Reactions of Charged and Neutral Recoil Particles Following Nuclear Transformations

Progress Report No. 11

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Table of Contents

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Introduction

The following is a report of the work completed during the period September, 1976 - August, 1977: 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 multiplicity 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 reactions. It was especially this latter topic which was thoroughly scrutinized during the recent contract periods.

We feel that the evaluation of the molecular properties of solvent molecules which appear to be responsible for their caging efficiency can significantly contribute to a better understanding of the photocatalytic cage effects and/or deexcitation processes. These factors may in turn substantially affect the yields of photochemical reactions used in photochemical energy conversion processes.

The importance of the search for direct non-synthetic methods to incorporate shortlived radionuclides into molecules of biochemical interest to prepare carrier free compounds of high specific activity to be used in nuclear medical research has long been recognized as an important goal in the nuclear science program.

Under this contract methods such as the excitation labeling which have been developed as a result of our basic hot atom chemistry program are tested as potential synthetic routes to prepare such radiopharmaceuticals.

An important aspect in our ongoing research program is related to the problems involved in power generation via nuclear fusion. Tritium released in this operation may eventually become incorporated into organic molecules or biomolecules which are components of essential enzyme systems.

The investigation of the various steps involved in this incorporation process from its initial state, T_2, to its final position in biomolecules will therefore be of great importance for an assessment of the potential health hazards presented by the expected tritium release.

Directly related to this aspect is the study of the chemical consequences of the nuclear decay of T (or other radionuclides) in these molecules, where the radiotoxicity has been found to depend on the amount of radiolysis caused by beta radiation as well on the subsequent reactions of the chemical species formed as a result of the transmutation.

Another aspect of hot atom chemistry most directly related to Energy Research and Development is the fact that energy generation via thermonuclear fusion processes in CTR's is strongly impacted by "hot atom phenomena". Hot ions and atoms produced in the plasma impinge with considerable kinetic energies on the vacuum walls of the CTR causing corrosion of the first wall resulting in plasma contamination.

The fate of hot atoms and ions incorporated into deeper layers of the materials and their reactions with the materials suggested as wall material or as protective curtain, such as graphite, and their potential effect on CTR operation is presently investigated under this contract.

In the following a detailed discussion of the present status of research and the results of our recent work will be given.

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 (1976)

Previous work in Prof. Stöcklin's laboratory had suggested that solvents may govern the stereochemical course of the ^{38}Cl for Cl exchange via a "conformational" effect i.e. the relative amounts of conformers present in the reaction mixture and their relative accessibility determine the mode of substitution leading to retention or inversion of configuration.

More recent evidence obtained in our laboratory indicated 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.

From a careful evaluation of the various properties of the solvents, the conclusion was reached in our laboratory 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.

Summary of Recent Work

Because of the great importance of the question as to how solvent 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 in our laboratory to accumulate more evicence for the detailed nature of the effect of solvents on the stereochemical course of hot halogen for halogen exchange reactions.

The strongest argument which we used against the conformational effect was that in the case of 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 stereochemistry of the chlorine-38 for chlorine substitution in this compound shows again a strong solvent dependence. (Appendix II)

In order to further substantiate these findings this investigation was extended to the study of the chlorine-38 for chlorine exchange following $^{37}(n,\gamma)^{38}$Cl in the diastereomeric 1,2 dichloro-hexafluorocyclobutanes, where the cis form exists only in one configuration, namely the axial-equatorial form, and where the trans form could potentially have two conformers. NMR investigations, however, showed no conformational effect when the trans form was dissolved in solvents with different dielectric constants. The fact that the ^{38}Cl for Cl substitution in these substrates results again in substitution products with ratios of retained and inverted configuration depending on the solvent used, clearly confirms our contention that the reaction is directly controlled by the solvent properties. (Appendix III)

Simultaneously, the investigation using the diastereomic 1,2-dichloro-1,2-difluoroethanes, which was started in cooperation with Prof. Rack's laboratory, was expanded to include more solvents and a detailed NMR analysis of the trans isomer was carried out. The experimental results in this study are consistent with the previously obtained results in the 2,3 dichlorobutane and 2,4 dichloropentane and further support our model.

Considerable effort was spent to assess the solvent effect on the stereochemical course of the ^{38}Cl for Cl substitution in optical isomers in solution, such as d and l CH_3-CHCl-CH_2OH, where the resulting products have the same thermodynamic properties.

