# Reactions of Charged and Neutral Recoil Particles Following Nuclear Transformations

Progress Report No. 10

ORO-3602-17

This work was supported by:

U. S. Energy Research and Development Administration
Contract No. E-(40-1)-3602

Principal Investigator: Hans J. Ache
Professor of Chemistry
Department of Chemistry
Virginia Polytechnic Institute
and State University

September 1976

## Table of Contents

## Introduction

The following is a report of the work completed during the period September 1975 - August, 1976: These studies were supported by the U. S. Energy and Development Administration, Division of Physical Research, under contract No. E-(40-1)-3602, and carried out at the Department of Chemistry of Virginia Polytechnic Institute and State University.

The various activities carried out under this contract during the past contract period and their main objectives can be summarized as follows:

## A. STUDY OF THE REACTIONS OF ENERGETIC PARTICLES GENERATED IN NUCLEAR REACTIONS.

### General Background

Chemical reactions in the gas phase and liquid phase are an essential part of basic energy related research and the ability to control them is of tremendous practical importance.

In order to control these reactions it is necessary to understand the mechanisms and kinetics involved in these processes which in turn requires the identification and structural determination of intermediates, measurement of rate constants for their formation, where intermediates could be defined as atoms, radicals, ion and ion molecules, the influence of three dimensional molecule structure on the rate constants, steric effects etc.

These are exactly the topics of modern hot atom chemistry and they are also the subject of this work.

Gas phase hot atom chemistry has been for years an extremely successful tool in the assessment of the parameters which determine the progress of chemical reactions which occur with kinetic energies greater than thermal and in chemical dynamics. The ultimate goal of hot atom chemistry and of non-Boltzmann chemistry in general has been characterized as "the description of chemical reactions in terms of the respective cross-sections for each of the various possible reactions at each of the energies at which the reaction is possible".

Within this framework our special interest is concentrated on the evaluation of the nature of the reacting species (ions or neutral atoms), its electronic state, the kinetic energy involved, the exact mechanism, configuration and lifetime of the intermediates and the stereochemical course of the reaction.

In the condensed phase the assessment of the detailed mechanism of the hot atom reactions is further complicated by the greater multipiicity of overlapping reactions and the enhanced presence of thermal processes which obscure the hot reaction channels.

Thus in addition to the objectives, as outlined above for gas phase reactions, other major considerations had to be included in our investigation,namely, the presence of caging effects and the effects of the solvent on the course of the reaction. It was especially this latter topic which was thoroughly scrutinized during the recent contract period. In the following a detailed discussion of the present status of research and the results of

## 1. Study of the stereochemistry of halogen atom reactions produced via (n,γ) nuclear reactions with diastereomeric molecules in the condensed phase.

### Status of research (1975)

In the past the results of the stereochemical course of the halogen for halogen substitution in diastereomers in the gas phase, which showed an almost complete lack of inversion of configuration, have been used as supporting evidence for the Wolfgang impact and inertial model for hot halogen substitution. This model postulates a direct replacement process on a time scale comparable to molecular transit times for the hot atom, i.e., $10^{-14}$ to $10^{-13}$ s, which would be too short to allow the movement of atoms at substituent groups necessary for Walden inversion.

A lower degree of stereospecificity was usually observed in the condensed state which was attributed to the presence of radical-radical recombination processes in the solvent cage.

If the time scale for the recombination of the radicals in the solvent cage becomes comparable to the time required to achieve planarity these thermal caged radical processes can lead to both retention and inversion of configuration.

Another interpretation for the reduced stereospecificity in condensed systems was given by Stöcklin et al. On the basis of a pronounced conformational effect these authors suggested a hot one-step substitution process, proceeding via a collision complex which is collisionally stabilized and has a lifetime sufficiently long to allow inversion of configuration ("direct replacement with collisional stabilization of the caged complex" model).

Further evidence for a hot one-step substitution process was obtained in our laboratory where the stereochemistry of bromine for chlorine substitution at asymmetric carbon atoms was studied in the pure liquid diastereomeric 2,3-dichlorobutanes and in organic solutions of these compounds.

The reactive bromine species were either energetic (hot)$^{80m}$Br atoms generated via the $^{79}$Br (n,γ)$^{80m}$Br nuclear process or bromine ions formed as a result of coulomb fragmentation of $^{80m}$Br- or $^{82m}$Br labelled molecules.

The results obtained in this study clearly indicate two different mechanisms by which the Br for Cl exchange in 2,3-dichlorobutane in the liquid phase proceeds. If the reactive bromine species is a "hot" bromine atom then the present evidence suggests in analogy to the findings by Stöcklin et al. in the Cl for Cl exchange reactions that the exchange occurs via a hot one-step substitution mechanism, whereas the exchange reactions of bromine species activated in isomeric transitions show distinctly different trends and may best be explained by assuming that Auger radiolysis leads to the formation of $CH_3\dot{C}HCHClCH_3$ radicals which may react with a neutral bromine to form the substituted product. In this case the stereochemistry will depend on the amount of time available for the organic radical to obtain its planar configuration before combination occurs.

## Summary of Recent Work

Because of the great importance of the question as to how solvents interact with reaction intermediates and determine subsequently the course, the stereochemistry, kinetics etc. of a chemical reaction in general, a deliberate effort was made during the past contract period to accumulate more evidence for the effect of solvents on the stereochemical course of hot halogen for halogen exchange reactions.

