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RESEARCH TRENDS IN HOT ATOM CHEMISTRY

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Discovered by Szilard and Chalmers in 1934, the chemical consequences of nuclear transformations or hot atom chemistry as it is often referred to, attracted considerable attention from researchers all over the world. The chemistry of the product nuclei that result from a nuclear transformation is governed by its excitation energy and thermalisation processes. The latter are dependent upon the nature of the phase in which the nuclear event occurs.

In the presentation, the trends in hot atom chemistry as they have emerged over the last 40 years are examined and the various models based on energy loss, excitation etc. are described. A brief mention is made of the reactions of hot atoms (nonradiative) produced by laser photolysis. The chemistry of ^{60}Co produced in solid metal complexes is reviewed in some detail towards the end.

Key Words: Recoil Energy; Phase; Effects-Annealing

INTRODUCTION

1984 marked the Golden Jubilee of discovery of Hot Atom Chemistry by Szilard and Chalmers.[1] The area of investigation is also referred to as 'Chemical Consequences of Nuclear Transformation' since from the beginning, it is the chemistry of the hot atoms that has attracted the attention of scientists. Szilard and Chalmers studied the irradiation of liquid ethyl iodide with neutrons from a small source.

$$C_2H_5\,^{127}I\,(n,r)\,C_2H_5\,^{128}I$$

In addition to the expected product as above, separable inorganic radioactive iodide was also isolated.

Since the advent of research reactors in many countries during the fifties, this area of study attracted considerable attention among chemists and physicists alike. India was no exception. Under the guidance of Dr Jagdish Shankar, work was initiated in 1952 on cobalt (III) complexes and in the next twenty years, a comprehensive study of these systems was undertaken, results analysed and models proposed.[2]

*Based on the author's presentation at the Symposium on 'Emerging Frontiers in Chemistry,' organised on the occasion of 75th Birthday Felicitation of Dr Jagdish Shankar.

If in the fifties and sixties the basic types of hot atom reactions and the chemical consequences thereof were discovered then in the seventies, it was the crucial role of the residual excitation or kinetic energy that was looked at, while the need to understand mechanisms, dominates the more recent studies. The concepts and techniques used in different phases have diverged in such a measure, that for e.g., work in gas phase reactions appears to bear little comparison with studies in the solid state. This paper reviews the work in all the phases, with special reference to Co(III) complexes.

The Recoil Effect

Szilard and Chalmers[1] conjectured that, "we might expect those atoms of the element which are struck by a neutron to be removed from the compound." This may be true of fast neutron collisions with the atoms of a compound, but since they were making use of thermal neutrons, the above view was a misconception. In 1935, Fermi & Coworkers[3] provided the correct explanation. The r-rays emitted during (n, r) events arise from the excited state of the product nucleus ($\sim$ 8Mev). Conservation of momentum, imparts to the radioactive atom a recoil energy of $\sim 10^2$ eV $E_{\text{max·recoil (in eV)}} = \dfrac{537\, E_r^2\ (\text{Mev})}{M}$,

where M is mass of the product nucleus in amu. In case of ^{128}I, $E_{\text{max . recoil}}$ $\sim$ 194eV is much larger than the C-I bond energy of $\sim$ 2eV. As such, the bond breaks and the hot atom (in terms of its kinetic energy) is freed from its moorings.

The discovery of Szilard and Chalmers was quickly followed by several researchers including Libby.[4] Some of the examples are,

$$C_4H_9\,{}^{80m}Br \xrightarrow[4.5\ \text{hrs}]{\text{IT}} C_4H_9\,{}^{80}Br + {}^{80}Br^- \quad (18\ \text{min})$$

$50Cn_{(n,r)}{}^{51}Cr$, in chromates,

$55Mn_{(n,r)}{}^{56}Mn$, in permanganates,

$59Co_{(n,r)}{}^{60}Co$, in Cobalt Complexes.

It was demonstrated that chemical effects following isomeric transition (as above) are due to internal conversion rather than to recoil energy and this could also apply to (n,r) events, where I.T. takes place after the capture r-cascade. Chemical effects of nuclear transformations were also studied in α and β decay, (n, p), $(n, 2n)$, (r, n), (n, f) and spallation reactions. Given the parameters like cross sections, the neturon flux and isotopic abundances, it became apparent that one could witness for the first time chemical events at essentially infinite dilution, a Chemist's dream. This amounts to chemical reaction analog of the cloud chamber.

