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CHEMICAL RESULTS OF THE BETA DECAY OF TELLURIUM-131 IN HYDROCARBON SOLUTIONS OF ORGANOTELLURIDES

by

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TABLE OF CONTENTS

INTRODUCTION

Hot Atom Chemistry

"Hot atom chemistry" is the study of the reactions of atoms exhibiting energies in excess of the ground state or thermal energies. The term "hot atom" will be used in this discussion to refer to all activated atoms, regardless of the charge possessed by the atom. The most common method of producing hot atoms has been by utilization of nuclear reactions. In any nuclear reaction the product nucleus receives recoil energy as a result of the absorption or emission of particles involved in the reaction. This recoil energy may be as high as several Mev.

In the last few years a rapid increase in the interest in the chemical behavior of hot atoms produced from radioactive decay by beta emission has developed. In rare cases the recoil energy resulting from beta decay may be as high as $\sim 10^4$ ev, i.e., B^{12} and Li^8. However, the recoil energy is usually on the order of chemical bond energies, and as such, the chemical effects which occur as a result of beta decay must, in a large percentage of decays, be due to other modes of excitation. The nature of these modes will be discussed below.

In order to be able to study processes of this type, there are two requirements which must be met:

1) Since hot atoms are formed in amounts that are smaller than those that can be chemically detected, it is necessary that the hot atom be radioactive.
2) There must be no exchange between the radioactive atom and stable atoms of the same element in the system.

Definition of Beta Decay

Beta decay is the process in which an electron and a nucleus interact, the result being the change in the atomic number of the nucleus by one unit while the mass number remains unchanged. There are three processes which are termed beta decay:

1) The emission of a negative electron.
2) The emission of a positive electron.
3) The capture by the nucleus of an orbital electron.

The chemical effects resulting from the first process were the object of this study.

Sources of Molecular Excitation

There are several factors which may determine the state of the daughter atom, in particular the excitation and charge of the atom, and the final forms of the atom under certain given conditions.

In the process of negative beta decay itself, excluding any other source of excitation or ionization, the immediate result is a transformed daughter atom bearing a single positive charge. If the decaying atom is a constituent of an isolated molecule, the primary product will be a molecular ion with a single positive charge. There are several secondary processes that may leave the daughter ion in a state of electronic, vibrational, rotational, or translational excitation, or with a larger positive charge due to loss of additional electrons. The most important of these are:

1) Direct collision of the beta particle with an orbital electron as the beta particle leaves the nucleus.

2) Vibrational and rotational excitation resulting from the recoil energy imparted by the beta emission.
3) The internal conversion of internal bremsstrahlung and the vacancy cascades which follow.
4) The "shaking" of the atomic core as a result of the sudden change in the nuclear charge.

Beta particle - orbital electron collision

Migdal, Feinberg, and others in the 1940's calculated theoretically the probability that the beta particle upon emission will interact with an orbital electron (1,2). Their calculations show this probability to be negligible. On the other hand, Grard (3) believes that in the case of heavy beta emitters, the beta particle after leaving the nucleus may interact with one of the electrons surrounding the nucleus to the degree that it does become important. Feinberg in 1965 (4) developed equations that show that direct collision of the beta particle with an atomic shell electron may in some cases play a predominant role over the shaking process in the ionization of the daughter atom.

Recoil energy

Usually the vibrational and rotational excitation which is observed in the daughter ion is a direct result of the recoil energy given to the daughter atom by the departed beta particle. The kinetic energy for the heavy particle does not require relativistic treatment, whereas that for the beta emission does.

For any particle, $E = \gamma m_0c^2 = m_0c^2 + T$, where m_0 is the rest mass, T is the kinetic energy, and c is the speed of light. This leads to

$$m = \gamma m_o = \frac{m_o}{\sqrt{1 - \beta^2}} \tag{1}$$

where $\gamma = \frac{1}{\sqrt{1 - \beta^2}}$ and $\beta = v/c$.

