12th INTERNATIONAL HOT ATOM CHEMISTRY SYMPOSIUM

ABSTRACTS

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FIFTY YEARS AFTER

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Fifty years ago last week a letter appeared in Nature that was to have a considerable impact on the interests of most of those present at this meeting. The various directions that work following Szilard and Chalmers discovery has taken will be outlined. Finally, a brief indulgence in speculation regarding future trends will be enjoyed.
WHAT DO WE WANT FROM A THEORY ANYWAY?

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One of the early attractions of hot atom chemistry was the prospect it offered for developing an understanding of the nature of reactive atom-molecule encounters above the threshold energy region. It is now more than 25 years since the earliest kinetic treatments were proposed for the analysis of the yields from recoil tritium reactions with simple hydrocarbons, and the nuclear physicists' concepts of moderating power, cross section and resonance escape probability adapted to the needs of hot atom chemistry. These treatments laid the foundations which should have enabled the theoretical calculation of hot reaction yields, and the subsequent years have seen much effort devoted to the calculation of hot reaction cross sections. However, it remains the case that even for the most elementary hot atom reactions (e.g. T + H₂) there is no quantitative agreement between theory and experiment.

This paper describes some of the techniques available for comparison between theory and experiment, and discusses some of the attempts which have been made to bring about satisfactory agreement - with particular emphasis on the nature of the failure. It is concluded that the principal reason for the disappointing progress lies in the concentration of effort on just one of the concepts mentioned above (the reaction cross section) to the exclusion of the other two. No definitive solution to this problem is offered, but some of the possible ways forward are discussed and their limitations considered.
Studies of thermal kinetics involving the accurate measurement of bimolecular rate constants for atom-molecule reactions often present challenging experimental problems. Atomic species are frequently very reactive and difficult to prepare with known concentration in a well controlled environment. Since the reactions of interest as well as competing processes have very fast rates, most methods for measurement depend on competitive kinetics. The moderated nuclear recoil method is one such technique which is relatively new but already shows promise in systems otherwise difficult to study. The advantage of this recoil technique lies in the ultratrace nature of the atomic reactant concentration and thus an experimental condition approximating infinite dilution. Because of the general attractiveness of this method, we have carried out model calculations which simulate the experimental conditions under which the nuclear recoil process is used. Here we present a refined approach to our recoil trajectory model in an environment containing competitive reactants and a large excess of nonreactive moderator to collisionally degrade translational energy. Excitation functions for the competitive reaction channels were varied to produce a substantial range of realistic thermal rate constants and to explore both the magnitude of hot reaction contributions to the thermal processes and the influence of the recoil process on the kinetic analysis. Based on these results, criteria are established for the most accurate method of relative rate constant determination in experiments of this type.
α-PARAMETER IN THE ESTRUP-WOLFGANG KINETIC THEORY

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One of the basic assumptions of the kinetic theory is that α-parameter (the logarithmic energy loss per collision) does not vary with energy within the region of interest i.e. where chemical combination takes place. This means that the HT/RT ratio (abstraction products/substitution products for the T+RH systems) should be independent of the nature of the moderator used in the moderation studies. However, as early workers started to analyse the results of their moderation studies certain anomalies (concerning the HT/RT ratio) were noticed especially when helium or deuterium were used as moderators.

In this paper we shall try to give a brief review of the various hypotheses which attempted to explain these anomalies with a particular emphasis on the hypothesis that deals with α parameter in the light of a recent evidence obtained from our moderation studies for the reaction of recoil tritium atoms with hydrogen and its isotopic variations.
NUMERICAL STUDY OF MATRIX MODERATOR EFFECTS ON HOT REPLACEMENT

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The effect of the hard-sphere slowing-down process on hot replacement in binary systems was studied. Estimations are given for hot chlorine reacting in C_6H_4Cl_2 - C_6F_6 mixtures of various concentrations assuming different excitation functions for ^38Cl-for-Cl and for ^38Cl-for-F replacement.

Numerical results suggest that the anomaly - enormously high ^38Cl-for-Cl replacement yields - found experimentally [1] in perfluorinated media cannot be explained on the basis of moderation effects of the two components.

MECHANISTIC STUDIES OF THE GAS PHASE REACTIONS OF $^{18}$F AND $^{38}$Cl WITH OLEFINS

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Gas phase studies of halogen atom addition to olefins have been made with $^{18}$F from the $^{19}$F(n,2n) nuclear reaction in SF$_6$ and with $^{38}$Cl from $^{37}$Cl(n,$\gamma$) in CCl$_3$. The addition of thermal $^{38}$Cl atoms, moderated in excess CClF$_3$, to CH$_2$=CHX (X = F, Cl, Br) can occur with the formation of either CH$_2$ClCHX* or CH$_2$CHX$^{38}$Cl* radicals. Collisional stabilization plus reaction with HI should then form CH$_2$ClCH$_2$X and CH$_3$CHX$^{38}$Cl. The yields of the various products have been studied over the pressure range from 50 to 4000 torr. With CH$_2$=CHF substrate, both stabilized radical products are observed, exhibiting a 2/1 preference for addition to CH$_2$ rather than CHF. With either CH$_2$=CHCl or CH$_2$=CHBr, the predominant product at 4000 torr is CH$_2$ClCH$_2$X, with yields >70% at low HI/olefin ratios. At low pressures, the main product in both cases is CH$_2$=CH$^{38}$Cl. The yields of CH$_2$CHX$^{38}$Cl are very small, even at high pressures, with about 1% for CH$_3$CHCl$^{38}$Cl and < 0.1% for CH$_3$CHBr$^{38}$Cl. The probable mechanism of reaction is approximately equal (50±10%) addition to CH$_2$ and CHX; the appearance of anti-Markownikoff addition in the products can be explained through isomerization after collisional stabilization of CH$_2$CHX$^{38}$Cl to CH$_2$ClCHX. All of these reactions are very fast with rate constants of about $2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$s$^{-1}$.

The addition of $^{18}$F to CH$_2$ClCH=CH$_2$ favors reaction with CH$_2$ by about 1.7 over central addition. The rate constant for loss of Cl from CH$_2$ClCHCH$_2$F* is so fast, estimated as >10$^{11}$ s$^{-1}$, that no stabilization of the radical is found at 4000 torr.

The addition of $^{18}$F to allylic side groups has been studied with Sn(allyl)$_4$, Ge(allyl)$_4$, and several Si(CH$_3$)$_x$(allyl)$_{4-x}$ substrates. The observation of CH$_2$=CH$^{18}$F in pressure-dependent yields between 500-4000 torr implies more rapid radical decomposition than expected for such large (C$_3$H$_5$)$_3$MCH$_2$CH$^{18}$FCH$_2$* radicals. The high rate is explained as the consequence of restriction of the excitation energy to the initial side group because of failure of energy transfer beyond the central M-C bonding.
The addition reactions of thermal $^{18}$F atoms have been studied with both cis- and trans-CH$_3$CH=CHCl substrates in the gas phase between 500-3100 torr total pressure. Energetic $^{18}$F atoms have been formed by the $^{19}$F(n,2n) reaction and moderated to thermal energies by collisions with SF$_6$ present as the major component. Approximately 20% of the $^{18}$F atoms react by addition to form CH$_3$CH=CHCl$^{18}$F$^*$ radicals, and are observed chiefly as cis- and trans-CH$_3$CH=CH$^{18}$F after loss of the Cl atom. Experiments with HI as a scavenger have shown that the fraction of stabilized radicals is 5%, indicating that the lifetime of the initial radical is $\ll 10^{-10}$ second. The cis compound is thermodynamically more stable for both chloro- and fluoro-propene, and the yield of cis-CH$_3$CH=CH$^{18}$F is greater than that of the trans product from $^{18}$F reactions with both cis- and trans-CH$_3$CH=CHCl. However, the cis/trans product ratio is 1.92 ± 0.10 from the cis substrate and 1.31 ± 0.03 from the trans substrate. The inequality in these ratios indicates: (a) the substitution process favors retention of the original geometric configuration; and (b) the loss of Cl is competitive with rotation about the C-C bond in the excited radical, with both faster than collisional stabilization which is estimated at about $10^{-10}$ second at 3100 torr.

Reaction of the $^{18}$F atoms with the central carbon atom gives about 20% stabilization products and only about 1% decomposition to form CHCl=CH$^{18}$F. Although loss of the CH$_3$ radical is also exothermic, it is very much slower than the loss of Cl following terminal addition.
AROMATIC SUBSTITUTION BY DECAY-GENERATED $^{76,77,80}\text{Br}$ CATIONS IN HIGH-PRESSURE MODERATED GAS PHASES

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Previous studies of substitution reactions of bromine species generated by $^{76,77}\text{Kr}$ decay with fluorobenzene were extended to high pressure systems containing noble gas or SF$_6$ additives. The yields of H- and F-substitution products increased with pressure to 12% at 15 bar (Kr, SF$_6$). The selectivity of isomer formation was also enhanced in all gases (o:m:p = 30:20:50). The isotopic ratio in the Br-for-H substitution yields ($^{76}\text{Br}/^{77}\text{Br} = 2.5$) reflects the primary charge distribution of each isotope. Fluorine substitution exhibits an isotope effect of $^{76}\text{Br}/^{77}\text{Br} = 0.4$, indicating a contribution from excited species.

The addition of pyridine as a cation scavenger suppressed the organic yield almost totally while the addition of oxygen did not influence yields or selectivity. Together with previous thermodynamic calculations, these effects indicate the reactions of thermalized bromine cations.

In highly-moderated systems, however, formation of $^{76,77}\text{Br}^+$ noble gas clusters are hypothesized to explain the high selectivity and yields. This cluster hypothesis is supported by a drastic decrease of products at elevated temperatures, and by the similar isomer distribution obtained with $^{80}\text{Br}$, formed via IT from $^{80}\text{Br}$.

The application of a linear free energy relationship (Hammett Plot) to the substitution yields of a series of monosubstituted benzenes resulted in a reaction constant of $\rho^+ = -1.5$ for $^{76,77}\text{Br}^+$, which is similar to that for $\text{CH}_3^{80}\text{Br}^+$ ($\rho^+ = -1.0$). Therefore, in both cases, $^{76,77}\text{Br}^+$-clusters or $^{80}\text{Br}^+$-molecular ions, rather than "naked" $\text{Br}^+$, are assumed to be the reactive electrophillic species.
DECAY-INDUCED REACTIONS OF IODINE-125 WITH GASEOUS ETHENE

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The EC-decay of $^{125}$Xe gives rise to iodine cations suitable for the study of electrophilic reactions with $\pi$-systems. In ethene as a model compound, only iodoethene was observed while the rest of the radioiodine was bound in oligomeric form as demonstrated by means of radio gel permeation chromatography. The yields of both products were enhanced with increasing pressure (1 bar) to 0.7% and 10%, respectively.

Dilution of the substrate with inert gases such as Ne, Ar, Kr, Xe, and SF$_6$ lead in each case to an increase of $^{125}$IC$_2$H$_3$ (e.g. 3.3% in 95 Vol % Ne). From the influence of noble gas or oxygen addition, and from thermodynamic considerations the formation of an intermediate ethene-iodonium complex (C$_2$H$_4$I$^+$) from iodine cations in different excited states ($^2$P$_1$, $^2$P$_0$, $^1$D$_2$, $^1$S$_2$) in hypothesized.

Further support for the intermediate molecule ion C$_2$H$_4$I$^+$ was found by the formation of addition products ICH$_2$CH$_2$X (X = OH, OCH$_3$, OC$_2$H$_5$) with yields of 2.5 to 5.5% in the presence of the corresponding nucleophilic compounds such as H$_2$O, CH$_3$OH, and C$_2$H$_5$OH. In the presence of HCl, up to 75% $^{125}$ICH$_2$CH$_2$Cl was formed. It was demonstrated, however, that the main part of this product originated from an addition of the first formed $^{125}$ICl with ethylene. This may be useful for n.c.a. exposure labelling of olefins. The addition of noble gases and of oxygen to the reaction mixture also leads to an increase in oligomer formation (up to 25%). Both additives cause a shift to smaller molecular weights, due to a dilution effect and a higher fraction of iodine radicals.
The dynamics of carbon atom reactions in the gas-phase by addition to a π-electron system and by insertion into a carbon-hydrogen bond have been addressed for simple localized bond systems. Understanding the dynamics of such reactions with more complex molecules such as benzene, has presented greater difficulties. The delocalized nature of the π-electron system in such a molecule enables reaction intermediates to rapidly interconvert by phenylcarbene rearrangements and cloud mechanistic interpretations. Fortunately, reactions of carbon atoms with toluene will yield intermediates which are converted to chemically stable products through intramolecular insertion reactions. Such reactions were studied in the gas-phase using high energy carbon-11 atoms generated via the $^{12}\text{C}(p,\text{pn})^{11}\text{C}$ and $^{14}\text{N}(p,\alpha)^{11}\text{C}$ nuclear reactions. The products were identified by radio gas chromatography. One of the most revealing products, $^{11}\text{C}$-benzocyclobutene, was chemically degraded to ascertain the positional distribution of carbon-11. This distribution was monitored as a function of the carbon atoms electron spin distribution and translational energy for experiments using admixtures of oxygen, xenon and neon. A complete report of these results will be presented along with a discussion of their significance to the fundamental understanding of the dynamics of carbon atom reactions in simple and complex systems. Research supported by the U. S. Department of Energy and Office of Basic Energy Sciences.
The yield of tritium-labelled molecules in adsorbed gas depends on the state of the target-molecule. In particular, if the molecule is attacked by a hot tritium atom in the adsorbed state, we observe a considerable (as compared to the gaseous phase) increase in the substitution reaction yield and a decrease in the probability of the molecule fragmentation into small labelled fragments. This process may be attributed to the dissipation of the excitation energy of the generated labelled molecules by means of exciton relaxation on the solid surface. Semiquantitative estimation of the yield of ethane labelling reaction by tritium on the surface of silicon oxide and molecular sieves confirms this assumption.
INTERRELATION BETWEEN THE STRUCTURAL CHARACTERISTICS OF THE
SOLID AND HOT TRITIUM ATOM REACTIONS

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The interaction of hot tritium atoms with a layer of gas (ethane) adsorbed on the porous solid (silica gel) surface is very peculiar. We have detected an essential dependence of the probability of formation of hot tritium interaction products on the structural characteristics of the solid, namely, on pore dimensions and on the specific surface magnitude, as well as on the hydroxyl group concentration on the solid surface.