The data analysis in this system is complicated by the fact, that the enantiomers have to be converted into the corresponding diastereomers via reactions with an optical active agent. This procedure as well as a rather time consuming gas chromatographic seperation, which is still not complete, makes an interpretation of the experimental results still somewhat doubtful. However the preliminary results would indicate the same general trends as observed in the other systems. These latter investigations will be continued.

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.

Although these investigations were aimed at the feasibility of detecting and measuring yields from caging reactions in nuclear recoil experiments, it stands to reason that the factors evaluated in this work are also the same which most likely control chemical reactions proceeding at slightly lower energies as in the case of the photochemical processes. Thus the understanding of the parameters which contribute to better caging efficiencies, which in turn may predominantly determine the chemical product yields in these reactions, has also a great practical importance.

It seems interesting to point out that a dependence on the same solvent parameters was found for the deexcitation of fluorescing molecules in solutions which also involves rapid energy transfer processes. 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 1976

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

In our laboratory experiments were carried out with the aim to develop methods by which radioactive bromine could be directly and rapidly introduced into biomolecules such as deoxyuridine, guanosine, cytidine, tyrosine, etc. resulting in a formation of carrier free radiobrominated biomolecules. 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 which suggested that Br^+ is not a very efficient brominating agent.

Thus it appeared necessary to convert the Br^+ which is generated as a result of the isomeric transition e.g. $^{80m}Br \rightarrow {}^{80}Br$, into a species which exhibits a greater reactivity in exchange reactions.

Such a species seemed to be a combination of bromine with chlorine. As discussed in detail in the previous progress reports, it was found that chlorine gas additives enhanced the exchange process drastically and exchange yields of more than 50-60% were easily achieved.

This suggested that intermediates such as BrCl may play an important role in the labelling process. 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.

This latter method is, however, not generally applicable, e.g. it does not work with deoxyuridine and deoxycytidine.

As shown in our laboratory bromine substitution can, however, be achieved if iododeoxyuridine instead of deoxyuridine is used as substrate. In this case labelling yields of greater than 80% have been obtained by the CF_3Br-$KBrO_3$ exposure technique. The yields observed are independent of the bromine source ($CF_3{}^{82m}Br$ or $CF_3{}^{80m}Br$).

Furthermore, a detailed study of the reaction conditions revealed the importance of factors, such as exposure or labelling time, amount of substrate used, on the radiochemical yields (see 1976 progress report).

Summary of Recent work

As described in the previous progress reports, the work in our laboratory has undoubtedly led to significant improvements in the technical aspects of the radiobromine labelling of the model molecules under investigation, by using the modified $CF_3{}^{80m}Br-Cl_2$ and $CF_3{}^{80m}Br-KBrO_3$ exposure technique.

However, as successful as these experiments may have been so far as the practical aspects of preparing radiobromine labelled molecules of high specific activity or carrier free in a fast and efficient way are concerned, they have provided only very little information about the nature of the reacting species and the reaction mechanism itself.

This information, however, is vital for a more general application of these techniques.

Therefore the research during the past contract period was centered on an evaluation of the nature of the bromine species which carry out the labelling process.

For this purpose the ^{80}Br exchange in a series of benzene derivatives via the various labeling techniques was investigated. If aniline was subjected to the direct $CF_3{}^{80m}Br$ exposure technique, it was found that the radiobromine incorporated by this method was overwhelmingly in the ortho-position and para-position 35% and 65%, respectively and only <1% in meta. The fact that the NH_2-group when attached to an aromatic ring is strongly ortho-para directing in electrophilic reactions would suggest that the substituting bromine species is electrophilic in nature.

A similar conclusion was reached as the result of the incorporation of radiobromine in aniline via the $CF_3{}^{80m}Br$-$KBrO_3$ gas exposure method. Here the incorporation occurs again mostly into the ortho and para position (on the average 45% ortho and 55% para, depending somewhat on the acid concentration).

Para and ortho substitution is also prevalent in the case of phenol, however, in this system more than 85% of ^{80}Br is found in the para position and only 15% in the ortho position. The direct labeling via the $CF_3{}^{80m}Br$ gas exposure technique yields in the latter system again mostly ortho and para product but in decidedly different amounts, 40% in ortho and 60% in para.

While the reactive ^{80}Br species in the direct labeling procedure might be a simple positively charged bromine ion, in the case of the $CF_3{}^{80m}Br$-$KBrO_3$ method it seems very likely that the Br^+ initially generated in the isomeric transition undergoes secondary reactions in the acidic solution to form species which will carry out the labeling process.