From the conservation of momentum we have

$$MV = mv \tag{2}$$

where M and V are the mass and velocity of the heavy particle and m and v are the mass and velocity of the beta-particle. Substitution of Equation 1 into Equation 2 and subsequent algebra leads to

$$E_R = \frac{(m + m_o)}{2M} E_\beta \tag{3}$$

This equation is still in an unuseable form since m, the relativistic mass, is not known. After rearranging $E_\beta = mc^2 - m_oc^2$ and substituting the result into Equation 3, the following equation is obtained,

$$E_R = \left(\frac{E_\beta + 1.02}{0.51}\right) \frac{m_o}{2M} E_\beta \tag{4}$$

which may be rearranged to the more familiar form of

$$E_R = \frac{548\ E_\beta(\text{max})}{M} + \frac{536\ E_\beta^2\ (\text{max})}{M} \tag{5}$$

where E (max) is in Mev and E_R is in ev (5).

The above formula is applicable only in those rare cases in which the neutrino emitted during beta decay removes no energy. Generally, the energy of the emitted beta particle varies from zero to a maximum value for a certain isotope. Thus, if the recoil energy is to be dealt with quantitatively, a recoil energy spectrum is involved. This recoil energy spectrum depends not only upon the total energy of the decay but also upon the angle between the two departing particles. Therefore, it is necessary to allow for the simultaneous emission of the beta particle and the neutrino in the calculation of the energy of the recoil atoms. The difficulties in calculating this energy spectrum are great, since there is very little data available on the angular correlation of the beta particle and the neutrino.

Suess (6) has shown specifically for the case of diatomic molecules that the recoil energy is not all available for bond rupture; that is, the recoil energy will be divided between the translational energy of the total mass, $E_{(m + M)}$, and the internal energy, E_i, which is available for activation or dissociation.

$$E_M = E_{(M + m)} + E_i \tag{6}$$

If the molecule does not instantaneously dissociate, its kinetic energy will be given by $E_{(M + m)} = p^2/2(M + m)$. The recoil energy given to the atom itself is $E_M = p^2/2M$, where the same value of p applies since there must be conservation of momentum. Substitution of these two equations into Equation 6 results in

$$E_i = \frac{m}{(m + M)} E_R \tag{7}$$

The consequences of the decay of Te^{131} as a constituent atom in diethyl telluride and in di-n-butyl telluride were the object of this study. Hence the application of these equations will be illustrated with the highest energy beta particle emitted by Te^{131}, which is observed in 60% of the transitions and has a maximum energy of 2.15 Mev (7). From Equation 5 a value of 27.9 ev is obtained as the recoil energy of the atom,

E_R, and from Equation 7 a value of 4.9 ev is found for E_i, if ethyl iodide is the primary product resulting from the decay of Te^{131} from diethyltelluride and if the ethyl radical and the iodine atom are assumed to be rigid bodies. Similarly, if n-butyl iodide is the primary product resulting from the decay of Te^{131} from di-n-butyl telluride and if the n-butyl radical and the iodine atom are assumed to be rigid bodies, E_i is calculated to be 8.2 ev. Since the average energy of the beta rays, $\overline{E}$, with a given value of E_{max} is approximately one-third of the maximum value (8), the average recoil energy transmitted to the two molecules, ethyl iodide and n-butyl iodide, will certainly be much less as was noted earlier.

Internal conversion

An alternative to the emission of a γ-ray as a means of de-excitation of the daughter atom is internal conversion. This is the process by which energy is transferred from the excited nucleus to an orbital electron, which is ejected from the atom (8). The ratio of the rate of the internal conversion process to the rate of γ-emission is the internal conversion coefficient, α. Generally, the internal conversion coefficient for any particular shell increases with decreasing energy, decreasing ΔI, and increasing Z. Since it is the inner electrons which are internally converted, the result is a vacancy which must be filled. This is accomplished by an electron of higher energy "falling" into this vacancy and emitting an X-ray in which $E_{X\text{-ray}} = E_i - E_f$. This X-ray may interact with another electron, the result being its ejection (Auger electron). This effects a cascade of vacancies, and the product atom may become highly charged.

