Reactions of Charged and Neutral Recoil Particles Following Nuclear Transformations

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

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Introduction

The following is a report of the work completed during the period September 1974 - August, 1975. These studies were supported by the U. S. Energy and Development Administration, Division of Physical Research, under contract No. AT-(40-1)-3602, and carried out at the Department of Chemistry of Virginia Polytechnic Institute and State University. The carbon-11 work was done at the Chemistry Department of Brookhaven National Laboratory in cooperation with Dr. A. P. Wolf.

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.

Background

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

In the future great emphasis will have to be put on the development of new methods or processes which can replace older, large amounts of energy consuming methods in the chemical processing industry. In order to find new pathways for making these kinds of products, such as synthetics, fibers etc., one will have to emphasize further research on reaction mechanisms. This will include predominantly the identification and structural determination of intermediates, measurement of rate constant 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 which have been studied by hot atom chemists for some time and which are also investigated in this work. It is obvious that this is an area in which hot atom chemistry can make a most significant contribution to the solution of the energy problem.

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

1. Study of the stereochemistry of halogen atom or ion reactions produced via (n,γ) or (I.T.) nuclear reactions with diastereomeric molecules.

Status of research (1974)

The stereochemical course of a hot reaction leading to an halogen for halogen exchange at a saturated carbon atom can provide important information on the basic mechanism of the substitution process.

Investigations of the stereochemical course of hot reactions have initially been made by Rowland et al. in gaseous meso and d,l-2,3-dichlorobutanes which showed a more than 95% retention of initial configuration. Similar results were observed by the same authors in gaseous d,l-or meso-$(CHFCl)_2$. These latter experiments were extended by Stöcklin etc. over a wide pressure range where they consistently found more than 93% retention. In the liquid phase, however, the stereospecificity of the substitution reaction was in both systems drastically reduced.

More recently Stöcklin et al. have shown in their studies on the "hot" ^{38}Cl for Cl exchange in the diastereomeric 2,3-dichlorobutanes that the addition of various solvents, which changes the conformational composition of the substrate molecules has a profound effect on the ratio of the ^{38}Cl-labeled products formed by ^{38}Cl for Cl substitution. They relate their results to the relative abundance of the various conformers, which varies with the dielectricity constant and concentration of the solvent, and the relative availability of the conformers for front side attack, leading to retention, and backside attack resulting in inversion of configuration. On the basis of these results Stöcklin et al. proposed their "direct replacement with collisional stabilization of the caged complex model".

Summary of Recent Work

Since the presence of the conformational effect would provide evidence for a one step substitution mechanism thus introducing a new concept for hot reactions in the condensed phase, where reactions were hitherto believed to occur mainly via a caged radical mechanism, 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 as well as nuclear decay induced halogen for halogen exchange reaction.

As described in detail in Appendix I, 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 labeled molecules. In the latter case it can be assumed that neutralization occurs before the bromine undergoes exchange reaction.

Distinct differences in the stereospecificity of the Br for Cl exchange have been observed depending on the type of nuclear process by which the reactive bromine species are formed and the nature of additives present.

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 predominantly via a direct replacement with collisional stabilization of the caged complex. In this case the relative concentration of the various conformers present in the reaction mixture and their (steric) availability for front- and backside attack will determine the stereochemical course of the reaction. In contrast to the Cl for Cl exchange, however, the system does not self-scavenge Br atoms which may increase the contribution made by radical-radical recombination in cages to the overall process and thus partly obscure the conformational effect.

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. The more time elapses before the reaction with Br takes place the more likely will the thermodynamically more stable diastereomer (erythro) be formed. One can argue that this time interval depends a) on the neutralization time of the initially charged Br^+ in the medium and b) on the density of the medium.

In cooperation with Prof. Rack's laboratory this investigation was extended to the study of the Cl for Cl substitution following $^{37}Cl(n,\gamma)^{38}Cl$ in the liquid diastereomeric $(CHFCl)_2$ systems.

The preliminary results indicate that 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 system, which is very similar to the trends observed by Stöcklin in the 2,3 dichlorobutanes.