This assumption is further supported by the fact that only $KBrO_3$ and not $KClO_3$ or KIO_3 is effective in this process and that this process requires an acidic medium. These finding again suggest that it is not a simple reactive Br species trapped on the surface of a crystal which reacts in the solution with the substrate molecule but that a reactive Br-intermediate is formed, whose formation and/or reaction shows a very subtle dependence on the experimental conditions.

Therefore a series of experiments was initiated to identify these species by ionic exchange and electrophorisis. Preliminary results seem to indicate that $H_2O\ Br^+$ species might be involved in the labeling process.

Significance

Even though the vast majority of radiopharmaceuticals to date have been prepared with radioiodine, in many cases bromine would be preferable. The C-Br bond is about 10-15 kcal/mole stronger than that of the corresponding C-I bond, and hence the label is more stable. From the neutron deficient bromine isotopes the nuclides with mass numbers 74 to 77 are potentially useful.

Unfortunately neither one of these isotopes can be produced with the facilities available at VPI and SU. However, the techniques ^{80}Br and ^{82}Br of radiobromine incorporation studied in this work are with slight modification also applicable to the ^{77}Br labelling of these compounds.

The studies in laboratory showed that 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 agent, 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.

3. Reactions of Energetic Tritium Species in Graphite.

Background and Status of Research 1976

Most directly related to the interests of ERDA in the field of energy generation is the fact that energy production via the thermonuclear fusion processes in CTR's is strongly impacted by "hot atom" phenomena.

One of the problems involved in the operation of Controlled Thermonuclear Reactors (CTR) is the erosion of metallic vacuum walls (first wall) by charged particles leaking from tokamac plasma and the effect of impurities resulting from these interactions on plasma operation. Since it was found that high-Z impurities have the most significant effect on plasma performance it has been suggested to protect the first wall in the CTR by using a graphite curtain between plasma and metallic vacuum wall.

Several investigation were carried out to study the gas content and hydrogen sticking probabilities for atomic and molecular hydrogen at thermal energies from which it was concluded that the vacuum properties of graphite would be compatible with the operating conditions prevalent in CTR.

However, very little attention has so far been given to the interaction of the energetic hydrogen, deuterium or tritium species leaving the plasma with the graphite and their potential effect on plasma contamination

Therefore, in order to simulate the CTR conditions where hydrogen isotope species, ions and atoms, with kinetic energies of 10-580 KeV are formed as a result of the fusion processes, we exposed various samples of graphite to tritium species generated in the $^3He(n,p)T$ reaction with maximum recoil energies of 194 KeV followed by heating the samples to temperatures up to 1000°C, i.e. temperatures expected to prevail in the projected carbon curtains during CTR operation.

The absolute and relative amounts of the gaseous products, mostly HT, CH_3T and C_2 hydrocarbons, under a variety of conditions were analyzed and an attempt was made to assess the fate of these energetic tritium species in graphite as well as its implication on CTR operation.

Summary of Recent Work

As described in greater detail in appendix I, in order to simulate some of the conditions present at the first wall of a Controlled Thermonuclear Reactor, recoil tritium from the $^3He(n,p)T$ reaction has been allowed to react with nuclear and non-nuclear grades of graphite. Graphite has been proposed as a protective curtain between plasma and the first wall to prevent contamination of the plasma by sputtered materials.

The tritiated gases formed on heating of the samples after irradiation were found to consist predominately of hydrogen (HT) and methane (CH_3T), with smaller amounts of all C_2 hydrocarbons and propane. The total and relative amounts of the gases varied depending on the type of graphite used. Heating of the samples prior to irradiation significantly reduced the total amount of labelled gases formed. This was taken to indicate that most of the gases released upon heating after irradiation arise from the reaction of these gases with tritium bound to the graphite. In the absence of the released gases, the tritium remains bound to the graphite. In relation to the first wall of the reactor, this would indicate that subsequent build up of the tritium in the graphite could, over an extended period of time, result in contamination of the plasma by formation of hydrocarbon products.

Significance

The preliminary results indicate that the more energetic (hot) fraction of the hydrogen species escaping the plasma becomes tightly bound to graphite and is not immediately released as H_2, HT etc., if the graphite has been thoroughly degasses, and present, therefore, little danger for a possible contamination of the plasma.