The efficiency for the ionization of an atom is shown by charge spectra of atoms which possess large internal conversion coefficients. The average charge for Xe^{131}, which results from the decay of Xe^{131m}, 98% internally converted, is +7.9 (9). An average charge state of +10.5 was obtained for the decay of Br^{80m} (from C_2H_5Br) (10).

Frequently low energy gamma rays accompany beta decay and the phenomenon of internal conversion may then become important to the chemical consequences of beta decay. The contribution which this process makes to systems observed in this study will be discussed in detail later.

"Shaking" theory

According to present theory the principal cause of excitation and ionization of recoil atoms resulting from beta decay is the "shaking" of the atomic core as a consequence of the sudden change in the charge of the nucleus. Because the beta particle leaves the nucleus in a time considerably shorter than the periods of electronic motion, the sudden change in the nuclear charge causes a perturbation of the electrostatic environment of the atomic core (1,2,11,12,13,14,15). Usually the electronic cloud is able to contract adiabatically to the increase in charge of the nucleus. However, there are instances in which excitation does occur, and the excitation energy for the nonadiabatic process is just that energy which in a normal adiabatic contraction would be carried away by the departing beta particle.

This excitation energy has been shown by Serber and Synder (16) to be the energy which would be carried away by the beta particle in an adiabatic process minus that energy which the beta particle actually carries away in the non-adiabatic process,

$$E = -\left[E(Z') - E(Z)\right] + e(Z' - Z)\,\phi(Z), \tag{8}$$

in which $E(Z)$ is the total energy of the parent atom, $E(Z')$ the energy of the daughter atom, and $\phi(Z)$ is electrostatic potential produced at the surface of the parent nucleus by the electrostatic cloud. They then derive an expression for the average excitation energy of a daughter atom following beta decay, as given by

$$E = 22.85Z^{2/5}(Z'-Z)^2 \text{ ev}. \tag{9}$$

This value is the average taken over the probability distribution for the transition from the ground state of the parent atom to the many final states of the daughter. This statistical model breaks down for light atoms. According to this model the average excitation energy of I^{131} which results from the beta decay of Te^{131} is 110 ev.

Generally, the published calculations of the probabilities of ionization due to the shaking effect are inaccurate because of the approximations that were made. The applicability of the non-adiabatic approximation to the inner shells of heavy atoms is satisfactory, but this is not so for the electrons in the outer shells. For the electrons in the outer shells the action is not so powerful because it is delayed. However, the probability of ionization in the outer shells is still more important, since electrons in these shells are less firmly held.

It is known that the accuracy of the non-adiabatic approximation decreases with increase in Z and with increase in the shell number.

Activation by the (n,γ) Process

Several preliminary experiments were performed in which solutions of an organotelluride in a hydrocarbon were prepared, irradiated, allowed to decay, and analyzed for the products resulting from the beta decay of Te^{131} to I^{131}. However, it is possible that some of the products observed in these experiments may have resulted from the (n,γ) reaction on Te^{130} rather than the beta decay. That is, a C-Te bond in the original organotelluride may have been ruptured as a result of the $Te^{130}(n,\gamma)Te^{131}$ reaction, so that the decay occurred from Te^{131} in a different chemical form.

When a thermal neutron is absorbed by a nucleus, a compound nucleus is formed which possesses an excess energy equivalent to the neutron binding energy of the nucleus. This energy is emitted in the form of one or more gamma rays. It has been found that on the average 3.4 gamma rays are emitted per neutron absorbed (17). If multi-gamma emission occurs, the energy that the nucleus receives will depend on the energies of the gamma rays as well as on the relative angles of emission.

The particular reaction in question is $Te^{130}(n,\gamma)Te^{131}$, and for this reaction the binding energy is 6.3 Mev. If this energy were emitted as one gamma ray, the Te^{131} nucleus would receive a recoil energy of $E_R = 536E_\gamma^2/131 = 164$ ev, where E_γ is the energy of the gamma ray in Mev and 131 is the mass in amu. The above equation was derived under the assumption that the recoil energy exceeds the bond energy sufficiently that the molecule is ruptured; and thus there is no need to consider the recoil energy to be absorbed by the whole molecule. However, if the energy available is of the same order of magnitude as that required for bond rupture, some of the energy may be dissipated as translational energy of the whole molecule, E_t, and bond rupture may be prevented. In the latter case, the internal energy is given by Equation 7. The recoil energy may be somewhat less than the calculated value due to the fact that some momentum may be canceled as a result of the relative angles of the gamma ray emission. Even then it would still appear that an extremely large fraction of the C-Te^{131} chemical bonds would be broken by the (n,γ) process. Studies of similar systems, i.e., the alkyl iodides, show bond rupture occurs in a large percentage of the neutron capture events.