Before the advent of high neutron fluxes in nuclear reactors, the effect was put to use for the preparation of high specific activity isotopes. For example, D' Agostino[5] was able to prepare high specific activity $^{56}Mn^{2+}$, from n-irradiated solid

$KMnO_4$ after a simple chemical separation. Exposing Indanthene Blue to the neutron flux from APSARA, Nath *et al*[6] prepared ^{60}Co with a specific activity of nearly 470μC/mg. However, this route for the preparation of high specific activity radioisotopes has now fallen into disuse.

It is but natural that the recoil ranges are different in different phases. Especially in the solid state as pointed out by Muller,[7] hot atom chemists have not realised till recently how short the ranges are for (n, r) recoils. In condensed phases, in a fair number of events, the atom either remains undisplaced or returns immediately to its site because of the short ranges of low energy recoils. Computational techniques employing screened Columb potential have been applied in combination with data on neutron capture r-rays to arrive at energy and range of recoil atoms. Experimental evidence of this is seen in the phenomenon of 'germinate recombination' discussed by Iyer and Martin.[8] B^- decay, electron capture and isomeric transition processes also produce very low energy recoils; however, their chemistry is influenced by secondary source terms for excitation.

Initial Retention

Once it was apparent that recoil energy is $\gg$ bond energy and bond rupture takes place, the question arose as to the reason(s) for a fraction of radioactive isotope to remain in the parent form, called the initial retention. Having studied a number of systems in the solid state Libby[9] found that the dissolution step of the irradiated crystals influenced the initial retention. For example, ^{56}Mn yield as $^{56}MnO_4^-$ depended, upon the pH of solubilising medium, Lu and Sugden[10] investigating C_4H_9Br in liquid phase found 30 to 40 per cent of ^{80m}Br as $C_4H_9\,^{80m}Br$. They invoked the "liquid cage" model proposed earlier for photochemical reactions by Frank and Rabinowitch.[11] Libby has also adopted this idea to formulate his "billiard ball concept"in the solid state. Libby[9] stated that Br atom or Br^- ion of high velocity on collision with atoms or groups of atoms loose large fractions of their energy to be left in the same reaction 'cage' with fragments of the struck molecules. Subsequent fast chemical reactions cause retention. In extending these ideas, Libby made use of equations analagous to the ones developed for slowing down of neutrons. On the other hand, to explain the product distribution in liquid phase, where ^{80m}Br was observed even initially in different chemical forms including the parent form, Willard[12] has advanced the 'randon fragmentation' hypothesis. These concepts have been extensively applied. During the fifties an important landmark was the conceptual interaction of hot atom chemistry in the solid phase with parallel developments in field of radiation damage in solids, specially in graphite and alkali halides. The groups from Brookhaven and Trombay were the pioneers in this effort. As Kinchin & Pease[13] have stated, in some of the collisions between moving atoms (generated due to collisions under fast neutron bombardment) and stationary atoms at lattice sites, the latter will be displaced, but the former is left with insufficient energy to escape from the vacancy so created. Known as replacement collisions, these could be responsible for, at least, a part of the initial retention.

Libby[9] has mentioned as early as 1947 of a small liquid droplet created due to dissipation of recoil energy. The concepts of thermal spike and displacement spike developed a few years later by Seitz and Kochler[14] and Brinkmen[15] have led the Brookhaven & Trombay Groups to propose in 1958–59, that chemical consequnces can be anticipated from such spikes formed by the recoil atom in its interaction with the neighbouring ions or molecules. Harbottle and Sutin[16] labelled the volume involved as the 'Hot Zone.' At Trombay, the author[17] made a detailed application of the concepts of Sietz & Brinkman to Cabalt (III) complexes, especially tris acetylacetone Co (III). The central region of a thermal spike for which Q is 500 eV (outer limit) could be far above the melting temperature (conceptually and not literally) of the Co complex during a time, t_0 given by

$$t_0 = \frac{r_s^2}{4D}, \text{ where } r_s \text{ is the mean}$$

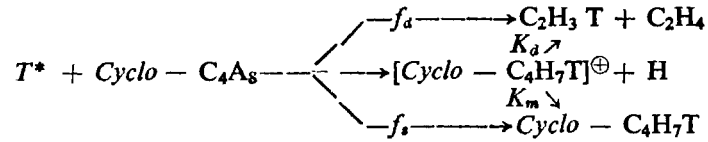
atomic radius ($\sim$ 1.35 Å) and D is thermal diffusion coefficient. The duration of such an energetic volume has been calculated to be 25 pico seconds.