It is established that the yield of hot substitution reactions with the formation of labelled ethane linearly increases with increasing specific surface of the solid and decreasing pore diameter. Meanwhile, the change of the silica gel surface hydration exerts a considerable influence on radiohydrogen yield.
NEW RESULTS IN HOT ATOM CHEMISTRY BY LIQUID ORGANIC COMPOUNDS

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In the past two years the understanding of muonium chemistry has greatly improved. One of the major questions is: does muonium (Mu) react as a hot or thermal atom. The results obtained with mixtures of benzene with several compounds can be understood by a two-step mechanism for muonic radical formation:

\[
\mu^+ + e^- \rightarrow \text{Mu} \quad \text{in } \mu \text{ ps} \quad \text{in C}_6\text{H}_6 \quad \text{in } 10 \text{ ps} \quad \text{C}_6\text{H}_6\text{Mu} .
\]

The neutralization step involves thermalization of \( \mu^+ \) ions and subsequent combination with end-of-track electrons.

Some progress has also been made in the study of reactions of recoil \( ^{11}\text{C} \) atoms with liquid organic compounds. From product analysis for reactions with \( \text{C}_6\text{H}_5\text{Cl} \) low yields of chlorotoluenes are found. There are also indications for reactions of \( ^{11}\text{CCl} \) or \( ^{11}\text{CHCl} \) intermediates. Gelfiltration and HPLC techniques provide further information regarding the composition of high-boiling species formed by the reactions of \( ^{11}\text{C} \) with alkanes, alkenes and arenes.

In addition the results of reaction studies on recoil \( ^{34}\text{Cl} \) and \( ^{38}\text{Cl} \) atoms with liquid chloroanilines will be presented. The presence of the \( \text{NH}_2 \) group has little effect on abstraction, substitution and addition reactions of recoil \( ^{38}\text{Cl} \) atoms, in contrast to the reactions of recoil \( ^{38}\text{Cl} \) atoms.
INTERMOLECULAR COMPETITION FOR HALOGEN REPLACEMENT BY RECOIL
\(^{38}\)Cl AND \(^{18}\)F IN LIQUID BENZENE DERIVATIVES

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As a further study of the role of the second substituent in the benzene ring on the halogen replacement, the relative \(^{38}\)Cl-for-F and \(^{18}\)F-for-Cl replacement yields in equimolar liquid mixtures of \(C_6H_5X - m\), p-\(C_6H_4XY\) (where \(X = F\) or Cl; \(Y = CH_3, F, Cl, I, CF_3, NO_2\)) have been determined. Interpretation of the data based on the Hammett relationship shows a significant difference in the influence of the electron density distribution on these replacement processes from that obtained in the previously studied systems [1].

SELECTIVITY IN THERMAL $^{34m}$Cl-for-Cl EXCHANGE IN SUBSTITUTED CHLOROBENZENES

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Thermal Cl-for-Cl exchange reactions can only be studied with isotopically enriched $^{35}$Cl, $^{37}$Cl atoms or radioactive $^{34m}$Cl, $^{36}$Cl, $^{38}$Cl atoms. Thermal exchange takes place with C$_6$H$_5$Cl, since from recoil $^{34m}$Cl and $^{38}$Cl experiments it is known that the yields of C$_6$H$_5$ $^{34m}$Cl and C$_6$H$_5$ $^{38}$Cl decrease from 30 - 50% in unscavenged C$_6$H$_5$Cl to 6 - 10% in I$_2$ scavenged C$_6$H$_5$Cl. Similar values were found for C$_6$H$_5$ClX (X = Cl, F, CH$_3$, CF$_3$) and C$_6$F$_5$Cl.

In 1 : 1 : 1 mixtures of ortho, meta and para-C$_6$H$_4$ClX (X = Cl, F, CH$_3$), thermal exchange proceeds mainly with the ortho and para isomers and for a negligible amount with the meta isomers, although exchange has been observed for the pure meta compounds. In the case of a 1 : 1 : 1 mixture of the C$_6$H$_4$ClCF$_3$ isomers, thermal exchange proceeds preferentially with the meta Cl atom.

Similar results as obtained with the 1 : 1 : 1 mixture of the three C$_6$H$_4$Cl$_2$ isomers were obtained from the three 1 : 1 mixtures of C$_6$H$_5$Cl with each of the C$_6$H$_4$Cl$_2$ isomers, for the three 1 : 1 mixtures of two C$_6$H$_4$Cl$_2$ isomers and from an equimolar mixture of C$_6$H$_5$Cl with the three C$_6$H$_4$Cl$_2$ isomers. The rates for thermal $^{34m}$Cl-for-Cl exchange are in the sequence ortho $\sim$ para-C$_6$H$_4$Cl$_2$ > C$_6$H$_5$Cl > meta C$_6$H$_4$Cl$_2$.

Thermal Cl-for-Cl exchange also takes place with C$_6$F$_5$Cl. The rate constant for this reaction, however, is much lower than that for exchange with C$_6$H$_5$Cl and C$_6$H$_4$Cl$_2$, as in 1 : 1 mixtures with these compounds no thermal exchange was found to take place with C$_6$F$_5$Cl.

From experiments with eight 1 : 1 mixtures of ortho-C$_6$H$_4$ClX compounds (X = Cl, F, CH$_3$, CF$_3$, NO$_2$), the rate constants for thermal $^{34m}$Cl-for-Cl exchange were found to decrease in the order: CH$_3$ > Cl > F > CF$_3$, NO$_2$.

Results obtained from three 1 : 1 mixtures of two meta isomers were found to be identical. The observed sequence for the reaction rates is consistent with an increase of the Hammett $\sigma$ parameters, indicating the electrophilic character of the thermal exchange process.
RECOIL $^{13}\text{N}$ IN LiH AND FROZEN CH$_3$X AND CH$_4$

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The experiments are undertaken in order to obtain information on the reactivity of atomic nitrogen in solids and to compare it to that of atomic carbon in LiH and the mirror systems $^{11}\text{C}/\text{NH}_4\text{X}$ and NH$_3$ (77 K).

$^{13}\text{N}$ is produced via the $^{16}\text{O}(p,\alpha)^{13}\text{N}$ process in Al$_2$O$_3$/LiH powder mixtures and via the $^{12}\text{C}(d,n)^{13}\text{N}$ process in frozen CH$_3$X (X=F,Cl) and CH$_4$ at 77 K. Analysis of products is performed via radio-GC and -HPLC.

In LiH a precursor molecule, most probably the nitrene $^{13}\text{NH}$, is formed which upon dissolving in acidic media yields $^{13}\text{NH}_4^+$ and in basic media $^{13}\text{NO}_2^-$. This behaviour provides interesting information on the pH dependence of $^{13}\text{N}$ recoil products in liquid H$_2$O. In contrast, $^{11}\text{C}$ in LiH yields mainly $^{11}\text{CH}_4$ irrespective of the working up procedure.

In CH$_3$X and CH$_4$ the main product is $^{13}\text{NH}_3$ (50-70 %) accompanied by some CH$_3$$^{13}\text{NH}_2$ (10-30 %). Disubstituted (CH$_3$)$_2$NH is not found, but CH$_3$CH$_2$$^{13}\text{NH}_2$ is identified, and attributed to chain elongation via reaction of the carbon part of the precursor molecule. In the mirror systems $^{11}\text{C}/\text{NH}_4\text{X}$ and NH$_3$ atomic carbon reacts up to 80 % to form $^{11}\text{CH}_3\text{NH}_2$ and more complicated products such as formamidine, cyanamide and guanidine. $^{11}\text{CH}_4$ is only formed to a minor degree.

When compared to those of $^{11}\text{C}$, solid state reactions of recoil $^{13}\text{N}$ seem to lead to smaller molecules. More abstraction and less insertion is observed.
REACTIONS OF THERMALIZED RECOIL PHOSPHORUS-32 ATOMS IN COMPLEX ORGANIC SYSTEMS

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Chemical transformations of thermalized recoil atoms determining the final products of stabilization represent a complicated scientific and practical problem.

A study is presented of thermal reactions of recoil $^{32}\text{P}$ atoms in complex organic systems including halohydrocarbons, alkyl alcohols, mercaptans and heterocycles. It is shown that the final products of stabilization - phosphorus acid-ethers, are formed through intermediate phosphororganic compounds, some of them being separated in a pure state.

The mechanism of formation of the complex phosphororganic ethers has been studied. The influence of the structure and of the conditions of neutron irradiation on the forms of stabilization of the recoil phosphorus-32 atom are shown.

The generation of recoil $^{32}\text{P}$ atoms was carried out by the $^{35}\text{Cl}(n,\alpha)^{32}\text{P}$ and $^{32}\text{S}(n,p)^{32}\text{P}$ reactions. Paper and thin-layer radiochromatography were used to separate and identify the products.
REACTIONS OF HOT $^{32}$P ATOMS WITH SOME LIQUID HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

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The reaction products of recoil phosphorus atoms with liquid C$_1$-C$_2$-chloroalkanes, C$_5$-C$_6$-n-alkanes, cyclohexane, benzene and hexafluorobenzene were studied. The hot $^{32}$P atoms were obtained by nuclear reaction $^{35}$Cl(n,$\alpha$)$^{32}$P in mixtures of CC$_1$$_4$ and the above compounds. Fragments $^{32}$P of one-coordinated P with C-P bond arise as a result of primary hot reactions. Secondary reactions of fragments form intermediates of two-coordinated phosphorus especially phosphinyl-radicals $^{32}$P. High-energy stripping and displacement of single atoms or atom groups by hot $^{32}$P atom, molecular fragmentation, and insertion of the hot atom in C-C and C-H bonds are characteristic of hydrogenous systems. In these systems the primary fragments $^{32}$P have unsaturated bonds (H$\tilde{C}$ - $^{32}$P, H$_2$$\tilde{C}$ - $^{32}$P, Cl$_2$$\tilde{C}$ - $^{32}$P). In systems without hydrogenated compounds (CC$_1$$_4$ - C$_6$F$_6$) the primary fragments being formed are as a rule hot substitution products of halogen atoms by recoil phosphorus and represent the phosphinidines with saturated carbon bonds (Cl$_3$C - $^{32}$P, F$_5$C$_6$ - $^{32}$P). Phosphinidines can be inserted in compounds with C-H bond but increasingly less so in those with C-Cl bonds and C-F bonds. Phosphinyl-radicals mainly react by recombination or abstraction of single hydrogen or halogen atoms.
RECENT APPLICATIONS OF RADIOACTIVE DECAY IN IONIC CHEMISTRY

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A nuclear technique, based on the radioactive decay of covalently bound atoms as a source of structurally well defined ions, free of solvation and counterions, ranks today among the most powerful tools for the study of ionic chemistry, both in the dilute gas state and in condensed media. Perhaps this area, more than any other, demonstrates the impact of fundamental principles of hot atom chemistry, deduced from theoretical, mass spectrometric and radiochemical investigations, on a wider domain of the basis research. In fact, the unique features of the decay technique, that allow, inter alia, direct comparison with theoretical models, have provided considerable insight in structural and mechanistic problems in the realm of physical organic chemistry. A few among the latest applications of the decay technique are outlined in the present review, focused on those results which appear most relevant to related areas, in particular to theoretical chemistry. The following topics are briefly illustrated:

i- Structure, reactivity and isomerization of tolyl and benzyl ions from the decay of suitably tritiated toluenes in gaseous and condensed systems.
ii- Automerization and reactivity of phenylium ions from the decay of 1,4-T2^-benzene in gaseous and liquid methyl halides and ethers.
iii- Generation and reactivity of vinyl cations from the decay of tritiated ethylene.
iv- Gas-phase protonation of five-membered heteroaromatic rings by HeT^+ ions from the decay of T2.
FREE CYCLOHEXYL CATIONS FROM THE DECAY OF MULTITRITIATED CYCLOHEXANE. REACTIVITY AND ISOMERIZATION IN GASEOUS AND LIQUID SYSTEMS

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The decay of a T atom of multitritiated cyclohexane, c-C₆X₁₂ (X=H,T), generates free cyclohexyl cations, c-C₆X₁₁⁺, whose reactions can be followed, and their final products identified, by radio gas chromatography. In particular, the isomeric composition of the daughter C₆X₁₁⁺ ions has been sampled allowing them to react with suitable nucleophiles (MeOH, 1,4-C₄H₈Br₂, Cl⁻) that yield structurally diagnostic products. The c-C₆X₁₁⁺ cations are formed in an excited state from the decay, since their structure, reminiscent of the parent cyclohexane molecule, is considerably deformed with respect to the most stable geometry. The excess internal energy, unless collisionally removed, allows the c-C₆X₁₁⁺ ions to overcome the barrier for isomerization to the more stable 1-methyl-1-cyclopentyl structure. Thus, quantitative formation of cyclopentyl derivatives is observed in the gaseous systems, except those at the highest pressure investigated, e.g. ca. 20% of the daughter ions retain their six-member ring in neopentane at 720 Torr. Isomerization can be entirely suppressed only when effective collisional deactivation is coupled to very fast quenching of the ions as in pure liquid methanol, where only cyclohexyl derivatives are formed. Partial isomerization is observed even in those liquid systems which contain a low molar fraction of the trapping reagents, its extent depending on the concentration of the latter and on the nature of the bulk constituent of the solution. The results of this study provide direct evidence for the existence of cyclohexyl cations in the dilute gas state, and unique information on the factors that control isomerization in various environments, as well as on the relative reactivity of the C₆X₁₁⁺ cations toward different nucleophiles.
PREPARING OF REACTIVE PARTICLES VIA $\beta$-DECAY

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The study of the problem of chemical changes during the processes of $\beta$-decay of atoms contained in the molecule allowed us to reveal the connection between the different characteristics of the initial substance and the primary molecule ions formed [1-4]. Based on these investigations new substances and reactive particles have been prepared. The nitronium-ion which is the main intermediate in nitration processes forms during the $\beta$-decay of $^{14}$CO$_2$.

The interaction of charged intermediates with different substances belongs to the class of ion-molecule reactions which are of great scientific and practical interest. The study of such reactions with the participation of ions obtained by the $\beta$-decay opens wide and sometimes unique possibilities: it removes difficulties in the explanation of the results connected with the structure of reactive particles; opens the possibility of studying the influence of the counter-ion and solvated shell on the rate-controlling step, steric effects and reaction course as a whole; it permits one to study, during the reaction, peculiarities depending on the aggregate state at a constant composition of the reaction mixture. The products of such reactions were studied by the radiometric method. The products of reaction between nitronium ions obtained by the $\beta$-decay and toluene in gaseous phase were identified by photoabsorption of the nitro-derivatives using the chromatographic technique.