Chemistry of Organotellurides

Alkyl and aryl tellurides tend to be quite reactive. Rochow _et_ _al_. (18) has provided one of the best reviews on the chemistry of organotellurium chemistry. A few reactions which are germane to the present study are mentioned here.

Alkyl and aryl tellurides react quite readily with oxygen upon exposure with air at room temperature to form R_2TeO. Only in the case of the dimethyltelluride does further oxidation to R_2TeO_2 occur.

Alkyl and aryl tellurides react with alkyl or aryl halides to readily form telluronium halides.

$$R_2Te + R'X \longrightarrow R_2R'TeX \qquad (10)$$

The telluronium halides are quite stable and are saltlike.

Alkyl and aryl tellurides add halogen readily to form diorganotellurium halides.

$$R_2Te + X_2 \longrightarrow R_2TeX_2 \qquad (11)$$

The most extensive tables of the properties of organotellurium derivatives to date is that of Krause and von Grosse (19).

Historical Background

Hot atom chemistry

Hot atom chemistry was born in 1934, at which time Szilard and Chalmers reported a study in which samples of ethyl iodide were irradiated with thermal neutrons from a radium-beryllium source (20). They found that a large fraction of the I^{128} activity could be extracted into an aqueous layer that contained a suitable reducing agent. This, of course, shows that enough energy had been aquired from the $I^{127}(n,\gamma)I^{128}$ process to break the C-I bond.

Since that time there have been a few hundred papers written on this subject as well as several excellent review articles (21-30).

There have been rather sophisticated theories presented for explaining the chemical reactions of hot atoms in the gaseous phase, such as the Estrup-Wolfgang theory (31,32). This mathematical model does not predict if a reaction will proceed by virtue of kinetic energy, charge, or electronic energy, but it can quantitatively predict the effects of inert moderators on "hot" reactions. Gordus and Hsiung (33) have discussed the activation of atoms joined to a molecule by a single bond, in the gaseous state. Data were presented for the beta decay of C^{14} and T on the net recoil energy needed for bond rupture, on the rotational and vibrational excitation energies received by the rupturing bond, on the internal energy of the radical originally bonded to the activated atom, and on the kinetic energy of the radicals. However, there is not at the present a good theory which will explain the mechanisms of reactions occurring in the condensed state.

Chemical consequences of beta decay

The first attempt to observe the chemical effects of beta decay was reported in 1934 by Martenson and Leighton (34), who studied the decay of Pb^{210}(RaD) to Bi^{210}(RaE) from the volatile compound, $Pb^{210}(CH_3)_4$. Some of the activity of Bi^{210}, as well as that of its daughter Po^{210}, was detected in the volatile fraction, signifying that there had not been complete decomposition of the original compound.

The study of the chemistry of "hot" atoms initiated by beta decay was not reported again until the late 1940's. The study of the chemical consequences of beta decay has since then been characterized by a wide variety of investigations.

The chemical results of all three modes of beta decay have been investigated. Burgus and Kennedy (35) studied the valence state of radiochromium produced by the positron decay of Mn^{51} from $CsMn^{51}O_4$, $Mn^{51}O_2$, and $Mn^{51}CO_3$ in solutions of the compounds as well as in crystalline form. Carlson and White (36), with the use of a special mass spectrometer, studied the chemical consequence of the decay of I^{125} by electron capture to Te^{125}. The decay was observed from CH_3I^{125} and $C_2H_5I^{125}$ and it was found that only ~1% of the Te-hydrocarbon ions remain intact, that in both cases tellurium ions were found with charges as high as +18 with an average of +9, and that singly, doubly, and triply charged carbon ions were found in greater abundance than the hydrocarbon ions. These results are due to the coulombic repulsions of the charge which was distributed over the entire molecule. The high charge is a direct result of the Auger processes which are initiated by the electron capture process.