Thus this investigation was extended to the study of the chlorine-38 for chlorine exchange following $^{37}(n,\gamma)^{38}Cl$ in the diastereomeric 2,4-dichloropentanes, 2,3-dichlorobutanes and in cooperation with Prof. Rack's laboratory, 1,2-dichloro-1,2-difluoroethanes and included a large number of different solvents.

The results from our laboratory are presented in appendices I and II. They are generally very similar to the trends observed by Stöcklin and in our laboratory in the 2,3-dichlorobutanes and indicated that e.g. upon addition of increasing amounts of bromine or methanol the retention/inversion ratios drastically increase in both diastereomers whereas the addition of n-pentane and c-hexane reduces the ratio in both systems. A total of about 30 different solvents were tested.

The first question to which we addressed ourselves to, was whether these results can be explained by the changes in the relative conformer population in the different solvent, and the relative availability of these conformers for front- or backside attack, leading to substitution with retention or inversion of configuration.

This question was answered by using two different approaches. In the first study we used the diastereomers of 2,4-dichloropentane, where predominantly only one conformer exist, whose concentration is affected only to a negligible degree by a change of solvent. The fact that the stereochemistry of the chlorine-38 for chlorine substitution in this compound shows again a strong solvent dependence provides clear evidence for the fact that the conformational structure of the substrate molecule is not determining the stereochemical course of the substitution. These findings were further supported by the results of a second series of experiments carried out with the diastereomeric 1,2-dichloro-1,2-difluoroethanes.

In order to correlate the experimental results to the conformational composition of the substrate molecules in the reaction mixture a elaborate conformational analysis of these mixtures was carried out by NMR spectroscopy.

As described in detail in appendix II no satisfactory correlation between conformer population and the retention/inversion ratios can be observed, which emphasizes the importance of other factors controlling the substitution process. From a careful evaluation of the various properties of the solvents, the conclusion was reached that the dielectric constant and the molecular size of the solvent molecules which in turn are related to the intermolecular interaction between reactants and solvent are responsible for the observed effect. The following hypothesis explaining the solvent effect in terms of a hot one-step substitution or a radical-radical recombination mechanism was suggested.

In terms of the first model the strong interaction between solvent and reactants may either lead to a rapid energy transfer in which case the high energy reaction channel will dominate (retention) and/or if one prefers the latter model the strong solvation will prevent the intermediate radical from obtaining planarity and recombination will result in a labeled molecule having the same configuration as the product formed in the primary displacement step.

Furthermore, the experimental results presented in this study clearly indicate that the stereochemistry is predominantly and directly governed by the properties of the solvent and not by an indirect solvent effect on the relative rotamer population of the substrate molecule.

## Significance

The major significance of the results of our study of the stereochemistry of the chlorine-38 for chlorine exchange in solutions is undoubtedly the fact that we have been able to identify the parameters which control the substitution. It is interesting to note that the factors involved, namely, magnitude of intermolecular interaction between reactants and solvent as well as the size of the solvent molecules, have been also postulated in computer simulations of photochemical reaction to be responsible for the caging efficiency of solvents. We, therefore, think that our studies have significantly contributed to a better assessment of the role of solvents in chemical reactions in general, a process whose details are still very little known.

## 2. Decay-Induced Labelling of Compounds of Biochemical Interest (Excitation Labelling)

(Study of non-synthetic methods of incorporating radioactive nuclides into compounds of biochemical interest.)

## Status of Research 1975

Organic molecules and biomolecules labelled with radioactive halogen have recently found increasing interest in biological and nuclear medical studies.

Because of the growing application of radiopharmaceuticals labeled with short-lived radionuclides and the requirements of high-specific activity or carrier free products in nuclear medical research direct and fast labelling techniques are of great importance.

Direct decay-induced labelling has been applied using reactive iodine species resulting from the decay of $^{123}$Xe and $^{125}$Xe on a surface coated with the substrate. The yields vary widely depending on the substrate and still very little is known about the nature of the species and reaction mechanisms involved.

Stöcklin found that certain biomolecules can be effectively iodinated if $^{123}$Xe is allowed to decay on a crystalline $KIO_3$ matrix, followed by dissolution in a 0.1 N HCl solution of the organic substrate.

In our laboratory a technique was developed by which radioactive bromine could be directly introduced into biomolecules such as deoxyuridine. Experiments in which the solid substrate was exposed to $CF_3{}^{80m}Br$ or $CF_3{}^{82m}Br$ showed that only a relatively small fraction of the $^{80}$Br or $^{82}$Br of the total number of Br produced was incorporated into the biomolecules. Better results were obtained when $Cl_2$ gas was added to the $CF_3Br$, which suggested that intermediates such as BrCl may play an important role in the labelling process. A modification of this method, the $CF_3Br$-

$KBrO_3$ exposure technique, where the $CF_3{}^{80m}Br$ or $CF_3{}^{82m}Br$ is allowed to undergo isomeric transition in the presence of solid $KBrO_3$ which subsequently is dissolved in 0.1 n HCl containing the dissolved substrate, leads to a similar improvement of the yields of radiobromine labelled substrate.

Summary of Recent work

During the past contract period the work on the development of methods for the direct labelling of biomolecules was continued as discussed in Appendices III and IV.

Additional model molecules such as deoxycytidine, guanosine, phenylalanine and L-tyrosine were included in this investigation. Furthermore, an attempt was made to expand the applicability of the $CF_3Br^{80m}$-$KBrO_3$ gas exposure technique which provides an extremely rapid and especially mild brominating agent, because it exposes the substrate only to a minimum of radiation, to the preparation of the bromoderivatives of deoxyuridine and deoxycytidine.