The study of the interaction between nitronium ions and toluene in gaseous phase showed that the nitration processes result in a qualitatively new composition of the products and an extraordinary correlation (compared with the classical) of nitrotoluene isomers.

SYNTHESIS OF TRITIUM LABELLED ORGANIC ONIUM DERIVATIVES OF V-VII GROUP ELEMENTS AS A CONSEQUENCE OF $\beta$-DECAY

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A new method of preparing organic onium derivatives of V-VII Group elements of the Periodic System generated by tritium $\beta$-decay has been proposed.

The formation of organic onium derivatives labelled with tritium includes ion-molecular reactions of the polytritiated phenyl-cations - generated by the tritium $\beta$-decay in hexatritiumbenzene - with electron pairs of fully substituted organic compounds of investigated elements and further stabilization of synthesized onium cations with anions. The equation of the reaction is:

$$C_6T_6 \xrightarrow{\beta^-} C_6T_5^+ + He \xrightarrow{R-nEl} [C_6T_5R_{8-n}El]^+ An^- \rightarrow [C_6T_5R_{8-n}El]^+An^-$$

The synthesis includes preparing polytritiated benzene, carrying out the interactions of phenyl-cations with substrates, purifying and identifying the obtained labelled compounds.

Phenyl onium derivatives of all elements of the main subgroups of the V-VII Groups of Periodic System (except astatine and polonium) were synthesized including onium chlorine, bromine, oxygen, bismuth derivatives and till recently unknown diphenylfluoronium and tetraphenylammonium compounds.

The influence of the phase, the nature of the anion and of the investigated substrate, as well as of the spatial factors on formation process of organic onium derivatives were investigated.

These compounds may be used for analytical purposes, and for biological and medical investigations.
RADON AND RADON DAUGHTER PRODUCTS: THEIR CHEMISTRY AFTER $\alpha$-DECAY

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Current investigations in the Radiochemistry Laboratory of Carleton University are focussing on chemical aspects of the adsorption of radon daughters on nearby surfaces. While most of the recent studies have looked at attachment to airborne dust and aerosols, we have been interested in attempting to use surfaces which are in principle chemically definable.

By studying the spatial distribution of radon daughters on metal strips exposed to a source of radon-222 or radon-220, using alpha spectroscopy, strip counting and autoradiography, we are able to show that adsorption of lead-212 occurs following diffusion and decay of radon-220, with very rapid decay of polonium-216. The distribution is thus controlled by the diffusion rate and the half-life of the radon parent. We find also that certain coatings markedly affect the adsorption. We conclude that the lead atoms display a distinct selectivity in the choice of their ultimate resting place. The questions of whether the selectivity is thermodynamic or kinetic and whether the attraction is chemical or physical have not yet been resolved.

It is known that, following $\alpha$ emission, the daughter nucleus is produced with a positive charge (+1 to +4 or more) and a high energy of recoil (up to 200 keV). The recoil energy will carry the atom (ion) a distance of some millimeters, by the end of which trajectory the ion will likely have a +1 charge. It will compete unfavourably for nearby electrons, and may act as a nucleus to cause condensation of water. In clean dry gases, these latter mechanisms are not available so the atom will migrate as a singly positive ion or as a molecule ion such as $\text{PoO}_2^+$, $\text{BiO}_2^+$, or $\text{PbO}_2^+$. 
SOLID STATE EXCHANGE REACTIONS

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A general insight into the chemistry of exchange reactions in solids is given with emphasis on recent trends. After recalling how this field has originated from hot atom chemistry and giving a brief survey of the systems studied so far, the major models which have been proposed to account for the results will be critically examined with some illustrative examples. Quantitative aspects will be developed on the basis of equations and concepts derived from solid state physics and chemistry.
THE INFLUENCE OF DOPANT $\text{PO}_4^{3-}$ ANIONS ON THE RETENTION AND THERMAL ANNEALING OF NEUTRON IRRADIATED $\text{K}_2\text{SeO}_4$

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In a preceding work, we studied the influence of aliovalent cation impurities ($\text{Ca}^{2+}$, $\text{Al}^{3+}$, $\text{In}^{3+}$) on the retention and thermal annealing of neutron irradiated $\text{K}_2\text{SeO}_4$. To explain the decrease of the initial retention after irradiating at 313 K and the changes in the annealing isochronals induced by the dopants, a model was proposed, based on $\text{Se}^{IV}$ oxidation by hole capture in the solid. The role of the dopants would be to introduce cation vacancies in the lattice, acting as hole traps during irradiation and releasing these holes upon heating.

In the present work, $\text{K}_2\text{SeO}_4$ solid matrices are doped with $\text{PO}_4^{3-}$ anions. As expected on the basis of the proposed model, the initial retention is not affected by the dopants when irradiating at 194.5 K, but is increased when irradiating at 313 K. The retention at 313 K increases with increasing dopant concentration (up to 723 atom ppm). Several possibilities are discussed to explain the changes induced in the annealing isochronals, involving the presence of electron and hole acceptors (or donors) introduced in the lattice when adding the dopant.

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DOUBLE-LABELLING EXPERIMENTS ON POTASSIUM CHROMATE

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Preparation of $^{48}$Cr in a suitable form has allowed a series of experiments with doubly labelled potassium chromate, in order to acquire a better insight in the chemistry of the recoil atom.

Two main results are here described:

a) Origin of the polymeric species observed on dissolution of neutron bombarded potassium chromate.

The recoil $^{51}$Cr(III) produced on reactor irradiation of chromate appears on analysis on ion exchange resins to be distributed over three fractions: a monomeric, a dimeric and a polymeric one. The question whether these species pre-exist in the solid, or whether they are formed on dissolution, is still open.

The present work reveals that, after neutron activated chromate has been dissolved in an aqueous solution containing carrier free $^{48}$Cr(III) in the monomeric form, the total of $^{48}$Cr remains unchanged and monomeric, while $^{51}$Cr(III) appears under the three forms. This seems to establish that the polymeric species are already as such present in the crystals as a consequence of the nuclear transformation.

This experiment also confirms that all exchange reactions in solution are extremely slow at ambient temperature and that they do not affect the precision of the measurements.

b) Annealing reactions in irradiated and doped potassium chromate.

Numerous results have shown the parallelism of behaviour on annealing of a species created by irradiation or introduced by a doping process.

It now appears that chemical doping of $\text{K_2CrO}_4$ by coprecipitation with a $^{48}$Cr(III) monomer leads to the formation within the crystal of dimeric and polymeric forms (20% and 5%, resp.). Isochronous annealing of such $^{48}$Cr(III) doped crystals which have been neutron irradiated allows a simultaneous tracing of the evolution of the two radio-isotopes, $^{48}$Cr and $^{51}$Cr.

It is then observed that "retention" and "transfer" ($^{51}$Cr(VI) and $^{48}$Cr(VI)) follow a parallel pattern. However, the distribution of $^{48}$Cr(III) and $^{51}$Cr(III) over the monomeric (M), dimeric (D) and polymeric (P) entities follows different paths: while the yields of doping $^{48}$Cr(III), D and P, increase on annealing, the recoil species $^{51}$Cr(III), D and P, show an inverse behaviour. Also monomeric $^{48}$Cr(III) constantly decreases with temperature, while $^{51}$Cr(III) M first increases to stabilize into a plateau value and starts to decrease again at higher temperature only.
THE TEMPERATURE DEPENDENCE OF RADIATION-PROMOTED TRANSFER ANNEALING IN $^{51}$Cr(III)-DOPED $K_2CrO_4$

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Radiation-promoted transfer annealing has been studied in $^{51}$Cr(III)-doped potassium chromate prepared by both the crystallization and precipitation techniques. Both the extent of radiation annealing and the apparent mechanism of the process depend strongly on the doping procedure. Thus, although in $^{51}$Cr(III)-doped crystals prepared by co-crystallization from a saturated, 100°C, solution of $K_2CrO_4$, only the $^{51}$Cr(III)-dimer appears to anneal to $^{51}$Cr(VI) upon radiation exposure at 0°C, in co-precipitation-doped crystals, only the monomeric form appears to contribute to the annealing. An intermediate behavior is observed with crystals prepared by co-crystallization from a 70°C solution.

Both types of crystals show a significant temperature coefficient to the radiation annealing process. In contrast to the hot atom case, similar $^{51}$Cr(VI) yields are obtained from low temperature gamma irradiation followed by a thermal pulse [$\gamma_0/\Delta T$] and from gamma irradiations at the higher temperature [$\gamma_T$]. However, the several $^{51}$Cr(III) species appear to show different behaviors.

The results can be discussed in terms of different temperature dependencies for the radiation annealing processes and different microstructures of the dopant atoms within the different crystal preparations.
TRANSFER ANNEALING OF $^{51}$Cr(III) IN $K_2SO_4$

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Samples of $^{51}$Cr(III)-doped potassium sulfate were prepared by co-crystallization and co-precipitation techniques for study of their thermal and radiation annealing processes, using a new ion-exchange chromatographic method which permits observing not only the traditional $^{51}$Cr(VI) and $^{51}$Cr(III) species but also the cationic and anionic chromium(III)-sulfate complexes.

For all annealing procedures, $^{51}$Cr(VI) forms more easily from samples prepared by co-crystallization than from those prepared by co-precipitation. Thus, transfer of the radioactivity from the (nominal) $^{51}$Cr(III)-form to a $^{51}$Cr(VI)-precursor occurs above 325°C for co-crystallization-prepared samples but only above 400°C for co-precipitation-prepared ones. Similarly, radiation transfer processes, to 50% $^{51}$Cr(VI), are essentially complete at 5 MGy for the co-crystallized samples but reach only 18% at this dose with the co-precipitation-prepared ones.

The species which appear to anneal to $^{51}$Cr(VI) are the monomeric (or dimeric) $^{51}$Cr(III) which are not complexed by sulfate. Thus, the presence of a Cr-O bond in the mono- and di-sulfato complexes does not appear to be conductive to oxidative transfer.

Financial support from CNPq is acknowledged.
It has recently been shown that $^{35}\text{S}$ diffused into alkali chloride crystals from the vapour broadly duplicates the behaviour of $^{35}\text{S}$ generated in such crystals by the (n,p) reaction. An auto-radiographic study has shown that the sulphur enters the crystals by at least two mechanisms. Even at room temperature the $^{35}\text{S}$ geometrical distribution is not static and examination of aged neutron generated $^{35}\text{S}$ doped samples provide some evidence of the room temperature reverse process to the vapour doping.
EFFECTS OF NUCLEAR TRANSFORMATIONS IN HALOGEN OXY-SALT SYSTEMS

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It is shown that halogen oxy-salt solid systems exhibit, a slight if any recoil effect as a consequence of nuclear reactions. Any damage would be better explained by Auger processes and subsequent relaxation steps where the final fate of the "hot atom" will be reached by chemical reactions very dependent on the physico-chemical environment. Unfortunately, wet chemical procedures cause alteration of the unstable forms and physical methods give only an indirect indication of the chemical species formed in the nuclear reaction. It is suggested that transfer annealing studies of doped or ion implanted crystals, by combination of thermal and irradiation treatments (on samples of the same crystalline batch), would allow one to investigate the sequence of thermal and electronic steps involved in the reactions when the "hot atom" comes to rest.
REATIONS OF HOT TRITIUM ATOMS IN LiF CRYSTALS

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Tritium hot atoms in LiF crystals interact with the defects of the crystal lattice and with the products of its radiolysis. The investigation of physical parameters characteristic of the irradiated crystal makes it possible to establish the probability of tritium trapping by traps of chemical and physical nature and to hypothesize possible mechanisms of these processes.
RETENTION OF $^{128}$I IN SOLID NaIO$_3$ AND NaIO$_4$ AFTER (n,$\gamma$) PROCESS

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Some calculations based on a few models for re-entry of recoil atoms have been made. The applicability of these models has been critically examined in view of the present experimental results. The contribution of the billiard-ball substitution to the over-all retention is found to be very small. Similarly, calculations based on "extreme back diffusion" model show a negligible contribution to over-all retention.

Calculations of the relevant parameters of "hot zone" model indicate that the reconstitution of the parent form is not a result of hot zone reactions but of the repair of zones of little disorder. The parent reformation and the yields of various forms can be explained on the basis of the "disorder" model where the intermediate molten state is assumed to be absent. It might be concluded that due to (1) the mean-free path of $^{128}$I being greater than the critical radius in the recoil energy range of 50-194 eV (2) the probability of thermalization of the recoil atom being comparatively low therefore not contributing to the population of recoil atoms below 50 eV and (3) the formation of focusons, the observed increase in retention on thermal annealing is not primarily due to initiation of quenched-in hot zone reactions.

These model-based calculations fail to explain some of the important aspects, e.g. the effect of thermal annealing on retention in view of which a physical cum chemical model is necessary to explain the re-entry phenomenon on the basis of solid state reactions.
A CONCEALED $(n,\gamma)$ EFFECT IN MOLYBDATES

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The chemical effects of $^{99}$Mo $\beta$ decay in neutron irradiated solid ammonium molybdate and molybdenum trioxide have been investigated. $^{99m}$Tc, formed in this way, was found mainly as a neutral species; the pertechnetate fraction was only 13% of the total amount of $^{99m}$Tc. The pertechnetate yield increased considerably when $\beta$ decay occurred in ammonium molybdate or molybdenum trioxide solutions. The proportion of pertechnetate varied from 70 to 81% depending on the solutions in which the molybdenum compounds were dissolved.

The high proportion of $^{99m}$Tc in species other than $^{99m}$Tc$^{4-}$, following $\beta$ decay of $^{99}$Mo in the neutron irradiated solid molybdenum compounds, is shown to be due to reduced $^{99}$Mo species not detectable after solution of the irradiated molybdenum compound in aqueous media.
EFFECTS OF ISOMERIC TRANSITION IN $^{95m}$Tc IN PERTECHNETATE SOLUTIONS

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Unexpectedly, the chemical distribution of the $^{95m}$Tc following isomeric transition in $^{95m}$TcO$_4^-$ proves to be sensitive to the concentration of the TcO$_4^-$ in the solution and even to the identity of the alkali metal cation.