An example of the variety of methods used for obtaining data on the chemical consequence of beta decay is a study done by Hashimoto and Hirotoshi (37), who studied the hot atom effects of the electron capture decay in cobalt(II) oxalate by using the Mössbauer transition in Fe^{57}. No evidence of hot atom effects were found, and the results were interpreted as due to the rapid reduction of high-charge recoil atoms by the oxalate ion.

Vacuum techniques were employed in studying the decay of C^{14} in ethane by labeling both carbon atoms and observing the products after one decay. In 47% of these decays the basic molecular structure was retained in the product, $C^{14}H_3NH_2$ (38). This retention was shown to be primary retention; that is to say, the product $C^{14}H_3NH_2$ was a result of failure to rupture any bonds rather than a recombination of fragments. The experimental retention agrees quite well with the theoretical value for the probability of non-dissociation due to beta decay of 0.60 ± 0.20 (39).

The distribution of radioarsenic, As^{77}, among products has been investigated in the beta decay of Ge^{77} and compared to the distribution of As^{76} among products resulting from the $As^{75}(n,\gamma)As^{76}$ reactions (40,41). It was shown that although the products tend to be the same, suggesting identical reaction mechanisms in both cases, their yields are not the same.

Since the primary product after negative beta decay has a charge one greater than the parent (atom or ion), several investigations have been performed in order to determine the fraction of decays which do result in a product with a single charge greater than the parent. The decay, $Ce^{144} \longrightarrow Pr^{144}$, (42) was studied using cerium acetylacetonate in solutions of CS_2, CCl_4, and water. No extensive irreversible rupture of the acetylacetonate molecule was found to occur when the decay took place in the crystalline form or in dry organic solvents. This was not the case, however, if the decay took place in organic solvents containing water and excess acetylacetone; some chemical change was noted. The authors presumed the excited daughter, $Pr^{144}A_3^+$ to react with any excess acetylacetone and the product to be hydrolyzed on contact with H_2O. The decay, $(La^{143})^{3+} \longrightarrow (Ce^{143})^{4+}$, was investigated (43) in nitric acid solution with the result that ~60% of Ce^{143} was found to be in the +4 state.

In a study of the decay of Se^{83} and Se^{84} in inorganic media Davies et al. (43,44) found that in the case of Se^{83} at pH 7 40% of the total Br^{83} formed was observed as BrO_3^-, and the results were quite similar for Se^{84}. In a similar set of experiments at pH 11 about 24-30% of the activity was found in the form of BrO_3^-. Since these fractions did not change regardless of the chemical state of selenium, $SeO_4^=$ or $SeO_3^=$, the authors felt this to indicate complete breakdown of the original ions.

Anderson and Knutsen (45) found 77% of the total Sb^{125} activity was in the form of Sb(V) when the beta decay occurred from the compounds K_2SnCl_6 and $(NH_4)_2SnCl_6$.

The decay of Ge^{77} from GeO_2 has been studied by several groups in attempts to determine the charge states of the resulting As^{77}. However, the reported results are quite different. Baro and Aten (46) found 69.2%

as As(III) and 28.8% as As(V) by using standard "wet-chemical" procedures for the separations. Fidelis et al. (47) found all of the activity as As(V) by using reversed phase partition chromatography as the method of separation. Finally, Genet and Ferradini (48) using a paper electrophoresis method found 85% as As(III) and 15% as As(V).

Experiments using the mass spectrometer have contributed to our knowledge of the chemical effects of beta decay, since this technique permits the observation of the primary products resulting from beta decay, free from intermolecular effects. Snell (49) studied the molecular dissociation following the radioactive decay of tritium from tritium hydride and found $(He^3H)^+$ to be present in 93% of all occurrences. Wexler (50) found the probability of occurrence for $(He^3H)^+$ from the decay of TH to be 89.5% and for $(THe^3)^+$ from TT to be 94.5%. The agreement between the two studies is assumed to be quite reasonable since the ion optics of the two mass spectrometers may have been greatly different. The fact that $(THe^3)^+$ is larger than $(HHe^3)^+$ is nicely explained by comparison of the zero point energies of TH and TT. A small difference in zero point energies may result in a large difference in probability of dissociation, as can be seen by invoking the Frank-Condon principle for the beta transition.