A detailed study of the optimum reaction conditions, such as length of exposure time, pressure, temperature, amounts of substrates etc. was carried out.

The results can be summarized as follows (Appendices III and IV.)

a.) The radiochemical yields of $^{80}Br$-5-bromodeoxyuridine and $^{80}Br$-bromoacetic acid obtained via the "$CF_3{}^{80m}Br$-$KBrO_3$" exposure techniques are consistently low (4.4 and < 1.0%). A drastic improvement of the amount of $^{80}Br$ incorporated into these compounds (41 and 75%) can be achieved if the labelling is carried out by applying the "$CF_3{}^{80m}$-$KBrO_3$" gas exposure technique to the corresponding iodo-derivatives to induce a $^{80}Br$ for I exchange in these compounds.

b.) The radiochemical yields obtained in the above procedure (a.) are also a function of the labelling time, which is defined as the time between elapsed dissolution of the exposed $KBrO_3$ crystals in a solution of the substrate and the subsequent HPLC separation. While the $^{80}Br$ for I exchange is a slow process which requires longer labeling times, the $^{80}Br$ for I exchange in iododeoxyuridine occurs very rapidly. Longer labelling times decrease the radiochemical yields because of secondary processes (hydrolysis etc.).

c.) Similar effects of the labelling time on the radiochemical yields as described in b.) can be observed if the $CF_3{}^{80}Br$-$KBrO_3$ technique is applied to induce a $^{80}Br$ for H exchange in L-tyrosine and guanosine.

d.) Since in some cases, e.g. in the labelling of proteins, insulin etc. by this method the substrate cannot be separated from the labelled product the amount of substrate used in these procedures has to be kept at a minimum. It was, therefore, important to study the effect of substrate concentration on radiochemical yields in the case of a few model molecules. The amount of substrate in the acidic solution used to dissolve the exposed $KBrO_3$ crystals proved to be indeed an important factor. While in the case of guanosine a concentration of about 2000 μg is required to obtain an optional yield, less than 50 μg are required for L-tyrosine. These results seem to reflect the interference of secondary processes, hydrolysis etc. The amount of $KBrO_3$ used in these experiments appeared to be less critical if more than 1 mg of the crystals were used.

Significance

Radioactive bromine can be conveniently and quite efficiently incorporated into organic compounds of biological interest by a simple fast and direct technique, the modified excitation labeling method using $CF_3{}^{80m}Br$ or $CF_3{}^{82m}Br$ as bromine source and in the presence of $Cl_2$ gas; or by the $CF_3{}^{80m}Br$-$KBrO_3$ technique which is an extremely rapid and especially mild brominating, because it exposes the substrate only to a minimum of radiation.

In the cases where the latter method does not give satisfactory radiochemical yields, better results can be obtained via a $^{80}Br$ for I exchange by using the iododerivatives of the corresponding substrate molecules as substrates.

All these methods produce carrier free radiobrominated molecules which can be subsequently used in biological or nuclear medical research.

($^{77}Br$ which would be better suited for biological or medical applications cannot be produced with the facilities available at VPI and SU. However, the techniques of radiobromine incorporation studied in this work would be also applicable to the $^{77}Br$ labelling of these compounds).

## B. THE CHEMISTRY OF THE POSITRONIUM

### Background and Status of Research 1975

In the past the behavior of Ps atoms in matter has mostly been discussed in terms of physical interactions between Ps and the surrounding matter and very little attention was given to the chemical reactivity of the Ps. Recent studies in our laboratory have shown that:

a) Positronium atoms behave in much the same way as normal chemical compounds. They undergo chemical reactions (equilibria and competition reactions) in reactive media, where (reversible) Ps molecular complex formation is strongly favored by the presence of appreciable amounts of intermolecular interaction energy. They are fairly unreactive in an environment where such forces are relatively small.

b) The activation energies for the complex forming step (I)

$$Ps + M \underset{II}{\overset{I}{\rightleftharpoons}} PsM$$

are very small ($\sim$ 1 Kcal/Mole). Differences in the observed rate constants have to be attributed to the preexponential Arrhenius factor.

c) The complex formation enthalpies range from $\sim$0 for toluene to -8 Kcal/Mole for the most reactive species studied (p-dinitrobenzene or p-benzoquinone).

d) Solvent effects are responsible for changes in the stability of the Ps-molecular complexes in different media. They can be contributed to changes in the entropies involved in the Ps complex formation.

e) The experimentally obtained average annihilation lifetimes of positrons bound in Ps-complexes are about 0.4 nsec, which is consistent with the ones predicted by quantum chemistry.

f) In the case of the inorganic (or organic) ions present evidence based on the existing correlation between the oxidizing capabilities of the ions and the observed reactivity toward Ps allows a satisfactory interpretation in terms of an electronic transfer when energetically possible; that is to say that the initial step leading to Ps complex formation with the ions is promptly followed by an electron transfer.

## Summary of Recent Work

The results of the work carried out during the past contract period can be found in Appendices V-VII:

They can be summarized as follows:

The study of the reactivity of Ps towards a number of organic molecules, known as strong acceptors in the molecule complex formation in conventional chemistry, has shown, that their reactivity towards Ps is strongly reduced when the acceptor molecule is present in the form of a molecule comples with a conventional donor.