The effects of pH, of dissolved oxygen and of the nature and amount of reduced technetium carried have been investigated. An attempt has been made to find out if local radiolytic effects, due to the Auger electrons, play any part.

The possible role of electron transfer exchange by the immediate product of isomeric transition with the $^{99}$TcO$_4^-$ carrier has been explored.
MÖSSBAUER EMISSION SPECTROSCOPY OF CHEMICAL AFTER-EFFECTS
OF NUCLEAR DECAY IN SOLIDS

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Chemical after-effects following the nuclear transformation of
$^{57}$Co(EC)$^{57}$Fe in cobalt labelled coordination compounds are studied by
Mössbauer emission spectroscopy, both in time integral and time-differential
mode. Among the various kinds of after-effects such as (a) change of
oxidation state, (b) change of inner coordination sphere, (c) metal-ligand
bond rupture, (d) change of spin state, and (e) long-lived non-equilibrium
populations within the ligand field ground manifold, which may be encoun-
tered in different matrices, the effects (d) and (e) have most actively been
studied in recent years. Examples of change of spin state will be describ-
ed, and the matrix influence on the nature and the intensity of the anoma-
lous spin states will be discussed. The results will be seen in the light
of observations by picosecond spectroscopy on such compounds.
NON-EQUILIBRIUM POPULATION AND RELAXATION OF LOW-LYING ELECTRONIC LEVELS OF Fe\(^{3+}\) AFTER THE ELECTRON CAPTURE IN \(^{57}\)Co


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Recently, at low temperatures and in high magnetic fields long-lived non-equilibrium populations of the Zeeman sublevels of the \(^6S\) electronic ground state of Fe\(^{3+}\) have been observed following the electron capture in \(^{57}\)Co in various hosts. Mössbauer emission spectra of LiNbO\(_3\):\(^{57}\)Co recorded at 4.2K ≤ T ≤ 100K and in 2T ≤ H ≤ 7T show this anomaly along with a population inversion of the two highest sublevels. The average populations and the line widths very weakly depend on temperature below 50 K. A considerable line broadening due to spin-lattice relaxation has been found at 100 K but the intensities still deviated from the Boltzmann equilibrium.

The observed population anomaly is fairly independent of the host and of the initial state of the Co ion /c.f. F. Tuczek et. al., this conference/ and may be explained either by /i/ preferred initial populations resulting from the Auger cascade or by /ii/ a slow residual relaxation of unknown origin with a correlation time close to the Mössbauer lifetime /141 ns/.
NON-EQUILIBRIUM POPULATIONS OF IRON(III) ZEEMAN LEVELS FOLLOWING THE $^{57}\text{Co(EC)}^{57}\text{Fe}$ DECAY IN COBALT ACETYLACETONATE


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Mössbauer emission spectra of $^{57}\text{Co}/\text{Co(acac)}_3$ (acac = acetylacetonate) have been recorded in external magnetic fields ($2 \text{ T} \leq H_{\text{ext}} \leq 4.5 \text{ T}$) at low temperatures ($4.2 \text{ K} \leq T_{\text{ext}} \leq 20 \text{ K}$). Each of the six Zeeman sublevels of the Fe(III) electronic ground state ($^6\text{A}_1$) contributes its own static hyperfine pattern the intensity of which is proportional to the average population of the respective level.

The spectra reveal:

(1) Over the whole range of temperatures and fields the Zeeman levels are populated out of equilibrium;

(2) the population of the $|S_z = + \frac{5}{2} \rangle$ level is higher than that of the $|S_z = + \frac{3}{2} \rangle$ level corresponding to a population inversion;

(3) the ratios of the intensities are temperature independent.

The two first observations are in agreement with results obtained by Doerfler at al. [1] from emission spectra of $^{57}\text{Co}/\text{LiNbO}_3$ in magnetic fields of $2 \text{ T} \leq H_{\text{ext}} \leq 7 \text{ T}$ at $4.2 \text{ K}$. This indicates that the observed phenomena are due to the specific electronic properties of the $3d^5$ system.


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NEW ASPECTS OF RECOIL CHEMISTRY IN NUCLEAR MEDICINE AND BIOLOGY

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The relevance of hot atom chemistry to medicine and biology is twofold. On the one hand, the increasing understanding of the chemistry of nucleogenic atoms has lead to the practical preparation of a wide variety of simple precursors for fast syntheses of more complex labelled compounds used in biological and medical research. This technique plays an important role in the labelling of radiopharmaceuticals with short-lived positron emitters (\(^{11}\)C, \(^{13}\)N, \(^{15}\)O, \(^{18}\)F) for studying physiological parameters in-vivo by means of positron emission tomography. Recent problems and potential future aspects are outlined.

On the other hand, radioactive decay in a labelled biomolecule can lead to specific chemical and biological consequences. Recent advances in the correlation of chemical and biological effects on a molecular basis provides a new approach to a selective radiation biology with radiological and therapeutic aspects. Specific examples are outlined emphasizing the relatively mild consequences of tritium decay and the drastic effects of "Auger-emitters". New results on the range and correlation of the chemical effects and strand breaks in \(^{125}\)I-labelled DNA are presented.
WHAT DOES THE LETHAL EFFECT OF INTRACELLULAR RADIONUCLIDE DECAYS REVEAL ABOUT DNA?

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Two systems will be discussed. The first will concern DNA of the S13 phage labelled with $^{33}$P, and the second two mammalian cells labelled with $^{64}$Cu or $^{67}$Cu.

1) Phosphorus: intrinsic component of DNA molecule - Experiments with S13 phage

In experiments with S13 phage labelled with $^{33}$P, the lethal efficiency of $^{33}$P decays is 0.73, whereas the single strand-break efficiency is 0.40 only. These two different values clearly point out that, besides the single strand-break, another lethal event must take place. We have shown that this second event has an efficiency of about 0.30 and corresponds to a local structural modification in DNA due to the substitution of a phosphate by a sulfate molecule ($^{33}$P → $^{33}$S$^+$). The presence of a sulfate in the DNA of phage S13 may lead to either a lethal single strand-break, or to a lethal structural modification or to another modification without any lethal consequence, since the lethal efficiency is less than 1. These three different consequences of a similar physical primary event seem to be related to the site where the decays have occurred.

2) Copper: associated to the DNA molecule - Experiments with mammalian cells

In experiments with two mammalian cells labelled with $^{64}$Cu or $^{67}$Cu, we observed a high lethal efficiency for these decays. The lethal efficiency is the same for these two isotopes in spite of their different decay processes. The lethal efficiency is different in the two cells studied and higher than that of $^{125}$I used in the form of IUdr (Iododeoxyuridine) under the same experimental conditions. Our results suggest that, in mammalian cells, copper ions reach the DNA molecule and that they are an essential component of the chromatin even if they are present in DNA in trace amount only. The question about the role of these atoms in the DNA is raised. One possible hypothesis will be discussed.
The original aim of Szilárd and Chalmers during their historical irradiation of ethyl iodide, producing inorganic $^{128}$I with enlarged specific activity, was to get with a simple laboratory neutron source radioisotopes suitable for possible utilization as tracers for detecting the thyroid. Even if it is not known whether their preparations were really applied to human beings, since its discovery the process has had a close relationship with the field that in the last decades satisfied the name "nuclear medicine" and "radiopharmaceutical production". There were trials in the past to use it as means for enlarging specific activity as well as for direct hot labelling of organic compounds. In routine production the process, unfortunately in contradiction to the original expectations, never played a significant role. Possibilities and limits of utilization of the process for radioisotope production in the future are reviewed.
THERMODESORPTIVE RADIOIODINATION OF FATTY ACIDS

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The so-called decay-induced labelling method of Stöcklin et al [1] carried out by keeping the material to be labelled in neutron-irradiated xenon atmosphere is very interesting from a scientific point of view as a hot atom reaction, but not suitable for the routine production of radioiodine-labelled compounds. If the labelling, as we supposed, is attributed to the chemical form of the recoil iodine species rather than to its recoil energy, similar results can be achieved by the thermolysis of iodine from a Pt-I surface compound. The expectation was justified by experiment.

We observed the formation of a stable platinum-iodine superficial compound on reduced platinum immersed in aqueous solution of even very dilute (e.g. NCA $^{125}$I, $^{131}$I) iodine ions according to the scheme

$$2 \text{Pt} - \text{H} + 2 \text{I}^- + \text{O}_2 \rightarrow 2 \text{Pt} - \text{I} + 2 \text{OH}^-$$

while the expected pH-increase was measured. The surface compound could be decomposed at 1200 - 1300 K, and the iodine species leaving the surface exhibited especially high labelling activity in electrophilic substitutions in absence of any oxidizing agents.

Several fatty acids, both unsaturated (oleic acid, prostaglandin F$_{2\alpha}$) and saturated (valeric and butyric) acids and a number of other compounds were iodinated in such a way while it was indirectly proven that the labelling of the unsaturated acids occurred without the cleavage of the double bonds.

An interesting possibility of "on-line" labelling during the routine thermodesorptive production of $^{125}$I is shown.

PHOSPHORILATION OF BENZIMINAZOLES BY RECOIL \(^{32}\text{P}\) FOR INVESTIGATING BEHAVIOUR OF PLANT GROWTH REGULATORS

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To investigate the behaviour of plant growth regulators by means of phosphorilation of the Benzimiazoles labelling of these compounds with high specific activity is needed.

A method is described for preparing tri(I-benzimiazole)[\(^{32}\text{P}\)]phosphate using recoil \(^{32}\text{P}\). It was shown that in the carbon tetrachloride - benzimiazole system recoil atoms were stabilized in the form of benzimiazoles of phosphorus, and phosphoric and trichloromethylphosphonic acids. A number of labelled \(^{32}\text{P}\) -benzimiazoles have been obtained. The specific activity of phosphor-organic compounds prepared by this simple method is more than 37 PBq/mole.

The recoil \(^{32}\text{P}\)-atoms have been generated in neutron sources and in nuclear reactor via \(^{35}\text{Cl}(n,\alpha)^{32}\text{P}\) process. Paper radiochromatography was used to purify and identify the products.

The behaviour of tri(I-benzimiazole)[\(^{32}\text{P}\)]phosphate in some plants has been investigated.
HOT HYDROGEN ATOMS IN RADIATION CHEMISTRY

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The formation and reactions of hydrogen atoms with excess energy were postulated many years ago to account for considerable amounts of unscavenged HD, produced in irradiated mixtures of hydrocarbons with deuterated compounds. But tentative estimations of the yields of hot H atom reactions as well as of contribution of other radiolysis processes, in spite of great number of experiments and mechanisms proposed, have not yet resulted in the building of satisfactorily complete radiolysis models even for most thoroughly investigated systems (e.g. hydrocarbons of different molecular structure, their mixtures).

Detailed investigations of recoil tritium atom reactions in such systems, beam studies and other approaches have enabled information to be obtained on the whole patterns of products including tritium atoms, the energetics of related reactions, etc. Based on these data it is possible to estimate the likely contribution of hot hydrogen atoms in radiolysis (and also the yields due to the other radiolysis processes resulting in the same final products).

Unlike recoil T atom chemistry, hot hydrogen atoms in radiolysis are produced from the parent compound under irradiation. Thus, it is also necessary to consider the special problems, of radiation chemistry - viz. the nature of excited precursors, their reactions or deactivation in the presence of additives. Since energy transfer is of extreme importance in radiation chemistry and the yields in the majority of investigated systems display significant deviations from linearity, the actual elucidation of the role of hot H atoms in radiolysis (together with other mechanisms' contribution) cannot succeed without better understanding of directions, mechanisms and limitations of energy transfer between excited molecules, transient species and other components in a variety of systems.
APPLICATION OF SPIN TRAPPING ESR SPECTROSCOPY IN HOT ATOM CHEMISTRY

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Radical scavengers typically used in HAC have a disadvantage of not furnishing any evidence as to the identity of the radical involved. This limitation can be overcome by using nitrone or nitroso compounds as scavengers. These compounds trap (scavenge) short-lived radicals to produce relatively stable paramagnetic adducts, nitroxides, the ESR spectra of which are characteristic of the radical trapped. We utilize the spin trapping ESR technique to study radicals formed by the decay of tritium incorporated in various organic molecules in the liquid phase.

In [methyl-³H]-methanol, with phenyl-t-butyl nitrone (PBN) as a spin trap, the ESR spectrum reveals the presence of methoxy and hydroxymethyl radicals. The relative intensity of the lines in the spectrum characteristic of the two spin adducts changes with the storage time of the sample, indicating that they are involved in different secondary reactions. In tritiated benzene, with PBN and nitrosodurene as spin traps, only phenyl radicals are observed. The evaluation of the relative role of the transmutation effect and internal β-radiolysis was achieved by a comparison of the yields of -Ph in ³H-benzene and in a solution of ³H-methanol in benzene. Radicals were also determined in dilute aqueous solutions of thymine tritiated in the methyl group or at the 6 position, with nitroso-t-butane as a spin trap.

The technique of spin trapping ESR spectroscopy can be utilized not only for the detection and identification of the decay-produced radicals, but also of those formed due to the interaction of recoil atoms with an organic medium. Examples will be discussed.
RADIATION CHEMICAL ASPECTS OF HOT ATOM CHEMISTRY OF HALOGEN OXYANION TARGETS: AN E.S.R. STUDY

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Halates and perhalates of chlorine, bromine and iodine were among the earliest targets for "hot-atom" studies and they still continue to be widely studied inorganic systems. In such researches nuclear activation by (n,γ), (n,2n) and (γ,n) reactions has been used to generate the radioactive recoil atoms of three halogens which are chemically stabilised in various forms.

It is well known that the chemical stabilisation of the hot atom in the parent (retention) and other chemical states (yield) is influenced remarkably by a variety of physical (thermal, radiation, mechanical defects and composition) and chemical (pH, other ions present, oxidising and reducing) treatments prior to or after the nuclear transformation. Also, it has emerged from such studies during the past over two decades that the unstable reactive intermediates (mainly paramagnetic and ionic/molecular) play an important role in the final chemical states of the recoil halogen atom in the oxyanion targets. These reactive paramagnetic species (\( \hat{X}_3O_4^- \), \( \hat{X}_2O_6^- \), \( \hat{X}_2O_7^- \), \( \hat{X}_3O_7^- \), \( \hat{X}_2O_8^- \), \( \hat{X}_3O_9^- \), etc.) have been recognised in gamma-neutron-irradiated halates and perhalates using the ESR technique as being relevant to the hot atom studies of these targets since some or most of these reactive intermediates are also produced during recoil activation due to concomitant radiation chemical effects.
HOT ALKYL RADICALS: PRODUCTION AND REACTIONS

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Data are presented on the reactivity of hot alkyl radicals $R^*$ ($CH_3^*$, $C_2H_5^*$, $n-C_3H_7^*$, iso-$C_3H_7^*$, $C_2H_4Cl^*$, $C_3H_4F_3^*$) obtained during gas phase photolysis of haloalkanes RX or on the addition of hot hydrogen atoms of different energy to certain olefines ($C_2H_4^*$, $C_2H_5Cl$, $C_3H_6$, $CF_3CH=CH_2$).