This situation however, may change if the structure of the graphite is drastically damaged by prolonged neutron or proton irradiation. Studies to evaluate these effects will be carried out in the near future.

B. THE CHEMISTRY OF THE POSITRONIUM

Positron Lifetime Measurements in γ-Irradiated Organic Solids

Background and Status of Research 1976

Positron annihilation techniques were frequently used in the past to study radiation defects in solid organic compounds. Several authors attempted to establish a correlation between positron lifetime characteristics and radiation produced radicals in these compounds. Thus in connection with our investigations of the results of the decay of radioactive nuclides in biomolecules (see previous research proposal), such as tritium or radioactive halogen labeled deoxyuridine, guanosine etc. positron annihilation techniques were evaluated in order to see whether this method can reveal further details about radiation induced species present in these substrates which cannot be detected by ESR techniques.

Summary and Significance of Recent Work

As discussed in detail in appendix V four organic solids, adamantane, guanosine, 2'-deoxyuridine and 5-iodo-2'-deoxyuridine were γ-irradiated in the dose range from 0 to 200 Mrad and their positron annihilation lifetimes and ESR signals measured, with and without subsequent thermal annealing. No consistent correlation between the positron lifetimes data, λ_1 and λ_2, and there associated intensities I_1 and I_2 and free radical concentration or absorbed radiation dose could be observed. On the basis of these results, it appears that the positron annihilation method is not a sensitive technique for the study of paramagnetic centers or radicals in irradiated solid organic materials because the interactions of positron or positronium with these species are relatively slow and are severely obscured by the response of the positron annihilation process to radiation induced structural changes in these solid materials.

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-)
   Dr. Edward D. Handel (April 1, 1977-)

3. Graduate Students
   Steven H. Wong (term. with Ph.D., Feb. 1977)
   Eugene S. Hall
   Jiann-long Wu (term. with Ph.D., May 1977
   Tobias R. Acciani (term. with Ph.D., Sept. 1977)
   Jack Mustaklem
   Belkacem Djermouni
   Onofre de Jesus

Publications (by the Principal Investigator)
(Sept. 1, 1976 - Oct 1, 1977)

A. Which have appeared during the Period October 1, 1976 to October 1, 1977).

1).	K. K. Taylor A. P. Wolf and H. J. Ache	Evidence for the Electronic States of Recoil Atoms Undergoing Reaction J. Amer. Chem. Soc., 98, 7176 (1976)
2)	S. H. Wong J. F. Mustaklem and H. J. Ache	On the Preparation of ^{80}Br-Biomolecules III: The Effect of Various Experimental Parameters on Radiochemical Yields Int. J. Appl. Rad. Isotopes, 27, 627 (1976)
3).	Y. C. Jean and H. J. Ache	Studies of Molecular Association in Biological Systems by Positronium Annihilation Techniques J. Amer. Chem. Soc., 99, 1623 (1977)
4).	R. E. Wild L. J. Bartal and H. J. Ache	Inhibition of Positronium Formation and Reactions of Positronium Atoms in Solutions J. Phys. Chem., 81, 941 (1977)
5).	Y. C. Jean and H. J. Ache	Search for Selectivity Between Optical Isomers in the Interactions of Positrons with Chiral Molecules J. Phys. Chem., 81, 1157 (1977)

6). J. L. Wu and H. J. Ache
On the Stereochemical Course of the Chlorine-38 for Chlorine Substitution in Diastereomeric Dichloroalkanes: 2,4-Dichloropentane and 2,3-Dichlorobutane
J. Amer. Chem. Soc. 99, 6021 (1977)

B. Which are accepted and in press

1). Positron Lifetime Studies in γ-Irradiated Organic Crystals Rad. Res. in press.

2). Positronium Reactions in Micellar Systems, J. Phys. Chem. in press.

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

4). Inclusion Systems Studied by Positron Annihilation Techniques J. Phys. Chem. in press.

C. Which are submitted

1). Reactions of Energetic Tritium Species in Graphite, J. Phys. Chem. submitted.

2). Ethylene-C^{11} Formation in Alkylchlorides. Mechanisms and Isotope Effects. J. Phys. Chem. submitted.

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.

4). On the Stereochemistry of the Chlorine-38 for Chlorine Substitution Reaction in 1,2 Dichloro-hexafluorocyclobutane. J. Phys. Chem. submitted.

D. Ph.D. Theses

Steven H. Wong:
Direct Bromine-80 or Bromine-82 Labeling of Biomolecules Via Excitation Labeling Methods: Preparation of Radiopharmaceuticals.