Thus by making use of these reactivity differences the positron annihilation technique can be applied to determine the complex formation constants for a series of molecule complexes such as tetracyanoethylene and nitrobenzene with hexamethylbenzene and mesitylene in benzene solution. This investigation was further expanded to studies of molecular association in biological systems, where the formation constants for complexes of vitamin $K_1$ and tocopherol-quinone with donors such as mono-, di- and tri-n-butylamines, indole and vitamin $D_3$ were investigated.

## Significance

On the basis of a simple gas kinetic mechanism it was possible to develop a general concept for the interactions of thermal Ps atoms with matter. An important part in these interactions, especially with organic molecules, is played by Ps-molecular complexes. Among others it is this very tendency of the Ps atoms to form Ps-molecule complexes which makes the reactions of the Ps with matter a viable technique or nuclear probe for the study of the details of the intermolecular forces responsible for molecular complex formation. The knowledge of the parameters which control the formation of these complexes is of utmost importance because of the participation of molecular complexes in all kinds of chemical reactions, such as catalysis, biochemical reactions, etc. Furthermore, the fact that the reactivity of the Ps toward an acceptor-donor complex is reduced in comparison with the reactivity which the Ps shows toward an uncomplexed acceptor molecule can be used as a method for determining the formation constant of these complexes.

This method might prove to be most useful in cases where the uncomplexed donor or acceptor absorb at similar wavelengths as the molecule acceptor or where the solvent absorption interferes with the spectrophotometric determination of the complex formation constant, a fact which quite commonly occurs in the case of acceptors or donors of biological importance.

## Personnel and Publications

### Personnel

1. Principal Investigator
   Dr. Hans J. Ache, Professor of Chemistry

2. Postdoctoral Research Associates
   Dr. Yan-ching Jean (Aug. 1, 1975 - )
   Dr. Thomas E. Booth (Sept. 1, 1976 - )

3. Graduate Students
   Ralph E. Wild (term. with Ph.D., May 1976)
   Steven Wong
   Gene Hall
   Jeff Wu
   Toby Acciani
   Jack Mustaklem
   Onofre DeJesus
   Belkacem Djermouni

### Publications (by the Principal Investigator)
(Sept. 1, 1975 - Oct. 1, 1976)

A. Which have appeared during the Period October 1, 1975 to October 1, 1976.

1) Ethylene Formation in Carbon Atom Reactions: Mechanisms and Isotope Effects. J. Amer. Chem. Soc., 97, 5970 (1975). Removed

2) Positronium Interactions in Binary Mixtures of Organic Compounds. Radiochem. radioanal. Letters, 23, 249 (1975). Removed

3) The Effect of Solvents on the Stability of Positronium Complexes in Solution. Radiochem. radioanal. Letters, 23, 283 (1975). Removed

4) Positronium and Muonium Chemistry, in "Hot Atom Chemistry Status Report", p. 81-105, IAEA, Vienna 1975. Removed

5) On the Preparation of $^{80}$Br or $^{82}$Br-Biomolecules via Excitation Labelling Methods. Int. J. Appl. Rad. Isotopes, 27, 19 (1976). Removed

6) On the Annihilation Lifetimes of Positrons in Positronium Complexes. J. Phys. Chem., 80, 451 (1976). Removed

7) On the Stereochemistry of the Bromine for Halogen Exchange Following $^{79}Br(n,\gamma)^{80m}Br$ and $^{82m(80)}Br$ (I.T.)$^{82(80)}Br$ in Diastereomeric 2,3-Dichlorobutanes. J. Phys. Chem., 80, 659 (1976). Removed

8) Positronium Formation in Binary Mixtures of Organic Compounds. J. Chem. Phys., 65, 247 (1976). Removed

9) Studies of Molecular Complex Formation by Positron Annihilation Techniques. J. Phys. Chem., 80, 1693 (1976). Removed

10) On the Preparation of $^{80}$Br-BiomoleculesII: $^{80}$Br for I Exchange in Iodo-Biomolecules. Int. J. Appl. Rad. Isotopes, 27, 379 (1976). Removed

11) Ethylene-C$^{11}$ Formation in Hydrogen-Alkylhalide Mixtures, Radiochim Acta, 22, 148 (1975). Removed

### B. Which are accepted and in press

1) Evidence for the Electronic States of Recoil Carbon Atoms Undergoing Reaction. J. Amer. Chem. Soc., in press. Removed

2) On the Preparation of $^{80}$Br-Biomolecules III: The Effect of Various Experimental Parameters on Radiochemical Yields Int. J. Appl. Rad. Isotopes, in press. Removed

3) Interactions of Positrons and Positronium with Inorganic Compounds in Solution. Proc. Fourth Symp. on Radiation Chem., Keszthely, Hungary, in press.

### C. Which are submitted

Removed

1) On the Stereochemical Course of the Chlorine-38 for Chlorine Substitution in Diastereomeric Dichloroalkanes: 2,4-Dichloropentane and 2,3-Dichlorobutane. J. Phys. Chem. submitted.

