CONFERENCE ON THE CHEMICAL
EFFECTS OF NUCLEAR TRANSFORMATIONS
(HOT ATOM CHEMISTRY)

August 19-20, 1948

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CHEMISTRY CONFERENCE #1

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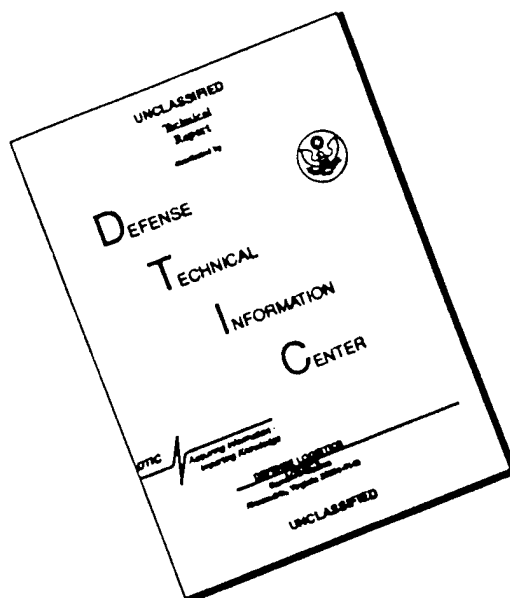
FOREWORD

The Chemistry Department of Brookhaven National Laboratory is sponsoring, from time to time, a series of small informal conferences on specific topics, at which individual workers present the results of research in progress. The particular subject taken up at any one conference is determined by the active research interest of the Department. We hope these conferences will serve as a stimulus to the research program of the Department, and invitations for papers are extended to individuals actively engaged in work from which we feel such benefit may be derived. We hope of course that our speakers and others attending the conferences will profit from the opportunity for intensive discussion which these meetings present.

The first conference in this series was held at Brookhaven on August 19 and 20, 1948 and dealt with the chemical effects of nuclear transformations (often called hot-atom chemistry). This report is a collection of the papers given, as submitted by the authors after the conference. Unfortunately, it has not been possible to include the many interesting and valuable comments and discussions which contributed greatly to the success of the meeting. We should like to express our appreciation to the speakers for their contributions, which made this conference possible.

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Committee on BNL Chemistry Conferences

N. Elliott

W.W. Miller

E. Shapiro

G. Friedlander, Chairman

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INTRODUCTORY REMARKS

R. W. Dodson*

Since I have been given the privilege of making introductory remarks at the start of this conference on hot atom chemistry, I should like to make some observations about the background of the subject and to indicate some of the problems which appear to be of present interest.

It is probably a safe generalization to say that most of the thousands of known nuclear transformations have significant chemical effects. This is automatically true for those reactions in which the nuclear charge changes, since then the product is a different chemical element. Whether or not this occurs, it is also the case that the net energy evolved is usually large compared to chemical bond energies and activation energies, so that one may expect bond rupture and other chemical reactions to occur if the energy is properly distributed among the various degrees of freedom. The energy is usually concentrated first on the particular atom in which the nuclear event occurred. The resulting energetic atom is called a " hot atom", which term has given the name to our conference.

It is appropriate to reflect on the reasons for our interest in the chemical behavior of hot atoms. It is easy to state a number of such reasons. First, the phenomena are interesting in themselves. Secondly, they are connected with problems in other branches of science, i.e. in reaction kinetics, in nuclear physics, and possibly in biology. And thirdly, the phenomena are of obvious practical importance in a technology based on nuclear reactions.

The first hot atom studies were made early in this century. The early workers with the natural decay series observed and studied the hot atoms which were physically displaced by recoil in alpha and beta decay. The first recorded

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observation known to me is that of Miss Brooks in 1904 (Harriet Brooks, Nature 70, 270 (1904), who found that an ionization chamber became contaminated with RaB and RaC when a source of RaA was placed inside it. It was apparently Rutherford who suggested that the RaB was set free by recoil in the alpha decay of RaA. In 1909 Hahn and others began an exploitation of the technique of recoil separations which turned out to be very important in unravelling the complexities of the natural decay series.

Proceeding to later developments, we take note of the historical contribution of Szilard and Chalmers in 1934 (Nature 134, 462 (1934)). They reported that radioiodine formed by neutron capture in ethyl iodide could be separated by aqueous extraction. They interpreted the result in terms of bond rupture caused by neutron capture, with the formation of free iodine atoms or ions. It seems from their paper that they were looking for a recoil effect due to the momentum of the captured neutron; however it was soon realized that the momentum of the emitted gamma ray is itself sufficient to cause bond rupture by recoil. This fact was specifically noted by Fermi and co-workers (Amaldi, et. al., Proc. Roy. Soc. 149, 538 (1935)), who used the Szilard-Chalmers technique in their early studies of neutron induced radioactivity.

It was also soon discovered (by Gluckauf and Fay, J. Chem. Soc. 390, (1936)) that the not atoms produced in the Szilard-Chalmers process may not remain free, but may enter into chemical combination, re-entering molecules of the parent type or synthesizing new substitution products. They also showed that the probability of reentry into the parent molecule was reduced by dilution with an indifferent solute. Lu and Sugden (J. Chem. Soc. 1273 (1939)) studied these hot atom reactions further, and developed methods of increasing the yield of the Szilard-Chalmers separation by adding diluents whose reactions might compete with the reactions leading to non-extractable compounds. Lu and Sugden also proposed the

operation of the "liquid cage" effect to account for the fact that a large fraction of activity is found in the parent molecule although the gamma recoil energy is about 100 times the bond energy and should cause bond rupture in every case. These ideas have been extensively developed by Libby, who has given a theoretical treatment of hot atom reactions in terms of the liquid cage.

Bond rupture and hot atom formation also happen in cases where recoil is insufficient to cause them, an effect discovered simultaneously by DeVault and Libby and by Segre, Halford, and Seaborg for the isomer transition in Br 80. In this case, bond rupture results from ionization caused by internal conversion and subsequent Auger processes. It has been rather convincingly shown in experiments of Friedlander, Kennedy, and Seaborg that internal conversion is a necessary and sufficient condition for bond rupture, and one feels that the primary process is understood quite well in its general outlines. Nevertheless it is a bit disconcerting to realize that no one has yet (prior to this conference) given convincing experimental evidence that the initial fragments are positively charged.

When we look at nuclear transformations involving the emission of a charged particle from the nucleus, we find that rather less is known about the hot atoms produced thereby. In the case of alpha decay one can readily calculate the kinetic energy of the recoiling atom; it is of course rather high, say about 100 Kev. The initial state of ionization is somewhat uncertain; it appears that three or four orbital electrons are ejected from the emitting atom as the alpha particle moves out. In beta decay the recoil energy is comparable to that in gamma emission, with the complication that recoil energy is distributed over an unknown spectrum determined by the angular correlation between the beta particle and the neutrino. Here again, the state of initial ionization is uncertain, although the initial charge must be at least plus 1.

The chemical effects of induced nuclear reactions in which heavy particles

are emitted have been studied but little. An interesting contribution has been made by Yankwich, Rollefson, and Norris who measured the yield of various compounds containing C-14 formed by N-n,p. The rather complicated results were plausibly rationalized by qualitative chemical arguments, but I believe the authors would be the first to say that only an initial step has been made in understanding what really happens in these systems. The chemical point of view adopted by them is quite different from the physical, billiard-ball-collision, liquid-cage picture used by Libby. It will be interesting when more and better data are at hand to see which point of view, or what combination of them best interprets the facts.

It is perhaps appropriate to close these introductory remarks by summarizing the types of knowledge we now have about the subject and the types of questions it would be well to ask of experiment and theory in order to amplify and extend this knowledge. We know:

(a) That recoil from the particle or quantum emitted by a nucleus (or for that matter, captured by a nucleus) may cause molecular fragmentation,

(b) ionization within the emitting atom may cause molecular fragmentation,

(c) some proportion of the hot atoms produced may react with the environment, especially in condensed phase.

Questions on which we would like more detailed information, qualitative and quantitative, are:

(1) In what manner is the energy evolved in the nuclear process communicated to the atom, i.e. by recoil, or by electronic loss or excitation, or by both?

(2) How is this energy distributed over the various degrees of freedom of the molecule?

(3) Does the molecule dissociate - if so into what fragments?

(4) Are the fragments neutral or charged?

(5) What are the kinetic energies of the fragments after dissociation, and what is the angular correlation of their motions?

(6) In what fashion do the fragments lose energy?

(7) In what chemical reactions do the hot atoms participate as they descend the energy scale?

(8) Finally, in what stable states of chemical combination do the fragments eventually find themselves after they have been degraded to thermal energies?

It is our hope that this conference will make known to us what problems are being undertaken, what sort of results are being obtained, what problems various workers in the field consider to be significant and suitable for study.

CURRENT WORK IN HOT ATOM CHEMISTRY AT THE UNIVERSITY OF WISCONSIN

Gerrit Levey, Robert Milham, William Rice and John E. Willard[*]

The work to be discussed here is work which is currently in progress at the University of Wisconsin. Results which are as yet incomplete or fragmentary will be included in the belief that exchange of such information among those working in a field is mutually helpful. The topics to be dealt with are:

(1) Chemical properties of monatomic sulfur formed by the $Cl^{35}(n,p)\,S^{35}$ reaction;

(2) Investigations of the chemical nature of Br^{80} and Br^{82} formed by the (n,γ) reaction on alkyl bromides;

(3) Reaction of low concentrations of HBr and Br_2 with residual impurities in purified reagents.

1. Chemical Properties of Sulfur Formed by the $Cl^{35}(n,p)\,S^{35}$ Reaction

Discussion of Results

It has been observed in our laboratory[1] and independently by Edwards and Coryell[2] and possibly by others that the S^{35} produced in crystals of KCl as a result of the $Cl^{35}(n,p)\,S^{35}$ reaction appears as $SO_4^=$ when the crystals are dissolved in water. The sulfate is obtained even when the water contains macro amounts of $S^=$, suspended S, and $SO_3^=$ as carriers and has been carefully degassed prior to dissolution of the KCl. Three possible hypotheses to account for the appearance of sulfur in this oxidation state are:

(1) the oxidation state of 6 is somehow stabilized by the KCl lattice;

(2) the sulfur is oxidized by elemental chlorine produced from KCl by the action of neutrons and gamma rays;

(3) atomic sulfur, S_1 (in contrast to the molecular forms (S_8) which are

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ordinarily dealt with at room temperature) is oxidized to sulfate by water.

None of the three hypotheses suggested is wholly satisfying. From considerations of ionization potentials alone it seems unlikely that the S^{35} atoms are held in a KCl lattice in a state which will produce sulfate by reaction with water, unless the water acts as an oxidizing agent. However, in order to test the hypothesis, we have determined the chemical form, after water extractions, of S^{35} formed by neutron bombardment of liquid and gaseous CCl_4 and of gaseous HCl. In each case the major portion of the S^{35} has been found to be in the form of sulfate. In these tests considerable care was taken to exclude oxygen during bombardment and until the bombarded material had been extracted with degassed water containing $S^=$, suspended S and $SO_3^=$ as carriers. These results seem to prove that the sulfur does not require a crystal lattice to preserve it in a form which will become sulfate when exposed to water. It has been suggested that the tracer amounts of S^{35} formed in these liquid and gas phase experiments might be oxidized by the small amounts of oxygen remaining in a system after even the best evacuation. Such an explanation does not appear satisfactory to explain the production of sulfate since the oxidation would ordinarily stop at SO_2 rather than proceeding to SO_3.

In considering the second hypothesis, it is difficult to estimate the amount of elemental chlorine which will be produced by radiation decomposition of KCl by gamma rays because of the very great uncertainty as to the relation between gamma ray energy lost and free chlorine produced. A rough estimate can be made of the amount of free chlorine produced in the irradiation of CCl_4 if it is assumed that the number of gamma rays entering a sample in the Oak Ridge pile or in the thermal column of the Argonne heavy water pile is equal to the number of neutrons and that one ion pair is formed per 30 ev of absorbed gamma ray energy

(taking the average gamma energy as 1 Mev and the average rate of absorption as 10^{-5} of the total energy per cm. of air equivalent) and that each ion pair results in the production of a Cl_2 molecule. If these assumptions are valid the number of moles of Cl_2 produced will be hundreds or thousands of times greater than the moles of S^{35}. Additional Cl_2 will be formed by other processes such as the dissipation of energy from (n,γ) and (n,p) recoils in the system. Chlorine so formed may result in the formation of S_2Cl_2, SCl_2 and SCl_4 but none of these compounds is known to hydrolyze in large percentage of sulfate and so they alone cannot explain the fact that a large fraction of the S^{35} appears as $SO_4^=$. The possibility that ClO^-, formed by hydrolysis of Cl_2, oxidizes an appreciable fraction of the S^{35} after the bombardment sample is extracted with water, is very improbable, since in these tests the tracer amounts of S^{35} were protected by macro amounts of $S^=$ and $SO_3^=$ in the water solutions. Experiments are planned to test the effect, if any, of elemental chlorine in investigations of this type, by determining the chemical form of the sulfur produced by neutron irradiation of mixtures of HCl and H_2, by irradiation of C_2Cl_4 and by irradiation of Cl_2. In the first case any chlorine produced may be expected to react with H_2 to reform HCl and in the second it may be expected to be removed by reaction with the double bond of C_2Cl_4.

Monatomic sulfur, like monatomic oxygen and monatomic chlorine might be expected to be much more reactive than the molecular form (S_8) of the element. To the best of our knowledge no one has ever had the opportunity of observing the properties of free sulfur atoms at room temperature except as they have been produced as isolated atoms by the transmutation of atoms of another element. The standard free energy change for the reaction $S + 4H_2O \rightarrow 2H^+ + SO_4^= + 3H_2$ may however be calculated from existing data. It is -6000 cal/mol and the actual free energy change at the concentration of S atoms present in the work discussed here

would be a much larger negative number. It is therefore possible that the $S^{35}O_4^=$ obtained is due to the direct oxidation of S atoms by H_2O, and this seems to be most attractive hypothesis available at present.

Experimental Method and Data

Our initial observation, that the S^{35} formed by the Cl^{35} (n,p) S^{35} reaction in KCl crystals appears as $S^{35}O_4^=$ when the crystals are dissolved in water, was made on a shipment of KCl from the Clinton Laboratories, which had been irradiated with a total exposure of 1.3×10^{18} neutrons/cm^2. Some of the crystals tested were as large as 2 mm. on a side. The ratio of S^{35} atoms in the crystal to K^+ and Cl^- ions was about 10^{-8}. In no case was less than 90 percent of the S^{35} found as $SO_4^=$. Sulfide carrier was removed from the water solution by precipitation as Ag_2S or CuS, and $SO_4^=$ was precipitated as $BaSO_4$. In some cases the bombarded crystals were ground with a solution of S in CS_2, with carborundum present as an abrasive, before being shaken with water. When the CS_2 was evaporated and the residual sulfur counted it was found to contain 0.5 percent of the S^{35} from the KCl sample. In some of these tests dissolved air was removed from the solvents before adding KCl and in one case NH_2OH was added to the H_2O.

Irradiation of gaseous CCl_4, HCl and H_2S and of liquid CCl_4 as well as samples of other chlorides and sulfides not yet analyzed has been carried out in quartz tubes 10 cm. long and 6 mm. i.d. in the thermal column of the Argonne heavy water pile for one hr. The irradiation was sufficient to cause considerable darkening of the quartz tubes. These tubes are opened by breaking the tip in an evacuated, degassed system under the surface of solvents containing appropriate carriers. Usually toluene was present, together with $S^=$, S, and $SO_3^=$ in alkaline aqueous solution. The mixture was shaken while still under vacuum and the water toluene and any other volatile components were distilled off in those cases where there was reason to believe that a significant fraction of the S^{35} might be present

in volatile form, as for example, in the bombardment of CS_2. The solid residue was then opened to the air and dissolved in water and toluene. The two layers were separated and the counting rate of the elemental sulfur determined from an evaporated portion of the toluene. NiS and $NiSO_3$ were precipitated and filtered from the water solution and $BaSO_4$ was precipitated from the filtrate after adding $SO_4^=$ carrier. The $NiSO_3$ was separated from Ni_2S by washing with NH_4OH.

Under the conditions used it was not found possible to obtain quantitative reproducibility of the amount of S^{35} recovered from identical samples exposed to the same bombardment or of the distribution of the S^{35} between different chemical forms. The results are, however, in qualitative agreement in indicating that the major portion of the S^{35} produced from gaseous CCl_4 or HCl is in the form of $SO_4^=$ after water extraction. They also indicated (on the basis of the limited evidence afforded by one experiment) that a large portion of the S^{35} formed by the $S^{34}(n, \gamma)S^{35}$ reaction on gaseous H_2S appears as elemental sulfur, while a large part of that formed from CS_2 is found in volatile sulfur compounds. These data are given in Table 1. The last column gives the ratio of the S^{35} recovered in all chemical fractions of each tube to the total S^{35} recovered from the irradiation tube which yielded the greatest amount of S^{35} per unit amount of chlorine irradiated. Since all the samples listed were irradiated at the same time in the same container, the S^{35}/Cl ratio should be constant. The variation may be due in part to variations in counting losses due to self absorption and "self focussing" of the counting samples (since only qualitative or semi-quantitative information was being sought in this work) and in part to incomplete removal of S^{35} from irradiation tubes (although each tube was heated with NaOH solution). The column labeled "$SO_4^=$ supnt" indicates that in some experiments S^{35} remained in solution after NiS, $NiSO_3$ and $BaSO_4$ had been precipitated. Until proven otherwise we are assuming that this is from $S^=$, $SO_3^=$, or $SO_4^=$ which escaped

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TABLE 1

Chemical Form of Sulfur Produced by $Cl^{35}(n,p)S^{35}$ Reaction on CCl_4 and HCl and by $S^{34}(n,\gamma)S^{35}$ Reaction on H_2S and CS_2

	$S^{=}$, %	S, %	$SO_3^{=}$, %	$SO_4^{=}$, %	$SO_4^{=}$ Supnt: %	Relative amt. of S^{35} recovered per Cl^{35} irradiated
CCl_4 gas[±]	2.8	2.4		72.2	0.9	1.00
"	12	6	3.6	38.4	40	0.27
"	3.3	3.3	0.5	92.5	0	0.58
"	1.6	25.7	1.7	69	1.7	0.06
"	0.8	1.9	0.5	11.4	84	0.25
"	0.1	0.1	1.3	93.8	4.5	0.63
"	0.1	0.1	0.2	87.0	12.4	0.39
HCl gas	6.5	5.5	0.6	56.9	30.5	0.82
H_2S gas[±±]	0.4	98.2	0.4	0.2	1.1	
CS_2 liq.	1.7	9	0.5	4	0	

[±] 19% of S^{35} appeared in water washes of quartz irradiation tube. 5% appeared in volatile sulfur compounds.