In the same set of experiments Wexler found that experimentally the probability of ionization resulting from the shaking effect was 1.7 to 2.3% (50) as compared to the theoretical value of 2.5% for the probability of ejection of the single electron in the decay of atomic T to the $(He^3)^+$ (1).

In sharp contrast to the large fraction of the bound daughter molecular ion, $(HHe^3)^+$, the behavior seen in the alkyl tritides is that of instability of the C-He bond in the daughter molecular ion which results from the decay of tritium in alkyl tritides. In a study of tritium beta decay from ethyl tritide Wexler and Hess (51) found that $(C_2H_5He^3)^+$ occurred in ~0.2% of the transitions and $(C_2H_5)^+$ in 78%. In the same paper the authors report a study of the fragments resulting from the beta decay of Br^{82} from $C_2H_2BrBr^{82}$, in which the major fragment was $(C_2H_2Br)^+$ in 69.8% yield. These results appear to indicate that the dissociation pattern shown in the tritiated organic compounds is not the result of peculiarities in the nuclear transition of H^3 to He^3. By making use of Rosenstock's quasi-equilibrium theory of unimolecular dissociation Wexler was able to estimate the molecular excitation energy available from the beta transformation of tritium in C_2H_5T.

In a later paper Wexler <u>et al</u>. (52) reported the fragment spectra of primary and secondary tritiated propane and of o-, m-, p-, and α-monotritiated toluene. In these studies the yield of the daughter molecular ion $(R\text{-}He^3)^+$ is also very small. The initial fragment ion, that is, the precursor to all other fragments, appears to be the molecular ion resulting from the loss of a neutral He^3 and corresponds roughly in all cases, to the values expected for the fraction of beta transitions to states with little or no excitation. If the fragment pattern had been different for the two isomers of tritiated propane and for the various isomers of tritiated toluene, it might have been possible to verify the localized excitation of the shaking process. However, it is known that radiationless transitions occur in times much shorter than periods of vibrational motion, and thus localized beta transitions may be obscured.

The quasi-equilibrium theory of unimolecular dissociation postulates transitions such as these as the vehicle by which excitation energy is randomly distributed throughout the whole molecule. The spectra of the corresponding isomers are similar, and this is taken as confirmation of the quasi-equilibrium theory of unimolecular dissociation.

White and Carlson (53) reported the probability of the occurrence of $(CH_3Xe^{131})^+$ from the nuclear decay of CH_3I^{131} to be 70%, which is in direct contrast to the decay of CH_3T in which hardly any $(CH_3He^3)^+$ was found (54). In a later paper the same authors reported a mass spectrometric analysis of the ions resulting from the nuclear decay of CH_3I^{130} and $C_2H_5I^{131}$ (55). They found the percent abundances for the parent ions, $(CH_3Xe^{130})^+$ and $(C_2H_5Xe^{131})^+$, to be 34% and 1.4%, respectively. The author's conclusions were that: 1) C_2H_5-Xe undergoes decomposition more readily than CH_3-Xe, 2) the greater bond severance of the C-Xe bond is due to the greater recoil energy present in the I^{130} decay, 3) coulombic shaking may be used to explain the appearance of the lower-charged Xe ions and most of the hydrocarbon fragments, and 4) multiple Auger processes following internal conversion are given as the cause for the more highly charged Xe ions. There were about 20 different fragments reported for each particular decay.

