclohexane, J. Phys. Chem., 67, 198 (1963).
6. E. P. Rack, C. E. Lang, and A. F. Voigt, Influence of Structure on Gaseous Products from C¹¹ Recoil Reactions in C₆ Hydrocarbons, J. Chem. Phys., 38, 1211 (1963).
7. J. A. Merrigan and E. P. Rack, Effects of Experimental Parameters on the (n, γ)-Activated Reactions of Bromine with Liquid Cyclohexane, J. Phys. Chem., 69, 2795 (1965).
8. J. A. Merrigan and E. P. Rack, Evidence for Bromine-82m Isomeric Transition Activated Reactions in Saturated Hydrocarbon and Alkyl Halides, J. Phys. Chem., 69, 2806 (1965).
9. J. A. Merrigan, W. K. Ellgren, Jr., and E. P. Rack, Reactions of Bromine Activated by Bromine-82m Isomeric Transition and Radiative Neutron Capture in Liquid and Solid Carbon Tetrachloride and n-Hexane, J. Chem. Phys., 44, 174 (1966).
10. J. A. Merrigan, J. B. Nicholas, R. M. Lambrecht, N. J. Parks and E. P. Rack, Isomeric Transition Induced Reactions of Iodine-130 in Cyclohexane, J. Phys. Chem., 70, 2417 (1966).
11. J. A. Merrigan, J. B. Nicholas, and E. P. Rack, Nature of (n, γ) and (IT)-Activated Bromine Reactions in Liquid Isomers of Hexane, Radiochim. Acta, 6, 94 (1966).
12. J. A. Merrigan, J. B. Nicholas, and E. P. Rack, A Radiochemical Experiment in Gas-Chromatography, J. Chem. Ed., 43, 543 (1966).
13. J. B. Nicholas, J. A. Merrigan, and E. P. Rack, Effect on Moderators on the Isomeric Transition Induced Reaction of Bromine-82 with Methane, J. Chem. Phys., 45, 1996 (1967).

14. R. M. Lambrecht and E. P. Rack, Isotope Effects of Iodine Reactions Activated by Radiative Neutron Capture and Isomeric Transition Processes in Liquid Hydrocarbons, J. Chem. Phys., **48**, 3735 (1968).
15. J. B. Nicholas and E. P. Rack, Nature of Isomeric-Transition Induced Bromine-82 Reactions with CH₄, J. Chem. Phys., **48**, 4085 (1968).
16. N. J. Parks and E. P. Rack, Substituent Effects of Iodine-130 Reactions Activated by (n,γ) and (IT) with Various Polyhalomethanes, Radiochemica. Acta, **10**, 26 (1968).
17. R. M. Lambrecht and E. P. Rack, Complicating Role of Reactions Induced by Isomeric Transitions in Neutron-Activation Analysis for Bromine-82 and Iodine-130, Analyst, **93**, 550 (1968).
18. R. L. Ayres, E. J. Kemnitz, R. M. Lambrecht, and E. P. Rack, Iodine Organic Yields in Hydrocarbons Matrices as an Indication of Clustering, Complexing and Fractional Crystallization at 77°K, Radiochim. Acta, **11**, 1 (1969).
19. R. M. Lambrecht, J. K. J. Hahn and E. P. Rack, Radiative Neutron Capture Organic Yields as an Indication of the State of Aggregation of ICl and I₂ and C₆ - Hydrocarbons Matrices at 77°K, J. Phys. Chem., **73**, 2779 (1969).
20. E. J. Kemnitz, H. K. J. Hahn and E. P. Rack, Isotope and Concentration Effects of Bromine in Polycrystalline Benzene at 77°K, Radiochim. Acta, **13**, 112 (1970).
21. H. K. J. Hahn, M. Yoong and E. P. Rack, Radiometric Analysis of Serum and Tissue Proteins, J. Lab. and Clin. Medicine, **76**, 965 (1970).
22. E. P. Rack, College Chemistry, Volume 1: An Orientation, Lincoln, Nebraska: Cliff's Notes, Inc., 1969.
23. R. L. Ayres and E. P. Rack, Szilard-Chalmers Organic Yields in Liquid and Solid Alkyl Iodines, Radiochem. Radioanal. Letters, **3**, (3) 213 (1970).
24. D. W. Oates, R. L. Ayres, R. W. Helton, K. S. Schwartz, and E. P. Rack, Isomeric Transition Activated Reactions of ⁸²Br with Gaseous Methyl Bromide, Radiochem. Radioanal. Letters, **4**, (3), 123 (1970).
25. O. C. Gadeken, R. L. Ayres, and E. P. Rack, Application of Isotopically-labelled Bromine for the Determination of Trace Unsaturation in Alkanes, Analytical Chemistry, **42**, 1105 (1970).
26. R. L. Ayres, C. J. Michejda, and E. P. Rack, Reactions of Iodine with Olefins: I. Kinetics and Mechanism of Iodine Addition to Pentene Isomers, J. Am. Chem. Soc., **93**, 1389 (1971).