In order to correlate our results to the conformational composition of the reaction mixture a conformational analysis of these mixtures is presently carried out by NMR spectroscopy.

Significance

The comparison study of the stereochemical course of hot atom or decay induced reactions on the liquid phase can help shed light on the details of the hot atom reactions as well as on Auger process in liquids. While the significance of the Auger effect in hot atom chemistry is obvious, the actual modes of post Auger processes in condensed phases are still obscur. Presently there exist reversal hypotheses, such as the autoradiolysis, thermal spike, etc., which have been found useful in the interpretation of certain experimental results.

From the present work it seems that the after effects of the isomeric transition followed by Auger radiolysis and Coulomb explosion lead to the formation of radicals with which the bromine species, which has become rapidly neutralized after being initially formed as an multicharged ion, can react. The type of reaction and nature of products formed will be controlled by the composition of the environment which involves factors such as caging, neutralization time for the ion, thermodynamical stability of the radicals etc.

The knowledge of the details of these reactions is not only important for the understanding of the mechanism of ordinary chemical reactions which includes the identification and structural determination of intermediates, measurement of rate constants for their formation and perhaps their removal, where intermediates could be defined as atoms, radicals, ions, and ion molecules, the influence of the three dimensional molecule structure on the rate constants, i.e. steric effects etc., but also for specific applications of the Auger effect with respect to a selective microsurgery on large biomolecules and its possible therapeutical use in nuclear medicine.

2. Study of nuclear decay induced reactions of halogen species with organic compounds in the gas phase

Status of Research (1974)

The isomeric transition (IT) of ^{80m}Br incorporated in organic compounds gives rise to vacancy cascades following internal conversion and eventually to a substantial fragmentation of the molecule via Coulomb explosion leading to ^{80}Br ions with multiple positive charges.

If these processes occur in the gas phase, the charge of the ^{80}Br ions will be rapidly reduced to unity by charge transfer processes, while the excess kinetic energy of some electron volts resulting from the Coulomb explosion or neutrino emission, respectively, is removed from the ions in nonreactive collisions. The resulting thermal $^{80}Br^+$ ions can subsequently undergo electrophilic reactions with organic substrate molecules.

The interactions of these species with alkylchlorides leading to a Br for halogen exchange have been found to be influenced by several parameters, predominantly however, by the electronic effect, i.e. by the electronic density around the attacked carbon atom, with a minor contribution coming from bond energy effects.

Data obtained for $^{80}Br^+$ or $^{125}I^+$ for halogen substitution in the racemic or meso forms of 2,3-dichlorobutane suggested the presence of an excitation-racemization mechanism which determines the stereochemical course of the substitution (see previous progress report). Following the attack of the halogen electrophile at the asymmetric C atom a molecule-ion complex is formed in an exothermic reaction which has a relatively long lifetime if no strong (gaseous) Brønsted base is present which can act as an acceptor for the Cl^+ ion (or proton) from the complex. The fact that in the presence of additives which can rapidly remove the Cl^+ ion and simultaneously the excess energy from the complex mostly the substitution product formed under retention of configuration is observed, indicates that the initial molecule ion complex is obtained

The structure of the intermediate complex may then resemble the triangular three centered bond structure as proposed by Olah for penta-coordinated carbonium ions.

If on the other hand no energy sinks are present the complex may undergo racemization as indicated by the ratio of the substituted diastereomers which under these circumstances approaches the relative concentrations as determined by the thermodynamical equilibrium conditions.

Summary of Recent Work

During the past contract period experiments were continued which were designed to eliminate some of the ambiguities inherent to the studies described above, namely: (1) the possible conformational steric effect due to the presence of two vicinal asymmetric centers in the 2,3-dichlorobutanes, which may have influenced the relative suitability of each diastereomer for front or backside attack by the electrophile and (2) the effect of differences in the thermodynamical properties of the two diastereomers on the final product distribution (as already documented in the observed isomerization of the primary complex).