[±±] 85% of S^{35} appeared in volatile S compounds.

precipitation.

2. Chemical Nature of Br^{80} and Br^{82} Formed by the (n,γ) Reaction on Alkyl Bromides

It is well known that following irradiation of liquid alkyl bromides with neutrons part of the Br^{80} and Br^{82} formed by the (n,γ) reaction is in organic combination and part may be removed from the parent organic liquid by water extraction. The possible chemical forms of the water-extractable radiobromine would seem to be limited to Br, HBr and Br_2. As far as we know, no one has established which of these species are present in such systems. It might be supposed that tracer amounts of HBr and Br_2 or Br in $C_2H_4Br_2$ could be distinguished by the preferential reaction of Br_2 and Br with Hg or Cu. However, Hg reacts with $C_2H_4Br_2$, and tests which we have made indicate that HBr as well as Br_2 reacts with freshly reduced Cu. These tests were made by mixing HBr formed by the action of phosphoric acid on neutron irradiated KBr with purified degassed $C_2H_4Br_2$ in the gas phase, passing the mixture through P_2O_5 supported on glass wool, and then through Cu turnings which had been reduced in a stream of hot hydrogen and preserved under vacuum, until exposure to the $HBr-C_2H_4Br_2$ stream. A total of 6.7 mg. of HBr was passed through the train. Six percent of the radiobromine was found in the P_2O_5 and glass wool, 66 percent on the Cu and 28 percent in $C_2H_4Br_2$ condensate on the effluent side of the train.

It may be that metallic silver could be used to effect a separation between elemental bromine and HBr, or that Hg would be a satisfactory reagent for the purpose in the presence of less reactive organic bromides than $C_2H_4Br_2$. A quite different method of distinguishing between Br, Br_2, and HBr would be on the basis of the characteristic activation energy of each with the parent solvent. It should be possible to determine the activation energy for the reactions of

HBr and of Br_2 with $C_2H_4Br_2$ to produce organic bromine compounds. It should also be possible to determine the activation energy for the reaction with $C_2H_4Br_2$ of the water extractable bromine formed by the (n,γ) reaction on $C_2H_4Br_2$ simply by heating sealed tubes of purified degassed neutron irradiated $C_2H_4Br_2$ at different temperatures before extraction with a water solution of Br^- or $SO_3^=$. If the " Szilard Chalmers bromine" is HBr the activation energy for its reaction should be the same as that obtained in the trial runs with $HBr^\pm$, and if it is Br_2 it should correspond to that found in the trials with $Br_2^\pm$. If it is Br it should be different than that obtained in either of the tests with available species.

As a preliminary indication of conditions under which Br_2, HBr and Szilard Chalmers bromine will react with $C_2H_4Br_2$ we have assembled in Tables 2, 3 and 4 pertinent data from past experiments which we have done on these systems. The data of Table 2 suggest that when HBr is present in presumably pure and degassed $C_2H_4Br_2$ at a concentration of about 10^{-5} moles/l, an appreciable fraction of the bromine may enter organic combination at room temperature and that this amount is independent of times of standing for periods over two hours. This behavior suggests the presence of a small amount of residual impurity such as an alcohol, and reemphasizes the role which impurities may play in " retention" experiments even at concentrations much higher than those met in work with Szilard Chalmers bromine. The data for the experiments at 100° suggests that the exchange reaction of bromine in HBr with bromine in $C_2H_4Br_2$ occurs at a measurable rate under these conditions. The columns labeled "1st ext.", "2nd ext." and "3rd ext." in Tables 2 and 3 show the percentage of the radioactive bromine which was removed by each of three successive extractions of 10 cc of the $C_2H_4Br_2$ with 10 cc of water containing 0.06 M $SO_3^=$ ion. These latter data indicate that the extraction was essentially complete in each experiment, and that the extractant

TABLE 2

Reaction of HBr in Purified $C_2H_4Br_2$ Solution

HBr m/1×10^{-6}	Treatment	Time between Mixing reagents and extraction, hrs.	Distribution of Activity,%			
			1st ext.	2nd ext.	3rd ext.	$C_2H_4Br_2$ layer
7.4	dark, R.T.	18	58.7	2.4	1.0	37.9
9	2 hr. at 100°	35	44.2	1.6	0.4	53.8
9.2	4 hr. at 100°	35	22.6	1.8	0.5	75.0
9.2	dark, R.T.	38	61.0	2.1	0.4	36.4

TABLE 3

Reaction of Br_2 in Purified $C_2H_4Br_2$ Solution
(Conc. approx. 2×10^{-3} molar)

Treatment	Time between mixing reagents and extraction, hrs.	Distribution of Activity, %			
		1st ext.	2nd ext.	3rd ext.	$C_2H_4Br_2$ layer
dark, R.T.	14	93.5	3.0	0.3	3.1
2 hrs. illumination*	14	56.6	1.9	0.5	41.1
dark, 2 hrs. at 105°	14	83.2	3.1	1.6	12.1
dark, 4 hrs. at 115°	89	53.8	2.7	0.5	43.0

*1000 watt Mazda lamp at 2 feet

TABLE 4

Retention of Bromine Produced by $Br^{79}(n,\gamma)Br^{80}$(4.4 hr)

Conditions	Retention in $C_2H_4Br_2$ layer %
extracted immediately	35
stood 6 hrs. with pentene at R.T.	80
2 hrs. at 100°	40
2 hrs. at 130°	91

did not cause appreciable liberation of water soluble bromine from the organically bound bromine.

The data of Table 3 indicate that there is very slight reaction of Br_2 with $C_2H_4Br_2$ in the dark at room temperature when the Br_2 is present at 10^{-3} molar but that reaction occurs in the light, or in the dark above 100°. In considering possible effects of impurities it must be noted that the concentration of bromine in the experiments of Table 3 is more than 100 times that in the HBr experiments of Table 2.

Szilard Chalmers bromine produced by neutron irradiation of purified degassed $C_2H_4Br_2$ reacts, at least in part, with pentene and at temperatures above 100° enters into organic combination when dissolved in $C_2H_4Br_2$, according to the data of Table 4.

Various investigators have made observations on the Szilard Chalmers bromine produced in alkyl bromides, which appear to be inconsistent with the supposition that it is in any one of the three forms HBr, Br_2 or Br. Such observations include the fact that the water-extractable bromine sometimes remains as a residue when the alkyl bromide is evaporated on a glass plate (Hamill and Davis), the fact that the radiobromine is not fractionated from the alkyl bromide by bubbling a stream of inert gas through the solution (Libby and Friedman) and the fact that the radiobromine migrates to the anode if electrodes are placed in the alkyl bromide. These observations suggest that trace amounts of impurities may play a major role in determining the form of the water-extractable bromine. Apparently impurities do not often play an important part in determing the percentage of the Br^{80} and Br^{82} which is organically retained, since retention values are qualitatively speaking quite reproducible.

3. Reaction of Low Concentrations of HBr and Br_2 with Residual Impurities in Purified Reagents

TABLE 5

Reaction of Bromine with Impurity in CCl_4

Solution	Purified by ClO_2-Cl_2 method several months before use, chlorinated just prior to test, distilled from P_2O_5				Purified by ClO_2-Cl_2 method just before test, distilled from P_2O_5						Analytical Reagent, distilled from P_2O_5	
	1a	1a	1b	1b	2a	2a	2b	2b	3a	3a	3b	3b
Time	10m	40hr	10m	40hr	10m	38hr	10m	38hr	10m	38hr	10m	38hr
Conc., m/1x10⁶	2.2	2.2	3.8	3.8	0.75	0.75	1.5	1.5	0.50	0.41	1.1	1.1
Tot.Counts/min.	2030	840	3649	1495	1425	662	2787	1312	934	315	2123	1072
% of Total Counts in:												
1st ext.	92.1%	83.1%	91.2%	85.0%	93.3%	32.3%	92.1%	24.8%	86.9%	34.3%	93.8%	68.7%
2nd ext.	4.0	7.9	5.4	9.2	3.9	2.6	3.7	3.3	9.6	1.9	2.9	2.1
3rd ext.	1.2	1.9	1.0	1.3	1.0	0.8	0.7	0.2	0.0	1.3	0.4	0.7
CCl_4	2.6	7.1	2.3	4.5	2.6	64.3	3.5	71.7	3.4	62.5	2.9	28.5
Organic Br, m/1x10⁶	0.057	0.16	0.087	.17	0.020	.48	0.053	1.1	0.017	.26	0.032	.31

Solution	Analytical Reagent, not distilled from P_2O_5				Technical Grade, distilled from P_2O_5	
	4a	4a	4b	4b	5a	5a
Time	10m	38hr	10m	38hr	30m	38hr
Conc., m/1x10⁶	0.50	0.50	0.98	0.98	0.75	0.53
Tot. Counts/min.	941	485	1801	882	1385	404
% of Total Counts in:						
1st ext.	92.3	84.9	91.0	87.2	87.5	71.0
2nd ext.	2.8	3.7	4.4	3.5	2.7	5.7
3rd ext.	.6	.6	0.0	.4	.3	1.7
CCl_4	4.3	10.7	4.6	8.8	9.6	21.5
Organic Br, m/1x10⁶	0.022	0.054	0.045	0.086	0.072	0.11

The data of Table 2, discussed in the preceding section, suggests that the $C_2H_4Br_2$ used may have contained about 3×10^{-6} moles/l of an impurity with which HBr could react readily at room temperature in the dark to form an organic bromine compound. The 3 percent reaction of Br_2 with $C_2H_4Br_2$ in the dark shown in Table 3 may represent reaction with an impurity. When some tests in which low concentrations of radiobromine were placed in supposedly very pure CCl_4 resulted in the production of organically bound bromine, we undertook a series of experiments to determine how the amount of such reaction varied with the method of preparation of the CCl_4, the concentration of the bromine and the time of contact.

In Table 5 the data for the experiments made with CCl_4 purified by different methods are differentiated by the numbers 1, 2, 3, 4 and 5. In all except the last case (Technical grade CCl_4) four tests were run, two at a low concentration where the bromine was allowed to stand with the CCl_4 for 10 minutes and 40 hours respectively and two at a higher concentration for the same two lengths of time. In each case the concentration of Br_2, the total counting rate (at about 3 percent counting yield), and the distribution of the radiobromine between three successive 11 cc portions of aqueous extractant containing 0.06 m $SO_3^=$, and the remaining organic phase are given. The final figure in each column shows the moles/l of bromine which were not extractable with sulfite solution and therefore may be assumed to have entered organic combination. The amount of bromine which could enter organic combination would be expected to be the same for both concentrations of bromine in CCl_4 if a limited amount of impurity is being completely brominated. This is approximately true (within a factor of 2) for all four types of CCl_4 which were tested at two concentrations of bromine, if the results for the longer times of contact are compared. However, the full explanation of the results is not clear. It may be noted that the only one of the five CCl_4 preparations which was not distilled from P_2O_5 showed the smallest reaction with Br_2. To test the

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hypothesis that the Br_2 reacts with some substance introduced from the P_2O_5, 35 cc of CCl_4 which had been purified by illumination with ClO_2 and Cl_2 were distilled from about 15 grams of P_2O_5 (Merck Reagent grade such as was used in the tests of Table 5). The liquid was divided into three fractions: the first third in the distillate, the second third in the distillate, and the remaining third which was removed from the distillation flask without distillation. Each of the three fractions was divided into two portions, to one of which was added a drop of water. Each portion was allowed to stand with radiobromine for 24 hours and then thoroughly extracted. From 1×10^{-7} to 3×10^{-7} moles per liter of Br_2 entered organic combination in the several cases, with no trend that could be ascribed to the added water or to the properties of the separate fractions.

It must be concluded that amounts of bromine of the order of $10^{-6} - 10^{-7}$ moles per liter react with something in carefully purified CCl_4 to form organically bound bromine. This cannot be due to a reaction of the type $Br_2 + CCl_4 \rightarrow CCl_3Br + BrCl$ since extensive studies on this reaction by A. A. Miller of our laboratory show that it has an activation energy of about 40 kcal/mole and does not proceed at a readily measurable rate below 150°C. It seems highly improbable that the reaction indicated by the data of Table 5 is a reaction between Br_2 and CCl_4 induced by the radiations from the decaying Br^{82}, since it may be calculated that only about 10^{-10} moles/liter of ion pairs would have been formed by this means in the 40 hour experiments, where between 10^{-7} and 10^{-6} moles per liter of bromine were observed to react.

References

1. Paper presented before the April 1946 Meeting of the American Chemical Society at Atlantic City.

2. Private communication.

SOME CONSIDERATIONS OF RETENTION IN THE LIQUID PHASE

J. M. Miller and R. W. Dodson*

This discussion will be concerned only with the hot atom chemistry that comes about as a consequence of radiative neutron capture. In particular we shall be interested in the neutron capture by $_{17}Cl^{37}$ in the chemical form of CCl_4.

Theory

Although there is little doubt that essentially all captures break up the molecule that contains the absorbing nucleus, nevertheless a good fraction of the radioactive chlorine is ultimately found as carbon tetrachloride. This fraction is known as "R", the retention. Our task will be to predict how this fraction "R" is influenced by the addition of other molecules to CCl_4.

The initially energetic (200ev) Cl atoms resulting from the breakup of the molecule must have a probability of exchanging with CCl_4 that is consistent with the observed value of "R". This reaction may involve atoms that are still being "cooled", or it may involve atoms that are in thermal equilibrium with their environment. We shall say that the reaction occurs with atoms having an energy distribution governed by the slowing down process rather than by thermal equilibrium. This statement can be substantiated by experimental evidence which unfortunately cannot be examined here.

"R" can be calculated in the event of a steady state, i. e. in the case that the number of atoms having a given energy is not a function of the time. If $N(E)dE$ is the number of collisions made per unit time by radioactive chlorine atoms having an energy between E and $E+dE$, P is the probability of hitting a Cl atom at a CCl_4 molecule in a given collision, $w(E)$ is the probability of a collision between an active Cl atom with an energy E and a CCl_4 molecule giving

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substitution of the atom in the molecule, and the retention is expressed as the number of atoms being retained per unit time per hot atom formed in unit time, one can immediately write

(1) $R = \int_0^\infty N(E)Pw(E)dE$

If ν is the activation energy of the exchange reaction and E_o the maximum energy of the Cl atoms, then $w(E)$ vanishes for $E < \nu$, and $N(E)$ vanishes for $E > E_o$. Equation (1) can be rewritten in the more useful form

(1) $R = \int_\nu^{E_o} N(E)Pw(E)dE$

To proceed it is necessary to make assumptions concerning the nature of the collisions in a liquid and the mechanism for the exchange of active Cl atoms with CCl_4. Initially let us use the assumptions given by Libby (1) to enable us to express explicitly these two functions of the energy. Briefly these assumptions are as follows:

(A) Every (n,γ) process produces a free recoil atom. The kinetic energy of this atom is such that it cannot participate in stable chemical combination until it has lost energy.

(B) Energy is lost solely by elastic collisions which are "billiard ball" collisions. Indeed, until chemical combination occurs, the recoil atoms behave as if they were travelling through an assemblage of free atoms and colliding with one atom at a time.

(C) If sufficient energy is transferred in a given collision the struck molecule will be dissociated into free radicals. Retention results from the combination of the recoil atom with one of these free radicals. However, this can occur only when the radical is trapped along with the radioactive recoil atom in a "liquid cage".

(D) If, after a given collision which dissociated the struck molecule, the recoil atom has a kinetic energy less than a critical amount ε, it will be trapped

in a cage and react with the radical trapped with it; otherwise it will escape and make more collisions which can lead to retention. If it has an energy below ν it cannot react in the subsequent collisions and will be extractable with water.

If a particle of mass M and energy E_i undergoes a "billiard ball" collision with a stationary particle of mass m, the energy of the initial particle after collision will be given by

$$(2) \qquad E_f = E_i \frac{M^2 + m^2 + 2Mm\cos\theta}{(M+m)^2}$$

where θ is the angle of scattering in the center-of-mass system. Further, since the scattering is spherically symmetric in the center-of-mass system, the probability of an angle θ is given by the solid angle at θ

$$(3) \quad P(\theta)d\theta = 1/2\sin\theta\, d\theta$$

By combining (2) and (3) it can be seen that the probability of a particle with energy E_i to have an energy E after collision is given by

$$(4) \quad P(E)dE = \frac{dE}{(1-\gamma)E_i}, \qquad \gamma = \frac{(M-m)^2}{(M+m)^2}$$

and is independent of E. This means there is uniform probability of the particle having any energy between E_i and γE_i. It is also clear that an atom with an energy greater than $\frac{\nu}{\gamma}$ cannot be cooled below ν in a collision with an atom of mass consistent with γ. If the energy is less than $\frac{\nu}{\gamma}$ but greater than ν, the probability of the energy falling below ν in a collision is evidently

$$(5) \quad \frac{\nu - \gamma E}{E(1-\gamma)}$$

Thus the masses of the atoms will have a decisive influence upon the form of $N(E)$. To illustrate this and its consequences we shall treat four cases.