Current Status of Modelling Studies

One can summarise the present thinking on the points discussed above as follows. The recoil atom ranges are rather short (2 to 3 molecular diameters) in the case of solids[7] and about 5–10 molecular diameters in a liquid phase in case of (n, r) events. Longer ranges are possible in $(n, 2n)$ and (r, n) processes. New equations for proton ranges in gas phase have been proposed,[18] which have the effect of reducing ^3H recoil range, specially in light gases such as He. There is enough evidence to indicate that billiard ball mechanism is ineffective in solids where there is large mass difference between the mass of the recoiling atom and other atoms. The hot zone model is to be understood in terms of a collective thermal excitation, rather than in terms of melting or of reaching a specific temperature. There are grounds for arguments concerning the role of thermal spike in promoting chemical effects. The disorder created by the recoil atom does play a significant role in post irradiation processes. While the physical models give a background to understanding, the chemistry in individual systems dominate the kinetics and mechanisms of post irradiation annealing process in solids.

Recent Developments in Gas Phase

The idea of Wolfgang[19] to use moderators for investigating the "energy shadowing", i.e., depletion of low energy recoils has been applied in several systems. The presence of charged and/or electronically excited species was deduced in case of recoil iodine from the product distribution of labelled species, when additives with particular ionisation energies were added. The effect of non-equilibrium excitation energy has been demonstrated in the breaking of C—C bond adjacent to $-CH_2T$ group in just formed neopentane.[18a] The following process illustrates the multiple pathways available to a hot tritium atom.[19]



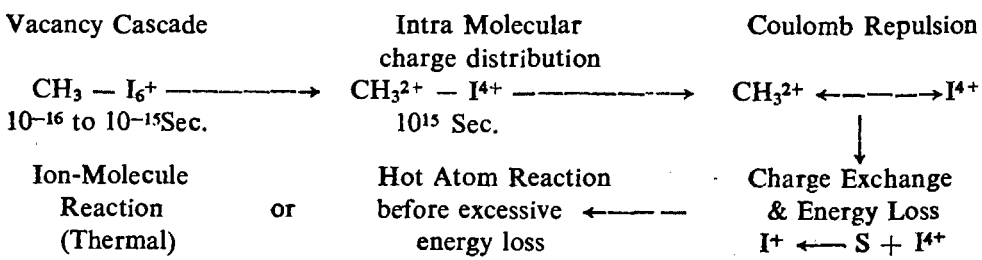
*Translational energy; (⊕) Internal excitation, f_d—High energy pathway; f_s—Low energy pathway, K_d—unimolecular decomposition and K_m—competitive collisional deactivation. In gas phase, recoil chemistry studies encompass ^{3}H, ^{11}C, ^{13}N, ^{18}F, ^{35}S, ^{38}S. ^{34m}Cl, ^{38}Cl, ^{78}Br, ^{80m}Br, ^{80}Br, ^{82m}Br, ^{82}Br, ^{123}I and ^{128}I. To mention only a few, it has been found that the reaction of ^{18}F recoil with 1, 1, 1 trifluoro ethane led to hydrogen abstraction to give HF in 84 per cent of the events, substitution of ^{18}F for F or H accounted for another 10 per cent, while substitution of CH_3 or CF_3 groups with ^{18}F was observed in 2.5 per cent cases.[21] Organo silicon chemistry using ^{31}Si has been studied,[22] with butadiene resulting in a 5-membered ring which incorporates ^{31}Si. An important observation by Wolf *et al.*[23] relates to the inversion at a Chiral centre when translationally excited ^{38}Cl interacted with *R* HCl. COCl.

Non-radioactive hot atoms can also be generated with laser flash photolysis, specially with excimer lasers.[24] A typical example is the production of hot hydrogen atoms from short pulse ArF excimer laser photolysis. The hot atom react with small molecules like HBr through collisional excitation.