Optically active halogen compounds, such as the d and l form of 2-chloropropionylchloride and 2-chloro-4-methylvalerylchloride were synthesized and exposed to gaseous $CF_3{}^{80m}Br$. Since a direct analysis of optically active compounds by chromatographic methods is still not feasible the two enantiomers formed in the bromine for chlorine substitutions process were allowed to react with an optically active reagent (d-valine) to form two diastereomers, which can be separated by gaschromatographic methods.

The initial results of the gasphase experiments seemed to indicate that the exchange of the halogen atom at the asymmetric carbon atom occurs overwhelmingly under Walden inversion,

$$\text{d-CH}_3\text{-CHCl-COCl} + \text{Br}^+ \rightarrow \ell\text{-CH}_3\text{-CHBr-COCl} + \text{Cl}^+$$

Inversion yields ranged up to about 75% in the case of d or l CH_3-CHCl-COCl and up to 91-98% in the d or l $CH_3CHBrCOBr$ systems (all oxygen scavenged).

The Br for Cl exchange in the l-2-chloro-4-methylvaleryl-chloride, which contains a bulky-$CH(CH_3)_2$ adjacent to the chlorine to the exchanged, occured also predominantly under Walden inversion (∿ 70%).

At face value these results resemble very much those obtained by Wolf, Rack and Pettijohn for the hot ^{38}Cl or ^{34}Cl for Cl exchange in the same system.

The present investigation was therefore extended to the "hot" Br for Br exchange in the liquid phase via the nuclear reaction $^{79}Br(n,\gamma)^{80m}Br$, where basically the same results were obtained (in presence of I_2 as scavenger):

Compound	Inversion %
l-$CH_3CHBrCOBr$	88
d-$CH_3CHBrCOBr$	76
l-$CH_3CHBrCOBr$ + 70% heptane	81
d-$CH_3CHBrCOBr$ + 70% heptane	76
l-$(CH_3)_2CHCH_2CHBrCOCl$	67
l-$(CH_3)_2CHCH_2CHClCOCl$(+Br_2)	68

Similar results were obtained if the source for the reacting bromine species was the $^{82m}Br(I.T.)^{82}Br$ isomeric transition (in presence of I_2 as scavenger):

Compound	Inversion %
l-$CH_3CHBrCOBr$	76±2
d-$CH_3CHBrCOBr$	86
l-$(CH_3)_2CHCH_2CHBrOCl$	87
l-$(CH_3)_2CHCH_2CHClOCl$	82

However, parallel to these investigations a very careful study of the possibility of chemical Br for Cl(or Br) exchange was carried out.

Such a chemical exchange could possibly occur at various stages during the experiment, during the irradiation or $CF_3{}^{80m}Br$ exposure, when the valine ester was prepared and thirdly during the gaschromatographic separation on the g.c. columns.

The results of this study seem to indicate that some of the brominated byproducts which are formed as a result of the n,γ or I.T. process can easily undergo exchange with the substrate molecules most likely on the g.c. columns or after condensation of the gaseous sample prior to the esterification. This exchange is very rapid and gives 70-90% inverted product. All attempts to eliminate this interfering process have failed so far.

Since the adjoining COCl group probably activates the Cl or Br atom and makes the latter very susceptive to exchange experiments have been initiated with a group of other molecules, such as:

d or l-CH_3-$CHCl$-CH_2OH

where the position of the halogen appears to be more stable and where these problems should therefore not exist. These optical active compounds are presently synthesized together with optical active acid chlorides with which the alcohols can react to give diastereomers which in turn can be separated by gaschromatographic methods. A major problem in these experiments is the gaschromatographic separation of the resulting diastereomeric esters, which requires an extensive search for suitable column materials.

Significance

The question whether in gaseous systems the attack of the reacting Br species, $^{80}Br^{+}$ or "hot" ^{80m}Br, occurs preferentially from the opposite side of the molecule involving a collision time sufficiently long to allow Walden inversion remains still open. One will have to wait for the results of the experiments in which a "chemical exchange" is not interfering with the hot or nuclear decay induced electrophilic reaction, before one can categorically state that not all hot-bromine substitution reactions are fast and involve a front-angle attack which would lead to retention of configuration. It furthermore doesn't yet invalidate the assumptions made by Rowland and Stöcklin that the hot substitution mechanism with inversion deposits an excess amount of vibrational excitation energy in the molecule resulting in (complete) secondary decomposition (in the gasphase).