Case I –Pure CCl_4

If we consider the collisions to be only with Cl atoms and express the steady state condition, we get

(6) $N(E_1)dE_1 = \delta(E_1-E_0)dE_1 + \int_{E_1}^{E_0} F(E) \frac{dE_1}{E} dE$

The term on the left represents the number of atoms leaving the energy range E_1 to $E_1 + dE_1$ per unit time, and the second term on the right gives the number of atoms entering this energy range from higher energies per unit time. The first term on the right is a Dirac Delta function and represents the source of hot atoms at an energy E_0. (For simplicity we shall assume that this is a given energy level of essentially no width.) This function vanishes for all values of E different from E_0 and becomes infinite at $E=E_0$, with the area under the function being unity. Expression (6) readily yields the solution

(7) $N(E_1) = \delta(E_1-E_0) + \frac{1}{E_1}$ (normalized to one hot atom formed per unit time.)

Case II CCl_4-SiCl_4

If we again consider only collisions with Cl atoms the result is identical with Case I.

Case III $CCl_4-?$

The " ? " represents a diluent for whose atoms $\frac{\nu}{\gamma} > E_0$, hence any one collision with the diluent can remove the Cl atom from the reactive range of energies. The steady state condition applied here gives

(8) $N(E_1) dE_1 = \delta(E_1-E_0)dE_1 + P\int_{E_1}^{E_0} F(E)\frac{dE_1}{E}dE + \frac{1-P}{1-\gamma} \int_{E_1}^{E_0} F(E)\frac{dE_1}{E} dE$

The term on the left and the first term on the right have the same significance as in (6), the second and third terms on the right represent the slowing down of Cl atoms by CCl_4 and the diluent respectively. Equation (8) has the solution

(9) $F(E_1) = \delta(E_1-E_0) + \frac{1-P\gamma}{1-\gamma}\left(\frac{E_0}{E_1}\right)^{\frac{\delta-P\gamma}{1-\gamma}} \frac{1}{E_1}$

Case IV $CCl_4-C_6H_{12}$

There are collisions of the hot Cl atoms with Cl and H atoms, but in

collisions with the latter only a small part of the energy of the hot Cl atom can be transferred. In this system the steady state condition is

(10) $\quad N(E_1)dE_1 = \delta(E_1-E_0)dE_1 + P \int_{E_1}^{E_0} N(E)\frac{dE_1}{E}dE + \frac{1-P}{1-\gamma} \int_{E_1}^{E_1/\gamma} N(E)\frac{dE_1}{E} dE$

It is important to realize that the upper limit of the second integral on the right becomes E_0 if $\frac{E_1}{\gamma} \geq E_0$. This physical aspect of the problem makes it necessary to solve (10) in regions, i.e. $E_0-\gamma E_0, \gamma E_0-\gamma^2 E_0, \ldots \gamma^{n-1} E_0-\gamma^n E_0, \ldots$ The solution in any of these intervals will depend upon the solutions in the preceding intervals. This method of solution of (10) for the Cl-H atom system involves about fifty intervals and therefore will not be undertaken at this time. For the moment we will take an asymptotic solution, which, as will be discussed in detail below, gives the correct form of R as a function of P. Hence we can write as a first approximation to the solution of (10)

(11) $\quad N(E_1) = \delta(E_1-E_0) + \frac{1}{E}\left(\frac{1}{P+(1-P)(1-\gamma)}\right)$

According to the criteria outlined above for the exchange of a hot Cl atom with CCl_4 in a collision, the energy of the Cl atom must fall from a value greater than ν to one below the energy ϵ necessary to penetrate the liquid cage. Using these criteria it is possible to express the retention in another way, viz. the number of atoms with energies falling below ϵ per unit time due to collisions with Cl atoms in CCl_4 divided by the number of atoms with energy falling below ϵ per unit time as a consequence of any possible kind of collision. At steady state this latter quantity must be equal to the number of active atoms formed in unit time. Hence, in the two component systems we have mentioned, the retention can be written as

(12) $\quad R = P \int_{\nu}^{E_0} N(E) \frac{\epsilon}{E} dE$

Using (7), (9), (11), and (12) R can immediately be written down for the four

cases of interest.

(13) Case I $R = \epsilon/\nu$

(14) Case II $R = P\,\epsilon/\nu$

(15) Case III $R = P\,\dfrac{\epsilon}{\nu}\,\left(\dfrac{E_o}{\nu}\right)^{\frac{\gamma(1-P)}{1-\gamma}}$

(16) Case IV $R = P\,\dfrac{\epsilon}{\nu}\,\left(\dfrac{1}{(P+(1-P)(1-\gamma))}\right)$ for $\dfrac{1}{E} <<< \dfrac{1}{\nu}$

The last three cases are plotted in Fig. 1.[*] There it is seen that the diluent
that is most efficient for cooling the hot Cl atoms is also the most efficient
in lowering the retention. It is evident that diluents that differ in mass from
the Cl atoms can effectively reduce the probability of collision with CCl_4, but
they also increase the number of collisions per unit energy interval and hence
cannot reduce the retention by a factor P, but instead by a smaller amount.
Therefore all curves of the type given in Fig. 1 must be concave downward for
diluents that differ in mass from the hot atom. Indeed, as the mass of the
diluent approaches either zero or infinity this family of curve approaches a
horizontal line at $R\,\dfrac{\nu}{\epsilon} = 1$.

Experiments

Experimental verification of the prediction for this model was sought by
investigating the retention of Cl activity in CCl_4 as a function of composition
in two binary systems $CCl_4 - SiCl_4$ and $CCl_4 - C_6H_{12}$. Some preliminary results
will be presented.

Case II $CCl_4 - SiCl_4$

The solutions were prepared in vacuum and bombarded with neutrons from the
Columbia cyclotron in sealed containers. After irradiation the solution was
slowly dropped into a concentrated NaOH solution; thus the $SiCl_4$ was hydrolyzed

[*]For case III γ was taken equal to 0.01 and $E_o/\nu = 100$.
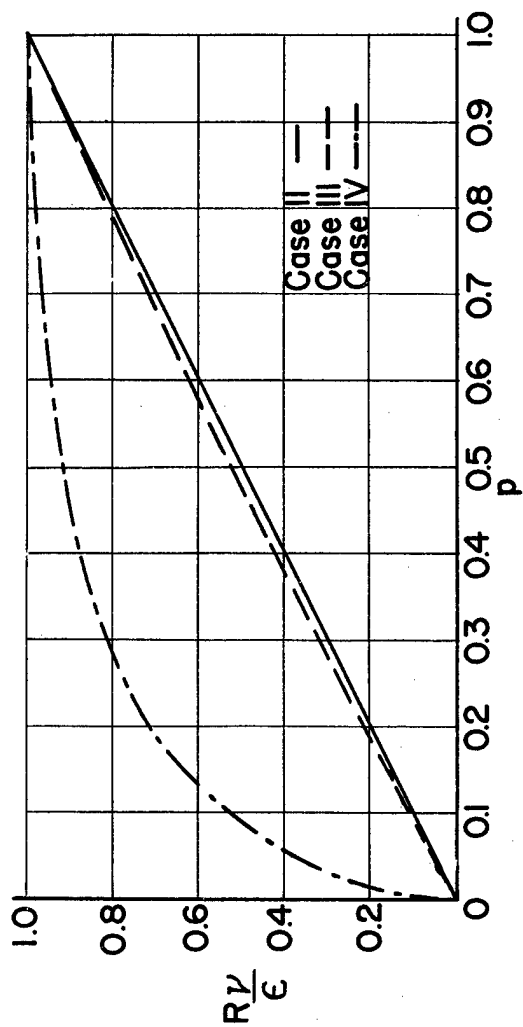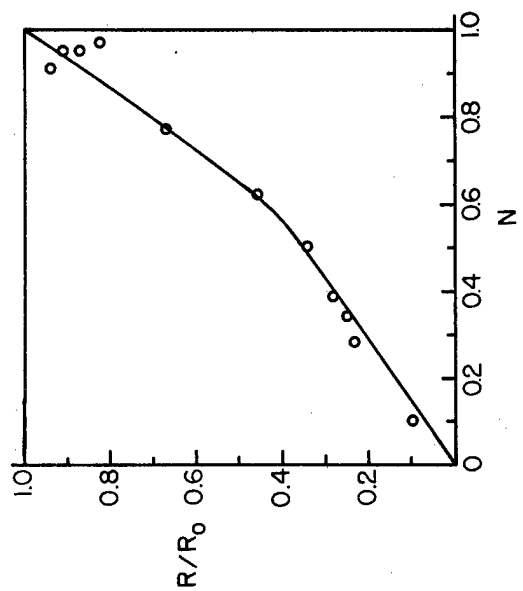 For case IV γ was taken equal to 0.9.

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Figure 2

Figure 5

Case II ———
Case III —·—
Case IV —··—

Figure 1

$\dfrac{R\nu}{\epsilon}$

A   total
B CCl_4
C   higher boiling
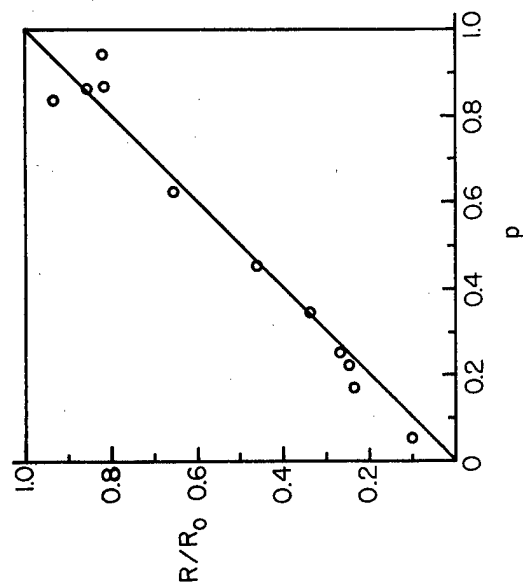
Figure 4

$\dfrac{\sigma_{C_6H_{12}}}{\sigma_{CCl_4}} = 6.25$
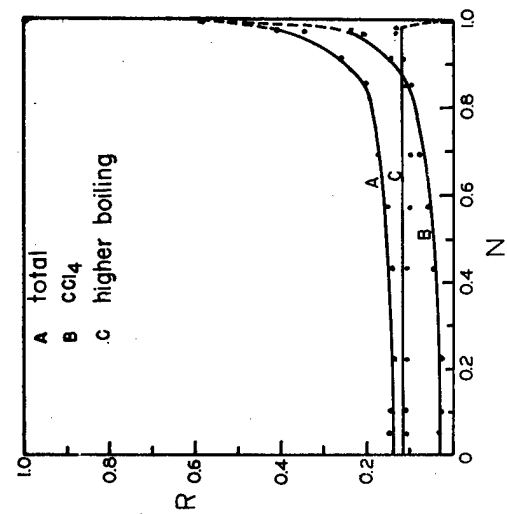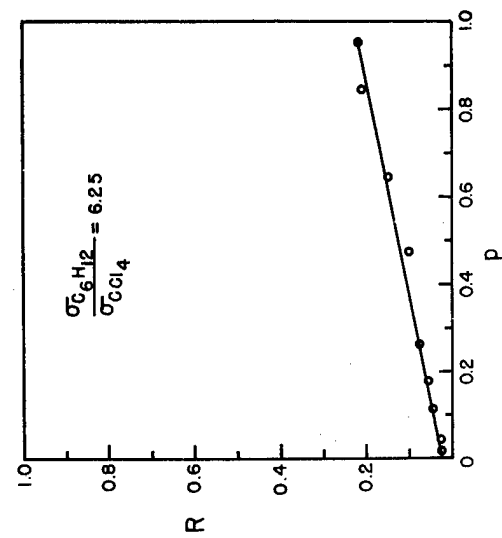
Figure 3

and the unbound active Cl extracted from the CCl_4. Any Cl activity that was

absorbed on the wall of the container was recovered by a rinse of the container

with a strongly alkaline aqueous solution. The organic and aqueous phases were

then separated and diluted to a known volume. The two liquids (organic and

aqueous) were counted in thin walled jackets placed around an ordinary silvered-

glass thinwall counter. The counting rate was corrected for the inevitable dif-

ferences among the jackets and for the density of the solution being counted.

The results are given graphically in Fig. 2, where the retention at mol fraction

N of CCl_4 divided by the retention of pure CCl_4 is plotted vs. N. It remains

to transform from the variable N to the variable P. To do this the relative

magnitude of the collision cross section of Cl atoms in $SiCl_4$ and CCl_4 must be

known. From (14) it can be shown that this quantity is equal to the slope at

the intercept divided by the intercept of a plot of 1/R vs. mol fraction $SiCl_4$/

mol fraction CCl_4. The value is found to be 1.96. By use of this number to

calculate P from N, the points in Fig. 3 are obtained. The experimental points

in Fig. 3 show fair agreement with the straight line that represents the prediction

of equation (14).

Case IV $CCl_4 - C_6H_{12}$

The solutions of known concentration were prepared in soft glass bottles by

the addition of measured volumes of the two components. After irradiation 6f

NaOH was added and the mixture thoroughly agitated, thereby extracting unreacted

Cl from the organic phase and adsorbed activity from the wall. After separation

of the phases $C_6H_{11}Cl$ was added to the organic phase and this organic solution

was fractionated. The bound activity was hence separated into two fractions,

one of which was CCl_4 and the other a higher boiling fraction. (The higher

boiling active fraction has been tentatively identified as indeed being cyclo-

hexylchloride.) The counting of the three liquids was done in the same way as

described above. The results are given in Fig. 4 where (A) the total retention, (B) the retention as CCl_4, and (C) the retention as higher boiling compounds are all plotted vs. mol fraction CCl_4. The dotted portions of the curve are interpolated to the situation that exists for pure CCl_4. These data illustrate strikingly that small quantities of cyclohexane are very efficient in lowering the retention. This is __inconsistent__ with the predictions given above. Further, it is to be noted that the decrease in retention of active Cl atoms by CCl_4 is not completely compensated for by the reaction of Cl atoms with cyclohexane to give unextractable organic halides. In this connection, it is interesting to see that the fraction of the active atoms forming cyclohexylchloride seems to be essentially independent of the composition of the bombarded solution over a large range of concentrations.

If the data on this system are treated in the same manner as the $SiCl_4 - CCl_4$ system in connection with the relative cross sections of these two compounds, it is found that the cross section of cyclohexane is 6.25 times that of carbon tetrachloride. Using this number to transform from N to P, the curve in Fig. 5 is obtained. The linearity of the experimental points is quite apparent. However, it must be pointed out that this line extrapolates to a value that represents only about $\frac{1}{2}$ the retention of pure carbon tetrachloride.

A comparison of the quantities in (1) with the experimental results can lead to the conclusion that $N(E)$ must be diminished in the region of energy where $w(E)$ makes its predominant contribution. Even with the abandonment of the "billiard ball" collision idea, it is not easy to see how small quantities of cyclohexane can diminish $N(E)$ so markedly unless the notion of chemical capture of the Cl atoms by cyclohexane is introduced. This reaction could be of the following well known sort

(17) $Cl + R-H \quad HCl + R\cdot$ (R$\cdot$ represents a free radical.)
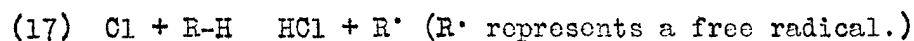
If this reaction occurs with good efficiency for Cl atoms with an energy higher

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than that where $w(E)$ is large, then the rapid reduction in retention is to be expected. This approach can be treated mathematically by using essentially the same mathematical apparatus as illustrated above except that a term corresponding to chemical capture must be introduced and $w(E)$ must be modified. (A capture term has to be added to the term for the " billiard ball" collisions to calculate $N(E)$, and $w(E)$ is said to be a constant over some energy range and zero elsewhere.) The result of this treatment is a retention curve that can fall off as rapidly as is desired by adjusting the many parameters available. But the curve is certainly concave upwards instead of downwards.

There is another approach that is at least qualitatively consistent with the data. This treatment asserts that the number of collisions made by Cl atoms in the energy range in which exchange can occur is independent of the composition of the solution. If we take 0.01 as the probability of the reaction in any one of these collisions, then to be consistent with the retention of pure CCl_4 the number of collisions in this range comes out to be about seven. When cyclohexane is added, if it is then asserted that reaction (17) occurs with a greater probability per collision in this energy range than 0.01, the retention as CCl_4 is again decreased quite rapidly. These simple considerations give for the retention

$$(18) \quad R= [1 - (1-PW_1 - (1-P)W_2)^{\eta}] \frac{PW_1}{PW_1 + (1-P)W_2}$$

W_1 is the probability of reaction of Cl with CCl_4 per collision, W_2 is the probability of reaction with cyclohexane per collision, and η is the number of collisions made by Cl atoms in the energy range in which reaction can occur.

Reference

(1) W. F. Libby, J.A.C.S., 69, 2523(1947).