The initial energies (1 - 3.5 eV) of excited radicals $R^*$ depend on the energy quantum (light wave 184.9 - 365 nm). Hot alkyl radicals $R^*$ at the photolysis of HI - olefine mixtures are produced in addition reactions of hot hydrogen atoms: $H + R-CH=CH_2 \rightarrow R-CH-CH_2$ (or $R-CH-CH_2^*$).

The energy of these species is $E_{R^*} = Q + E_{H^*}$, where $Q$ is the heat of the addition reaction, $E_{H^*}$ the energy of hot $H$ hydrogen atoms.

While introducing inert moderators (He, Ar) into the HI - olefine mixture, possibility arises to vary widely the energy of $H^*$ atoms (from several eV to thermal energies at full thermalization).

Hot alkyl radicals $R^*$ react in different ways:

$$R^* + R' \rightarrow RH + R'$$
$$R^* + M \rightarrow R^* + M$$
$$R^* \rightarrow R' + R''$$

The ratios of rate constants for different types of reactions were determined. In the process of photochemical decay of $CH_3I$ in the presence of $HCl$ (irradiation by monochromatic light 250 - 285 nm) the reactivity of the excited $CH_3^*$ radicals was studied. The average energy of these radicals was changed by collision deactivation with $M$ (He or Ar). It has been shown that as the mole fraction of $M$ increases in irradiated mixture the energy of excitation of $CH_3^*$ decreases. The effective energy of activation of reaction $CH_3^* + HCl \rightarrow CH_4 + Cl$ rises from 0 (in the absence of $M$) to $2.5 \pm 0.5$ kcal/mole (at very high concentrations of $M$) which is in good agreement with literature data for thermal methyl radicals.

The influence of the structure of hot alkyl radicals on their activity in gas phase reactions is discussed.
POSSIBILITY FOR EVALUATING SOME RADIATION-CHEMISTRY CONSTANTS BY NANOSECOND FLUORIMETRY WITH POSITRON SOURCE

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The experiment resembles pulse radiolysis, but only with single particles (positrons), in which the lifetime distributions of fluorescence (excited by these particles) are studied with time resolution of about 1-2 ns [1].

The experimental procedure includes sample irradiation with positrons from \(^{22}\)Na radioactive source and nanosecond fluorimetry based on the single photon counting technique.

Solvents of anthracene in hexane with various amounts of electron scavengers - carbon tetrachloride, nitrobenzene - have been studied[2]. Fluorescence life-time distribution analysis in combination with the known rate constant of positron trapping by carbon tetrachloride enables evaluation of the recombination rate constants of the spur electron with positive anthracene ion \((k = 0.9 \times 10^{12} \text{ s}^{-1})\) and of anthracene ion with negative hexafluorobenzene ion \((C_{14}H_{10...C_{6}F_{6}}) - k = 1.810^{10} \text{ s}^{-1} [3].

Chemical reactions and interactions are of great importance in various areas of fusion technology. These include mainly the fields of:

1. First-wall technology, where material problems are caused in the first wall by plasma-wall interactions, i.e. by energetic particles escaping the plasma.

2. Blanket technology, where the reactions of neutrons with the breeder material (mostly Li-compounds) lead via $^6\text{Li}(n,\alpha)\text{T}$ nuclear reactions to energetic tritium species which will eventually form $\text{T}_2$, but which might also interact with impurities present and form a variety of different compounds. The extraction and purification process of the breded tritium including the detritiation of the cooling system involve again a number of chemical processes.

3. Tritium technology, where materials are exposed to considerable amounts of tritium, which via decay or radiation induced reaction can become partially incorporated into these materials. This field also includes the purification of the plasma exhaust gases and storage of the tritium.

An attempt will be made to discuss the various chemical aspects including the recoil chemistry in these systems.
COLLISION PROCESSES IN THE FORMATION OF EXOTIC HYDROGEN ATOMS

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A systematic analysis is presented of the possible elementary processes determining the fate of heavy negative particles (muons, pions) stopped in hydrogen-containing samples. The effect of particle transfer is analysed on the capture probabilities of muons and pions by heavy atoms in the presence of hydrogen. Using a phenomenological description in comparison with the available experimental information on pion capture in hydrogen, it is shown that the formation and decay of $\pi^-$ atoms in compounds $Z\text{H}_n$ are determined mainly by the processes of Auger capture in a molecular orbit $Z\text{H}_n^-$, transition from molecular to atomic orbit, transfer of pions to atoms $Z$ in collisions $\pi^- + Z$, and nuclear capture in collisions $\pi^- + \text{H}$ [1]. The recent assumption by D.F. Jackson et. al. [2] of a considerable role of the processes of radiative atomic capture in bound hydrogen atoms, nuclear capture of pions by protons from the molecular state $Z\text{H}_n^-$, or "inner transfer" of the pion via tunnelling through the bond $Z$-$\text{H}$ is not supported by the theory and contradicts the experimental data.

PION TRANSFER FROM $\pi^-$ ATOMS AS A RESULT OF HOT ATOM REACTION IN BINARY MIXTURES OF HYDROGEN WITH NOBLE GASES

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Pionic hydrogen ($\pi^-$) is a short-lived hydrogen isotope with a negative pion replacing the electron. It is formed when negative pions are stopped in a sample containing hydrogen. The pionic hydrogen can either decay by pion capture in proton

$$\pi^- + n \rightarrow n^0 + n\gamma$$  \hspace{1cm} (1)

or the pion can be transferred to other atoms

$$\pi^- + Z \rightarrow p + Z\pi^-.$$  \hspace{1cm} (2)

The probability $W$ of the charge-exchange reaction (1) can be measured experimentally [1]. In $H_2 + Z$ mixtures $W$ as a function of the relative atomic concentration $C_z$ of atoms $Z$ can be approximated as

$$W(C_z)/W(0) = P(C_z)[1-Q(C_z)],$$  \hspace{1cm} (3)

where $P(C_z)$ and $Q(C_z)$ are the probabilities of the atomic capture and the transfer of pions, respectively. The approximation

$$P(C_z) = 1/(1 + A_z C_z),$$  \hspace{1cm} (4)

where $A_z$ is the atomic capture ratio for pions, proved to be valid in our recent experiments [2].

Here we report on the determination of the relative pion transfer rates $A_z$ in $H_2 + Z$ ($Z = $ noble gases) mixtures. The available experimental data [3] were analysed using a phenomenological hot atom reaction model [4], according to which the pion transfer probability could be approximated as

$$Q(C_z) = [1 - (1 - e^{-A_z C_z})/A_z C_z].$$  \hspace{1cm} (5)

The results are: $A_z = [(4.5 \pm 0.4)(Z^{1/3} - 1) + 1]$ ; $A_z = (8.3 \pm 0.5)(Z^{1/3} - 1)$; $\chi^2 = 1.642$.

This approximation is in better agreement with the experimental data than the earlier one [3], which resulted in a concentration dependent $A_z = A_z^{1/3} + 1$ with $A_z = (7.1 \pm 0.1)(Z^{1/3} - 1)$ and a higher $\chi^2 = 2.825$.

[3] Petrukhin, V.I., Suvorov, V.M., ZheTF (USSR) 55, 1145 (1976), [JETP (sov.phys.)- 43, 595 (1976)]
HIGH SPIN-LOW SPIN TRANSITION IN [Fe(phen)₂(NCS)₂] COMPLEXES STUDIED BY POSITRON ANNIHILATION


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Positrons injected into condensed media annihilate mostly with lifetimes 0,1-0,5 ns characteristic of the electron density of the surroundings encountered. In case of positronium (Ps)-formation, however, lifetimes can reach 1-10 ns as well.

Earlier results have demonstrated an interaction - resulting in a decrease of this lifetime - between iron(II) ions and positronium in solutions depending on the spin state of the iron complexes involved. In this work results referring to temperature induced high spin-low spin transition of [Fe(phen)₂(NCS)₂] solid complexes in powder form are reported. The data indicate a strongly spin depending interaction (e.g. o-Ps → p-Ps conversion) between the outer molecular electrons and Ps. The intensity of the long-living component increases with grinding time of the powder suggesting that in solid phase Ps-atoms trapped in structural defects (and not hot Ps) are affected by this spin depending interaction.

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EFFECT OF THE DIELECTRIC CONSTANT OF THE REACTION MEDIUM ON THE ORTHO-POSITRONIUM QUENCHING REACTIONS

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The ortho-positronium quenching reaction promoted by K[CoEDTA] (potassium ethylenediaminetetraacetate cobaltate) was investigated in different solvents and at different temperatures. It was found that in each solvent the reaction is diffusion controlled and that the value of its rate constant $k$ is dependent on the dielectric constant $\varepsilon$ of the reaction medium.

The functional form of $k$ on $\varepsilon$ is: $k = k_0 \exp(\nu/\varepsilon)$ where $k_0$ is the rate constant for $\varepsilon \to \infty$ and $\nu$ is a constant whose expression depends on the model used for calculating the electrostatic interaction between the o-Ps atom and quencher.

The $\varepsilon$ effect seems to be relevant not only "per se", but also for the procedure to be applied for ascertaining whether a reaction is diffusion controlled. Moreover it offers an alternative explanation for the experimental results used for supporting the hypothesis that a significant fraction of o-Ps atoms diffuses in quasi free states at room temperature.
POSITRONIUM FORMATION-, DIFFUSIVITY- AND LIFETIME PARAMETERS IN MICELLAR SOLUTIONS

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A microscopic model was formulated to describe positronium lifetimes in micellar solutions with the following two assumptions:

a) positronium lifetimes are different in the two phases and positronium undergoes normal diffusion;

b) the low atomic density region of the micellar boundary serves as an effective positronium trap.

A non-exponential positronium lifetime density function has been derived by approximately solving a diffusion problem with randomly distributed spherical absorbers.

Positronium formation-, diffusivity- and lifetime parameters are estimated by fitting this lifetime density function to positron lifetime spectra obtained from various sodium dodecylsulphate solutions at different temperatures.

Because of the similarity in the basic assumptions, the method can readily be utilized to determine the same parameters for other short-living objects such as exotic atoms and radicals.
REATIONS OF HOT TRITIUM ATOMS AND POSITRONIUM IN THEPORES OF SOLIDS

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The reactions of hot tritium atoms, as well as of positronium in the pores of solid dielectrics are characterized by certain peculiarities as compared with the respective reactions in the gaseous phase. Both cases exhibit the mechanism of excitation energy dissipation on the solid surface. Comparison of tritium or positronium processes allows us to make suggestion on the mechanism of transformation of the excited molecules PsO₂ and C₂H₅T.
EFFECT OF \text{ClO}_4^- \text{IONS ON INTERACTIONS BETWEEN CATIONS AND POSITRON}

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When ions interact with positron it has to be taken into account that electrolytes always contain cations as well as anions. In order to separate cation from anion effects various salts have to be compared with the same anion. The influence of the \text{ClO}_4^- ion on the annihilation process was investigated by dissolving salts with different cations (Li$^+$, Na$^+$, Mg$^{2+}$, Ba$^{2+}$). The solvents used were acetonitrile (AN) and propylene carbonate (PC). In these investigations use was made of the dependence for electrolytes [1] in which the intensity I of the amount of o-Ps formed is related to the concentration c of the salt

$$I = \frac{I_0}{1 + kc}.$$

The relative variation between the different cations shows that ions with larger surface charge density also exhibit a larger influence on the intensity. In order to estimate the contribution of the \text{ClO}_4^- a cation with a very low surface charge density has to be used; the tetrabutylammonium ion (TBuA$^+$) served this purpose. In AN the electrolyte TBuAClO$_4$ caused no changes in the annihilation parameter. This means that in AN neither the TBuA$^+$ nor the ClO$_4^-$ has any effect on positron annihilation, thus the variation of positron annihilation in electrolytes with perchlorates belongs only to the cations and acts as a measure of the different degree of solvation of cations.

REACTION OF MUONIUM WITH AROMATIC COMPOUNDS

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Positive muons \( (t_1/2 = 1.5 \mu s) \) formed in the decay of positive pions \( (t_\pi = 18 \text{ ns}) \) can during their slowing down become neutralized, resulting in neutral muonium atoms (\( \text{Mu} \)), light isotopes of hydrogen \( (m_{\text{Mu}} = 0.11 m_H) \). Chemical reactions of \( \text{Mu} \) can be followed by means of the \( \mu \text{SR} \) (muon spin rotation) technique.

In transverse magnetic fields three entities can be distinguished by measuring their precession rates through the detection of the energetic decay positrons \( (E < 52.8 \text{ MeV}) \):

a) free \( \text{Mu} \) (fraction \( P_M \)), frequency of 13.9 GHz \( T^{-1} \),
b) free \( \mu^+ \) or \( \text{Mu} \) bound in a diamagnetic compound by abstraction or substitution (fraction \( P_D \)) with a frequency of 0.136 GHz \( T^{-1} \),
c) \( \text{Mu} \) bound in a paramagnetic compound by addition (fraction \( P_R \)), frequency dependent upon radical structure.