1. $H\,Br + h\nu\ (193nm) \longrightarrow H^* + Br$ (Hot atom generation)
2. $H^* + CO_2 \longrightarrow Co_2^* + H$ (Wibrational excitation)
   $CO_2^* \longrightarrow h\nu\ (4.3\mu m) + CO_2$ (IR fluorescence)
3. $H^* + HCl \longrightarrow HCl^* + H$ (Vibrational excitation)
   $HCl^* \longrightarrow h\nu\ (3.3\mu m) + HCl$ (IR fluoroscence)
4. $H^* + CO_2 \longrightarrow CO + OH$ (Hot atom reaction)

Recent Results in Liquid Phase

Hot atom chemistry in the liquid phase pioneered by Willard[12] and other scientists appears to some of having been at cross roads for a while. It has several disadvantages such as greater multiplicity of overlapping initiations, thermal processes obscuring hot reaction channels with little information on energy and charges states. Studies on (*n*, *r*) and I.T. activated iodine recoils are focussed to some extent on the molecular explosion model as detailed below.[25]



The effect of caging of an ice lattice on high energy recombination of halogen recoils with biomolecules has been investigated by Arsenault *et al.*[26] to show that these large molecules exist within the ice lattice in monomolecular caged or trapped condition. Recombination is efficient by virtue of the caging effect. For example in the liquid phase, with monoiodotyrosine and dilodotyrosine the absolute product yields of ^{128}I labelled MIT and DIT decreased with decreasing solute concentration, while in the frozen phase, the absolute yields remained constant over a 100-fold concentration range. Such processes in frozen medium can be applied to labelling for nuclear medicine and "molecular neutron activation analysis."

Iyer and Hari Mohan[27a,b] have investigated the recoil chemistry consequent upon (n, r), $(n, 2n)$ and I.T. reaction of iodine atoms in hydrocarbon diluents. To assess the total radiation damage due to (n, r) process, the extent of added iodine scavenger consumption per nuclear event has been sought to be determined. Using ^{131}I labelling gas chromatographic analysis of the product iodide coupled with spectrophotometry showed that a very large number ($\sim 10^{10}$) of iodine molecules were consumed for every (n, r) event on ^{127}I. The above work was extended to studies of the recoil chemistry following ^{127}I $(n, 2n)$ ^{126}I, and ^{130m} I (I.T) ^{130}I in cyclohexane, hexane and heptane. The (n, r) reaction of iodine in aqueous methyl iodide solution was studied in the presence and absence of O_2, I_2 and H_2O_2. Different organic yields were observed in each case. The results indicated that the organic yield observed in oxygen saturated system has a 20 per cent component due to germinate recombination. Hari Mohan and Iyer[28a,b] have also studied ^{80m}Br (I.T) ^{80}Br reactions in inorganic bromide-hydrocarbon systems with emphasis on the variation of the organic yield with the solvent as well as with the inorganic bromide, when of ^{80m}Br present as NH_4Br, $MgBr_2$, Sr Br_2, Zn Br_2 or $HgBr_2$ underwent an I T reaction in *n*-hexane, the observed organic yields did not follow the trend expected from the differences in the kinetic energy of the ejected ^{80}Br. It was concluded that the resultant positive charge on ^{80}Br at the time of its break from its original partner determined the final chemical stabilisation of the radionuclide. Taking ^{80m}Br present in $SrBr_2$ as a representative inorganic bromide, 12 other organic solvents, both aliphatic and aromatic hydrocarbons, were used to look for the solvent effect on the organic yield of ^{80}Br. It ranged from 5 per cent in CCl_4 to 39 per cent in tetradecane.

The isotopic effect of ^{82}Br and ^{80m}Br was investigated by Mishra and Singh[29] in bromobenzene, bromoform, 1, 2-dibromoethane, ethyl bromide, *n*-propyl bromide and 1-propyl bromide. A marked decrease of isotope effect and its near disappearance at high concentration of bromine was observed. Charged plate collection technique was developed and used to study the fate of bromine recoils. The successful application of this technique to pure organic bromides established an isotope effect first between charged species of ^{82}Br, ^{80m}Br and ^{80}Br. For example the recoil bromine in bromobenzene and *n*-butyl bromide showed a marked difference in the relative collection of isotopes or isomers.

In addition the scavenging action of bromine on the reaction of ^{82}Br with benzene cyclohexane and carbon tetrachloride was investigated. This showed that in the case of benzene, there was no sharp fall of organic retention for small concentration of bromine scavenger.