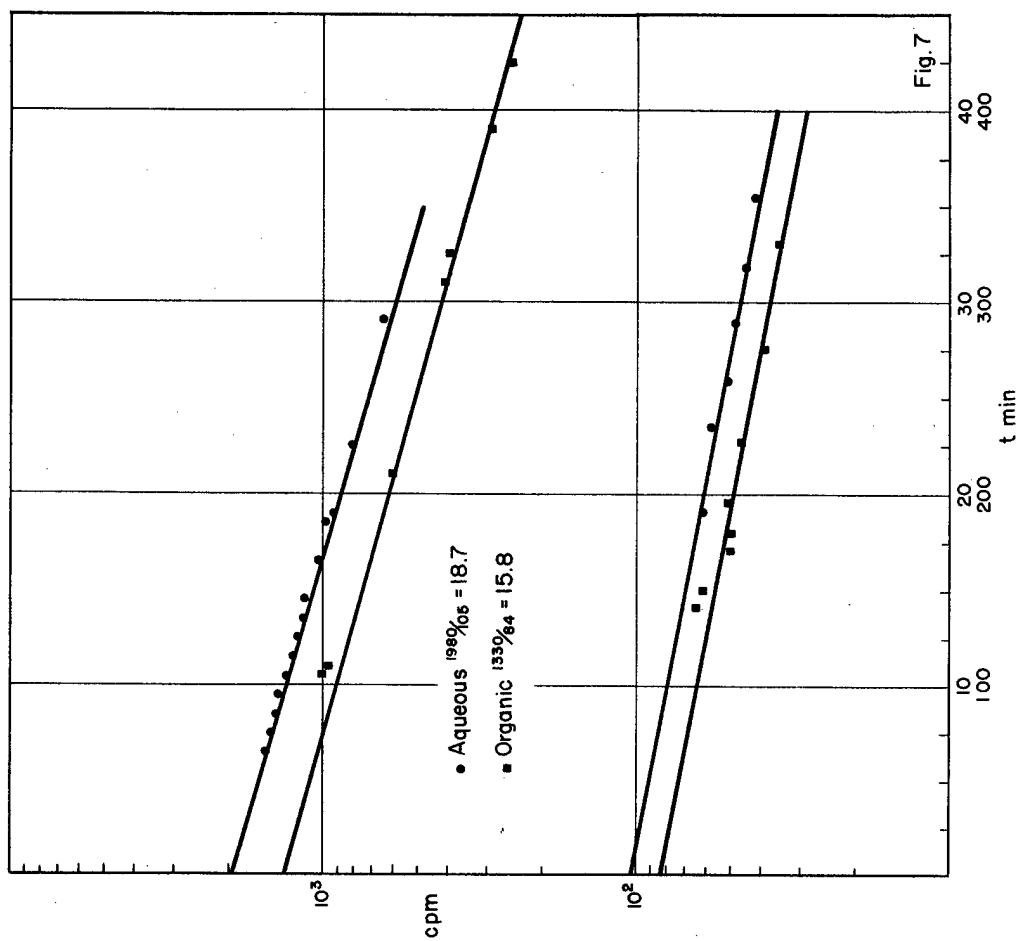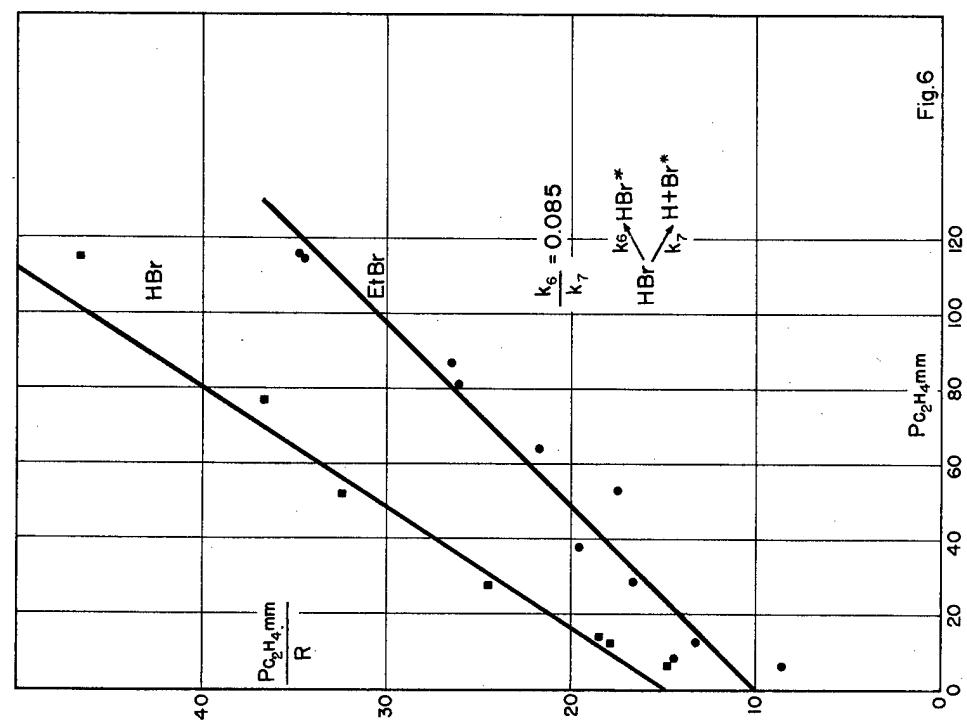# CHEMICAL CONSEQUENCES OF THE (n,γ) PROCESS
FOR GASEOUS BROMIDES

R. R. Williams and W. H. Hamill*

This work is a preliminary survey and conclusions are tentative. It was our intention to repeat and verify part of Suess's work before progressing to other related investigations of the (n,γ) process for gaseous bromides.

For neutron bombardment a 300 mc Ra-Be source, with paraffin moderator, was centrally located within a 2.5l soft-glass bottle surrounded by water and shielded from light. The bottle was connected by rubber stopper to a simple vacuum line with mercury manometer. Exposures lasted 10 min. unless otherwise stated. Exposed samples were condensed into a flask, containing measured amounts of water and ethyl bromide as required to bring each phase to approx. 3.5 ml volume, and provided with a ground joint and stopcock. The flask was removed from the line, the contents were melted and well shaken, and each layer counted in a jacketed G-M tube. Background averaged approx. 100 cpm (due to the exposed source) and sample counts averaged 1500 during 4 min. ($\sim$300 cpm above background.) The jacket was rinsed with ethanol after removal of each sample. All count rates were extrapolated to the time of removal from the source and corrected to a common volume and density of liquid sample. The major gaseous component was always added last to purge the line of minor components. Pressures refer to those prevailing in the 2.5l bottle. Matheson C_2H_4 and HBr were twice frozen and pumped on the line. Eastman-Kodak pure ethyl bromide was similarly treated, then distilled from P_2O_5.
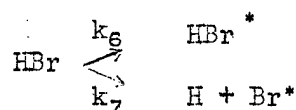
In the series "Et Br" (Fig. 6), $P_{HBr} = 48 - 50$mm, $P_{EtBr} = 180-190$ mm, $P_{C_2H_4}$ varies as shown. In the series "HBr" (Fig.6) $P_{EtBr} = 4-6$ mm, $P_{HBr} = 170-190$ mm, $P_{C_2H_4}$ varies as shown. During neutron bombardment the temperature of the sample was 20 - 25°C.

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Fig. 7

Aqueous $^{198}\%_{05} = 18.7$
Organic $^{1330}\%_{84} = 15.8$

Fig. 6

$$\frac{k_6}{k_7} = 0.085$$

$$HBr \underset{k_7}{\overset{k_6}{\rightleftarrows}} \begin{array}{l} HBr^* \\ H + Br^* \end{array}$$

HBr

EtBr

$P_{C_2H_4} mm$

$$\frac{P_{C_2H_4} mm}{R}$$

Our kinetic treatment is based upon Suess's, but explicitly includes the (n, γ) process in steps 6, 7 and retains all terms in (HBr). We postulate that the processes 1-7 are necessary and sufficient to account for our present results. In these equations A refers to C_2H_2 or C_2H_4, S* refers to $C_2H_3Br^*$ or $C_2H_5Br^*$

$$HBr + Br^* \xrightarrow{k_1} HBr^*$$

$$A + Br^* \underset{k_3}{\overset{k_2}{\rightleftarrows}} ABr^*$$

$$ABr^* + HBr \xrightarrow{k_4} AHBr^*$$

$$ABr^* + HBr \xrightarrow{k_5} ABr + HBr^*$$

$$HBr \underset{k_7}{\overset{k_6}{\lessgtr}} \begin{array}{l} HBr^* \\ H + Br^* \end{array}$$
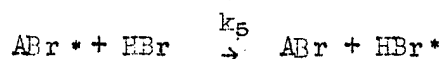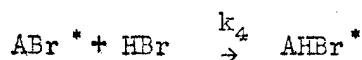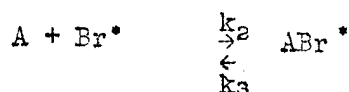
$$dS^*/dt = k_4(ABr^*)(HBr)$$

$$dHBr^*/dt = k_1(Br^*)(HBr) + k_6(HBr) + k_5(ABr^*)(HBr)$$

$$(ABr^*) = \frac{k_2(A)(Br^*)}{k_3 + (k_4 + k_5)(HBr)}$$

$$dBr^*/dt = 0 = k_7(HBr) + k_3(ABr^*) - k_1(Br^*)(HBr) - k_2(A)(Br^*)$$

$$(Br^*) = \frac{k_7(HBr)}{k_2(A) + k_1(HBr) - \dfrac{k_2 k_3(A)}{k_3 + (k_4 + k_5)(HBr)}}$$

$$\frac{S^*}{HBr^*} = \frac{k_4 k_2(A) \big/ [k_3 + (k_4 + k_5)(HBr)]}{k_1 + \dfrac{k_5 k_2(A)}{k_3 + (k_4 + k_5)(HBr)} + k_6 \dfrac{k_2(A) + k_1(HBr) - k_3 k_2(A)\big/[k_3 + (k_4 + k_5)(HBr)]}{k_7(HBr)}}$$

$$R = \frac{S^*}{HBr^*} = \frac{(A)}{\dfrac{k_1}{k_4}\left(1 + \dfrac{k_6}{k_7}\right)\left(\dfrac{k_3 + (k_4 + k_5)(HBr)}{k_2}\right) + \dfrac{k_5}{k_4}\left(1 + \dfrac{k_6}{k_7}\dfrac{k_4 + k_6}{k_5 \quad k_7}\right)(A)}$$

$$b = \frac{k_1 k_3}{k_2 k_4}, \quad \beta = \frac{k_1(k_4 + k_5)}{k_2 k_4}, \quad M = \frac{k_5}{k_4} \quad \rho = \frac{k_6}{k_7}$$

$$(A)/R = [b + \beta(HBr)](1 + \rho) + M(1 + \rho + \rho/M)(A)$$

From some of our experiments at constant (A) and variable (HBr) we find,

contrary to Suess, that $\beta \cong 0.027$, not zero. Using this constant with the results which appear in Fig. 6 we have (expressing concentrations in pressure units)

for the series " Et Br", (HBr) $\cong 50$ mm, b = 8.7

for the series "HBr", (HBr) $\cong 185$ mm, b = 8.0*

average b = 8.4

Assuming $\rho = 0$ for the series " Et Br"

$$\frac{M(1 + \rho + \rho/M)}{M} = \frac{0.31}{0.205} \quad ; \quad \rho = 0.08_5$$

If the (n, γ) process fails to rupture the HBr bond in 1/10 of all cases for Br^{80} (18m.) it is possible that one may obtain a different result for Br^{80} (4.5 h.) or Br^{82}. We have tested only the former possibility.

Using the procedure described above we performed two additional experiments. In the first we introduced 5mm of Et Br, 7mm of C_2H_4, 366 mm of HBr and in the second 6mm of Et Br, 9mm of C_2H_4 and 415mm of HBr. Both samples were exposed to the source for 61 min. From the first we obtained for the ratio of the counting rates at an arbitrary zero time referred to the end of exposure

$$\frac{cpm\ (18m)}{cpm\ (4.5h)} = 18.7$$

using the aqueous layer. From the second we obtained, similarly,

$$\frac{cpm\ (18m)}{cpm\ (4.5h)} = 15.8 \text{ (see Fig. 7)}=$$

From the ratio of these ratios we have

$$\left[\frac{cpm\ (18m)}{cpm\ (4.5h)}\right]_{Aqueous} \Bigg/ \left[\frac{cpm\ (18m)}{cpm\ (4.5h)}\right]_{Organic} = \frac{(A)/R_{4.5h}}{(A)/R_{18m.}}$$

Qualitatively it is evident that $\rho_{18m.} > \rho_{4.5h}$

*This figure is a second approximation, anticipating the result $\rho = 0.085$.

Considering the poor precision of the "Et Br" and "HBr" series of experiments, we can only expect qualitative agreement between the two types of experiment. We find adequate agreement by choosing, as a minimum $\rho_{4,5h} = 0$ and so predict the ratio of counting rate ratios as 1.23 which agrees adequately with the experimental ratio $\frac{18.7}{15.8} = 1.18$.

Summary

There is evidence, based upon kinetic postulates, for failure to rupture the HBr bond during the (n,γ) process forming $Br^{80}(18m)$ in a small fraction of such events. Corroborative evidence, independent of any kinetic postulates, follows from the experimental fact of unequal $Br^{80}(18m) / Br^{80}(4,5h)$ ratios for different chemical species. We do not find it necessary to attribute exceptionally high energies or durations to atomic Br^{80} as a reactant in the gas phase.

THE HOT ATOM CHEMISTRY OF THE PROPYL BROMIDES*

Lewis Friedman** and W. F. Libby***

Abstract

The chemical effects of the recoil from the capture gamma radiation produced by the (n,γ) reaction on bromine 81 in both normal and isopropyl bromides have been investigated. It is found that the principal part of the radiobromine resisting aqueous extraction, that is, organically combined, is propyl bromide. The ratio of normal to isopropyl bromide formed by irradiation of either normal or isopropyl bromide is found to be about 2.5. The irradiation of propyl bromide cooled to liquid nitrogen temperatures produced no change in the yield of normal and isopropyl radiobromides, as compared with the results for the liquids at room temperature. In direct contrast, however, the yield of the dibromides requiring hydrogen substitution was much larger in the case of the low temperature solid, the percentage yield of dibrom rising about three-fold. These results are interpreted as evidence that the bromine substitution is a reaction occurring largely in the energy range where the chemical bonds involved are negligible, and that the hydrogen substitution occurs in the lower energy range where the recoiling bromine atoms collide with the molecule as a whole in an inelastic manner rather than with a single atom, as is postulated in the high energy range. The difference in temperature dependence of the two types of substitution reaction would appear to arise from the difference in magnitude of the energies involved. The fact that the irradiation of isopropyl bromide produces 2.4 times as much normal bromide as iso bromide, and the same

relative amounts are observed in the irradiation of normal propyl bromide, is taken as further evidence of the extremely energetic nature of the bromine substitution reaction, the free radical apparently having sufficient energy to isomerize before recombination occurs in the solvent " cage".

Introduction

The capture of a slow neutron by bromine 81 to form 34-hour bromine 82 involves the emission of the order of 8 million volts energy as gamma radiation nearly instantaneously. It is not known whether this energy is emitted in the form of one gamma ray or whether there are several involved. If one is involved the recoiling bromine will possess an energy of about 420 electron volts. If a cascading process occurs the recoil energy will vary between this limit and zero, the chance of zero recoil energy being extremely small unless a very large number of gamma rays are involved in the cascade. It is well known that the radiobromine atoms are ejected from the molecules in which they resided before the neutron capture [1a,b,c,d,e,f], the evidence being that the irradiation of a liquid organic halide allows about half of the radiohalide to be extracted into an aqueous solution [1a,b,d], and that the irradiation of a gaseous organic halide allows the extraction of over 95% [1c,e,f], and that the irradiation of a dilute solution of an organic halide in an organic solvent reduces the fraction of the radiohalide found in the mother molecule to zero as the concentration is decreased [1b,d]. The mechanism by which the radioactive halogen atoms are reincorporated into organic molecules may be of considerable interest both in radiochemistry and indirectly in chemical kinetics. It has been proposed [1d,e,2] that the broad features of this type of reaction can be explained by a mechanism which considers the chemical bonds to be of strength negligible with respect to the energy of the recoiling bromine atom, and that the re-entry process consists of an essentially head-on collision of the recoiling bromine atom with a bound bromine atom, the radioactive bromine atom transferring its

momentum nearly completely to the inactive atom and being itself left with a relatively small energy in the immediate vicinity of the free radical formed by the removal of the non-radioactive atom, both the free radical and the radio-bromine atom being contained in the same solvent "cage"[3] and being free to recombine, with a dissipation of their excess energy to the solvent through the cage.

Substitution for hydrogen atoms in an organic halide has been explained as occurring near the end of the range of the recoiling bromine atom, where the energy is still somewhat larger than the chemical bond energy but not a great deal larger; that is, the energy is sufficient to cause both to rupture, but is insufficient to warrant treatment of the collision as a process occurring essentially between free atoms. This allows the molecule as a whole to act in an inelastic manner to stop the radiobromine atom in the same solvent "cage" and to itself dissociate, for example, by losing a hydrogen atom, the whole process resulting in a replacement of hydrogen by bromine to form a more highly halogenated product. This type of process can be dominant apparently when the medium contains a very low concentration of either combined or free halogen, as Reid[4] has shown by studying very dilute solutions of iodine in pentane and establishing that 38% of the radioiodine appears as amyl iodide. This result has been confirmed in this laboratory by Mr. W. H. Johnston, who found 37% under similar conditions and observed that no significant decrease in iodine titre occurred. A similar experiment with 0.10 gms of Br_2 in 100 cc of liquid pentane was performed, and a retention of 31% observed. The yields of hydrogen substitution products reported in the literature for the organic halides in general are considerably less than this, though they vary with experimental conditions, as we shall see later in this paper. It appears therefore to be necessary to explain the increase in effectiveness of the hydrogen substitution reaction with diminution in halogen concentration. Such an explanation seems to follow from the collisional type of

theory referred to above. According to this theory hydrogen entry can occur only for those halogen atoms which possess an energy between one and several times the bond energy. If there are no halogen atoms in the solution, energy loss occurs entirely by collisions with much lighter atoms, so that every halogen atom will move through this critical energy range, thereby having an opportunity to substitute by the inelastic molecular collision mechanism described. If, however, an appreciable fraction of the cooling collisions occur with atoms of equal mass, the chance of the atoms jumping discontinuously through this energy interval is appreciable, and the result is a considerable fraction of the atoms having no opportunity for hydrogen substitution. The whole problem is analogous to that of resonance capture in neutron physics.