The study of the chemical consequences of beta decay from organometallic systems has been receiving increased attention. These compounds have definite advantages. After the study by Martenson and Leighton (34) on the beta decay of Pb^{210} from $Pb^{210}(CH_3)_4$, no other work was reported in this particular phase of the field until 1948. At that time Edwards and Coryell (56) studied the same system in the gas phase and found the fraction of the bonds ruptured, 8%, to be independent of the pressure of the parent compound. The reason for this value was not evident. In 1953 Edwards et al. (57) examined the Pb^{210} system in more detail. This time they observed the decay of $Pb^{210}(CH_3)_4$ in solutions of benzene, octane, and CCl_4 and found the occurrence of Bi^{210} in the non-volatile fraction to be 60-80%. The authors thought this fraction occurred because of bond rupture resulting from internal conversion and vacancy cascades.

Nefedov reported the first study of beta decay involving aromatics (58). He used the carrier method in separating the decay products from $Pb^{210}(C_6H_5)_4$ and $Pb^{210}(C_6H_5)_3Cl$. The most exciting factor here was the discovery of the complex organometallic compounds $Bi(C_6H_5)_3$ and $Bi(C_6H_5)_3Cl_2$. The system $Pb^{212} \longrightarrow Bi^{212}$ was also studied by the same authors (59) for the same compounds, $Pb^{212}(C_6H_5)_4$ and $Pb^{212}(C_6H_5)_3Cl$. Nefedov et al. (60) also studied the chemical state of Bi^{210} obtained by the beta decay of Pb^{210} from $(PbPh_3)_2$, $PbPh_3NO_3$, and $PbPh_2(NO_3)_2$.

Nefedov et al. (61) then studied Pb^{214} from $PbPh_3Cl$ and $PbPh_4$ and compared the results to those from the decay of Pb^{210} and Pb^{212} from the same compounds. The ratio of the inorganic yields from Pb^{210}, Pb^{212}, and Pb^{214} in both compounds was the same as the ratio of the total internal conversion coefficients of Pb^{210}, Pb^{212}, and Pb^{214}. Identical experimental conditions were used in all cases.

Because previous studies had been done using the isotopic carrier technique, all of the complex features of the chemical changes could not be reproduced. In order to study these features in more detail paper chromotography was used by Nefedov (62) to again study the decay products of $Pb^{210}(C_6H_5)Cl$.

It had been suggested that the appearance of $BiPh_3$ and $BiPh_3Cl_2$ might, in part, be due to the interaction with the surrounding molecules. In order to illuminate the situation, Nefedov et al. (63) studied the decay of radical deficient $Pb^{210}(C_6H_5)_2Cl_2$, and they found the yield of $BiPh_3$ and $BiPh_3Cl_2$ to be very low. Thus in this case the chemical changes accompanying beta decay do not involve the surrounding molecules.

Duncan and Thomas (64) were the last to examine the $Pb^{210}(CH_3)_4$ system and did so under conditions in which the products were not under the influence of neighboring molecules. One hundred percent of the daughter Bi^{210} was deposited on the walls of the containing vessel. This was taken to mean that the daughter $Bi(CH_3)_4^+$ disproportionates to yield charged bismuth containing fragments rather than $Bi(CH_3)_3$.

In other beta decay studies of organometallic compounds, Merz observed the chemical reactions following the decay of tetraphenylgermane (Ge^{77}) (65), and Nefedov et al. (66) observed the chemical reactions following the decay of Sb^{125} from some phenyl and tolyl derivatives.

Chemical effects of beta decay of tellurium isotopes

In 1952 Keneshea and Kahn (67) irradiated a solution of $TeCl_4$ dissolved in benzene and examined the chemical state of I^{131}. Eighty-seven percent of the activity was extracted into an aqueous layer, while 10% was found to be C_6H_5I. The study of the chemical consequences of beta decay of the tellurium systems was dormant then until the 1960's.

In 1961 Cummiskey et al. (68) reported separating the I^{132} products resulting from the decay of Te^{132} in an inorganic media. The separation was accomplished by using the carrier method, and the products observed were of three different types -- reduced forms, iodate, and periodate. Later a method for studying the behavior of iodide, iodate, periodate, tellurite, and tellurate ions in NaOH and NaCl solutions by the use of low voltage and high voltage paper electrophoresis was reported (69). Gordon (70) again studied the decay of Te^{132}, and this time the separations were accomplished using paper electrophoresis. Whereas Cummiskey had found a considerable amount of periodate resulting from the decay of Te(IV), Gordon found the quantity of periodate to be quite small. Gordon suggests that this small quantity of periodate results from the complete severance of bonds due to the large internal conversion coefficient of Te^{132}. Therefore, any amount of periodate present must be due to the reaction of the excited iodine species with the medium.