2) Ethylene-C$^{11}$ Formation in Alkylchlorides Mechanisms and Isotope Effects. Radiochim. Acta, submitted. Removed

3) On The Stereochemistry of Chlorine-38 for Chlorine Exchange Following $^{37}(n,\gamma)^{38}$Cl in Diastereomeric 1,2-Dichloro-1,2-difluoroethanes in Solutions. J. Phys. Chem., submitted. Removed

4) Studies of Molecular Association in Biological Systems by Positron Annihilation Techniques. J. Amer. Chem. Soc., submitted. Removed

5) Inhibition of Positronium Formation and Reactions of Positronium Atoms in Solutions. Int. J. Radiat. Phys. Chem., submitted. Removed

### D. Ph.D. Thesis

Ralph E. Wild: On the Reactions of Ortho Positronium Atoms and the Inhibition of Positronium Formation.

## Papers Presented at Scientific Meetings and Invited Seminars (During the period Oct. 1, 1975 - Oct. 1, 1976).

1) "Positronium Formation in Mixtures of Organic Compounds", 27th Southeast-31 Southwest Regional Meeting of the American Chemical Society, Memphis, Tennessee, Oct. 29-31, 1975.

2) "On the Reactions of Bromine Species Activated by the $^{80m}Br \rightarrow ^{80}Br$ Isomeric Transitions or $^{79}Br(n,\gamma)^{80m}Br$ Nuclear Reaction with Halogenated Hydrocarbons". First Chemical Congress of the North American Continent, Mexico City, Nov. 30-Dec. 5, 1975.

3) "The Energetics and Mechanisms Involved in the Reactions of Energetic Carbon-11 Atoms with Simple Organic Molecules", 12th International Symposium on Free Radicals, Laguna Beach, Calif., Jan. 4-9, 1976.

4) "The Chemistry of the Positronium Atom", 12th International Symposium on Free Radicals, Laguna Beach, Calif., Jan. 4-9, 1976.

5) "New Aspects of Positronium Chemistry", Seminar, University of Nebraska, Lincoln, Nebraska, Jan. 23, 1976 (Invited).

6) "The Application of Modern Radiochemical Methods for the Preparation of Radiopharmaceuticals". Seminar, Old Dominion University, Norfolk, Va., April 21, 1976 (Invited).

7) "Studies of Molecule Complex Formation by Positron Annihilation Techniques", Annual Meeting of the Virginia Academy of Sciences, Fairfax, Va. May 11-14, 1976.

8) "On the Stereochemistry of the Bromine and Tritium for Chlorine Exchange in Liquid Diastereomeric 1,2-Dichloro-1,2-difluoro-ethanes", Annual Meeting of the Virginia Academy of Sciences, Fairfax, Va., May 11-14, 1976.

9) "The Effect of Solvents on the $^{38}Cl$ for Cl Exchange Mechanisms in Diastereomeric and Optical Isomeric Organic Molecules", Annual Meeting of the Virginia Academy of Sciences, Fairfax, Va., May 11-14, 1976.

10. "Interactions of Positrons and Positronium Atoms with Inorganic and Organic Molecules". Fourth Symposium on Radiation Chemistry, Kewzthely, Lake Balaton, Hungary, June 1-5, 1976.

11. "Application of Positron Annihilation Techniques in Chemical Research", Eötvös University of Budapest, Budapest, Hungary, June 7, 1976 (Invited).

12) "Recent Results in Positronium Chemistry", Seminar, Hungarian Academy of Sciences, Central Research Institute of Physics, Budapest, Hungary, June 8, 1976 (Invited).

13) "On Positronium Formation in Binary Mixtures of Organic Compounds" Fourth International Conference of Positron Annihilation, Helsingor, Denmark, Aug. 23-26, 1976.

14) "On the Annihilation Lifetimes of Positrons Bound in Positronium Complexes", Fourth International Conference on Positron Annihilation, Helsingor, Denmark, Aug. 23-26, 1976.

15) "Molecular Complex Formation between Positronium and Organic Molecules in Solutions", Fourth International Conference on Positron Annihilation, Helsingor, Denmark, Aug. 23-26, 1976.

16) "Studies of Charge-Transfer Complex Formation in Biological Systems by Positron Annihilation Techniques", Fourth International Conference on Positron Annihilation, Helsingor, Denmark, Aug. 23-26, 1976 (Invited).

17) "On the Preparation of $^{80}$Br- or $^{82}$Br-Biomolecules via Excitation Labeling Methods," First International Symposium on Radiopharmaceutical Chemistry, Brookhaven National Laboratory, Sept. 21-24, 1976.

18) "New Aspects of Positronium Chemistry" Seminar,Academy of Sciences of the U.S.S.R., Moscow, Sept. 8, 1976 (Invited).

19) "Reactions of Hot Carbon-11 Atoms", Seminar Academy of Sciences of the U.S.S.R, Moscow, Sept. 9, 1976 (Invited).

20) "Advances in Positronium Chemistry", Seminar, University of Zürich, Zürich, Switzerland, Sept. 17, 1976 (Invited).

21) "The Application of the Positron Annihilation Technique as Nuclear Probe is Solid State Chemistry", Symposium on Nuclear Methods in Solid State Chemistry , German Chemical Society, Jülich, Germany, Sept. 20-23 (Invited).

## Other Activities of the Principal Investigator

Chairman of the Organizing Committee for the 9th International Hot Atom Chemistry Symposium, Blacksburg, Virginia, Sept. 1977.

Referee for J. Amer. Chem. Soc., J. Phys. Chem., Chem. Physics, Radiochimica Acta, Appl. Phys., Petroleum Research Fund, NSF and ERDA.

Session Chairman at the Fourth International Conference on Positron Annihilation, Helsingor, Denmark, August 23-26, 1976.