27. R. L. Ayres, O. C. Gadeken, and E. P. Rack, Reactions of Iodine with Olefins: II. Radiative Neutron Capture Induced Reactions of ^{128}I with Various C_5 Isomers: Evidence for a Mechanism Other than Autoradiolysis in the Condensed State, J. Phys. Chem., **75**, 2880 (1971).
28. R. W. Helton, W. Yoong, and E. P. Rack, Kinetic Energy Isotope Effects of Bromine Reactions Activated by Radiative Neutron Capture in Gaseous CH_3F and CH_3I , J. Phys. Chem., **75**, 2072 (1971).
29. M. Yoong, Y. C. Pao and E. P. Rack, Systematics of (n,γ) -Activated Hot ^{128}I Reactions in Gaseous Methane and Halomethanes. The Energy Degradation Factor, J. Phys. Chem., **76**, 2685 (1972).
30. R. R. Pettijohn and E. P. Rack, Reactions of Iodine with Olefins. III. Radiative Neutron Capture Induced Reactions of Iodine-128 with Gaseous Ethylene and Propylene, J. Phys. Chem., **76**, 3342 (1972).
31. *J. B. Nicholas, M. Yoong, and E. P. Rack, Reactions of ^{130}I Activated by Radiative Neutron Capture and Isomeric Transition in Gaseous CH_4 and CD_4 , Radiochim. Acta, **19**, 124 (1973).
32. *R. W. Helton, W. M. Grauer, and E. P. Rack, The Gas to Liquid to Solid Transitions in Halogen Hot Atom Chemistry I. Reactions of (n,γ) -Activated Bromine-80 in Methyl Fluoride, Radiochim. Acta, **19**, 44 (1973).
33. *R. W. Helton, D. W. Oates, and E. P. Rack, Reactions of ^{82}Br Activated by Isomeric Transition in CH_4 : A Re-Evaluation, Bull. Chem. Soc., Japan, **46**, 2877 (1973).
34. *A. J. Blotcky, L. J. Arsenault and E. P. Rack, An Optimum Procedure for the Determination of Selenium in Biological Specimens Using ^{77}Se Neutron Activation, Anal. Chem., **45**, 1056 (1973).
35. *W. M. Grauer, E. P. Rack and R. M. Lambrecht, Radiative Neutron Capture and Isomeric Transition Isotope Effects in Bromine Reactions with Liquid Cyclohexane and Carbon Tetrachloride. A Re-Evaluation. Radiochim. Radioanal. Letters, **16**, 289 (1974).
36. *A. J. Blotcky, D. M. Duven, W. M. Grauer, and E. P. Rack, Determination of Iodine in Urine by Neutron Activation Analysis. Application of the Szilard-Chalmers Effect, Anal. Chem., **46**, 838 (1974).

*New publications in Current Reporting Period.

In Press or Submitted Manuscripts

1. M. E. Berg, W. M. Grauer, R. W. Helton, and E. P. Rack, The Gas to Liquid to Solid Transitions in Halogen Hot Atom Chemistry. II Systematics of Bromine Reactions Activated by Radiative Neutron Capture and Isomeric Transition with Halomethanes, J. Phys. Chem.

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List of References

1. L. Szilard and T. A. Chalmers, Nature (London), 134, 462 (1934).
2. O. U. Anders, Phys. Rev., 138, 81 (1965).
3. J. F. Emery, J. Inorg. Nucl. Chem., 27, 903 (1965).
4. D. D. Wikley and J. E. Willard, J. Chem. Phys., 44, 970 (1966).
5. J. E. Willard, Symposium on Chemical Effect Associated with Nuclear Reactions and Radioactive Transformations, Vol. I, p. 221, IAEA, Vienna (1964).
6. M. Yoong, Y. C. Pao and E. P. Rack, J. Phys. Chem., 76, 2685 (1972).
7. J. B. Nicholas, J. A. Merrigan and E. P. Rack, J. Chem. Phys., 46, 1996 (1967).
8. J. B. Nicholas and E. P. Rack, J. Chem. Phys., 48, 4085 (1968).
9. Oates, Ayres, Helton, Schwartz and Rack, Radiochem. Radioanal. Letters, 4, 123 (1970).
10. R. W. Helton, M. Yoong, and E. P. Rack, J. Phys. Chem., 75, 2072 (1971).
11. J. B. Nicholas, M. Yoong, and E. P. Rack, Radiochim. Acta, 19, 124 (1973).
12. R. R. Pettijohn and E. P. Rack, J. Phys. Chem., 76, 3342 (1972).
13. R. W. Helton, D. W. Oates, and E. P. Rack, Bull. Chem. Soc. Japan, 46, 2877 (1973).
14. M. E. Berg, W. M. Grauer, R. W. Helton and E. P. Rack, J. Phys. Chem., (submitted for publication).
15. J. Franck and E. Rabinowitsch, Trans. Far. Soc., 30, 120 (1934).
16. W. F. Libby, J. Amer. Chem. Soc., 69, 2523 (1947).