Recoil Chemistry in Solid State

Hot atom chemistry in the solid state which was at its peak in the sixties and seventies, appears to have reached a stage where only carefully thoughtout experiments are likely to give results which are either new in themselves or shed light on mechanisms. Following the discovery of radiation induced back reaction by Williams[30] in 1948 and thermally stimulated recombination processes by Maddock *et al.*[31] in 1949, most of the researchers including researchers at Trombay, Pune and Varanasi have focussed attention only on such investigations, rather than on the 'hot' reactions. It is this emphasis on post-recoil processes that distinguishes the work in solid phase in contrast with the other two phases. The disruption or damage caused by the recoiling atom moving with an initial average energy of about 100eV (given that the threshold displacement energy for atoms/ions in solids range from 10–25eV) can be preserved in this phase and if required by merely preserving the samples in a freezer.

Looking at the 'hot' reactions that might take place, it seems that initial retention (a major part of which can be due to hot reaction) ranges from 10 to 65 per cent. The higher end of the range observed in oxyanions such as chromates and permanganates leads one to suspect whether the yields are due to 'hot' reaction at all or they are due to thermal and radiation stimulated processes occurring during neutron irradiation itself. To get over this difficulty, Shankar *et al.*[32] have conducted, short term (30min) low temperature (—70 °C) irradiation of tris acetylacetene Co(III) in APSARA and measured Ro in terms of ^{60m}Co, and a few hours later in terms of ^{60}Co. The observed Ro of 2 to 4 per cent indicates that (a) bond rupture due to recoil is nearly complete and (*b*) contribution of 'hot' reaction is of a low order, at least in this system. The most recent direct evidence for 'hot' reactions, in solid metal complexes which could be preferably labelled as 'replacement reactions', following Kinchin & Pease[13] is provided by the studies on Zn [Co(III) EDTA]$_2$ by Zeba Abbas[33] who measured [^{65}Zn EDTA]$^{2-}$ formed initially on neutron irradiation of the complex in addition to [^{60}Co(III) EDTA)$^-$. Here is an example, where the Zn recoil atom originating outside the coordination sphere was able to replace the Co(III) in the complex. The 8–10 per cent yield of [^{65}Zn EDTA]$^{2-}$ in terms of total ^{65}Zn produced indicates the significance of hot or replacement reactions. It may also be mentioned that ^{65}Zn participated in post-recoil thermally stimulated process (hereinafter referred to as annealing).

Regarding annealing it has been shown under 'Liquid Phase' that concepts of radiation damage in solids have influenced the thinking of researchers in fifties and sixties. There is a close parallelism between the thermal annealing patterns of fast neturon induced damage in graphite and (*n*, *r*) recoil effects in *tris*-acetylacetone