In addition to these processes in the hot or high energy range and in the 1 to 4 or 5 chemical bond energy range, which we might call " epithermal" in analogy to the neutron nomenclature, we may have reactions proceeding in the thermal range between the solution and those halogen atoms which do manage to enter the thermal range without chemical combination, i.e., halogen atoms are notoriously reactive and the possibilities of their combining with impurities, walls, and the principal species in the solution may be considerable, and care must be taken in work in the field of hot atom chemistry to guard against mis-interpreting such phenomena as occurring in the hot or epithermal ranges. A further type of reaction which is not characteristic of or to be attributed directly to the hot or epithermal chemistry is the type of reaction discovered by Sugden[5], in which the addition of small amounts of aniline to an organic halide greatly reduced the retention in organic forms. This has been inter-preted[1d,c,2] as a reaction between the excited, reformed organic halide and aniline present in the solution in such concentrations as to have a good chance of collision with the excited organic halide before it cools. It is to be

expected that this type of reaction will be found to be quite common. Fortunately, the result can generally be predicted by experiments with macroscopic quantities, for example: the ability of aniline to react with organic halides to form anilonium salts in which the halogen is ionically bound is well known. This reaction is known to occur at elevated temperatures in ordinary organic systems. In addition, a third type of essentially thermal reaction which must be borne in mind in the interpretation of experiments on hot atom chemistry is thermal exchange reactions between halogen atoms and organic halides. It is probable that in most cases studied so far this effect has been negligible, but it is not unlikely that in certain cases, for example the benzyl or allyl halides, this effect will be expected to be serious.

The present research was undertaken to elucidate some of the doubtful points in the theoretical structure described above. The 34-hour bromine activity was selected because of its convenient half life, and the availability and stability of the organic bromides. The propyl bromides were selected from the various organic bromides for the ease of separation of the products by distillation techniques, at the same time retaining the possibility of isomerization.

Experimental

Pure normal propyl bromide and isopropyl bromide samples were obtained from Paragon Testing Laboratory. These were redistilled and their refractive indices found to check with those for the pure products within 1 part per ten thousand. The irradiations were conducted in 500 cc soft glass bottles near the cyclotron target with an intervening 10 cm. of paraffin for neutron moderation, and 2 inches of lead to eliminate radiochemical effects due to gamma radiation. Exposures usually lasted one hour, at a mean flux of about 10^8 thermal neutrons per square centimeter per second. The beam current on the cyclotron usually averaged 20 microamperes. A beryllium target was used. The bottle was

approximately 18 inches from the target. After exposure, the samples were returned immediately to the chemical laboratory and extracted within 5 minutes with aqueous sulfite containing bromide carrier, after which 25 cc of the irradiated liquid was mixed with 25 cc of the mono brom isomer, 25 cc of the 1,2-dibrom propane, and 25 cc of the 1,3 dibrom propane. The distillation was conducted by taking middle cuts of 10 cc for each of the 4 constituents. The 1, 1 and 2, 2-dibrom propanes were not added and apparently were not formed in any appreciable yield because the material balance obtained for the radiobromine in the four cuts listed accounted within the accuracy for the entire radiobromine content of the organic fraction left after the aqueous extraction. The boiling points of the 1,1 and 2,2 compounds are sufficiently different to insure their not being included in the center cuts for the four compounds used. The radioactivity measurements were made with a standard type of liquid cell counter, 10 cc of liquid being measured. Precautions were taken to allow the 18 minute and 4.5 hour bromine activities to decay, and a lead shield of 2 mm thickness was used as a combination absorber of the 18 minute radiation and radiator for the 34 hour gamma radiation, for those experiments where the decay period was in sufficient. Measurement of the rate of decay of the radioactivity showed it to be essentially pure 34 hour. Table I presents the major portion of the experimental results.

The upper half of the table refers to experiments in which isopropyl bromide was irradiated and the lower half to those belonging to normal propyl bromide. The second column gives the percentages of the total 34-hour radiobromine found in the various chemical forms indicated by the designations in the first column. The last row in each half of the table refers to the total retention in organic form as experimentally observed after the aqueous extraction, the symbol R being used. The third column of the table contains the data for

the experiments at liquid nitrogen temperatures. In general, the data in the table are accurate to about $\pm$ 1 unit, e.g., the isopropyl fraction found in normal propyl irradiations at room temperature would be 12.0 $\pm$ 1.

Table I

Principal Data on Propyl Bromide

	Isopropyl Retentions		
	25°	-196°	1 g Br_2/100 cc
Iso	10.0	11.2	7.9
Normal	23.7	23.5	2.6
1,2 Dibrom	3.8	20.0	6.7
1,3 Dibrom	4.6	11.5	4.8
R	42.1	66.0	21.4

	Normal Propyl Retentions		
Iso	12.0	11.3	4.0
Normal	30.6	28.5	9.0
1,2 Dibrom	3.8	20.2	8.4
1,3 Dibrom	4.5	18.2	5.4
R	50.0	78.2	28.8

In addition some study was made of the effect of concentration of added bromine on total organic retention in the case of isopropyl bromide. The numbers were as follows: for 3.5 grams per 100 cc bromide a 22.7% organic retention; for 1.0, 21.4; for 0.35, 26.5; and for 0.035, 39.4. Thus it is seen that the effect of added bromine is essentially saturated at 1 gram per 100 cc and has essentially disappeared at 0.035 grams per 100 cc. The fourth column of Table I contains the detailed retention data for this concentration. Checks on loss of titre of elemental bromine were made and very little loss of titre occurred during the course of the experiment.

It was necessary to extract the irradiated halides immediately after exposure in order to avoid a very considerable increase in the observed retention. For example, allowing a solution irradiated at room temperature to stand overnight

would result in retentions of about 80%, and in a rather irreproducible fashion, and it was discovered that reproducibility could be obtained only by immediate extraction after relatively short exposure. To test the efficacy of our adopted procedure one experiment was performed in which extraction occurred continuously throughout the irradiation. The organic and aqueous layers were placed together in a sealed glass tube which was rotated with a motor end over end throughout the exposure. Normal propyl bromide was used and the observed total organic retention was 50.0%, in good agreement with that observed at the end of one hour of exposure and a 5-minute extraction interval, the bromide carrier in the aqueous layer being less than .1% in the total bromine in the system. The retention in this case was measured by comparing the activities in the aqueous layer with that in the organic layer, in contrast to our usual procedure of counting the liquid before and after aqueous extraction. The thought occurred to us that the addition of Br_2 might well stabilize the system, it being considered possible that the slow growth in retention was due to the reaction of unusual species such as atomic bromine with impurities in the system. An experiment was performed with normal propyl bromide in which 0.7 grams of elementary bromine per 100 cc was added. The irradiation was conducted and the solution allowed to stand in a dimly lit room for 24 hours, nearly the same conditions of illumination being used as had obtained throughout the research. The result was an increase in retention from 28.8% to 42.8%, with a sharp increase in the 1,2 dibrom yield. A loss in titre of the Br_2 and a macroscopically observable yield of 1,2 dibrom propane as indicated by a refractive index measurement was found. The total distribution data are given in Table II below. This experience led to the thought that the slow thermal rise in retention might involve the presence of air in the solutions as well as the illumination, so an experiment was performed in which air was carefully excluded, other conditions being

unchanged from the standard procedure. These and the other data supplementary
to Table I are given in Table II, and it is clear that the exclusion of oxygen
had no effect within experimental error.

Table II

Supplementary Data on Propyl Bromide Retentions

A. Effect of added Br_2 on Retention; Isopropyl Bromide

Concentration (g/100 cc)	3.5	1.0	0.35	0.035
Retention (%)	22.7	21.4	26.5	39.4

B. Effect of Standing in Dim Light 24 Hours after Irradiation;

Normal Propyl Bromide with 0.7 g Br_2/100 cc

	Immediate (1.0 g Br_2)	24 hr. Delay (0.7 g Br_2)
Iso	4.0	6.5
Normal	9.0	10.3
1,2 Dibrom	8.4	17.8*
1,3 Dibrom	5.4	8.2
R	28.8	42.8

*Macroscopic yield of about 1% 1,2 dibrompentane
corresponding to observed loss in Br_2 titre was
observed.

C. Effects of Excluding Air and of Continuous Extraction
during Irradiation;

Normal Propyl Bromide

	Usual Procedure	Air Excluded	Cont. Extraction
Iso	12.0	9.7	---
Normal	30.6	29.7	---
1,2 Dibrom	3.8	3.8	---
1,3 Dibrom	4.5	6.8	---
R	50.0	51.0	50.0

Experiments were performed with various amounts of lead shielding and with
a 0.5 gram radium-beryllium source, instead of the cyclotron, which show the
retention pattern to be independent of radiation intensity. We take this as

evidence that secondary reactions with free radicals generated by gamma rays or fast neutrons were negligible.

Discussion

The type of explanation previously proposed for hot atom phenomena and referred to above in the Introduction appears to be capable of explaining many of the data obtained in this research.

1. <u>The temperature independence of the yields of mono brom derivatives.</u>

The data in Table I reveal that the yield of mono brom products is independent of the temperature during exposure, in sharp contrast to the dibrom derivatives. To recapitulate, the explanation of the predominance of the reactions leading to the re-formation of the bombarded molecule in the hot atom chemistry of organic compounds, particularly the organic halides, has been that the recoiling halogen atom while still in the hot range, that is, possessing an energy several times the chemical bond energy, makes a nearly headon collision with bound bromine in an organic halide molecule, driving the inactive bromine onwards with a transfer of momentum to it and leaving the radioactive bromine atom in the same solvent cage with the free radical so produced. In our case this free radical would be propyl radical, and the radiobromine would be expected to recombine with the propyl radical to form a mono brom derivative. It seems that the efficacy of the cage in this high energy range must be a matter mainly of the density of solvent molecules in the cage walls rather than any adhesive forces operating between them, for the reason that the residual energy of the bromine atom probably is large compared to any such binding energy. A rough theoretical calculation[2] of the bromine atom energies involved indicates that these are of the order of 1/2 to 2/3 the chemical bond energy, which is large with respect to the intermolecular adhesive energies. Therefore, the only temperature effect one might expect in this range is a slight difference in molecular density. It

would appear from these results that the dependence on density is less than the first power in any case, though one could hardly predict this theoretically. The re-entry to form the mono brom derivatives leaves the bromine so energetic on the average that the question of whether it is reflected from the walls is not connected with the question of how tightly the wall particles are held to one another, but is a matter of reflection of the bromine on the individual wall molecules. These collisions probably are somewhat inelastic, the cooling of the bromine atom occurring through molecular excitation of the wall molecules. After the cooling has proceeded to a certain point, recombination occurs, a certain number of collisions with the wall having preceded the recombination. The freshly re-formed molecule is excited and then it in turn cools by wall collisions.

2. <u>The formation of both the normal and isopropyl isomers in ratio of 2.4 to 1 from both normal and isopropyl mother molecules</u>.

The data reveal that the ratio of the yields of normal and isopropyl bromide is nearly the same for both normal and isopropyl bromide bombardments, the average value being $2.4 \pm .2$, and there being some slight indication that the ratio for iso is slightly less than that for the normal, as though there were indeed some slight tendency to form that isomer identical with the mother molecule - a certain memory for the configuration existing before the hot atom collision.

The explanation proposed for this observation is that during the period of existence of the free radical, that is, the interval between the initial collision forming the free radical and the instant of recombination after the cooling period for the energetic radiobromine atom, the propyl radical itself is free to isomerize to essentially the equilibrium state it would have at extremely high temperatures. It is thought probable that the propyl radical will itself receive considerable excitation energy in the rupturing collision forming it from the propyl bromide, and that this energy of excitation will be so high as

to promote free isomerization so that the radical retains very little memory of its original configuration when formed, and that when recombination does occur the final product will reflect only slightly the nature of the original radical. Some slight memory is found due to those few cases where essentially immediate recombination occurs because the bromine was left relatively cool by virtue of a chance almost exactly head-on collision. It would seem that the truly high temperature distribution ought to be 3 to 1, since there are 6 methyl hydrogen and 2 methylene hydrogen positions. The facts that it is 2.4 to 1 instead and that there is evidently some remembrance of the nature of the mother molecule probably have the same explanation.

3. The yield of the di brom derivatives is much larger for the solids at liquid nitrogen temperature than for the liquids at room temperature.

Table I shows further that the yields of the hydrogen substitution products increase 3 to 5 fold on cooling, in sharp contrast to those for the halogen substitution products, the only exception being the 1,3 di brom formed from isopropyl for which the factor is 2.5 versus about 5 for 1.2 from isopropyl and both 1,2 and 1,3 from normal propyl.

It has been proposed that hydrogen substitution in an organic halide is brought about by the halogen atom colliding with the molecule as a whole with an energy which we have termed epithermal, and defined as being above the bond energy but not extremely large as compared to it, amounting perhaps to 5 times the bond energy, though this limit is rather indefinite. The essential point is that as the halogen atom reaches the end of its range the collisions become less a matter of collision with individual atoms in the molecule and more a matter of inelastic collisions with the molecule as a whole or groups thereof, until the thermal range is reached when truly elastic collisions with the molecule as a whole occur. In the epithermal region the molecule is able to stop the

bromine atom in the same solvent cage, and due to its high degree of internal excitation shed hydrogen and bromine atoms and whole radicals*. With this model one notices that the residual energy of the bromine is very likely to be much less than in the case described above where the mono brom derivatives are formed, and that therefore any change in the adhesive energies and densities of packing of the molecules constituting the cage wall will be more important. The greater dependence on density and strength of the cage wall in the case of these lower energy atoms can perhaps be seen best in the following way. In the higher energy case the bromine has sufficient energy to melt or vaporize the whole cage in any case. It matters little therefore in this case whether one starts from a solid or from a liquid, but in the case of the epithermal processes this probably is not true, and so the strength of the cage and its general efficacy will depend considerably on whether the cage is compact and more tightly bound, as in the low temperature solid, or whether it it more attenuated and less tightly bound, as in the liquid. Further experiments must be performed at intermediate temperatures to settle whether the density, i.e., the phase, is more important than the mean temperature. It seems not unlikely that if one cools through the melting point a rather abrupt change in the yield of the di brom derivatives may occur.

The observation that the increase in yield of 1,3 di brom product from isopropyl bromide at liquid nitrogen temperatures is less than for the 1,2 and the same as the 1,2 and 1,3 yields for the normal propyl bromide appears to be a definite result. One notices that the formation of the 1,3 product from the

* Some evidence has been obtained for this type of phenomenon in another research on the hot atom chemistry of dilute bromine solutions in pentane where a small yield of propyl bromide has been observed, amounting to some 4% of the total bromine activity where the total organic retention was 40% . It must be said, however, that no evidence in the course of the research on propyl bromide has appeared for the formation of such products as 1 or 2 carbon alkyl bromides.

isopropyl requires a very considerable shuffling of the atoms in the molecule, and particularly that the carbon-bromine bond on the central carbon atom must be broken. This requirement does not occur for the other three cases, of the 1,2 from the isopropyl and the 1,2 and 1,3 from the normal propyl. With this observation in mind, an obvious explanation seems to be that this shuffling process can occur only for the most energetic of the collisions, and that a good fraction of them do not possess sufficient energy to allow it. It might also be taken as evidence that the actual process involved in a good fraction of the cases is not only the ejection of a hydrogen atom but also of the bound bromine atom, and that then one has an inactive bromine atom, the radioactive bromine atom, and the propylene di radical all loose in the cage and recombination of these three constitutes the last step of the reaction.

4. <u>The lower retention in isopropyl as compared to normal propyl irradiations.</u>

It is clear from Table I also that the total organic retention in the isopropyl case appears to be definitely less than for the normal propyl case, and that this ratio apparently is independent of temperature, both temperatures giving the value of 1.2 for the ratio of the retentions.

The most obvious explanation of this observation is that the bromine is somewhat more shielded by the methyl radical in isopropyl bromide than by the ethyl radical in normal propyl bromide. Examination of Fischer-Hirschfelder models seems to bear this out.

5. <u>Very little 1,1 and 2,2 di brom propane formed.</u>

The agreement between the total for the individual organic fractions as separately determined with the experimentally determined total organic retention shows that the yield of 1,1 and 2,2 di brom propyl products could not have exceeded 2 units in any of the runs. It would seem quite clear therefore that

particularly in the liquid nitrogen run these products are excluded as being significant components.

This result is in line with the well known difficulty of preparing these substances by ordinary bromination of hydrocarbons and organic halides. It appears the molecules would prefer to brominate to positions on other carbon atoms than that already brominated. This situation would be further accentuated by the relatively high temperatures involved in the syntheses involved in this research.

6. <u>The presence of bromine in the irradiated organic bromide greatly reduces the total retention, the main decrease occurring in the mono brom derivatives.</u>

Tables I and II show that the addition of bromine greatly reduces the total retention, the main reduction occurring in the primary products, with some increase in the hydrogen substitution occurring.