In general a fraction \( P_L \) of the muons is missing:

\[
P_L = 1 - P_M - P_D - P_R
\]

The formation of radicals was investigated with 33 monosubstituted arenes at the Swiss Institut for Nuclear Physics (SIN). For 26 compounds the addition of \( \text{Mu} \) to the aromatic ring - forming the ortho, meta and para muonic cyclohexadienyl radicals - was observed. Only in the case of \( \text{C}_6\text{H}_5\text{CF}_3 \) also ipso addition was found. No radicals were detected in \( \text{C}_6\text{H}_5\text{CHO}, \text{C}_6\text{H}_5\text{COC}_6\text{H}_5 \) and \( (\text{C}_6\text{H}_5)_2\text{NNH}_2 \), whereas \( \text{C}_6\text{H}_5\text{C}==\text{CH}, \text{C}_6\text{H}_5\text{CH}==\text{CH}_2, \text{C}_6\text{H}_5\text{N}==\text{NC}_6\text{H}_5 \) and \( \text{C}_6\text{H}_5\text{NO}_2 \) radicals are formed by \( \text{Mu} \) addition to the substituent. Addition to the ortho positions occurs with a somewhat higher than statistical probability. The values of \( P_D \) range between 0.15 \( (\text{C}_6\text{H}_6) \) and 0.76 \( (\text{C}_6\text{H}_5\text{SH}) \), the values of \( P_R \) between 0.65 \( (\text{C}_6\text{H}_6) \) and 0.08 \( (\text{C}_6\text{H}_5\text{I}) \). The results can qualitatively be understood when \( \text{Mu} \) is formed by the neutralization of thermalized \( \mu^+ \) ions.
In hot atom chemistry the usual procedure of obtaining information on the relative probability of different reaction channels is to obtain it from the spectrum of the end-products.

A method using induced resonance fluorescence is employed for the direct measurement of concentrations of active particles formed during stationary photolysis. The sensitivity of the method ($\sim 10^8 \text{ cm}^{-3}$) enables one to study the processes involving highly reactive particles ($\sigma \sim 10^{-15} \text{ cm}^2$).

The hot atoms were obtained through photolysis in the reaction vessel and the stationary concentrations of active particles were measured by their induced resonance fluorescence.

Dependence of atom concentrations on the presence of thermorelaxators provides data on the rate of energy losses and the reactivity of hot particles.

The possible ways of applying this method are demonstrated by means of methylamine and hydrogen iodide steady-state photolysis and by reactions between oxygen and hydrogen atoms and methane.
REACTIONS OF RECOIL $^{38}\text{Cl}$ ATOMS WITH DICHLOROTOLUENES

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Reactions of recoil $^{38}\text{Cl}$ atoms with dichlorotoluenes are investigated. Lower $^{38}\text{Cl}$-for-Cl substitution yields arising from thermal ipso-attack on dichlorotoluenes than from ipso-attack on chlorobenzenes and chlorotoluenes are explained on the basis of substituent effects. Combination experiments suggest higher reaction probability of $\text{I}_2$ with thermal recoil $^{38}\text{Cl}$ atoms than that of $\text{C}_6\text{H}_6$ in the mixtures of the latter with chlorobenzenes as compared with the corresponding mixtures with chlorotoluenes. Reactivity parameters of recoil $^{38}\text{Cl}$ atoms are evaluated using the model proposed by Urch and are discussed in terms of the accompanying chemical processes.
CHEMICAL CONSEQUENCES OF L SHELL PHOTOELECTRIC IONIZATION IN LIQUID C₆H₆-I₂ SYSTEMS

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C₆H₆ - I₂ solutions were irradiated by quasimonochromatic X-rays with limited energies between 4.5 keV and 8.0 keV using an X-ray generator containing Cr as anticathode material. The maximum voltage applied was 12 kV. The characteristic X-ray energy of Cr (5.412 keV) agrees well with the photoelectric excitation energy of the L shell electrons of iodine atoms (5.118 keV).

Each solution absorbed a radiation dose (R_D) between 10.21 krad and 74.31 krad depending on irradiation time and I₂ concentration.

The irradiated solutions were analysed by a gas chromatograph with an FID detector and the only product observed was iodobenzene.

In the low I₂ concentration region a large fraction of R_D (>95%) is essentially absorbed by the benzene molecules thus the yield of iodobenzene (Y_iodo) can be compared with the scavenger effect of I₂ in the radiolysis of benzene. These comparisons clearly indicate that the formation of iodobenzene observed in the present work effectively depends on the Auger activation of iodine atoms.

On the other hand, the absence of any aliphatic iodide compounds shows that the Auger activation of iodine atoms starting with L shell photoelectric ionization causes only the production of the phenyl radicals, not the aromatic ring rupture.

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TRITIUM LABELLING BY CATALYSED WILZBACH METHOD

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Exposure to gaseous tritium in the presence of Pt or Pd black is a promising modification of the Wilzbach method. The reagents excited by the β-radiation of tritium make only a small contribution to the overall yield of the reaction. The process may be explained by hydrogen atoms arising from the dissociative adsorption of H₂ on Pd in the H₂(Pd) organic compound system diffusing into the compound layer and entering into chemical reactions with it [1]. Various processes are discussed that possibly determine the yield of the reaction: poisoning of the catalyst by the reaction product, de-activation of catalyst surface by chemisorbed hydrogen, recombination of hydrogen atoms and their disappearance in the repeated reaction:

RH + H' → R' + H₂
R' + H' → RH, etc. (1)

A model of the process has been constructed where the distribution of H⁺ atom concentration C in the organic compound is determined by reaction (1). Equations have been written for unidimensional (Wilzbach method, bombardment of targets with H⁺ atoms, etc.) and three-dimensional (catalysed Wilzbach method, eq. (2)) processes:

\[ C(r) = k_p C_s r_o^2 \exp \left[ \frac{\sqrt{r_o^2 - r}^2}{Dr(1 + r_o \sqrt{r/Dr})} \right] \] (2)

\( r_o \) is the radius of the metal crystallite, \( r \) is the distance from the crystallite centre, \( k_p \) is the rate constant of H⁺ penetration through the boundary, \( C_s \) is the H⁺ concentration on the metal surface, \( k \) is the rate constant of reaction (1), \( D \) is the diffusion coefficient. We have plotted the dependence of the reaction zone radius on \( r_o \) and the dependence of the minimum metal content ensuring 100% yield on \( r_o \) for a series of \( \sqrt{r/Dr} \) values. The effects of the crystallite size and metal content on the tritium labelling yield in the \(^3\)H₂/Pd black/organic compound system have been studied (\( r_o \) was measured by means of an electron microscope).

STERILIZATION OF ALUMINA FOR PRODUCTION OF $^{99m}$Tc-GENERATORS

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$^{99m}$Tc-generators were prepared using chromatographic alumina sterilized by gamma radiation, dry heat sterilization, or steam sterilization. This article deals with a comparison of the various methods of sterilization and their influence on the chromatographic properties of alumina. It is essential that in all cases the alumina was sterile and that absorption capacity of the alumina for molybdate was not disturbed significantly. The sterilization effect can reduce elution yields of $^{99m}$Tc eluates. The best yield of $^{99m}$Tc was obtained by commercial, unsterilized alumina. It was found that gamma sterilization of alumina reduced elution yield of $^{99m}$Tc more than dry or steam sterilization.
$^{99m}$Tc-GENERATOR-PREVENTION OF RADIOLYTICALLY INDUCED REDUCTION OF ELUTION YIELD

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For the $^{99m}$Tc-generator activities ranging from 74-92.5 GBq, an adsorbent consisting of a mixture of alumina and silica gel was modified by copper addition. The quantity of copper adsorbed on alumina was in the range of 10-15 mg Cu/g alumina. It was found that saline solution does not influence the performance of the column. A high elution yield of $^{99m}$Tc and good quality of the eluate was obtained both for the "wet" and "dry" column.
EFFECTS OF $^{35}\text{Cl}(n,p)^{35}\text{S}$ REACTION

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In the present work $^{35}\text{S}$ was obtained via $^{35}\text{Cl}(n,p)$ reaction in $\text{CCl}_4$, $\text{CHCl}_3$ and $\text{C}_2\text{HCl}_3$ with irradiation being carried out in a TRIGA MARK III reactor. Radiochemical analysis showed the main $^{35}\text{S}$ product to be absorbed in $\text{S}$. Gas chromatographic analysis was performed on the residual material after separating the $^{35}\text{S}^0$ from the neutron irradiated organic chlorine compounds.

Results for the different compounds are given.
MODEL OF REACTIONS OF At(I)-COMPOUNDS IN AQUEOUS SOLUTION

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Based on investigating the electromigration of $^{217}$At-compounds in dilute aqueous solutions [1] the synthesis mechanism, characterization and complex formation of At(I)-compounds as well as their behaviour in alkaline electrolytes are discussed. Oxidation of $^{217}$At in acidic solutions containing $\text{Cr}_2\text{O}_7^{2-}$ or $\text{S}_2\text{O}_8^{2-}$ results in At(I)-cation formation with $pK_\text{S} = 1.55 \pm 0.15$ in $\text{At}(\text{H}_2\text{O})_2^+ + \text{H}_2\text{O} = \text{At}(\text{H}_2\text{O})_{2-} + \text{H}_3\text{O}^+$ system [2].

Anionic and neutral complexes $\text{AtX}^{2-}_n$, $\text{At}^-$, $\text{At}(\text{ClO}_4)_n^-$ ($X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-$; $Y = \text{Cr}_2\text{O}_7^{2-}$, $\text{S}_2\text{O}_8^{2-}$; $n = 1, 2$, [1,2]) and cationic species $\text{At}(\text{th})^+_n$, ($\text{th} =$ thiourea and some thiourea derivates; $n = 2, 3$; [3,4]) are described. Stability constants and - for the At(I)-diiodocomplex formation as an example - their dependences on temperature were determined. Results were compared with literature data. The observed tendency in the complex constant values characterizes At(I) cation as a typical soft Lewis acid. There are strong correlations with parameters of analogous Ag(I) compounds.

In acidic and some neutral ligand containing solutions $\text{AtO}_x$ and $\text{At}^-$ turn into At(I) complexes, too [5]. The easy shift in the $\text{At}^{-2} \rightleftharpoons \text{AtO}_x \rightleftharpoons \text{At}^+$ system is possible because of oxidation via air-$\text{O}_2$ in these solutions connected with the stabilization of the At(I) status in complex formation.

At (I) compounds are stable up to pH 9-11. Their individual existence in a wide pH range complies with the values of their brutto stability constants. In alkaline solutions ligand exchange with $\text{OH}^-$ was observed. The unstable At(I)-dihydroxo-complex in alkaline solutions free of oxidation agents undergoes reaction to At-anion, whose electromigration is identical with that of astatide. In alkaline solutions containing oxidation agents like $\text{S}_2\text{O}_8^{2-}$, products of most probably $\text{AtOX}^-$ ($x =$ 2,3,4) chemical form were observed.

ION-MOLECULAR CHARGE TRANSFER AND REACTIONS WITH CATION-RADICALS STUDIED BY OPTICALLY DETECTED ESR OF RADICAL PAIRS

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The effects of ion-molecular charge transfer in a new method of optically detected ESR (ODESR) of radical pairs have been studied. Broadening and collapse of the hyperfine structure have been observed experimentally depending on the concentration of neutral acceptors. Ion-molecular charge transfer rate constants have been calculated for some radical-anions and cations from experimental data. ODESR signals of the monomer cation-radicals $A^+$ and dimer cation-radicals $A_2^+$ are observable in the case of acceptors of the positive charge. The dimer cations production rates were calculated from analyses of the ODESR spectra.
An efficient method has been developed which allows the preparation of various tritium labeled compounds including proteins, polypeptides, aminoacids, nucleic acids, nucleoproteins, fatty acids, protein modifiers, etc. of rather high specific radioactivity: 1-10 Ci/mmole. The method takes advantage of hydrogen-tritium exchange in solid organic compounds upon treatment with activated tritium atoms which are generated on hot tungsten filament. The exchange proceeds only within the monomolecular surface layer thereby allowing the method to be used for structural analysis of the tertiary structure of proteins, conformational transitions, topology of membrane proteins.
GEMINATE RECOMBINATION OF ELECTRONS TRAPPED AND SOLVATED WITH CATION-RADICALS IN NONPOLAR LIQUIDS

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The recently developed ODESР method was used to study processes of geminate recombination of electrons trapped and solvated by polar solutes with cation-radicals in nonpolar liquids. This method allows one to obtain data on the interactions of an electron with a trap during recombination at times above 100 ns after barning.

The temperature dependences of the signal intensity of each type of electrons (trapped or solvated) corresponded to those of mobilities.

The line width dependences on temperature, microwave power and (for solvated electrons) concentration of polar solutes obtained describe the mechanism of electron motion.
RECOIL ATOM REACTIONS IN VARIOUS ORGANIC SOLIDS INDUCED BY IMPLANTED TRITIUM FROM THE GAS PHASE

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Recoil atom reactions in various organic solids induced by implanted tritium from the gas phase were studied using naphthalene derivatives, pyrrole, dimethyl pyrrole and uracil. The tritium recoil source was $^3$He-gas filled in a quartz tube. Neutron irradiation was performed in the nuclear reactors, JRR-2, 3 and 4. The $^3$He(n, p)$^3$H reaction gave a sufficient amount of tritium implanted in wall materials in the tube.

The most interesting point revealed in this study is inhomogeneous distribution of tritium in rings of naphthols, naphthoic acids, pyrrole, dimethyl pyrrole and uracil. It shows a correlation with electron density in the ring positions. These results obviously differ from those obtained in many substances which showed homogeneous tritium distribution. Nonselective hot reaction as was considered previously in aromatic rings is not always correct. In our case it is most probable that tritium was trapped by the rings in a considerably lower energy range which allowed orientation effect in ring hydrogen substitution reactions.

Intramolecular hydrogen bonding in naphthoic acid influenced tritium trapping.
SOME EXPERIMENTAL PROBLEMS IN THE T + H$_2$ SYSTEMS

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During the study of the T + H$_2$ systems certain experimental problems were resolved. Some of these problems are specific to the hydrogen systems while others could be found in most gas-phase recoil chemistry.

In this paper we shall try to discuss the following problems:
1. The damage caused to the components of the sample as a result of the ampoule-sealing process.
2. Post-irradiation thermal reaction of bromine scavenger with hot products as well as the decomposition of ICl scavenger.
3. The detection of hydrogen and its isotopes when helium is used as a carrier gas after the separation of the components at liquid nitrogen temperature.
PRODUCTS OF $^{50}\text{Cr}(n,\gamma)^{51}\text{Cr}$ NUCLEAR REACTION IN SOLID INORGANIC CHROMIUM COMPOUNDS. EXPERIMENTAL DATA AND THERMODYNAMIC CALCULATIONS.