Received an International Travel Grant to attend the Fourth International Conference on Positron Annihilation, Helsingor, Denmark, Aug. 23-26, 1976 and to present lectures at the Academy of Sciences of the U.S.S.R., Moscow, in September 1976.

Organizer and Symposium Chairman of the Symposium on "Positronium and Muonium Chemistry" at the combined Meeting of the American Chemical Society and Canadian Institute of Chemists, Montreal Canada, June 1977.

Research Collaborator with the Chemistry Department of Brookhaven National Laboratory, Upton, New York.

Running List of Papers Published before October 1, 1976

Ache, Hans J.

Publications:

| | | |
|---|---|---|
| 1. | K. Alder,<br>H. J. Ache<br>and F. H. Flock | Diels-Alder Reactions with Spiro- 2,4- heptadiene-(1,3)<br>Chem. Ber. 93, 1888 (1960). |
| 2. | K. Alder and<br>H. J. Ache | The Formation of Santene and Other Substituted Bicyclo-1.2.2 - heptenes<br>Chem. Ber. 95, 503 (1962). |
| 3. | K. Alder and<br>H. J. Ache | Thermal Rearrangements in the Bicyclo- 1.2.2 -heptene System<br>Chem. Ber. 95, 503 (1962). |
| 4. | H. J. Ache | The Diels-Alder Reaction of Substituted Cyclopentadienes with Ethylene and Thermal Rearrangements in the Bicyclo-1.2.2 -heptene System<br>Dissertation, University of Cologne, 1959 |
| 5. | H. J. Ache,<br>A. Thiemann<br>and W. Herr | Radiogaschromatographic Analysis of Tritium-Labelled Aromatic Nitro- and Chlorocompounds at Higher Temperatures<br>Z. analyt. Chem. 181, 551 (1961) |
| 6. | H. J. Ache,<br>W. Herr and<br>A. Thiemann | Gaschromatographic Studies on the Distribution of Tritium in Labelled Toluene<br>Chemical Effects of Nuclear Transformations Vol 2, p. 111, I.A.E.A., Vienna (1961). |
| 7. | H. J. Ache,<br>W. Herr and<br>A. Thiemann | Study on the Position of Tritium in Aromatic Molecules Labelled by Different Methods<br>Tritium in the Physical and Biological Sciences Vol 2, p. 21, I.A.E.A., Vienna (1962) |
| 8. | H. J. Ache,<br>A. Thiemann<br>and W. Herr | The Catalytic Effect of Iodine in the $H^3$-Labelling via the Wilzbach Method<br>Angew. Chem. 73, 707 (1961) |
| 9. | H. J. Ache<br>and W. Herr | The Mechanism of the $\beta^-$-decay induced $H^3$-Labelling of the Toluene Molecule<br>Z. Naturforsch. 17a, 631 (1962) |
| 10. | H. J. Ache<br>and A. P. Wolf | Reactions and Mechanisms Involving Hot Carbon Atoms and $N_2$-$H_2$, $N_2$-Alkane and $N_2$-Alkane-Moderator Systems Including their Relationship to Other Simple Systems<br>Chemical Effects Associated with Nuclear Reactions and Radioactive Transformations, I.A.E.A., Vol. 1, p. 107, Vienna (1965) |
| 11. | H. J. Ache<br>and A. P. Wolf | Reactions of Energetic Carbon Atoms with Nitrogen Molecules<br>Radiochimica Acta, 6, 32 (1966) |

| | | |
|---|---|---|
| 12. | H. J. Ache<br>and A. P. Wolf | Radiogaschromatographic Separations of the Isotopic Ethylenes<br>Z. Analyt. Chem., 230, 19 (1967). |
| 13. | H. J. Ache<br>and A. P. Wolf | Bond Energy Effects and Acetylene Production in the Reactions of Energetic Carbon Atoms with Alkylhalides and Propane<br>J. Am. Chem. Soc., 88, 888 (1966) |
| 14. | H. J. Ache<br>and A. P. Wolf | The Effect of Radiation on the Reactions of Recoil Carbon-11 in the Nitrogen-Oxygen Systems<br>J. Phys. Chem., 72, 1988 (1968). |
| 15. | H. J. Ache | The Effect of Rare Gases and Aromatic Admixtures on the Self-Induced Isotopic Exchange of Tritium with Toluene<br>J. Phys. Chem., 71, 3388 (1967). |
| 16. | H. J. Ache<br>and A. P. Wolf | Reactions of Energetic Carbon$^{11}$ atoms in Fluorohydrocarbon Systems<br>Radiochimica Acta, 10, 41 (1968). |
| 17. | C. T. Somma<br>and H. J. Ache | Self-induced Tritium Labeling in Cyclohexane Benzene Mixtures<br>Radiochimica Acta, 10, 49 (1968). |
| 18. | H. J. Ache<br>D. R. Christman,<br>and A. P. Wolf | Mechanisms and Isotope Effects in the Reactions of Energetic Carbon Atoms with Hydrocarbons and Alkylfluorides<br>Radiochimica Acta, 12, 121 (1969). |
| 19. | H. J. Ache<br>and A. P. Wolf | Production and Reactivity of Carbon-11 in Solid Compounds<br>J. Phys. Chem., 73, 3499 (1969). |
| 20. | R. D. Finn,<br>A. P. Wolf<br>and H. J. Ache | Chemical Effects Following $N^{14}(n,p)C^{14}$ in Magnesium nitride<br>J. Phys. Chem., 73, 3928 (1969). |
| 21. | Y. S. Wu<br>and H. J. Ache | On the Mechanism of the Self-induced Exchange of Tritium with Halogenated Organic Molecules I. Halogenated Aromatic Hydrocarbons<br>J. Phys. Chem., 73, 2424 (1969) |
| 22. | T. L. Williams<br>and H. J. Ache | Positronium Chemistry in Aqueous $KMnO_4$<br>J. Chem. Phys., 50, 4493 (1969) |
| 23. | T. L. Williams<br>and H. J. Ache | Radiation Damage Dependence of Positron Lifetimes in Sodiumhalide Crystals<br>J. Chem. Phys., 51, 3536 (1969) |
| 24. | V. Carr<br>and H. J. Ache | On the Mechanism of the Self-induced Exchange of Tritium with Halogenated Aliphatic Hydrocarbons<br>Radiation Res., 41, 15 (1970) |