The explanation proposed for this is that of exchange occurring during the cooling process either before or after the reformation of the molecule, the re-formed molecule being excited. It is well known that all organic halides exchange at sufficiently high temperatures with either the halogen or the halide ion, the activation energies being 18.12 K cal/mole for normal propyl and 22.94 for isopropyl against bromide ion[6]. The exchange between bromine atom and Br_2 is of course extremely rapid, so we have the interesting possibility that if the concentration of bromine is sufficiently high so that each solvent cage contains a bromine molecule or that a bromine molecule be within one or two layers of the solvent cage one might expect the radioactivity to be "washed out" into the Br_2 and so made water-extractible with a consequent reduction in the overall retention. It seems that exchange of the bromine atom must proceed only with a bromine molecule in the solvent cage itself, in other words, occur only at the

high bromine concentrations, but that the re-formed organic bromide may retain some of its energy of excitation for a sufficiently long time to be able to exchange with the Br_2 within one or two layers of the solvent cage. It is interesting to observe in Table II that the effect seems to be saturated at about 0.5 grams of organic bromide per 100 cc of propyl bromide. Of course, at much higher bromine concentrations another effect will occur where an appreciable probability for collisions of the hot bromine with Br_2 itself will enter, with a necessary reduction in organic bromide retention. The concentrations used here, though, would involve not over 5% reduction by this effect.

7. <u>The inversion by the presence of bromine during irradiation of the usual ratio of normal to isopropyl products in the case of isopropyl bromide.</u>

The indications are that the usual ratio of normal to iso products is unchanged in the case of normal propyl bromide irradiations by the addition of bromine, but it is indeed inverted in the case of isopropyl bromide.

The explanation of this point is not clear. It is possible that the lower activation energies of the exchange reaction for the normal product is involved, it being remembered that to form the normal from the iso requires that the free radical isomerize and therefore that more energetic processes be involved than in the direct formation of the iso.

8. <u>The delayed rise in retention.</u>

The observed increase in retention from about 50% to nearly 80% on standing for 24 hours in a dimly lit room at room temperature is probably connected with photochemical or oxygen promoted chain brominations of the alkyl halide itself. It is possible that the effect is due to impurities in the alkyl halides and reactions of either atomic bromine or Br_2 or HBr with these. This type of effect has been reported previously and is rather widely recognized by workers in hot atom chemistry. It is quite clear from these results that one must be careful

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in working with 34 hour bromine and weak neutron sources to eliminate this effect occurring during long exposure. By using the cyclotron it was possible to obtain sufficient intensity with short exposures.

Summary

The study of the hot atom chemistry of the propyl bromides has revealed evidence for isomerization proceeding during the formation of the mono brom derivatives and of temperature independence of the yield of these derivatives. In direct contrast, the formation of the di brom derivatives by hydrogen substitution is either strongly temperature dependent or strongly dependent on the phase, for the yields obtained at liquid nitrogen temperatures are very much larger than those obtained in the liquid at room temperature. In addition certain effects of the presence of Br_2 during irradiation have been found. These results seem to be explicable in the main by a billiard ball type of collisional theory previously proposed for other cases. Certain points seem to strain this theory considerably, but for the present it seems to be the most tenable.

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BETA DECAY OF Ce^{144} AS THE ACETYLACETONATE TO Pr^{144}

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A study was undertaken of covalent bond rupture in cerium acetylacetonate on decay of cerium to praseodymium. Use was made of the 275d Ce^{144}, which decays by emission of β-rays of 0.348 Mev maximum energy to 17m Pr^{144}, which in turn can be followed by means of its 3.07 Mev β-rays. The transformation of Ce^{144} is not complicated by γ-rays or conversion electrons[1].

Of the many advantages found in this system, one of the most striking is the speed with which studies may be made after the medium for decay is selected. In a period of two hours, essentially all of the Pr^{144} has been replaced by a new growth, so that examined after such a period is known to have been formed under the conditions applied. Following the decay period, a fractionation yields samples which will, if any chemical separation is achieved, show either radioactive growth or decay, and the extent of the growth or decay to the constant activity in secular equilibrium with Ce^{144} is a direct measure of the degree of chemical separation of Ce and Pr. Graphic examples of this determination are given below.

Since Ce acetylacetonate is obtainable in crystalline form, this system presented an opportunity for study of bond rupture accompanying β decay in the solid state, as well as in organic solutions. Extractability of the Pr daughter by water, or its separation to the vessel walls were taken as criteria for bond rupture, although reactions of an excited Pr acetylacetonate molecule or ion with materials in the medium could not be excluded in every case.

The maximum recoil energy for the Pr^{144} in the β decay process will be 1.8 ev or 41 kcal/mole, which may be near the energy of the Pr-O bond in Pr acetylacetonate.

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However, if the equation of Suess[2] is applied, assuming the three acetylacetonate fragments act as a mass unit, we find that only about 0.4 ev should be available for internal excitation. This almost certainly does not approach the energy of even one bond, so that disruption in the recoil process itself should not be highly probable. Thus extensive bond rupture in the absence of chemically disturbing influences must be attributed to a high degree of ionization in the decay processes, analogous to the explanation offered for rupture in isomeric transition reactions. Where reactions with the medium are likely, however, the internal energy gained in the recoil process may serve as activation energy, leading to selective reaction of the excited (radioactive) species.

Experimental

Preparation of Ce^{144} Acetylacetonate

In experiment 1, Ce acetylacetonate was prepared as follows: A solution of cerous nitrate (200 mg Ce) in 20 ml 1 M HNO_3 was prepared, and about 1 μc of Ce^{144} as the Oak Ridge carrier-free tracer added. Ce was then precipitated as the hydrous oxide by addition of an excess of 16 F NH_4OH. The precipitate was centrifuged off, washed twice with 20 ml EtOH to remove most of the water, and then 0.5 ml of acetylacetone was added to form a thick sludge. About 20 ml of this mixture was then added to 5 ml C.P. CS_2 for the experiment.

The sample Ce-AA-I was prepared as follows: To a solution of cerous nitrate (10 mg Ce-ml) in 20 ml 1 N HNO_3 was added 1 ml of a Ce tracer solution containing about 20 μc Ce^{144}. The Ce was then precipitated as the hydrous oxide by addition of an excess of NH_2OH. The precipitate was redissolved in a minimum of 1 N HNO_3. A solution of ammonium acetylacetonate (20 ml acetylacetone, 20 ml H_2O, and 20 ml 16 F NH_4OH) was then added until a pH of 8 was reached. The resulting solution (about 20 ml) was placed in a refigerator for 20 hours. The crystalline precipitate that had formed was centrifuged off and washed twice with EtOH to

remove water, then dissolved in 10 ml warm CCl_4, the solution centrifuged, and the insoluble residue discarded. About 30 ml n-hexane was then added, and the solution placed in the refrigerator overnight for crystallization. The crystals were centrifuged off, washed once with n-hexane, and dried in air. This preparation was considered to be free of excess acetylacetone.

The sample Ce-AA-II was prepared in a similar manner to that just described, except that the final precipitate was dissolved in CS_2 immediately after centrifugation.

For the final experiment of this series, the sample Ce-AA-III was prepared as follows: A solution of 20 ml cerous nitrate in 1 M HNO_3 was added to a carrier-free Ce^{144} solution containing about 1 uc in 10 ml of dilute HNO_3. A concentrated solution of ammonium acetylacetonate prepared as described above was then added to yield the crystalline Ce acetylacetonate. The precipitate was centrifuged off, washed once with 10 ml H_2O, twice with 10 ml EtOH, and twice with 10 ml ethyl ether. After drying in air at room temperature, 20 ml CS_2 was added, and the mixture heated over steam. The undissolved residue was filtered off, and the saturated solution collected for use.

A sample of inactive Pr acetylacetonate was prepared from a Pr nitrate solution as just described for the Ce compound. A saturated solution of this material in CS_2 was also prepared.

Experimental Procedures

Most of the experiments with the Ce-Pr pair were conducted with mixtures of organic solvent and water, with the radioactive Ce compound initially in the organic phase. The assumption was made that Pr daughter atoms ejected from the molecules would favor the aqueous phase, and that a good separation of bonded and non-bonded Pr would be obtained by separating the two liquid phases. Consequently, samples of radioactive Ce acetylacetonate were dissolved in the specified

organic solvents, water and, in some cases, excess acetylacetone were added, and the resulting mixtures were shaken mechanically in glass stoppered Erlenmeyer flasks for periods of time sufficient to allow essentially complete replacement of the 17m Pr daughter, usually not less than two hours. After this period, samples of the organic phase were evaporated in 1 inch Al planchets for counting. Counts were taken with a thin mica-window Geiger-Mueller tube, with 90 mg/cm^2 of Al between source and counter window, so that only the harder (3 Mev) radiation of Pr^{144} was actually counted. In this manner, as counts were taken as function of time after separation of the phases, growth curves were obtained, which, when extrapolated to the time of separation, indicated the extent of Pr removal from the organic phase. Evaporated samples of the aqueous phase exhibited decay, but quantitative interpretation of the data was difficult because of the extent of hydrolysis of the Ce compound during the course of the experiments. Consequently, the data obtained from counting the samples of organic phase only are presented here for most of the experiments.

Results

Experiment 1

The first experiment was designed simply to determine the partition of the Pr^{144} daughter between H2O and CS2. A sample of 2 ml CS2 solution of Ce^{144} acetylacetonate, prepared as described in the experimental section, containing excess acetylacetone, was added to 2.4 ml H2O and shaken mechanically for 2 hours. At the end of this period, 1 ml of the CS2 phase and 2 ml of the H2O phase were evaporated separately in Al planchets, and counted for growth and decay, respectively. The results are plotted in Figure 8, together with the derived curves extrapolated to zero time, showing that about 7000 c/m of Ce^{144} was in the CS2 phase at the end of the experiment, and that essentially this amount of Pr^{144} had been removed from the organic phase. Only about 30% of the Pr counts missing

from the organic phase were recovered in the aqueous phase, indicating some loss from the system, perhaps by deposition on the vessel walls. In any case, it is clear that the Pr daughter was completely removed from the CS_2 phase, presumably as Pr ion. The extent of hydrolysis of the Ce compound (about 20%) is indicated by the equilibrium value for the aqueous phase, 2600 c/m. Because of this hydrolysis and the poor material balance, the practice of counting evaporated samples of the aqueous phase was abandoned.

Experiment 2

To determine whether free Pr ions formed in the decay process survive in CCl_4 solution, a sample of 2.8 mg Ce-AA-I was dissolved in 5 ml CCl_4 and allowed to stand for one hour. At the end of this period, 1 ml was evaporated in an Al planchet and counted as a function of time. No radioactive growth was observed, indicating that no separation of Pr to the vessel walls was effected.

The remaining 4 ml of CCl_4 solution was extracted with 4 ml H_2O in 30 seconds shaking, and 1 ml of the CCl_4 phase evaporated and counted as above. Again no growth was observed, indicating that no extractable Pr (free Pr ions) existed in the organic phase after more than one hour of standing.

Experiment 3

The third experiment was designed to determine whether Pr^{144} ions are formed in crystalline Ce^{144} acetylacetonate. About 5 mg Ce-AA-I was dissolved in 10 ml CCl_4, 5 ml H_2O immediately added, and the mixture shaken for 30 seconds in a separatory funnel. The phases were then separated, and 2 ml of the CCl_4 phase evaporated for counting. No growth was observed, indicating either that no Pr ions are formed in the solid Ce^{144} acetylacetonate, or that such ions exchange with Ce carrier, assuming the central positions in acetylacetonate molecules.
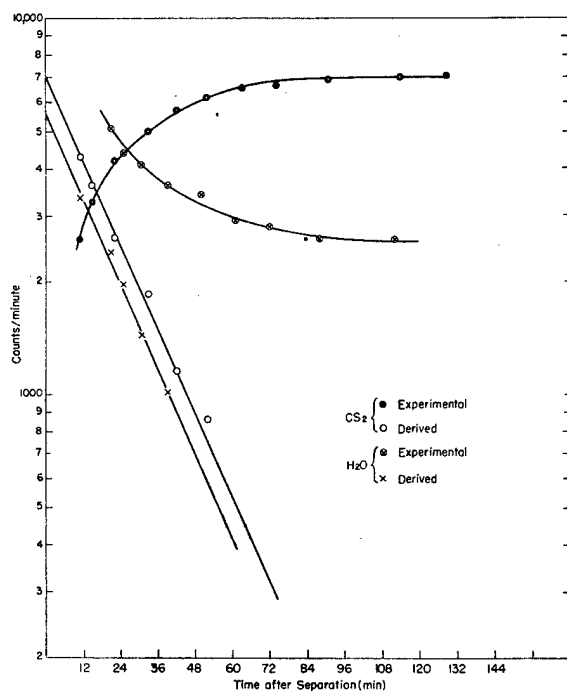
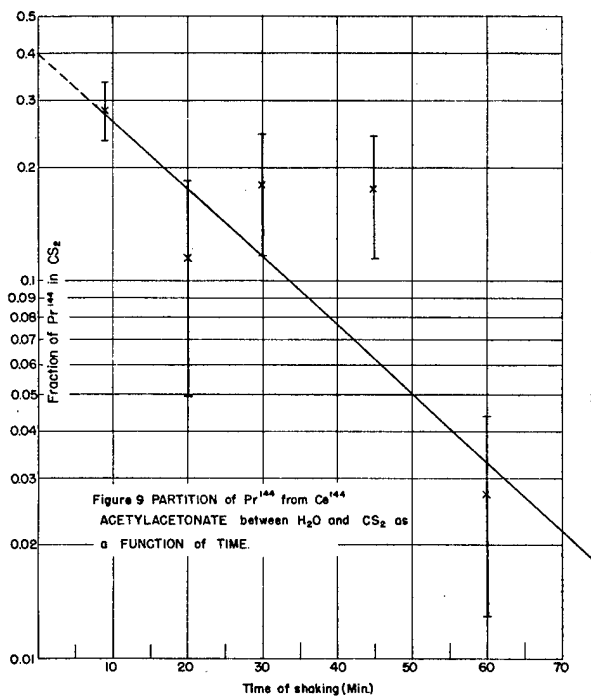Figure 8 Separation of Carrier-Free Pr[144] to Aqueous Phase from Ce[144] Acetylacetonate in CS_2

Figure 9 PARTITION of Pr[144] from Ce[144] ACETYLACETONATE between H_2O and CS_2 as a FUNCTION of TIME.
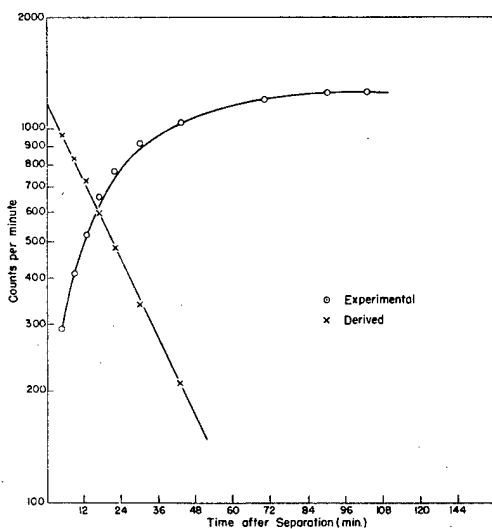

Figure 10 Separation of Pr[144] to Aqueous Phase from CS_2 Containing Ce[144] Acetylacetonate and Pr Acetylacetonate Carrier
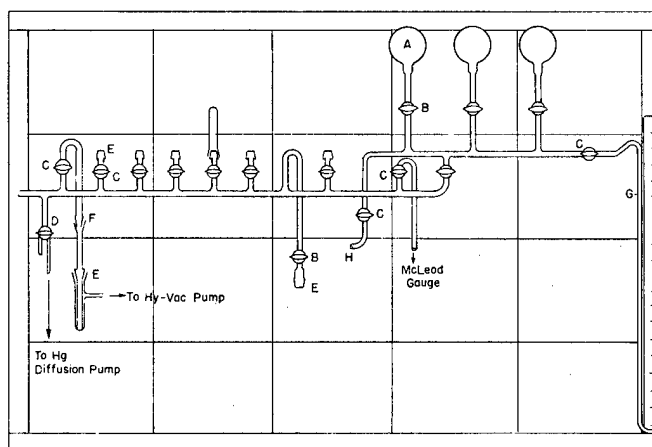

Figure 11 Apparatus for Determination of Bond Rupture in the Gas Phase

Experiment 4

To determine whether free Pr ions are formed and can exist in CS_2 solutions for reasonable periods of time, about 10 mg Ce-AA-I was dissolved in 10 ml CS_2, and the solution allowed to stand for 18 hours in a glass stoppered Erlenmeyer flask. A 2 ml sample of the solution was then evaporated in an Al planchet for counting. No growth was observed, indicating that no separation of Pr^{144} to the walls from CS_2 solution occurred.

The remaining 8 ml of CS_2 solution was extracted with an equal volume of H_2O in 30 seconds shaking, and 2 ml of the organic phase evaporated for counting. A deficiency of 220 c/m of a total of 705 c/m was observed, indicating either (a) that 30% of the Pr existed in CS_2 as free ions, or (b) that the Pr compound is much more rapidly hydrolyzed in its carrier-free state than the Ce compound at reasonable concentrations.

Experiment 5

The fifth experiment was disigned to determine the effect of excess acetylacetone on the Ce-Pr separation. Two samples of Ce-AA-I in CCl_4 (10 mg in 5 ml) were prepared, and 5 ml H_2O added to each. To one of these mixtures was added 1 ml acetylacetone, and then both were shaken mechanically for 1 3/4 hours. Samples of 1 ml of each of the organic layers were evaporated and counted. No growth was observed in the sample which was free of acetylacetone, but growth indicating complete removal of Pr^{144} from the organic phase was observed in the sample which had contained excess acetylacetone, similar to the result obtained in experiment 1. Thus it is clear that an excess of acetylacetone assists in the Ce-Pr separation.