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The products of $^{51}\text{Cr}$ stabilization in $\text{Cr}_2\text{O}_3$, $\text{CrO}_3$, $\text{K}_2\text{CrO}_4$, $\text{K}_2\text{Cr}_7\text{O}_7$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{KCr(SO}_4)_2 \cdot 12\text{H}_2\text{O}$ were studied. Traditional methods of coprecipitation as lead chromate and chromium phosphate as well as the specially developed express high-voltage paper electrophoresis (EHVPE) and mercury amalgamating method were used.

Data obtained by EHVPE agree reasonably well with those achieved using traditional coprecipitation methods. Experimental data are compared with thermodynamic calculations by multi-atom excited complex model (MEC). For all the studied compounds a definite correspondence between calculated and experimentally obtained data was observed. However, the experimental values of $^{51}\text{Cr}$ yield in the VI-valency state are higher than the theoretical ones for potassium chromate and bichromate. Accordingly, $^{51}\text{Cr}$ yields for the lower valency states, especially for Cr(II) and for undissociated Cr(III) compounds are decreased. This difference can be explained by annealing processes which are observed both under irradiation in the reactor and during the analytical procedures. Comparison with the calculation data shows that Cr(IV) yield is increased at the expense of the parent yield.

The MEC model enables the estimation of the products of chemical transformation in solids due to exposure to heavy particles or to implanted ions.
THERMAL ANNEALING IN CrO$_3$ CRYSTALS IRRADIATED BY NEUTRONS

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CrO$_3$ crystals are the simplest systems for investigating the behaviour of recoil $^{51}$Cr during thermal annealing and for testing the annealing model mechanism activated by defects (AAD).

Samples of CrO$_3$ were irradiated in a thermal neutron flux of $2.5 \times 10^{12}$ n cm$^{-2}$ s$^{-1}$ for 24 hours at a temperature of 30°C (fast neutron flux of $4 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$, $\gamma$-dose of $1.4 \times 10^6$ R). The irradiated samples were annealed at 60, 80, 100, 120, 140, 150, 160, 180 and 196°C in argon atmosphere and at 120, 140, 160 and 180°C in air for 20 and 40 min. and for 1, 2, 4, 6 and 8 hours. The CrO$_3$ samples were analysed by express high-voltage paper electrophoresis. Experimental data, treated by the composite equivalent curve method, sections method and method of distributed activation energy provide average values of activation energy which are in good agreement with each other. The obtained values correspond to the activation energy for vacancy transport.

The experimental data can be expressed by:

$$\Delta R = K \ln n, \\
n = b.t.f.E\Sigma n_i = b.t.z.v.E\Sigma n_i.e^{-E/kT},$$

where $\Sigma n_i$ is the total quantity of defects, $t$ is time, $f$ is the jumping frequency, $z$ is the number of equal neighbour sites, $v$ is the frequency factor, $b$ and $K$ are constants.

At similar annealing times, the linear sites on the curves of $^{51}$Cr yield in the III- and VI-valency state are observed to be dependent on temperature. Extrapolation of linear sites into the low temperature region to their intersections gives the irradiation temperature of samples. Thus, annealing can be used for monitoring thermal conditions of irradiation.
THERMAL ANNEALING OF CHROMIUM-51 IN NEUTRON-IRRADIATED Cr(tfa)$_3$

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Neutron-irradiated tris-(1,1,1-trifluoro-2,4-pentanedionato-0,0')-chromium(III), Cr(tfa)$_3$, was thermally annealed isochronically (70 min) and isothermally (95°C and 115°C). The annealed samples were dissolved in chloroform, with and without the presence of excess tfa, and then analyzed by an alumina column chromatographic method with appropriate eluents which revealed the presence of parent, two different ligand-deficient species and free Cr(III) species. The presence of excess tfa in the dissolution solution affects the absolute values somewhat, but not the general trends observed. Both isochronal and isothermal annealing data suggest that a stepwise reassembly of fragments occurs in the crystalline Cr(tfa)$_3$ matrix. These observations are in contrast to those reported in the literature [Mathieu and Vargas, Radiochem. Radioanal. Lett. 28 (1977) 145] but are similar to those already observed for Cr(acac)$_3$ and Cr(hfa)$_3$ [Collins and Goetz, 10th IHAC, 1979].

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ISOTOPE EXCHANGE IN A MIXED VALENCE COMPOUND: Tl₄Cl₆

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Chemical analysis and physical methods are combined to unravel the mechanism of isotope exchange in solid Tl₄Cl₆. The results suggest that this compound is a superconductor. The reaction would proceed by fast diffusion of the cations with apparently two pathways, either in the bulk of the crystals or in disordered regions.
GAMMA IRRADIATION EFFECTS ON THE ELECTRICAL CONDUCTIVITY BEHAVIOUR OF HEXACYANO HEXA-AMINE DOUBLE COMPLEXES


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Gamma irradiation effects on the electrical conductivity of the double complexes [Co(NH$_3$)$_6$][Co(CN)$_6$], [Co(NH$_3$)$_6$][Al(CN)$_6$] and [Co(NH$_3$)$_6$] [Mn(CN)$_6$] were investigated. A comparison is made between the rates and the activation energies of thermal annealing influencing the electrical properties of pure and $\gamma$-irradiated samples. The sign of charge carriers was shown to be negative and the isothermal annealing curves are due to annealing of thermal electrons in the lattice. The conductivity of solid double complexes increases with temperature, decreases with radiation dose and remarkably increases when the transition metal of the negative component of the double complex changes from Al to Mn to Co. However, the results show that the rate constants and activation energies of thermal annealing of defects in these systems are not significantly affected by gamma irradiation.
SOME REACTIONS DUE TO INTERACTION OF IMPLANTED IONS WITH SOLID SURFACE

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Some results on phase transformations in the implanted surface layers of metals and alloys obtained by X-ray diffractometry are presented.

The samples were irradiated by different ions in wide dose and energy ranges using an ion accelerator (ILU-3).

It is estimated that multiphase nitride and carbide layers are formed on the surface of the metal during nitrogen and carbon ion implantation as a result of radiation-induced chemical interaction between implanted N⁺, C⁺-ions and atoms of the target.

Amorphous metal glass was produced by metalloid implantation into stainless steel.

It is shown that ion irradiation followed by phase formation is accompanied by changes in some physical and mechanical properties.
TIME DIFFERENTIAL MÖSSBAUER APPARATUS FOR THE STUDY OF AFTER-EFFECTS FOLLOWING ELECTRON CAPTURE

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Chemical after-effects (e.g. creation of anomalous metastable oxidation states, that of short lived anomalies in the lattice, anomalous population of spin states) following the electron capture (EC) of $^{57}$Co incorporated in various matrices lend themselves to be studied by time differential Mössbauer emission spectroscopy. For that purpose the 122keV γ-ray populating the 14.4 keV level is used as start time marker while the Mössbauer spectrum is registered sampling the decay of the 14.4 keV niveau. In order to improve the time resolution and the rate capacity a fast-fast coincidence system employing NaJ(Tl) and NE 102 A scintillators has been developed. The data are collected with an LSI-based 64 x 1024 channels on-line system providing data evaluation possibilities as well.

Test measurements have yielded in ~4 ns FWHM time resolution to be compared with literature data of 9-25 ns FWHM characteristic for earlier measurements performed with slow-fast coincidence systems.

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RECOIL RADON ATOMS FOR INVESTIGATING PHASE AND CHEMICAL TRANSFORMATIONS OF CONDENSED MEDIA

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The singularities of evolution of recoil atoms of gases from substances under investigation are generally used for the study of the matrix itself and of chemical and phase conversions in it. Due to alpha-decay of Th or Ra in samples recoil atoms of radon (emanation) are formed. The recoil energy incorporates them into the lattice of the solid. The hot radon atoms may also be implanted into the sample directly from solution. The measurement of the evolution rate of radioactive noble gases from sample constitutes the principle of emanation method. The emanation ability is characterized by emanating coefficient E. By solving the corresponding diffusion equations we have established that the diffusion coefficient does not depend on the function of initial distribution nor on the form and size of particles. The changing of radon diffusion conditions - determined by phase conversions - can be estimated. For diffusion coefficient vs temperature (or time) in the region of the phase transition an approximate expression has been obtained enabling the pre-exponential factor and activation energy of radon diffusion to be calculated. The suggested mathematical models of emanating, the improvement of installation and the employment of computers have raised the structural sensitivity of the method thereby allowing liquids to be studied. Thus, in Fe-S, Co-S, Ni-S melts some fine effects were revealed, e.g. the existence of microheterogeneities, by evaluating the viscosity vs composition and temperature functions (emanation data). The use of emanation analysis together with DTA and TGA and developed models enable one to calculate thermodynamic functions and thus, from radon diffusion data, to obtain information on the state of the matrix.
FORMATION OF COMPOUNDS AFTER METALLOID ION IMPLANTATION IN TITANIUM, ZIRKONIUM AND HAFNIUM

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Thin foils (50 - 100 nm) of Ti, Zr or Hf were implanted with the metalloids B, C or N using doses from $10^{16}$ to $10^{18}$ ions cm$^{-2}$ at room temperature. The implantation energy was in all cases 50 keV. The phase composition and the microstructure of the implanted metal foils were investigated by high-voltage electron microscopy in transmission and selected area diffraction and examined as a function of the implanted dose and of the annealing temperature after implantation. A special device in the microscope enabled a defined tempering and annealing regime to 600 °C.

The analysed foils show that besides the carbides and nitrides of Ti, those of Zr and Hf were also synthesized at room temperature by metalloid implantation. We obtained only crystalline compounds. After annealing at about 600 °C we found a growth of precipitations in the vicinity of dislocations and grain boundaries.
CHEMICAL EFFECTS OF CHROMIUM-51 - NEUTRON CAPTURE RECOILS IN K₃Cr(C₂O₄)₃ - K₃Al(C₂O₄)₃ AND K₃Cr(CN)₆ - K₃Al(CN)₆ MIXED CRYSTALS

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The chemical effects of chromium neutron capture recoils produced in mixed crystals of the type K₃Cr(C₂O₄)₃ - K₃Al(C₂O₄)₃ and K₃Cr(CN)₆ - K₃Al(CN)₆ have been investigated. The initial chromium parent retention in the investigated mixed crystals has been determined using solvent extraction techniques and making use of 0.32 MeV photopeak for ⁵¹Cr produced as a result of thermal neutron capture. It was found that the initial chromium parent retention varies linearly with parent mole fraction in the mixed crystals. The retention and non-retention results have been discussed in view of a mechanistic model involving metal and ligand vacancies exchange and substitution reactions.
GAMMA IRRADIATION EFFECTS ON THE ELECTRICAL CONDUCTIVITY BEHAVIOUR OF N,N' - ETHYLENE BIS METAL SALICYLIDENEIMINE

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Gamma irradiation effects on the electrical conductivity behaviour of some newly prepared mono-, homo bi- and hetero bi-nuclear metal chelates of tetralentate salicylideneimine were investigated. The variation of the electrical conductivity with temperature is characteristic of semiconductors. The rate constants for isothermal annealing reaction and activation energies for semiconduction in the various metal chelate complexes of irradiated and unirradiated metal chelates were calculated and are discussed.
PHYSICO-CHEMICAL PHENOMENA OF ELECTRON CAPTURE WITH $^{57}$Co AS AN EXAMPLE

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The physico-chemical consequences of some nuclear transformations, such as electron capture of $^{57}$Co, are induced primarily by electron processes (Auger cascades), since the recoil energy associated with neutrino emission is smaller than typical lattice displacement energy. However, processes following the inner electron capture could be similar to those occurring at the final stage of recoil atoms or atoms with excess kinetic energy slowing down.

The present talk deals with the following phenomena triggered by the electron capture: excited states of molecules, the influence of various factors on their yield, intermolecular transfer of electrons, radiolytic effects of nuclear decay, mobile electron participation in hot atom stabilization, energy transfers, etc.

The after-effects of nuclear transformations may be investigated by means of Mössbauer spectroscopy, generally in solid phases at low temperatures. This virtually permits one to neglect solid diffusion processes and thus to minimize the number of elementary interactions.

The available experimental data suggest a striking similarity between traditional hot atom chemistry and the chemistry of high energies.
THERMAL STABILITY OF SILVER ATOMS ON THE SURFACE OF GAMMA-IRRADIATED ALUMOSILICATES

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The influence of temperature, of the quantity of silver ions and the influence of the method of their introduction into alumosilicates as well as the effect of irradiation doses on the kinetics of thermal changes and stability of paramagnetic particles of silver on the surface of gamma-irradiated alumosilicates modified by different metals and non-modified alumosilicates were studied. As a result of gamma-irradiation, in all the studied matrices, ESR spectra of different forms of stabilization of atomic silver particles were observed. The existence of several types of silver atoms and complex Ag was established. The quantitative relationship between different paramagnetic conditions of silver particles and their stability is governed by method of introduction of silver ions, quantity of ions introduced, thermal and vacuum pre-treatment, irradiation dose and the character of the modifying additive. It has been shown that ESR spectra of silver particles in gamma-irradiated alumosilicates and in alumosilicates modified by additives such as calcium, magnesium, yttrium and lanthanum oxides and containing silver ions introduced by ion exchange can be observed at higher temperatures (up to 353 K) than in matrices prepared by adsorption equilibrium of silver ions (up to 223 K).
KINETICS OF THERMAL CHANGES OF SILVER ATOMS ON THE SURFACE OF GAMMA-IRRADIATED SILVER-CONTAINING MATRIX

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An investigation of kinetics of thermal changes of silver atoms on the surface of gamma-irradiated silver-containing matrix by ESR method has shown that in post-irradiation processes there is an increase in the number of silver atoms along with their recombination. On heating gamma-irradiated samples additional formation of silver atoms takes place as a result of the reaction of the excess silver atoms with the electron-donor centres which appear in the matrix on gamma irradiation. The general view of the dependence of the number of silver atoms adsorbed on the surface of gamma irradiated carriers and stabilized in frozen water solutions of silver salts on time in the range of the studied temperatures, is a curve passing through the maximum. In the first stage of kinetic dependence an increase can be seen in the number of silver atoms, then the maximum is reached and for longer periods of investigation the number of silver atoms does not practically change. The observed step-like kinetic curves represent extreme dependences in which the maximum position exists for very short periods which equal the time taken for a sample to reach the specified temperature.