17. P. R. Geissler and J. E. Willard, J. Phys. Chem., 67, 1615 (1963).
18. Cole, Mia, Miller and Shaw, Radiochem. Acta, 9, 194 (1968).
19. D. L. Bunker and B. S. Jacobson, J. Amer. Chem. Soc., 94, 1843 (1972).
20. R. M. Noyes, J. Chem. Phys., 18, 999 (1950).
21. Lampe and Noyes, J. Amer. Chem. Soc., 76, 2140 (1954).
22. C. Walling and A. R. Lepley, Int. J. Chem. Kinet., 3, 97 (1971).
23. Richardson and Wolfgang, J. Amer. Chem. Soc., 92, 3480 (1970).
24. M. D. Loberg and M. J. Welch, J. Amer. Chem. Soc., 95, 1075 (1973).
25. M. D. Loberg, K. A. Krohn and M. J. Welch, J. Amer. Chem. Soc., 95, 5496 (1973).
26. C. Bekzadi, J. G. Kuhry and Ch. Heitz, Radiochem. Radioanal. Letters, 11, 19 (1972).
27. Ernstberger, Kuhry and Heitz, Radiochem. Radioanal. Letters, 12, 345 (1972).
28. Kuhry, Lagarde and Heitz, Radiochem. Radioanal. Letters, 13, 185 (1973).
29. C. M. Wai, C. T. Ting and F. S. Rowland, J. Am. Chem. Soc., 86, 2525 (1964).
30. F. S. Rowland, C. M. Wai, C. T. Ting, and G. Miller, Chemical Effects of Nuclear Transformations, "Vol. 2, International Atomic Energy Agency, Vienna, 1965, p. 333.
31. C. M. Wai and F. S. Rowland, J. Phys. Chem., 74, 434 (1970).
32. L. Vasaros, H.-J. Machulla, and G. Stöcklin, J. Phys. Chem., 76, 501 (1972).
33. H.-J. Machulla and G. Stöcklin, J. Phys. Chem., 78, 658 (1974).

34. G. F. Palino and F. S. Rowland, Radiochim. Acta, 15, 57 (1971).
35. K. Fukushima, Nippon Kagaku Zasshi, 80, 1828 (1959). Chemical Abstracts, 53, 21163h (1959).
36. M. Henschman and R. Wolfgang, J. Am. Chem. Soc., 81, 2991 (1961).
37. M. Henschman and D. Urch, and R. Wolfgang, Can. J. Chem., 38, 1722 (1960).
38. D. Urch and R. Wolfgang, J. Amer. Chem. Soc., 83, 2982 (1961).
39. R. A. Odum and R. Wolfgang, J. Amer. Chem. Soc., 85, 1050 (1963).
40. R. Wolfgang, "Progress in Reaction Kinetics", Vol. 3, G. Porter, ed., Pergamon Press, Oxford, 1965, pp. 97-169.
41. L. Spicer, J. F. J. Todd, and R. Wolfgang, J. Am. Chem. Soc., 90, 2425 (1968).
42. L. Spicer and R. Wolfgang, J. Am. Chem. Soc., 90, 2426 (1968).
43. (a) D. L. Bunker and M. D. Pattengill, Chem. Phys. Letters, 4, 315 (1969).
(b) D. L. Bunker and M. D. Pattengill, J. Chem. Phys., 53, 3041 (1970).
44. R. W. Helton, W. M. Grauer, and E. P. Rack, Radiochim. Acta, 19 44 (1973).
45. R. L. Ayres, C. J. Michejda and E. P. Rack, J. Amer. Chem. Soc., 93, 1389 (1971).
46. R. M. Lambrecht and E. P. Rack, Analyst, 93, 550 (1968).
47. A. J. Blotcky, L. J. Arsenault and E. P. Rack, Anal. Chem., 45, 1056 (1973).
48. A. J. Blotcky, D. M. Duvon, W. M. Grauer and E. P. Rack, Anal. Chem., 46, 838 (1974).

49. H. K. J. Hahn, M. Yoong and E. P. Rack, J. Lab. and Clin. Medicine, 76, 965 (1970).
50. O. C. Gadeken, R. L. Ayres and E. P. Rack, Anal. Chem., 42, 1105 (1970).