In general the study of the reactions of (ionic) halogen species generated by the isomeric transitions or as a result of an electron capture process can significantly enhance our knowledge of the detailed reaction mechanisms, parameters, nature and energy contents of the intermediate involved in electrophilic substitution reactions at (saturated) carbon atoms in the gasphase.

This technique can be of special importance in cases where other methods such as ion cyclotron resonance or high-pressure mass spectrometry cannot provide the necessary information, i.e., in cases where one wishes to study the stereochemistry of the reaction or where several isomers may result from the substitution.

3. 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 1974

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

Although the half-life of most of the radioisotopes used so far, e.g. ^{123}I ($t_{1/2}$ = 13.3h) and ^{125}I($t_{1/2}$ = 60d) allows a preparation of these labelled molecules by chemical synthesis, direct labelling via decay induced species (excitation labelling) can be of great advantage if compounds of high specific activity or carrier free products are required.

In the past mostly modified classical halogenation methods have been used for incorporating radioactive halogen into aromatic systems, which worked well when the halogen species initiating the labeling are present in macroamounts. However carrier free halogenation is often unsatisfactory.

The iodine-monochloride technique has been successfully modified for carrier free ^{123}ICl produced via the decay of ^{123}Xe

in Cl_2 by the Brookhaven group but gives only poor results for the iodination of some heteroaromatic systems as reported by Stöcklin's group.

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 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 experiments were carried out with the aim to develop methods 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.

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 Appendix II.

Additional model molecules such as deoxycytidine, guanosine, phenylalanine and tyrosine and other labelling methods such as the $CF_3{}^{80m(82m)}Br$-$KBrO_3$ exposure techniques were included in this investigation.

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

The results can be summarized as follows:

a) The direct CF_3Br gas exposure technique gives consistently rather low yields ranging from 1% for bromodesoxyuridine to 11% for bromoacetic acid.

b) The modified CF_3Br-Cl_2 gas exposure technique improves the yields in most cases considerably (up to 80%) for bromoguanosine and bromo-L-tyrosine.

c) 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.

Bromine substitution can be achieved if iododeoxyuridine instead of deoxyuridine is used as substrate. In this case labelling yields of greater than 80% have been obtained. The yields observed are independent of the bromine source ($CF_3{}^{82m}Br$ or $CF_3{}^{80m}$ Br).

The analysis and separation of the labelled compounds is achieved by high pressure liquid chromatography in combination with discontinuous radioactivity assay of the effluent.

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 labelling method using $CF_3{}^{80m}Br$ or $CF_3{}^{82m}Br$ as bromine source and in the presence of Cl_2 gas. In addition to that the CF_3Br-$KBrO_3$ technique provides also an extremely rapid and especially mild brominating agent, because it exposes the substrate only to a minimum of radiation.

4. The Energetics and Mechanisms Involved in the Reactions of Highly Energetic Carbon-11 Atoms with Simple Organic Molecules

(This work is being done in cooperation with Dr. A.P. Wolf Chem. Dept., BNL)

Status of Research (1974)

The basic reactions of hot carbon atoms with saturated hydrocarbons which result in the formation of acetylene and ethylene have been discussed within the mechanistic framework of the hot carbon atoms into a carbon-hydrogen bond:

I. Acetylene formation:

An energetic carbon atom inserts into a carbon hydrogen bond resulting in an excited intermediate which decomposes to acetylene and other products:

$$^{11}C^* + CH_3-CH_2-CH_3 \rightarrow [CH_3CH_2CH_2{}^{11}CH]^* \qquad (1)$$

$$[CH_3CH_2CH_2{}^{11}CH]^* \rightarrow CH_3CH_2 + {}^{11}CH\equiv CH + H \qquad (2)$$

Experimental evidence using double label techniques now strongly supports formation of acetylene by this intramolecular mechanism.