| | | |
|---|---|---|
| 25. | C. M. Wang<br>and H. J. Ache | Positron Annihilation in Helium and the System of $e^+$He Bound State<br>J. Chem. Phys., 52, 4023 (1970). |
| 26. | C. M. Wang<br>and H. J. Ache | Temperature and Phase Dependence of Positron Lifetimes in Choline Chloride<br>J. Chem. Phys., 52, 5492 (1970). |
| 27. | C. S. Tumosa<br>and H. J. Ache | Recoil Atoms from (n,$\gamma$) Reactions<br>Radiochimica Acta, 14, 83 (1970) |
| 28. | H. J. Ache | The Application of Positron Annihilation as a Chemical Probe<br>Proc. VIth International Symposium on Microtechniques, Vol. D, 133 (1970). |
| 29. | R. D. Finn,<br>A. P. Wolf,<br>and H. J. Ache | The Effect of Radiation on the Reactions of Recoil Carbon-11 in the Perfluorocarbon-Oxygen Systems<br>J. Phys. Chem., 74, 3194 (1970). |
| 30. | C. S. Tumosa<br>J. B. Nicholas<br>H. J. Ache | The Interactions of Positrons with Defects in Sodium Chloride Crystals<br>J. Phys. Chem., 75, 2030 (1971). |
| 31. | R. D. Finn<br>D. R. Christman<br>H. J. Ache and<br>A. P. Wolf | The Preparation of Cyanide-$^{11}$C for Use in the Synthesis of Organic Radiopharmaceuticals<br>Int. J. Appl. Radiot. Isotopes, 22, 735 (1971). |
| 32. | H. B. Swordsma<br>C. S. Tumosa<br>and H. J. Ache | The Effect of $\gamma$-Radiation on the Oxidation State of Manganese in $KMnO_4$<br>Radiochimica Acta, 16, 112 (1971) |
| 33. | H. J. Ache | The Chemistry of the Positron and Positronium<br>Angew. Chem., 84, 234 (1972); Int. Ed. 11, 179 (1972). |
| 34. | L. J. Bartal<br>J. B. Nicholas<br>and H. J. Ache | The Reactions of Energetic Positronium Atoms in Solutions<br>J. Phys. Chem., 76, 1124 (1972). |
| 35. | J. B. Nicholas<br>and H. J. Ache | Phase and Temperature Dependence of Positron Annihilation in Liquid Crystals<br>J. Chem. Phys., 57, 1597 (1972). |
| 36. | R. D. Finn<br>H. J. Ache<br>and A. P. Wolf | The Effect of Rare Gas Additives on the Reactions of Energetic Carbon-11 Atoms Following $^{12}$C (p,pn)$^{11}$C in Saturated Hydrocarbon Systems<br>Radiochimica Acta, 17, 131 (1972). |
| 37. | L. J. Bartal<br>and Hans J. Ache | Reactions of Energetic Positronium Atoms in Oxidizing Solutions.<br>Radiochimica Acta, 17, 205 (1972). |