Experiment 6

To compare the time dependence of the Pr extractability with the period of the nuclear transformation, an experiment was designed to show the rate of

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disappearance of Pr^{144} from the organic phase as a function of time after the beginning of the shaking period. A sample of 5.5 ml of the CS_2 solution of Ce-AA-II was added to 2 ml H_2O and 1 ml acetylacetone in a 25 ml Erlenmeyer flask, and the mixture shaken mechanically. At various times, 0.5 ml samples of the CS_2 phase were taken, and evaporated in Al planchets for growth determinations. Such samples were prepared at 9, 20, 30, 45, 60, and 90 minutes after preparation of the mixture. Each of these samples was then counted as a function of time after sampling, yeidling data which permitted caluclation of the extent of depletion of Pr in the organic phase. Figure 9 shows the results, plotted as the fraction of the equilibrium value of Pr^{144} which was found there after various times of shaking. Treatment of the data in this manner involved some magnification of the experimental (counting) errors* as indicated by the bars on each point, but it is seen that the data are not inconsistent with a 17 minute half-life for the loss of Pr^{144} from the organic phase, corresponding to the straight line drawn in Figure 9.

Experiment 7

The final experiment of this series was designed to determine whether the extraction of Pr^{144} to the aqueous phase was due merely to its rapid hydrolysis in the carrier-free state, testing the tacit assumption that the Ce compound would serve as its carrier. If this were the case, then one would expect that addition of carrier amounts of Pr acetylacetonate to the organic phase would prevent the Ce-Pr separation, since little difference is expected between the rates or equilibrium values for the hydrolysis of Ce and Pr acetylacetonates.

A solution was prepared consisting of 5 ml Ce-AA-III solution in CS_2, 5 ml

*The error given is the standard error (statistical) for a given number of counts (N), numerically equal to $\sqrt{N}$. Subtraction of values one from the other, as performed with these data, increases the error considerably.

Pr acetylacetonate solution (see Experimental), and 1 ml acetylacetone. This solution was added to 5 ml H_2O in a 25 ml glass stoppered Erlenmeyer flask, and the mixture shaken for two hours. One ml of the CS_2 phase was then evaporated in an Al planchet, and counted for growth. The results, shown in Figure 10, again show essentially complete removal of radioactive Pr from the organic phase, although the Ce compound, and presumably therefore the Pr carrier compound, was only partially (about 60) hydrolyzed. These data indicate selective disruption of the "hot" Pr acetylacetonate molecules or ions in the presence of a normal molecular carrier.

Discussion

The results of this series of experiments seem to indicate (a) that no extensive irreversible rupture of the acetylacetonate molecules occurs in the solid or in dry organic solvents, and (b) that some chemical change occurs when Ce^{144} decays as the acetylacetonate in organic solvents in contact with water and in the presence of excess acetylacetone. Whether this latter combination of conditions prevents recombination of fragments or merely serves as a medium for hydrolysis of the excited species is not clear.

On the basis of the results of experiments 2, 3, 4, and 5 it appears unlikely that the Pr daughter is separated from the molecular bonds at the instant of decay, since separation to the aqueous phase would have been expected in all of these cases, perhaps to varying degrees. Again, if this separation of Pr from the molecule occurred in every event, one would expect that an excess of acetylacetone would serve to aid in reforming the acetylacetonate molecule, decreasing rather than increasing the probability that the Pr daughter will be found in the aqueous phase.

If, however, the separation of Pr^{144} to the aqueous phase is dependent on its selective hydrolysis, it is clear that the hydrolysis requires excess

acetylacetone. This requirement is not readily explained chemically, but it is conceivable that some intermediate compound which is readily hydrolyzable is formed between the "hot" Pr ion and acetylacetone, whereas stabilization may occur by other mechanisms in the absence of excess acetylacetone. For example, we may assume that the decay process proceeds with the minimum of chemical change, as expressed by the equation:

$$\overset{*}{C}eA_3 \longrightarrow \overset{*}{P}rA_3^+ + \beta^-$$
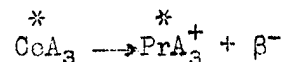
where A is the acetylacetonate ion. In the absence of acetylacetone, the most prominent solute in the organic phase is CeA_3, and oxidation potentials are undoubtedly favorable for the stabilization reaction:

$$\overset{*}{Pr} A^+_3 + CeA_3 \longrightarrow \overset{*}{Pr} A_3 + CeA_3^+$$
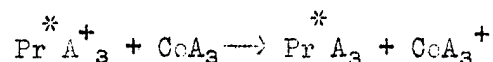
In the cases where acetylacetonate was added, however, its concentration was much higher than that of CeA_3, so that the following reaction should have been highly probable:

$$PrA_3^+ + HA \longrightarrow PrA_4 + H^+$$
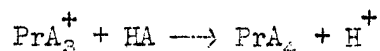
In this case the PrA_4 might have been reasonably stable in the non-polar solvent, but certainly would undergo reactions on reaching the aqueous phase. Such reactions should involve both hydrolysis and reduction, and may be expressed for example by the equation:

$$PrA_4 + 3 H_2O \longrightarrow PrO^+ + 4HA + OH^- + HO$$
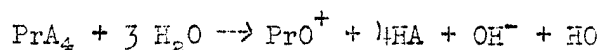
Although the explanation offered here is not detailed, it seems acceptable, particularly in view of the dissimilarity of the "hot" Pr species and its carrier and of the low recoil energy (1.8 ev maximum). Also, the results presented in the following paper indicate that no extensive ionization occurs in the emission of low energy β particles, so that the postulation of a PrA_3^+ fragment seems reasonable.

An additional possible explanation of the results is that the acetylacetone

serves as a water-carrier, transporting H_2O molecules into the organic phase where the nuclear events occur. Water so transported would be capable particularly of hydrolyzing the excited Pr daughter species, since the recoil certainly provides an energy comparable with the activation energy of a reaction which, judging from the results of experiment 1, proceeds at an appreciable rate at room temperature.

References

The references for this and the following paper are listed on page 70

EFFECTS OF BETA TRANSFORMATIONS IN THE GAS PHASE

R. R. Edwards and C. D. Coryell[*]

Extension of the studies of the chemical effects of beta decay to gaseous systems follows logically from the difficulties in interpreting the data from liquid systems. The omnipresent solvent molecules in condensed media provide reaction cages for the excited species to occupy for relatively long periods of time, and in many cases themselves undergo reactions with the newly-formed species, obscuring the true nature of the effects due to the transformation itself.

Recombination of fragments to form the parent compound in cases of neutron capture and isomeric transition has been discussed in paper 6, and it was seen that dilution of a liquid target with compounds of lighter elements diminished this effect. Suess[2] has studied these processes with Br^{80} in gaseous compounds (HBr and C_2H_5Br) finding that recombination is negligible, and that essentially all of the radioactive atoms (resulting from (n, γ) reactions or isomeric transition with internal conversion) are ejected from the parent molecule.

It was therefore expected that much clearer results concerning the rupture of covalent bonds in the β decay process could be obtained with gaseous compounds. Extensive bond rupture could be attributed to the energy of recoil, as in the (n, γ) reactions, or to a high degree of ionization, as in the internal conversion process. In the gas phase, particularly at low pressures, no obscure solvent reactions can occur as in the Se-Br case, and no hydrolysis or cage-recombination effects are expected, such as those possible in the cerous acetyl-acetonate studies.

The radioactive pair $Pb^{210}-Bi^{210}$ (RaD-RaE) was chosen as the first system for gas phase study since the radio-nuclides are readily available, since their radiation characteristics and half-lives are favorable, and since both are known to form volatile alkyl compounds. Experiments were planned on the assumption that

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the radioactive Bi from ruptured $Pb(CH_3)_4$ molecules in the gas phase would deposit on the vessel walls and could be detected there by means of its β radiations.

This system has been studied previously by Mortenson and Leighton[3], who found that essentially all of the Bi (RaE) daughter and Po (RaF) granddaughter of RaD decaying as $Pb(CH_3)_4$ in the liquid state (presumably in the absence of air) existed after the decay period as volatile compounds. The conclusion from these data that no bond rupture occurs in either of these transitions is, however, unwarranted, since it has now been demonstrated that a large fraction of the products of nuclear reactions reform the parent molecule in condensed media.

The 22y Pb^{210} is readily obtained from spent radon seeds. It decays by the emission of β^- particles of maximum energy 0.025 Mev to the 5.0d Bi^{210}. Several γ rays accompany the transition, the principal one with an energy of 46.7 kev reported to appear in 2.8% of the transitions, and its conversion electron in 8% of the transitions. No information is available concerning conversion of the weaker γ rays, but five others are said to occur with energies between 7 and 45 kev, all of relatively low intensity[4]. Conversion in the K shell is impossible for the known γ rays, and conversion in the L shell apparently is not extensive, since the total intensity of γ rays above the L edge is about 1.8%, exclusive of the principal γ ray mentioned above.

Because of its low decay energy Pb^{210} is particularly suited for studies of bond rupture in the β decay process, since either of two main processes may be responsible for the rupture of bonds, viz. recoil processes or ionization. The latter is a factor of unknown importance, since the disposition of the orbital shrinkage energy is not established, and since no experimental data concerning ionization are at hand. In the case of the decay of a nuclide of mass 210, and β energy 0.025 Mev, however, the maximum recoil energy is about 0.068 ev, which

is barely above thermal energies, so that no bond rupture due to the recoil process is possible; thus bond rupture observed in the decay of Pb^{210} as $Pb(CH_3)_4$ to Bi^{210} can be attributed unequivocally to ionization processes, whatever their origin.

Dependence of the bond rupture on pressure of the parent compound, $Pb(CH_3)_4$, or of the daughter compound, $Bi(CH_3)_3$, might be positive, negative, or absent, depending on the nature of the important bond rupturing and recombination processes. If bond rupture depends chiefly on intermolecular collisions between the excited and normal species (not a likely condition when the initial recoil energy is far less than the bond energies), then the extent of rupture would be expected to increase, with increments in the total pressure of the system. If, on the other hand, reaction of free daughter atoms or ions with molecules of the parent compound, or with (carrier) molecules of the daughter compound can reconstitute an important fraction of the ruptured molecules, the apparent bond rupture would decrease with increasing pressure. The third and seemingly most attractive possibility in the case at hand is that collisions will contribute little to the rupture, since kinetic energies of the newly-formed species are so low, and little to recombination, since (1) no " cage" reactions can occur analogous to those in condensed media, and (2) too little energy is available in the recoil process to account for the rupture of bonds in neighboring molecules necessary to produce reactive (alkyl) fragments to participate in the recombination. If this third condition applies, little or no pressure dependence of the bond rupture is expected. Dependence of the apparent rupture on pressure of inert gases would of course distinguish rupture and recombination effects if an important pressure dependence is found.

Experimental

Apparatus

An all-Pyrex apparatus was designed and built, with provisions for introducing and storing the gases in vessels previously evacuated to 10^{-4} mm Hg. Seven reaction tubes of 50 cc capacity were provided for pressure variation studies. The apparatus is shown schematically in Figure 11. Gaseous materials were introduced at E from 50 ml distilling flasks equipped with 10/30 standard taper joints, and stored temporarily in the flasks A. The items marked B are pyrex 4 mm oblique stopcocks, C are 2 mm stopcocks, D are 2 mm three-way stopcocks, E are 29/42 standard taper joints (one reaction tube is shown in place), F is a 19/38 standard taper joint, and G is a mercury manometer. The trap below F was used for condensing the gases removed from the system after an experiment. Samples of the gas admitted to the system were sometimes collected for condensation and analysis in a tube attached to E at the left of H. The system was evacuated by a mercury diffusion pump, supported by a Welch Duo-Seal pump. Pressures during the evacuation were determined with the McLeod gauge, while pressures in the experiments were determined with the manometer.

Preparation of Materials

Lead tetramethyl containing the 22y Pb^{210} was prepared by the method of Calingaert[5] involving reaction of dry $PbCl_2$ with a methyl Grignard reagent, as described below.

A sample 70 g of $Pb(NO_3)_2$ containing Pb^{210} at a specific activity of about 180 c/m-mg at 20% geometry was dissolved in dilute HNO_3 and metathesized to the chloride by addition of a large excess of concentrated HCl. The resulting precipitate was collected on a Buechner filter, washed several times with cold water, and dried in air at 110° for 24 hours.

Methyl magnesium bromide was prepared by passing CH_3Br through a 16 inch

$CaCl_2$ tube into 100 ml absolute ethyl ether containing 19 g Mg turnings (cooled in an ice bath) to complete reaction of the Mg. The mixture was then stirred with a mercury seal stirrer, and 50 g $PbCl_2$ added slowly, with continued cooling in ice. The mixture was then heated on a steam bath for two hours under a reflux condenser. The excess Grignard reagent was then decomposed with chipped ice, and the aqueous and ether phases separated. The ether phase was dried over $CaCl_2$, and the ether distilled off over a steam bath. The $Pb(CH_3)_4$ was then distilled over at a boiling temperature of about 109-110°C, yield about 7 ml (14 g).

Analytical and Radiometric Procedures

(a) Analysis of $Pb(CH_3)_4$ for Bi^{210}:

For the determination of the total amount of Bi^{210} present in a sample of radioactive lead tetramethyl, 0.02 ml of the liquid was treated with Br_2 in a CCl_4 solution, in the presence of a few ml of 1 M HNO_3 containing about 10 mg Bi^{III} from a standardized solution to serve as carrier. The CCl_4 and Br_2 were then boiled off, and an excess of neutral Na phosphate solution added to precipitate $BiPO_4$, which was centrifuged down, washed with H_2O and EtOH, then transferred to a tared Al planchet, dried under an infra-red lamp, weighed, and then mounted for counting. The fraction recovered was determined by comparing the sample weight with the standard weight of $BiPO_4$ obtained from the aliquot of the carrier solutions, thus allowing a correction for chemical yield of the analysis.

In several cases, attempts were made to perform this analysis on the material trapped out after a decay period in the gas phase, but material balances and duplicates were poor, so that this practice was abandoned. This technique, therefore, was used only to determine the Bi^{210} titer of the material used in the experiments at the time of its use.

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(b) Counting of BiPO$_4$ Samples:

Samples prepared as described in (a) above were mounted on standard white cards, covered with a polystyrene film, and counted in the first shelf (20% geometry) below a thin mica window Geiger-Mueller tube. The β particles of Bi^{210} are energetic enough that a sample weight of 8-12 mg did not contribute appreciable self-absorption.

(c) Determination of Bi^{210} Deposited on Vessel Walls:

In the experiments designed to determine bond rupture in Pb(CH$_3$)$_4$ in the gas phase, the material was introduced into the 50 cc reaction tubes at various pressures, and the Pb^{210} allowed to decay for a period of several days to form Bi^{210} in an appreciable fraction of the amount in secular equilibrium. At the end of this decay period, the Pb(CH$_3$)$_4$ was pumped out with the vacuum pump into a trap cooled with liquid nitrogen. Air was then admitted to the reaction tubes, and they were removed from the system. The material deposited on the walls of the vessels was then counted _in situ_ with a special counting arrangement. A glass walled, 3/4 inch cylindrical Geiger-Mueller tube (Eck and Krebs, wall thickness about 35 mg/cm^2) was mounted on a wooden base concentrically with a 29/42 standard taper joint (inner part). The reaction tubes were lowered over the G. M. tube and seated on the ground glass joint for counting, with the whole arrangement placed inside a conventional cylindrical lead shield. While the geometry of this counting arrangement must have been near 50%, tests with a set of standard evaporated RaE samples indicated an effective geometry of 15$\pm$2%, including absorption in the tube walls. The standard samples were prepared by evaporation of Pb(NO$_3$)$_2$ solutions containing a known amount of Bi^{210} on the walls of the 50 cc reaction tubes by irradiation with an infra-red lamp while the tube was undergoing slow mechanical rotation.* Four such samples were prepared and counted, with an average deviation as shown above. Consequently values obtained

*Some additional error was probably introduced by non-uniformity of the evaporated samples.

by counting the tube walls were multiplied by the factor 1.33 (20/15) for comparison with those obtained from counting solid $BiPO_4$ samples at 20% geometry.

Results

Two experiments were performed to determine the fraction of Bi^{210} daughter appearing in non-volatile form after the decay of Pb^{210} as gaseous $Pb(CH_3)_4$. In each case the liquid parent compound was frozen in a 25 ml distilling flask attached to the system, and this flask evacuated with the entire system to a pressure of 10^{-4} mm before the vapors were introduced into the reaction tubes. The total amount of $Pb(CH_3)_4$ in each reaction tube was determined from the pressure-volume relationship, and its specific activity with respect to Bi^{210} was determined by analysis of aliquots of the original liquid. By performing these analyses on several days, it was found that the radioactive compound was initially free of Bi^{210} after preparation* , so that in the first experiment, when the compound was fresh, all the Bi^{210} was formed in the gas phase. In the second experiment, the preparation was two weeks old, and thus contained a considerable quantity of the daughter. Since analysis of the residual gas proved impractical, this factor was unimportant, requiring only the assumption that the $Bi(CH_3)_3$ already existing in the preparation is not adsorbed appreciably as such on the vessel walls. This assumption is supported by comparison of the results of the two experiments.

The results of these two experimental series are shown in Table I. It is interesting to note that although tubes 6 and 8 had admitted air through stopcock leaks to near atmospheric pressures (as determined by the pressure transmitted to the entire system at the end of experiment II) no significant differences in the results were observed.

*Analysis of 0.01 ml (20 mg) aliquots of the liquid for Bi^{210} gave the following results: Fourth day, 134.8 c/m-mg Pb, 47.4% of saturation, theoretical value 47.5%. Eighth day, 196 c/m-mg Pb, 66.4% of saturation, theoretical value 67.0%.