II. Ethylene formation:

Insertion of a hot carbon atom results in the formation of an intermediate carbene (eq. 1), subsequent decomposition of the carbene leads to methyne formation (eq. 3).

$$[CH_3CH_2CH_2{}^{11}CH]^* \rightarrow [CH_3CH_2CH_2] + {}^{11}\underline{CH} \qquad (3)$$

Methyne $[{}^{11}CH]$ inserts into a carbon-hydrogen bond to give an intermediate which undergoes unimolecular decomposition to give ethylene directly

$$[{}^{11}CH] + CH_3CH_2CH_3 \rightarrow [CH_3CH_2CH_2{}^{11}CH_2]^* \qquad (4)$$

$$[CH_3CH_2CH_2{}^{11}CH_3] \rightarrow CH_3CH_2 + CH_2={}^{11}CH_2 \qquad (5)$$

Experimental evidence as documented in last year's progress report shows that the observed deuterium isotope effects on ethylene formation are the opposite of what one would predict if vinyl radicals were the immediate precursors and therefore convincingly supports the methyne insertion mechanism.

Furthermore from the investigation of the electronic states of the carbon atoms involved in these reactions it was concluded (see last year's progress report) that:

The major reaction of hot ^{1}D carbon atoms is to form methyne which then inserts into the carbon-hydrogen bonds to ultimately yield ethylene. The principal reaction of hot ^{3}P carbon results in the formation of acetylene. At lower energies acetylene can no longer be formed by C(^{3}P) but can be produced by C(^{1}D) as can ethylene.

Summary of recent work:

In an attempt to further evaluate the electronic state of the reacting carbon atom and the detailed mechanism of C-11 ethylene formation, energetic carbon-11 atoms were allowed to react with specifically deuterated alkylchlorides and with mixtures of protonated and perdeuterated alkylchlorides. The doubly labelled ethylenes (^{11}C and D) formed in this process were radiogaschromatographically analyzed (Appendix IV).

The observed ^{11}C distribution in the isotopic ethylenes is consistent with previously proposed "methyne insertion and decomposition mechanism". The results further suggest that in addition to methyne formation following C(^{1}D) insertion into carbon-hydrogen bonds a certain fraction of methyne may be formed via hydrogen abstraction involving C(^{1}D) and C(^{3}P). Chlorine containing compounds seem to be able to divert C(^{1}D) from forming methyne by chloromethyne formation.

In another series of experiments, the yields of the isotopic ^{11}C-ethylenes were determined in gaseous systems in which hydrogen was mixed in varying ratios with ethane-d_6 and with neo-pentane-d_{12} in the presence of 4.5 mol % oxygen scavenger. Other mixtures contained D_2-ethane, D_2-ethyl chloride and D_2-ethyl fluoride.

The results show a linear correlation of the ethylenes formed via CH or CD insertion in carbon hydrogen bonds with the collision fraction of H_2 or D_2, which indicates that methyne (CH) formation is not a function of the number hydrogen atoms available in the hydrogen source. It furthermore would imply that methyne formation from H_2 or D_2 is only slightly less favored than formation from an alkane or alkylhalide. (Appendix III)

Significance

The major significance of these recent results is that they further strengthen the experimental evidence presented for the first time in the previous progress report of the importance of the electronic state of hot carbon atoms on its chemical reactivity, that is to say that the type of chemical reaction which they will undergo following an encounter with the substrate molecule depends not only on the amount of kinetic energy associated with the carbon atom but also on its electronic state.

They also present a first attempt to evaluate the role of halogenated compounds as spin converters and to assess the relative cross section for methyne formation in a variety of molecules.