| | | |
|---|---|---|
| 38. | J. B. Nicholas<br>L. J. Bartal<br>R. E. Wild<br>and H. J. Ache | Effect of Complex Formation on the Reactions of Positronium Atoms with Inorganic Ions<br>J. Phys. Chem., 77, 178 (1973) |
| 39. | C. S. Tumosa<br>C. M. Wang<br>and H. J. Ache | Annihilation of Positrons in Hydrocarbons and Halogenated Hydrocarbons Adsorbed on Silica Gel<br>J. Chem. Phys., 58, 1833 (1973) |
| 40. | J. B. Nicholas<br>C. S. Tumosa<br>and H. J. Ache | Thermal Annealing of Radiation Damage in NaCl Crystals Studied by Positron Annihilation Techniques<br>J. Chem. Phys., 58, 2902 (1973) |
| 41. | L. J. Bartal<br>and H. J. Ache | Reactions of Carboniumions with Positronium Atoms in Solution<br>J. Phys. Chem., 77, 2060 (1973) |
| 42. | L. J. Bartal<br>and H. J. Ache | Hot Atom Chemistry of Ps-atoms in Aqueous Solutions of Inorganic Compounds<br>Radiochimica Acta, 19, 49 (1973) |
| 43. | S. H. Daniel<br>and H. J. Ache | Electrophilic Substitution Reactions of Bromine Ions with Halomethanes in the Gasphase<br>Radiochimica Acta, 19, 132 (1973) |
| 44. | L. J. Bartal<br>and H. J. Ache | Reactivity of Positronium Atoms Towards Some Cobalt(III) Complexes in Aqueous Solutions<br>J. Inorg. Nucl. Chem., 36, 267 (1974) |
| 45. | L. J. Bartal<br>and H. J. Ache | On the Energetics of the Positronium Oxidation Process in Aqueous Solutions of Inorganic Ions<br>J. Inorg. Nucl. Chem., 36, 922 (1974) |
| 46. | W. J. Madia<br>A. L. Nichols<br>and H. J. Ache | Study of the Electron Donor-Acceptor Properties of Diamagnetic Organic Molecules via Positronium Reactions<br>J. Chem. Phys., 60, 335 (1974) |
| 47. | W. J. Madia<br>A. L. Nichols<br>and H. J. Ache | Positronium Reactions with Diamagnetic Organic Molecules<br>Applied Physics, 3, 189 (1974) |
| 48. | W. J. Madia<br>A. L. Nichols<br>and H. J. Ache | Study of Electron Donor-Acceptor Properties of Organic Molecules via Positronium Reactions<br>Ber. Bunsenges. Physik. Chem., 78, 179 (1974) |
| 49. | S. H. Daniel<br>G. Stöcklin<br>and H. J. Ache | On the Stereochemistry the Decay-Induced Gas Phase Halogen Exchange in Diastereomeric 2,3-Dichlorobutanes<br>J. Phys. Chem., 78, 1043 (1974) |
| 50. | A. L. Nichols<br>L. J. Bartal<br>R. E. Wild<br>and H. J. Ache | Positronium Atom Reaction in Aqueous Solutions of Fe(III) Complexes<br>Applied Physics, 4 , 37 (1974) |

| | | |
|---|---|---|
| 51. | A. L. Nichols<br>W. J. Madia<br>and H. J. Ache | Reactivity of Aromatic compounds Toward Positronium Atoms, J. Phys. Chem., 78, 1881 (1974). |
| 52. | Y. Y. Su<br>C. Metcalfe<br>and H. J. Ache | On the Reactions of Bromine Species Activated by the $^{82m}$Br → $^{82}$Br and $^{80m}$Br → $^{80}$Br Isomeric Transitions with Cycloalkylbromides<br>Radiochem. radioanal. Letters 18, 349 (1974). |
| 53. | W. J. Madia<br>A. L. Nichols<br>J. C. Schug<br>and H. J. Ache | Approximate Molecular Orbital Study of Organic Positron and Positronium Complexes<br>J. Phys. Chem., 78, 2682 (1974). |
| 54. | H. J. Ache | Chemical Reactions of the Positronium Atom,<br>Nachr. Chem. Techn, 23, 108 (1975). |
| 55. | W. J. Madia<br>A. L. Nichols<br>and H. J. Ache | Molecular Complex Formation Between Positronium and Organic Molecules in Solutions.<br>J. Amer. Chem. Soc., 97, 5041 (1975). |
| 56. | K. K. Taylor<br>A. P. Wolf<br>and H. J. Ache | Ethylene Formation in Carbon Atom Reactions: Mechanisms and Isotope Effects.<br>J. Amer. Chem. Soc., 97, 5970 (1975). |
| 57. | R. E. Wild<br>and H. J. Ache | Positronium Interactions in Binary Mixtures of Organic Compounds<br>Radiochem. radioanal. Letters, 23, 249 (1975). |
| 58. | E. Hall<br>W. J. Madia<br>and H. J. Ache | The Effect of Solvents on the Stability of Positronium Complexes in Solution<br>Radiochem. radioanal. Letters, 23, 283 (1975). |
| 59. | H. J. Ache | Positronium and Muonium Chemistry, in "Hot Atom Chemistry Status Report", p. 81-105, IAEA, Vienna 1975 |
| 60. | S. H. Wong<br>and H. J. Ache | On the Preparation of $^{80}$Br or $^{82}$Br-Biomolecules via Excitation Labelling Methods<br>Int. J. Appl. Rad. Isotopes, 27, 19 (1976). |
| 61. | W. J. Madia<br>and H. J. Ache | On the Annihilation Lifetimes of Positrons in Positronium Complexes.<br>J. Phys. Chem., 80, 451 (1976). |
| 62. | Y. Y. Su<br>and H. J. Ache | On the Stereochemistry of the Bromine for Halogen Exchange Following $^{79}$Br(n,γ)$^{80m}$Br and $^{82m(80m)}$Br (I.T.)$^{82(80)}$Br in Diastereomeric 2,3-Dichlorobutanes<br>J. Phys. Chem., 80, 659 (1976). |
| 63. | R. E. Wild<br>and H. J. Ache | Positronium Formation in Binary Mixtures of Organic Compounds<br>J. Chem. Phys., 65, 247 (1976). |

64. Y. C. Jean and H. J. Ache — Studies of Molecular Complex Formation by Positron Annihilation Techniques J. Phys. Chem., 80, 1693 (1976).

65. S. H. Wong, J. F. Mustaklem and H. J. Ache — On the Preparation of $^{80}$Br-Biomolecules II: $^{80}$Br for I Exchange in Iodo-Biomolecules, Int. J. Appl. Rad. Isotopes, 27, 379 (1976).

66. K. K. Taylor, A. P. Wolf and H. J. Ache — Ethylene-C$^{11}$ Formation in Hydrogen-Alkylhalide Mixtures Radiochim Acta, 22, 148 (1975).