Counts were taken of the tubes from experiment I at intervals of a few days for about 20 days (four Bi^{210} half-lives) after completion of the experiment, and no evidence of long-lived contamination, which could have resulted from decomposition of the parent compound, was detectable.

It is clear that, within the pressure limits and under the conditions applied, no pressure dependence of the bond rupture is observed. The average value of the percentage counted on the walls is 8.7 ± 1.6, where 1.6 is the probable deviation (50% error) in the series. If recombination were responsible for the high retention observed (about 91%), then some significant pressure dependence within the limits applied might have been expected.

Several attempts to determine the volatility of the Bi^{210} formed in liquid lead tetramethyl (in a glass stoppered Erlenmeyer flask) led to values which indicated considerably more bond rupture than found in the gas phase experiments, and much more than reported by Mortenson and Leighton[3], whose experiments apparently were performed in the absence of air. Two 0.01 ml samples of the $Pb(CH_3)_4$ (20 days old) were evaporated on 1 inch watch glasses, (a) in air at room temperature, and (b) in air under an infra-red lamp. Immediately after evaporation, (a) exhibited 53% of the theoretical Bi^{210} count, and (b) showed 59% . These samples decayed with the characteristic Bi^{210} half-life. In another experiment, a sample of $Pb(CH_3)_4$ was frozen in the upright tube attached to the system shown in Figure 11, and the entire apparatus evacuated through the trap at F. The trap was then cooled in liquid nitrogen, and the sample allowed to warm up to room temperature, then the entire sample was vaporized and pumped into the trap for condensation. Analysis of the trapped material showed that only about 5% of the Bi^{210} had been trapped there, whereas the tube from which the material was distilled showed about 60% of the total. The filtrate from the $BiPO_4$ precipitate in the distillate showed a strong test for Pb (H_2S), while

TABLE 1

FRACTION OF BISMUTH DAUGHTER DEPOSITED ON WALL IN DECAY OF LEAD AS LEAD TETRAMETHYL

Sample	Experiment	$Pb(CH_3)_4$ Pressure mm Hg	$Pb(CH_3)_4$ Weight mg	Day Removed	Bi^{210} Total (20% geom) (calc) c/m	Bi^{210} on Wall* (15% geom) c/m	Minutes Counted	Percent Bi^{210} on Wall
1	I	40	28	5	3200	160	8	7
2	I	40	28	7	3820	258	10	9
3	I	34	24	11	4520	161	20	5
4	I	18	13	11	2435	152	20	8
5	I	13	9	8	1400	73	25	7
6	II	18 (air)	13	4	1224	88	10	9
7	II	18	13	3	988	110	13	14
8	II	8 (air)	6	4	547	39	20	9
9	II	4	3	4	274	21	20	10

*The background of the tube wall counter varied between 34 and 38 c/m.

that from the material in the distilling tube gave a negative test, indicating that essentially all of the Pb was volatilized as $Pb(CH_3)_4$.

Discussion

The apparent bond rupture observed in the decay of Pb^{210} as $Pb(CH_3)_4$ in the liquid state can scarcely be attributed to the nuclear transformation, since no conceivable processes whereby rupture could be more extensive in the liquid than in the gas phase are at hand. The results of Fortenson and Leighton[3], furthermore, indicate no extensive rupture in the liquid state in the absence of air. Considering the results of the gas phase experiments reported here, however, little effect of air is allowed. A more likely hypothesis is that a small amount of water was in solution in the $Pb(CH_3)_4$, and that the carrier-free $Bi(Ch_3)_3$ is hydrolyzed. A test experiment with water showed that this hydrolysis occurs readily.

The fraction of bonds ruptured in the decay of Pb^{210} as $Pb(CH_3)_4$ to Bi^{210} in the gas phase is remarkably independent of the pressure of the parent compound, and coincides rather closely with the reported minimum extent of internal conversion (8%) in the nuclear transition. Since it is known from earlier experiments that ionization sufficient to set up bond-rupturing electrostatic repulsions occurs in the internal conversion process, and since parent-daughter separations in this process are easily effected, it is reasonable to assume that essentially all of the bond rupture observed here was effected by ionization due to internal conversion processes.

These considerations lead to the conclusion that ionization in the β^- decay process, at least for such a low energy particle (0.025 Mev), is not as extensive as in the conversion process, and probably not nearly so extensive, since conversion is generally conceded to lead to far more ionization than necessary to rupture simple chemical bonds. Considering only the primary effects of the β^-

transition, one would not predict a higher degree of ionization in the case of more energetic spectra.

The nuclide Pb^{210} is of particular interest with regard to the orbital shrinkage energy, which must be about 10 kev. Since the maximum decay energy is not much above that value (25 kev) it is difficult to see how interactions between the departing β particle and the orbital electrons could lead to the formation of Bi^{210} in its (atomic) ground state, unless indeed the actual mass difference between the two nuclei is only about 15 kev. If the daughter is left in a highly excited atomic state, dissipation of the stabilization energy must lead to a degree of ionization which is incompatible with the results reported here. Thus for the present, the shrinkage process must be considered either (a) adiabatic, leading to the ground or a low-lying excited state, or (b) non-adiabatic, leading to stabilization by emission of very soft (non-ionizing) radiation.

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THE OXIDATION STATES OF CHROMIUM ARISING FROM POSITRON DECAY OF MANGANESE

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Of factors which may influence the chemical properties of atoms arising from beta or positron decay, one of the more important is the recoil energy imparted to the decaying atom by the departing particles, the electron and neutrino, or the positron and antineutrino. Because of the present lack of knowledge of neutrino-beta angular correlations, calculations of recoil spectra are nearly impossible.

A second factor which may influence the chemcial properties of atoms produced in beta or positron processes, involves the readjustment of the orbital electrons to the new nuclear charge. If the decay process consists of independent ejection from the nucleus of a beta particle or a positron, then readjustment of the orbital electrons to the new nuclear charge will be quite different for beta decay than for positron decay. In the former case, the electronic arrangement which describes the ground state of the parent, becomes an excited state for the daughter. In the latter, a sub-normal electronic state would result, and energy would need to be introduced to bring the electrons up to the ground state for the daughter atom. The difficulties encountered in picturing the β^+ decay in this way are immediately obvious, and the true picture involves sufficient interaction of the electrons with the particles involved in the decay process to leave the electrons in at least a ground state for the daughter atom. It may also be possible for some of the electrons to be raised to excited levels, and even for ionization to occur. Probabilities of ionization from various levels for processes involving both increase and decrease in nuclear charge have been calculated by Migdal[1]. A more elaborate calculation for probability of ionization from the K-shell has been carried out by Feinberg[2].

Another factor which may play on important role in determining the chemical

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properties of atoms undergoing beta or positron decay is the chemical oxidation state of the parent species. If the parent atoms were in a given oxidation state, and no serious electronic disturbance were to occur during decay in a chemically inert medium, then the daughter of a beta emitter might be expected to exhibit an oxidation number one higher than that of its parent, while the daughter of a positron emitter might be expected to have an oxidation number one lower.

In addition to the above factors, which may directly influence the chemical properties of daughter atoms of beta or positron emitters, there may also be secondary or indirect factors, which may play important roles in determining final chemical forms. As a result of the primary processes, the daughter atoms may be found at tracer concentrations in a chemical form not ordinarily encountered at macro concentrations. Studies of such phenomena have been meager and little is known about this subject called "tracer solution chemistry". However, if such a chemical species could exist it could conceivably undergo further reactions which could determine the final chemical state of the daughter. One of these reactions might be exchange with another chemical form of the element added as carrier. Thus the bulk of the daughter atoms originally in one state would ultimately exhibit the chemistry of another-the added carrier (providing this particular carrier did not exchange with other carriers also present).

Another secondary process of great importance in determining the ultimate chemical form of the daughter of a beta or positron emitter, is chemical reaction of the daughter atoms with the surrounding medium. This may occur as a result of one or more of the primary processes of ionization, electronic excitation, or high recoil energy, or as the result of the appearance of the daughter in a non-stable chemical oxidation state. By allowing decay to occur in the gaseous state at low pressures the importance of such reactions may be minimized.

However, gaseous experiments may not always be possible, and reactions with other molecules must often be tolerated.

From the preceding considerations, it is clear that the final chemical forms in which daughter atoms of a beta or positron emitter are found may be determined by one or more of several important and possibly competing factors. The object of the present investigation was to determine the chemical forms assumed by chromium, when it is formed by positron decay of manganese. By adjusting variables such as the oxidation state of the manganese, the temperature, the composition of the medium in which decay occurred, etc., it was hoped to learn something of the nature and importance of two of the factors which may determine the chemical form of the chromium, viz. the oxidation state of the parent, and subsequent reactions of daughter atoms with other molecules.

For this study the positron-decaying manganese isotope of mass number 51 was used. Emitting positrons of 2.0 mev. maximum energy, this isotope decays to Cr^{51}, which in turn decays by K-capture to stable V^{51}. The latter decay also involves 0.32 mev gamma emission occurring in about 3-5% of the transitions. Some of these gamma rays are internally converted, and in this study the Cr^{51} was detected by means of these conversion electrons and of the x-rays following K-capture.

Mn^{51}, produced by deuteron-bombardment of metallic chromium at the Washington University cyclotron, was isolated from the target and cleaned of all Cr^{51} grown during the isolation procedure, and initially present due to a competing reaction. The Mn^{51}, with added carrier, was placed in a definite oxidation state and allowed to decay. In cases of decay in solution, carriers for Cr(III) and Cr(VI) were always present. For decay in the solid states, the manganese salt was permitted to decay in the absence of Cr carriers. To effect separations the Cr carriers were added afterwards when the salts were dissolved.

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Cr(III) and Cr(VI) were shown to undergo only a very slow exchange of chromium, so no error was introduced by this exchange. Cr(II) was not looked for, because of its expected exchange with Cr(III), and because of the difficulties of Cr(II) chemistry. Separation of the daughter Cr^{51} into Cr(III) and Cr(VI) fractions was made by precipitation of lead chromate at pH 2. After separation, extensive purification of each fraction from foreign activities was necessary.

The results of the decay experiments are summarized as follows: Decay of Mn^{51} incorporated into solid dry $MnCO_3$ and then dissolved (after decay) in 0.1 f nitric acid containing Cr carriers yielded $(70.2 \pm 2.1)\%$ of the Cr^{51} as Cr(III) and $(29.8 \pm 1.1)\%$ as Cr(VI).

Decay of Mn^{51} as manganous ion in aqueous solutions produced nearly all of the Cr^{51} in the trivalent form, with only about 1% separable as Cr(VI). This distribution between Cr(III) and Cr(VI) in aqueous solution was independent of the pH of the solution between pH 4.56 and a pH equal to that of 8.45 f nitric acid. In each case essentially all of the daughter Cr^{51} was in the form of Cr(III).

By cooling solutions to liquid air temperature and allowing decay to occur at that temperature, then melting and separating, the Cr(III) fraction was found to have $(95.4 \pm 1.9)\%$ of the total Cr daughter and the Cr(VI) fraction to have $(4.6 \pm 0.6)\%$.

Another condition in which decay of Mn^{51} as manganous ion resulted in some daughter activity being in the higher oxidation state was obtained when the aqueous solution in which decay occurred was diluted with organic solvents. In an acetone-water solution in which the mol fraction of acetone was 0.60, $(88.2 \pm 2.7)\%$ of the daughter appeared in the Cr(III) fraction while $(11.8 \pm 1.4)\%$ appeared in the Cr(VI) fraction. In a dioxane solution in which the mol fraction of dioxane was 0.565 the Cr(III) contained $(89.7 \pm 2.8)\%$ of the daughter atoms and the Cr(VI) contained $(10.3 \pm 1.8)\%$.

Decay of Mn^{51} as MnO_4^- in aqueous solutions showed that in all solutions between pH 1.17 and 0.28, $(50 \pm 3)\%$ of the daughter appeared as Cr(III) and a like amount as Cr(VI). While it is thermodynamically possible to oxidize Cr(III) with MnO_4^- at the concentrations employed, spectrophotometric studies showed that this did not occur at a sufficiently rapid rate to be important. Further, because no dependence of the per cent of daughter in Cr(VI) fraction upon MnO_4^- concentration was found, oxidation of daughter by MnO_4^- was shown to be unimportant. By freezing to liquid air temperature the solution in which Mn^{51} as MnO_4^- decay occurred, the amount of Cr(VI) increased from 50% to $(62.4 \pm 1.4)\%$.

Summarizing the results, it can be said that decay of Mn^{++} as dry $MnCO_3$ yields a considerable fraction of the daughter atoms (30%) in a state which, when dissolved, can form, or exchange with $CrO_4^=$. When decay of Mn^{++} ion occurs in solution, the water effects chemical reduction of this 30% to a form which follows Cr(III) chemistry. When the solutions are frozen to liquid air temperature a small fraction remains in an oxidized state. Likewise addition of organic solvents results in less reduction.

Decay of MnO_4^- leaves about one-half of the daughter in a state which forms $CrO_4^=$ or can exchange with it. Again, freezing in liquid air reduces the fraction of daughter atoms chemically reduced to a form exchanging with or carried by Cr(III).

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THE EXTENT OF INTERNAL CONVERSION IN Br^{80*}

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Chemical reactions induced by isomeric transition in Br^{80*} have previously given yields up to about 90%, indicating that internal conversion must be at least this extensive.[1,2] Recently reported physical measurements have indicated that the transition proceeds in two steps, one of which is completely converted, as evidenced by failure to detect the appropriate unconverted gamma ray.[3,4] We have attempted two methods of isomer separation selected to provide, if possible, a reliable estimate of the maximum extent of conversion, and therefore, of chemical reactivity.

Separation of isomers by ion collection in an electrostatic field is an obvious choice for such a determination, since ionization can be expected only with internal conversion. Further we wished to use a substance such as hydrogen bromide, which would be expected to show no separation of a purely chemical nature. Briefly, the plan of the experiments was as follows: Gaseous hydrogen bromide of high specific activity (4.4h Br^{80*}) is placed in an evacuated electrolysis chamber consisting of a cylindrical outer electrode and an axial wire. Imposition of a high field at gas pressures such that the mean free-path will be at least as large as the electrode separation should remove ions formed in the gas phase during decay. The proposal was to remove and count the gaseous sample after an appropriate growth period, but this point was not attainable. Extensive loss of activity (4.5 h) occurred in the chamber, probably due to absorption and chemical reactions with construction materials, and it is feared that these effects and the property of no ordinary chemical separation of isomers may be inseparable.

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The second method of attack consists in a choice of the most favorable conditions for a chemical separation. This we believe means gas phase experiments, to avoid cage effects leading to retention, and the introduction of an acceptor molecule which will readily combine or exchange with nascent daughter particles. Finally, it must be possible to remove Br^{80} (18 m) and begin counting Br^{80} (4,5 h) within a brief interval, since the ratio of counting rates at zero time (moment of separation) is a measure of the conversion efficiency. The following procedure proved to be satisfactory: The total Br* activity, as AgBr*, was converted to $AlBr_3$* and exchanged with CH_3Br; water was added to destroy $AlBr_3$ and CH_3Br* was then distilled from P_2O_5 and HBr (0-50 mole%) added. This gaseous mixture remained at room temperature for two hours. The CH_3Br* was transferred within an interval of ten seconds, to the cold finger of a gas sample holder surrounding a thin wall counter; HBr was removed during transfer by an interposed soda-lime tube. Counting of the gas sample, at a fraction of its vapor pressure, started within thirty seconds and continued through the decay of Br^{82} (34 h). In the counting arrangement used, the counting efficiency of Br^{80} (4.5 h) is quite negligible, and therefore its activity must be measured through its 18 m. daughter.

After correcting for a small Br^{82} (34 h) contribution and for background, the residual growth and decay curve may be expressed in the usual exponential form. The analytical results of the data for four separate runs are given in the accompanying table. The figures given for separation efficiency must be 1.00 or less. The average of the four values may be given as 0.98 ± 0.02. It is interesting to note that the experiment with no HBr also gives rather complete separation, although this might be expected to be low due to absence of the acceptor. Although no attempt was made to follow in detail the fate of the daughter particles, it was repeatedly observed that a considerable fraction of

the 18 m daughter remained in the counting chamber after removal of CH_3Br*.

Summary of Data

Conditions		Activities at 0 time		Separation
MeBr	HBr	4.4 h.	18 m	Efficiency
15 mm Hg.	16 mm Hg.	1478 c/m	0 to -230 c/m[x]	1.00
12	6	1328	-35	1.00
20	12	375	-15	0.96
15	0	1206	-45	0.96

[x]Uncertainty due to inadequate location of zero time.

These experiments agree with the latest physical measurements, in indicating a conversion efficiency of nearly unity in this isomeric transition, and, as further pointed out by Dr. W. F. Libby, deny the presence of an independent beta decay of 4.5 h Br^{80*}.

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RECOIL BROMINE ATOMS IN NEUTRON CAPTURE BY GASEOUS ETHYL BROMINE*

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Ethyl bromide at several microns pressure was irradiated with neutrons in the
Argonne pile. Usually the container was a quartz cylinder 2 cm. in diameter, 40
cm. in length, lined with metal foil and containing a central metal rod. After
irradiation no radiobromine was detected in the gas phase, a result indicating in-
variable rupture of the C-Br bond on neutron capture. Evidence was obtained for
re-emission of the bromine recoils after collision with several ordinary metal
surfaces, but attachment at first wall collision apparently occurs with foils of
amalgamated copper. By varying the electric field imposed across the central rod
and surrounding field, the distribution of radiobromine on the metal surfaces changed
as if 15-40% of the recoil fragments reach the surfaces as positively charged par-
ticles, the remainder as neutrals. The proportion of cationic species found varied
with the particular bromine isotope studied. The results are tentatively ascribed
to internal conversion of soft γ-rays emitted in neutron capture.