B. THE CHEMISTRY OF THE POSITRONIUM

Background and Status of Research 1974

In the past the behavior of Ps atoms in matter has been mostly discussed in terms of physical 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 (see also previous progress reports) have shown drastic differences in the reactivity of thermal Ps atoms towards various categories of chemical compounds. The first group which is relatively unreactive towards Ps comprises among others, the aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, aliphatic nitro compounds and inorganic ions in aqueous solution having a standard redox potential $E_o < -0.9$ eV. This is in sharp contrast to a second category of molecules, such as nitroaromatics, quinones, maleic anhydride, tetracyanoethylene, halogens, carbonium ions and certain inorganic ions in solutions, the latter having a standard redox potential of $E_o > -0.9$ eV, which react very rapidly with Ps atoms.

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.

No such obvious relationship seems to exist between the measured Ps reactivities and the electron affinities of various groups of organic molecules.

On the other hand a clear chemical selectivity exists if Ps atoms are allowed to react with various derivatives of nitrobenzene, which indicates the predominance of ordinary chemical parameter controlling the progress of the interaction between Ps and substrate molecule.

Summary of Recent Work

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

They can be summarized as follows:

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)

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

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

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.

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. Since the Ps atom is a relatively simple entity and steric hindrance in its reactions can be neglected, it is extremely suitable for the experimental testing of quantum mechanical models of intermolecular interactions. Furthermore positronium reactions provide a rather simple technique to investigate the stabilizing effect of solvents on molecular complexes and could be used to set up a scale for the effective solvating power of solvents.

It should be added that because of its extremely small mass Ps reactions are also uniquely suited for an experimental investigation of the quantum mechanical tunnel effect.

Personnel and Publications

Personnel

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

2. Postdoctoral Research Associates
   Dr. Ying-yet Su (Jan. 1, 1974 - Dec. 31, 1975)
   Dr. Yan-ching Jean (Aug. 1, 1975 -)

3. Graduate Students
   Ralph E. Wild
   William B. Madia (term. with Ph.D., May 1975)
   Steven Wong
   Gene Hall
   Jeff Wu
   Toby Acciani
   Jack Mustaklem

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

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

1. Approximate Molecular Orbital Study of Organic Positron and Positronium Complexes. J. Phys. Chem., 78, 2682 (1974).

2. On the Reactions of Bromine Species Activated by the $^{82m}Br \rightarrow {}^{82}Br$ and $^{80m}Br \rightarrow {}^{80}Br$ Isomeric Transitions with Cycloalkyl bromides. Radiochem. radioanalyt. Letters, 18, 349 (1974).

3. Neues über chemische Reaktionen des Positronium Atoms, Nachr. Chem. Techn. 23, 125 (1975).

4. Molecular Complex Formation Between Positronium and Organic Molecules in Solutions. J. Amer. Chem. Soc. 97, 5041 (1975).

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

B. Which are accepted and in press

1. Evidence for the Electronic States of Recoil Carbon Atoms Undergoing Reaction. J. Phys. Chem.

2. Positronium and Muonium Chemistry. Proc. Panel on Theory of Hot Atom Chemistry, IAEA, Vienna 1974.

3. On the Preparation of ^{80}Br or ^{82}Br-Biomolecules via Excitation Labelling. Int. J. Appl. Rad. Isotopes.

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

5. On the Annihilation Lifetimes of Positrons Bound in Positronium Complexes. J. Phys. Chem. Removed

6. Positronium Interactions in Binary Mixtures of Organic Compounds. Radiochem. radioanal. Lett. Removed

7. The Effect of Various Solvents on the Stability of Positronium Complexes in Solution. Radiochem. radioanal. Lett. Removed

C. <u>Which are submitted</u>

1. ^{11}C-Ethylene Formation in Hydrogen-Alkane and Hydrogen-Alkylhalide Mixtures. Radiochem. radioanal. Lett. Removed

2. On the Positronium Formation in Binary Mixtures of Organic Compounds. Chem. Phys. Removed

D. <u>Ph.D. Thesis</u>

William J. Madia: Positronium Reactions with Nitroaromatics Via Complex Formation

Papers Presented at Scientific Meetings and Invited Seminars (During the period Oct. 1, 1974 - Oct. 1, 1975)

1. "On the Reactions of Bromine Species Activated by the $^{82m}Br \rightarrow {}^{82}Br$ or $^{80m}Br \rightarrow {}^{80}Br$ Isomeric Transition with Cycloalkylbromides." 26th Southeastern Regional Meeting of the American Chemical Society, Norfolk, Va., Oct. 23-25, 1974.