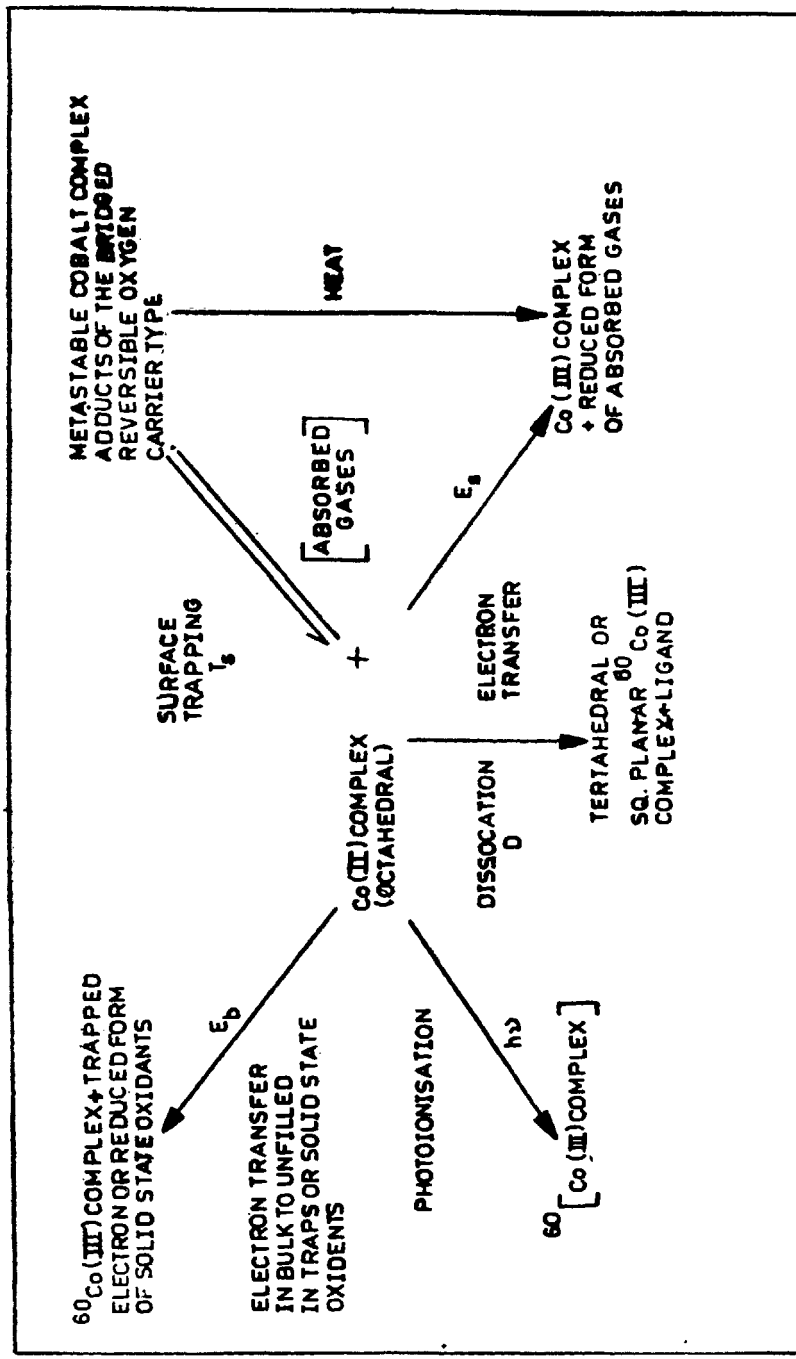


FIG 1 Post recoil annealing in cobalt complexes.

Co(III).[17] The behaviour of ^{60}Co in this complex (R_0 10—20 per cent—R_∞ 90 per cent) is typical of a number of octahedral complexes. The planar or sandwitch type Co complexes, however, show a somewhat different pattern, with low values of R_0 and R_∞.[34] Notable effects observed at Trombay relate to the effect of dilution in the solid state with isomorphous Al(III), Rh(III) and Mn(III) complexes,[32] the finding on the equivalance of thermal and radiation annealing,[35] the influence of oxygen in inhibiting the annealing in some complexes while promoting it in some others[36–38] and the effect of hydration in increasing R_0 and R_∞.[39]

Annealing was markedly reduced or even absent when tris acetylacetone Co(III) was diluted with the isomorphus Al(III) complex. In retrospective, this looks to be forerunner of such a behaviour in frozen systems later on as mentioned under 'Liquid Phase'. On the other hand dilution with tris acetylacetone Mn(III) has just the opposite effect.[33] This led to conclusion that solid state oxidation processes a play a prominent role in annealing.

For a while, the oxygen effect was puzzling as it was seen to influence the course of annealing in both directions, depending upon the complex. An explanation was proposed by the authors[40] based on the formation and relative stability of an oxygen carrying intermediate $^{60}Co(II)$ complex. Since in solid state oxidation, electron movement is involved, it was more easy to rationalise the positive effect hydration. The schematic model of chemical processes that could occur during annealing in Co(III) complexes developed by the author is given in Fig. 1.

A brief mention has to be made of solid state isotopic exchange.[41] When radioactive tracer such as ^{51}Cr or ^{58}Co is applied to a solid powder of chromates or cobalt(III) complexes and heated after intimate mixing, subsequent chemical separation results in a part of the radioactivity appearing as labelled chromate or Co complex. At one stage, this was believed to be the main reason for annealing, the reasoning behind being the microthermal decomposition of the parent form and the reaction of those fragments with the added trace or recoil. Ramshesh[42] put forward this view in a more cognet way. However, in the judgment of the present author the comparison between annealing and solid state exchange is more qualitative than definitive. It is quite possible that solid state exchange might form a small part of the total annealing process. For example, recently Abbas[33] demonstrated that while micro TG data on α, α′ *cis*-dichloro triene Co(III) shows no decomposition (80 to 120 °C) there has been annealing of ^{60}Co recoils in that complex, in the same temperature range.

To sum up, it is clear that hot atom chemistry studies in different phases have reached a stage, where further experimentation without better thought out models might only result in the accumulation of data. The need is for more and more theoretical work that would lead to a comprehensive understanding of the mass of information already existing in the literature.

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