The character of the kinetic features of silver atoms adsorbed on the surface is determined by the temperature, the content of silver ions in the matrix and the method of their introduction, the composition and character of modifying additives, as well as by the conditions of thermal and vacuum treatment of systems before irradiation and by the irradiation dose. By changing these parameters it is possible to have kinetic dependences of a different type within temperature range from 77 to 350 K.
CHEMICAL EFFECTS IN IRRADIATED AND IMPLANTED METAL SELENITES STUDIED BY THE EPR METHOD


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EPR spectroscopy has been used to study chemical effects in some polycrystalline metal selenites (SrSeO$_3$, CdSeO$_3$) and in elementary selenium irradiated with gamma-rays, thermal neutrons, or implanted with accelerated ions.

In the EPR spectra of irradiated selenites signals from various radicals, depending upon irradiation temperature and measurement, have been identified. At room temperature a relatively strong signal from the SeO$_2^-$ radical and a weak one from the Se$^0$ radical have been observed. At a low temperature (77 K), signals from SeO$_2^-$ and SeO$_3^-$ radicals and a weak signal from the Se$^0$ radical have been obtained.

In the EPR spectra of the selenites, implanted with Se$^+$ and Cd$^+$ ions ($E = 20 - 40$ keV, $D = 10^{17}$ ions/cm$^2$), signals from the SeO$_2^-$ and Se$^0$ type radicals have been observed.

Analysis of the EPR spectra of elementary selenium, implanted with Se$^+$ and O$^+$ ions ($E = 40$ keV, $D = 10^{17}$ ions/cm$^2$), showed that radicals of various types are produced, depending upon the implanted ion. Implantation with Se$^+$ ions gives rise to radicals like those found in gamma-irradiated selenium (in both cases a wide signal from the Se$^0$ radical has been observed), and implantation with O$^+$ ions gives rise chiefly to SeO$_2^-$ radicals.

Values of the EPR spectral parameters (g-factors, superfine structure constants) have been determined. Recombination kinetics of radicals during thermal annealing was studied, and the reaction velocity and activation energy constants were determined.

A possible mechanism of radical production during irradiation and implantation of selenites and elementary selenium has been considered, as well as recombination processes during thermal annealing.
HOT ATOMIC REACTIONS IN THE COSMOS

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High energy reactions might be important for cosmic chemistry with respect to accelerated particles in solar or stellar winds, cosmic rays, colliding interstellar gas and dust clouds, etc. The formation of approximately 56 molecules observed in space has chiefly been attributed to ion molecule reactions and to photo- and radiolytical processes to a lesser extent. The criteria for these processes are exothermicity and low activation energies. Hot atom chemistry, hitherto unknown to astrophysics, could introduce a new perspective to cosmic reactions and add to the explanation of some of the exotic molecules in the interstellar medium. It allows for endothermic reactions with high activation energy and atom molecule interactions. The latter is of interest, since the vast majority of species in space are neutral.

Even more than to gas phase reactions could hot atom chemistry contribute to the new and expanding field of cosmic solid state research, where processes in or at the surface of interstellar dust and ice grains, comets, outer planets and their satellites are studied. One of the major goals is to explain the formation of organic compounds with respect to problems of potential extraterrestrial life and the evolution of life on our planet. Recoil chemistry, especially that of carbon, lends itself for terrestrial simulation of chemical processes in space. In combination with ion implantation and spectroscopy, it may even help to assign spectra of interstellar solids. A review is given which shows the overlap of T, C, N, O, P and S recoil chemistry in gas and solid phase with the problems of cosmic chemistry. Special emphasis is laid on recent experiments with carbon atoms in gaseous and frozen water, ammonia, and mixtures thereof, leading to high yields of formaldehyde, nitriles and NCN group containing compounds (formamidine, cyanamide, guanidine). These compounds are precursors for sugars, amino acids and nucleotides, and could lead to the abiotic formation of even more complex biomolecules.
CHEMICAL APPLICATIONS OF HOT ELECTRONS

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Hot electrons, such as the beta particles emitted during radioactive decay, cause physical and chemical effects in the materials through which they pass. These effects may be justifiably regarded as close (although adjacent) to the area of interest in hot atom chemistry. Probably the two best known effects of hot electrons are the production of electronically excited species which may subsequently fluoresce (as exploited in liquid scintillation counting), and the direct production of photons (the Cerenkov effect). We have been interested for some years in the application of these two effects for analytical purposes, principally allied to the separation technique of liquid chromatography.

This paper discusses two novel chromatographic detection systems based on hot electron processes, emphasising particularly the advantages offered by instruments constructed around sealed radioisotope sources - such as the low external power requirement, the low cost and weight, and the exceptionally high medium-term stability of the sources. The beta-induced fluorescence detection system is illustrated with high sensitivity chromatograms recorded for polynuclear aromatic hydrocarbons and for fluorescent derivative of amino acids, and a number of beta-induced fluorescent spectra are discussed. A Cerenkov photon absorption detection system is illustrated with a range of chromatograms recorded by monitoring Cerenkov absorption at 200, 215 and 254 nm.
SURFACE STUDIES AT THE MOLECULAR LEVEL USING RECOIL-LABELLED ADSORBATES

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The application of hot atom chemistry to the study of molecular dynamics on surfaces using positron annihilation surface detection (PASD) is a technique recently introduced to the field of surface science. PASD utilizes the nuclear recoil method to prepare molecular concentrations of potential sorbates labelled with short-lived positron-emitting radionuclides such as carbon-11. Positron annihilation by surface bound species allows facile detection. Thus a non-disruptive measurement of dynamic surface processes such as molecular sorption and diffusion where sorbate-sorbate and sorbate-surface interactions could result in energy transfer and alter equilibrium conditions is possible. The sensitivity of PASD is unattainable by any present state-of-the-art surface spectroscopic method. Sorbate concentrations as low as \(10^{-12}\) of a monolayer result in a resolution using PASD that allows the detection of changes in concentration below \(10^{-4}\) of a monolayer per second. An application of PASD to the investigation of parameters controlling catalyst selectivity during alkyne cyclotrimerization over support Cr\(^{+6}\) surfaces will be addressed, with particular attention given to the molecular dynamics of acetylene-propyne co-trimerization. Research supported by the U. S. Department of Energy and Office of Basic Energy Sciences.
A new method is presented to study the dynamics of chemical reactions with high threshold energies combining hot atom production by laser photolysis and very fast and state selective product detection by laser induced fluorescence.

The nascent OH rotational, vibrational and fine structure state distributions produced in the reactions

\[ \text{H} + \text{O}_2, \text{CO}_2, \text{H}_2\text{O}, \text{NO}_2 \rightarrow \text{OH} (k,v,f) + \text{O}, \text{CO}, \text{H}_2, \text{NO} \]

have been measured at collision energies up to 60 kcal/mol (C.M.-system) with hot H atoms from the Excimer laser photolysis of HBr, HCl and H_2S. Absolute reaction cross sections have been obtained for the first three reactions by measuring reactant and product densities at short times.

For the reaction H + O_2 the experimental results are compared with extensive trajectory calculations on an ab initio potential surface (Melius, Blint 1979). The comparison shows that only very specific initial conditions (planar impact parameters of a well confined range etc.) lead to reaction at high collision energy.
THIRTY SIX YEARS OF HOT ATOM CHEMISTRY SYMPOSIA

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In 1948 interest in Hot Atom Chemistry had grown sufficiently to lead R.W. Dodson to organize a meeting on "Chemical Effects of Nuclear Transformations" at Brookhaven National Laboratory. The meeting is documented in the U. S. Atomic Energy Commission publication AECU-50. While this meeting was not truly international in scope, it heralded a recognition of Hot Atom Chemistry as an area of research appealing to a growing community of scholars with common research interests.

This meeting is the twelfth in a series of meetings begun in Louvain-la-Neuve, Belgium and held at the University of Louvain in 1959. There was no uniformity of title, nor any special regularity in occurrence in the subsequent meetings which are listed at the end of this abstract. The field grew and prospered with the passing years. Another milestone of early efforts at providing a forum for scientists in Hot Atom Chemistry was the meeting sponsored by the International Atomic Energy Agency and held in Prague, Czechoslovakia, October 24 - October 27, 1960. This meeting resulted in a two volume work published by the IAEA in 1961 as "Chemical Effects of Nuclear Transformations", STI/PUB 34, Vienna, Austria. What made this meeting remarkable, aside from the broad representation of scientists from multiple scientific disciplines, was the great increase of interest in theory and in organic systems. However, the applied aspects of Hot Atom Chemistry were yet to surface as a significant outgrowth of Hot Atom Chemistry. The second meeting sponsored by the IAEA on Chemical Effects of Nuclear Transformations (CENT) was held in Vienna, December 7-11, 1964, again resulting in a two volume work with the same title (vide supra) IAEA STI/PUB 91, 1965.

Beginning in the sixties many of the national societies representing the community of chemists organized symposia on Hot Atom Chemistry within their own national meeting structures. This has continued up to the present. However the International Symposia of which this is the twelfth,
were the cement that brought together the many diverse interests in Hot Atom Chemistry and provided a continuity that still exists today in research on the chemistry of excited species whose commonality is translational energy.

It is interesting to trace the literature which forms a basis for progress in this field. Perhaps the first chapter in a chemistry text devoted to Hot Atom Chemistry specifically can be found in "Radioactivity Applied to Chemistry" by F. C. Wahl and N. A. Bonner, John Wiley, New York 1951. I draw your attention to Chapter 8. In 1963, another important milestone came to the fore, the bibliography on "CENT" by A. Siuda published by the Polish Atomic Energy Commission as report No. 6 and covering the years up to 1963. This was followed by a series of bibliographies published by J.-P. Adloff of the Centre de Recherches Nucleaires, Strasbourg, France and covering the period 1963 to the end of the seventies. The most notable texts solely devoted to Hot Atom Chemistry began with "Chemie Heisser Atome" by G. Stöcklin, Verlag Chemie, Weinheim, 1969. This was later expanded and published in a French version. In 1979 "Chemical Effects of Nuclear Transformations in Inorganic Systems" edited by G. Harbottle and A.G. Maddock appeared. It was published by North-Holland in the Netherlands. Two recent books have appeared, "Modern Hot Atom Chemistry and Its Applications" by T. Tominaga and E. Tachikawa, Springer-Verlag, Berlin, 1981 and "Hot Atom Chemistry" edited by T. Matsurra, Kondasha-Elsevier, Tokyo, 1984. One might also mention the "Hot Atom Chemistry Status Report" published as an IAEA Panel Proceedings in 1975, STI/PUB 393. To be sure there have been reviews too numerous to mention and published in many languages, especially in the period 1960-1980.

In recent times, there has been increasing emphasis on drawing attention to the successes of Hot Atom Chemistry in the applied field. The first extensive presentation in this area occurred at the 9th meeting in Blacksburg in 1977 although application in the biological area goes back much further than that glimmerings of which can be found in earlier meetings. In some senses it is strange that applied Hot Atom Chemistry found more fertile ground in presentation to scientific audiences at meetings with other main themes, eg. the IAEA meeting in Venice in 1964.

In addition to the chronological and historical aspects of these meetings a discussion of changing interests and emphasis on succeeding IHAC
meetings will be presented with a view toward relation to advances in chemical thinking and in particular the impact of Hot Atom Chemistry on the parent body of advances in chemistry.

The IHAC have provided stimulus and excitement to those of us who have worked in this area for any length of time. I'm certain that with the success of this meeting we all look forward to the 13th International Hot Atom Chemistry Symposium.

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LISTING OF INTERNATIONAL HOT ATOM CHEMISTRY SYMPOSIA

1. 1959 - University of Louvain, Louvain-la-Neuve, Belgium
2. 1963 - Institute of Nuclear Physics Research, Amsterdam, Netherlands
3. 1966 - Purdue University, Lafayette, Indiana USA
4. 1967 - University of Kyoto, Kyoto, Japan
5. 1969 - Cambridge University, Cambridge, United Kingdom
6. 1971 - Chemistry Department, Brookhaven National Laboratory, Upton, New York, USA
7. 1973 - Institute for Nuclear Chemistry, Atomic Research Center, Jülich, FRG
8. 1975 - University of Louvain, Louvain-la-Neuve and Spa, Belgium
9. 1977 - Virginia Polytechnic Institute and State University, Blacksburg, Virginia USA
10. 1979 - Loughborough University of Technology, Loughborough, United Kingdom
11. 1982 - University of California, Davis, California USA
12. 1984 - Central Research Institute for Physics, Budapest and Balatonfüred, Hungary
There is some confusion in the literature arising due to misunderstanding of our model regarding fragmentation of molecules vis-a-vis models proposed by other scientists. An attempt would be made to clarify the picture and suggest some new experiments to gain further insight. The crucial question as to how unfragmented molecules may dispose off their large excitation energy rapidly, would be discussed.
DETERMINATION OF SOLUTE ION - BIOMOLECULE ASSOCIATION BY A RADIOMETRIC RECOIL ATOM TRACER TECHNIQUE

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Hot atom chemistry has had practical applications in such areas as neutron activation analysis and radiopharmaceutical chemistry. Utilization is made of the activation event where a radioactive atom born in the nuclear transformation acquires a high kinetic energy which can result in unique chemical reactivity. In a sense a "hot atom" can be utilized as an interactive tracer especially in multiphase systems where site information can be determined. It is important that the hot atom has distinctly different chemical reactivities with the phases.

We report a radiometric recoil atom technique employing biomolecules containing $^{127}$I and iodide-$^{129}$ ions for determining biomolecule - biomolecule and iodide-ion - biomolecule association in liquid and frozen aqueous solutions of slightly soluble biomolecule solutes.

The distributions of radio iodo-labelled products ($^{128}$I and $^{130}$I) produced by radiative neutron capture in liquid and frozen aqueous solutions of uracil, 5-iodouracil (5IU), 3-iodo-L-tyrosine (MIT), and 3,5-diiodo-L-tyrosine (DIT), all containing iodide-$^{129}$ at various biomolecule solute concentrations were determined by liquid chromatography.

For both uracil and DIT, liquid or frozen aqueous solutions, the only observable product containing $^{130}$I activity is the iodide ion. On the other hand, in liquid and frozen aqueous solutions of 5IU and MIT, containing iodide-$^{129}$, the $^{130}$I labelled parent was produced, in addition to the labelled iodide ion.

No other labelled organic products were observed. Recoil $^{128}$I born within the biomolecule aggregates produces in addition to labelled iodide and parent, other $^{128}$I labelled products indicative of recoil atom reactions within the aggregates. Perhaps the $^{129}$I associates with iodo biomolecule at the surface as only the labelled parent is formed.
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