2. "On the Preparation of Radiopharmaceuticals by Novel Direct Labelling Methods" 26th Southeastern Regional Meeting of the American Chemical Society, Norfolk, Va., Oct. 23-25, 1974.

3. "On the Interactions of Positrons and Positronium Atoms with Organic Molecules" 26th Southeastern Regional Meeting of the American Chemical Society, Norfolk, Va., Oct., 23-25, 1974.

4. "The Chemistry of Positronium: Mechanisms and Kinetics", Seminar, University Kiel, Germany. Dec. 16, 1974 (Invited).

5. "On the Preparation of ^{80}Br or ^{82}Br-Biomolecules via Excitation Labeling Methods", 169th National Meeting of the American Chemical Society, Philadelphia, Pa. April 6-11, 1975. Removed

6. "The Application of Positron Annihilation Techniques to the Study of Radiation Effects in Crystals as Related to Hot Atom and Radiation Chemistry", 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6-11, 1975 (Invited).

7. "On the Present Status of Nuclear Decay Induced Reactions", Panel Meeting on Hot Atom Chemistry: Present Status - Future Directions, Brookhaven National Laboratory, April 11, 1975 (Invited).

8. "The Application of Modern Radiochemical Methods for the Preparation of Radiopharmaceuticals" Seminar, Virginia Commonwealth University, Richmond, Va., April 25, 1975 (Invited).

9. "Solvent Effects on Positronium Complex Formation", Annual Meeting of the Virginia Academy of Sciences, Harrisonburg, Va., May 7-9, 1975.

10. "On the Reactions of Energetic Bromine Species with Cycloalkylbromides," Annual Meeting of the Virginia Academy of Sciences, Harrisonburg, Va., May 7-9, 1975.

11. "On the Formation and Interactions of Positronium Atoms in Organic Mixtures", Annual Meeting of the Virginia Academy of Science, Harrisonburg, Va., May 7-9, 1975.

12. "On the Interactions of Positrons and Positronium Atoms with Organic Molecules", 23rd Annual Meeting of Radiation Research Society, Miami Beach, Fla., May 11-15, 1975.

13. "Physical Methods in Hot Atom Chemistry", 8th International Symposium on Hot Atom Chemistry, Spa, Belgium, May 25-30, 1975. (Invited).

14. "Isotope Effects in Carbon Atom Reactions," 8th International Symposium on Hot Atom Chemistry, Spa, Belgium, May 25-30, 1975.

15. "On the Reactions of Bromine Species Activated by the $^{80m}Br \rightarrow {}^{80}Br$ or $^{82m}Br \rightarrow {}^{82}Br$ Isomeric Transitions with Halogenated Hydrocarbons", 8th International Symposium on Hot Atom Chemistry, Spa, Belgium, May 25-30, 1975.

16. "On the Preparation of ^{80}Br or ^{82}Br biomolecules via Excitation Labeling Methods", 8th International Symposium on Hot Atom Chemistry, Spa, Belgium, May 25-30, 1975.

17. "Chemical Reactions of Positronium Atoms", Seminar, Université de Strasbourg and Laboratoire de Chimie Nucleaire Strasbourg-Cronenbourg, France, June 16, 1975 (Invited).

18. "Chemical Reactions of Positronium Atoms", Gordon Research Conference on Radiation Chemistry, New Hampton, N.H., July 14-18, 1975 (Invited).

19. "Positronium Chemistry in Solutions" 170th National Meeting of the American Chemical Society, Chicago, Illinois, Aug. 24-29, 1975 (Invited).

20. "The Importance of the Positron Annihilation Process for the Solution of Chemical Problems". National Meeting of the German Chemical Society, Cologne, Germany, Sept. 8-13, 1975.