Jiann-long Wu:
On the Stereochemical Course of the Chlorine-38 for Chlorine Substitution in Diastereomeric and Enantiomeric Compounds.

Tobias R. Acciani:
The effect of Solvents on the Stereochemistry of the Chlorine-38 for Chlorine Replacement Reactions in 1,2 Difluoro 1,2 dichloroethane and 1,2 Dichlorohexafluorocyclobutane.

Papers Presented at Scientific Meetings and Invited Seminars (During the period Oct. 1, 1976 - Oct. 1, 1977).

1). "Studies of Molecular Association by Positron Annihilation Techniques", 28th Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, Oct. 27-29, 1976.

2). "Direct Bromine-80 (or 82) Labelling of Biomolecules via Gas Exposure Techniques", 28th Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, Oct. 27-29, 1976.

3). "On the Stereochemical Course of Chlorine-38 for Chlorine Substitution in Diastereomeric Molecules in Solution", 28th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, Oct-29, 1976.

4). "Recent Developments in Positronium Chemistry", Seminar, North Dakota State Universtiy, Fargo, North Dakota, Nov. 9, 1976. (Invited)

5). "Positron Annihilation as a Chemical Probe", Seminar, Wake Forest University, Winston-Salem, N.C., Nov. 17, 1976. (Invited)

6). "Positronium Chemistry in the Liquid Phase and Solutions", 173rd National Meeting of the American Chemical Society, New Orleans, March 20-25, 1977. (Invited)

7). "The Effect of Solvents on the Stereochemistry of the ^{38}Cl for Cl Exchange in Halogenated Organic Molecules", 173rd National Meeting of the American Chemical Society, New Orleans, March 20-25, 1977.

8). "Exotic Atom Chemistry", Seminar, Sweet Briar College, VA, April 14, 1977. (Invited)

9). "Radiopharmaceuticals: Their Preparation and Use in Nuclear Medicine", Sweet Briar College, VA, April 14, 1977. (Invited)

10). "Reactions of Positrons and Positronium Atoms in Micellar Systems", 25th Annual Meeting of the Radiation Research Society, San Juan, P.R., May 8-12, 1977.

11). "Positronium Chemistry: Present Status - Future Directions", Joint CIC-ACS Conference, Montreal, Canada, May 29-June 2, 1977. (Invited)

12). "Radiation Effects in Organic and Biomolecules Studied by Positron Annihilation Techniques", Joint CIC-ACS Conference, Montreal, Canada, May 29-June 2, 1977.

13). "Temperature Dependent Complex Formations between Ortho-Positronium and Various Nitroaromatics", Joint CIC-ACS Conference, 14). "Positronium Reactions in Micellar Systems" Gordon Research Conference on Micellar and Macromolecular Catalysis Wolfeboro, New Hampshire, Aug. 15-19, 1977. Invited!

15). "Positron and Positronium Reactions and their Relationship to Radiation Chemistry" 174th National Meeting of the American Chemical Society, Chicago Aug. 28 - Sept. 2, 1977.

16). "Caging in High Energy Reactions" 9th International Symposium on Hot Atom Chemistry Blacksburg. VA Sept. 18-23, 1977. (Invited)

17). "Reactions of Energetic Tritium Species in Graphite" 9th International Symposium on Hot Atom Chemistry, Blacksburg, VA, Sept. 18-23, 1977.

18). "Direct Bromine-80 or 82 Labeling of Biomolecules via Excitation Labeling Methods" 9th International Symposium on Hot Atom Chemistry, Blacksburg, VA, Sept. 18-23, 1977.

Other Activities of the Principal Investigator

Chairman of the International and 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, ERDA, Guggenheim Memorial Foundation.

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, 1977

Ache, Hans J.

Publications:

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

12.	H. J. Ache and A. P. Wolf	Radiogaschromatographic Separations of the Isotopic Ethylenes Z. Analyt. Chem., 230, 19 (1967).
13.	H. J. Ache and A. P. Wolf	Bond Energy Effects and Acetylene Production in the Reactions of Energetic Carbon Atoms with Alkylhalides and Propane J. Am. Chem. Soc., 88, 888 (1966)
14.	H. J. Ache and A. P. Wolf	The Effect of Radiation on the Reactions of Recoil Carbon-11 in the Nitrogen-Oxygen Systems 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 J. Phys. Chem., 71, 3388 (1967).
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