21. "Hot Atom and Positronium Chemistry at Virginia Polytechnic Institute and State University". Instituut voor Kernphysisch Onderzoek, Amsterdam, Netherlands, Sept. 15, 1975 (Invited)

22. "Positronium Chemistry" Seminar, Max Planck Institut für Kohleforschung, Mülheim a.d. Ruhr, Germany, Sept. 22, 1975 (Invited).

Other Activities of the Principal Investigator

Member of the Executive Committee for the Organization of the 8th International Hot Atom Chemistry Symposium, Spa, Belgium, 1975.

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

Discussion leader at the Gordon Research Conference on Radiation Chemistry, New Hampton, N.H., July 1975.

Session Chairman at the National Meeting of the German Chemical Society, Cologne, Sept. 1975.

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

Lecturer and Organizer of a 2 day short course for college teachers on "Radiotracer Techniques and Modern Applications of Radionuclides in the Physical and Life Sciences", February 1975, VPI and SU, Blacksburg, Virginia.

Running List of Papers Published before October 1, 1975

Ache, Hans J.

Publications:

1.	K. Alder, H. J. Ache and F. H. Fiock	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 and A. P. Wolf	Reactions of Energetic Carbon Atoms with Nitrogen Molecules Radiochimica Acta, 6, 32 (1966)

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).
16.	H. J. Ache and A. P. Wolf	Reactions of Energetic Carbon^{11} atoms in Fluorohydrocarbon Systems Radiochimica Acta, 10, 41 (1968).
17.	C. T. Somma and H. J. Ache	Self-induced Tritium Labeling in Cyclohexane Benzene Mixtures Radiochimica Acta, 10, 49 (1968).
18.	H. J. Ache D. R. Christman, and A. P. Wolf	Mechanisms and Isotope Effects in the Reactions of Energetic Carbon Atoms with Hydrocarbons and Alkylfluorides Radiochimica Acta, 12, 121 (1969).
19.	H. J. Ache and A. P. Wolf	Production and Reactivity of Carbon-11 in Solid Compounds J. Phys. Chem., 73, 3499 (1969).
20.	R. D. Finn, A. P. Wolf and H. J. Ache	Chemical Effects Following $N^{14}(n,p)C^{14}$ in Magnesium nitride J. Phys. Chem., 73, 3928 (1969).
21.	Y. S. Wu and H. J. Ache	On the Mechanism of the Self-induced Exchange of Tritium with Halogenated Organic Molecules I. Halogenated Aromatic Hydrocarbons J. Phys. Chem., 73, 2424 (1969)
22.	T. L. Williams and H. J. Ache	Positronium Chemistry in Aqueous $KMnO_4$ J. Chem. Phys., 50, 4493 (1969)
23.	T. L. Williams and H. J. Ache	Radiation Damage Dependence of Positron Lifetimes in Sodiumhalide Crystals J. Chem. Phys., 51, 3536 (1969)
24.	V. Carr and H. J. Ache	On the Mechanism of the Self-induced Exchange of Tritium with Halogenated Aliphatic Hydrocarbons Radiation Res., 41, 15 (1970)

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

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

51.	A. L. Nichols W. J. Madia and H. J. Ache	Reactivity of Aromatic Compounds Towards Positronium Atoms, J. Phys. Chem., 78, 1881 (1974).
52.	Y. Y. Su C. Metcalfe 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 Radiochem. radioanalyt. Letters 18, 349 (1974).
53.	W. J. Madia A. L. Nichols J. C. Schug and H. J. Ache	Approximate Molecular Orbital Study of Organic Positron and Positronium Complexes J. Phys. Chem., 78, 2682 (1974).
54.	H. J. Ache	Chemical Reactions of the Positronium Atom, Nachr. Chem. Techn, 23, 108 (1975).
55.	W. J. Madia A. L. Nichols and H. J. Ache	Molecular Complex Formation Between Positronium and Organic Molecules in Solutions. J. Amer. Chem. Soc., 97, 5041 (1975).
56.	K. C. Taylor A. P. Wolf and H. J. Ache	Ethylene Formation in Carbon Atom Reactions: Mechanisms and Isotope Effects. J. Amer. Chem. Soc., 97, 5970 (1975).