The interest in the chemical effects of the tellurium systems in organic media was revitalized in 1961 by Halpern (71). This study was concerned with the bond rupture resulting from the beta decay of dibenzyltelluride(Te^{131}). The dibenzyltelluride was prepared by the action of benzyl chloride on sodium telluride(Te^{131}), which had been prepared following neutron irradiation of tellurium powder. The percentages of the I^{131} activity as benzyl iodide, methyl iodide, phenyl iodide, iodotoluene, and inorganic forms were determined by using carriers and fractional distillation to accomplish the separations. The retention (ratio of I^{131} atoms existing in benzyl iodide to the total number of I^{131} atoms) was found to be 1.8% in solid dibenzyltelluride, indicating that the C-Te bond was ruptured in 98% of the events. This indicates that the shaking effect or the large charge resulting from internal conversion may have been responsible for the bond rupture. Even if recoil energy had been responsible, essentially all the kinetic energy would have been used in the bond rupture leaving the liberated I^{131} atom thermalized.

Halpern also reported scavenger studies on the dibenzyltelluride(Te^{131}) systems. Allyl iodide and molecular iodine were both used as scavengers; the conclusions were that 28% of the I^{131} atoms were born with thermal energies and that the other 72% of the I^{131} atoms are epithermal, that is, they possess excess energies of 1-~20 ev. In all the experiments, however, 53-77% of the products formed were unidentified.

Adloff (72) reported some interesting although quite qualitative, work in 1962. Functional groups were studied by dissolving $Te^{132}Cl_4$ in various alcohols and toluene, and it was found in the case of alcohols that rupture occurs mainly in the C-C bond of the carbon atom of the functional group.

A study reported by Halpern (73) in 1963 compared the chemical effects of the beta decays of Te^{131} and Te^{132} in solutions of $TeCl_4$ in toluene. Although the recoil energy is greater in the case of the Te^{131} $Te^{131} \longrightarrow I^{131}$ transition as a result of the difference in the beta energies, the reactivity of the I^{132} atom appears to be greater. This comparison was based on the results that 25% of the total I^{131} and 68% of the I^{132} activities were found in the organic fraction after the decay. In both cases a rather large fraction of the activity was found in the form of methyl and phenyl iodides indicating bond rupture between the benzene ring and the methyl radical. Approximately one-third of the organic activity was found to be in an unidentified higher boiling fraction. The relative yields of the organic iodides in each particular experiment differed very little and this was taken to indicate independence of the product distribution on the kinetic energy of the atoms.

Both elemental iodine and allyl iodide were used as scavengers in the above study. The organic yield of I^{131} decreased from 25% to 11% and that of I^{132} decreases from 68% to 15% upon addition of 10^{-4} mole fraction of elemental iodine. Halpern suggested that this may be due to the recoiling atom losing its unique charge properties by a charge exchange between the recoiling atom and a molecule of iodine:

$$(I_{recoil})^{+} + I_2 \longrightarrow I_{recoil} + I_2^{+}$$

Upon addition of 10^{-2} mole fraction of allyl iodide the total organic yield increased to ~90% in both cases. Since the scavenging action of allyl iodide occurs only by way of its rapid exchange with the thermalized recoil atom, the majority of recoil atoms must possess kinetic energy in the thermal region.

In Halpern's study the two solutions were prepared by different procedures for this comparison. A solution of $Te^{132}Cl_4$ in toluene was prepared and allowed to stand for 50 hours while the decay occurred. However, in the case of $Te^{131}(T_{\frac{1}{2}} = 25 \text{ min})$ the solution of $TeCl_4$ in toluene was prepared and then activated in the thermal column of a reactor for a period of 20 min. Under these conditions Te^{131} is the principle activity. Halpern asserted that all of the Te^{131} formed might not be in the form of

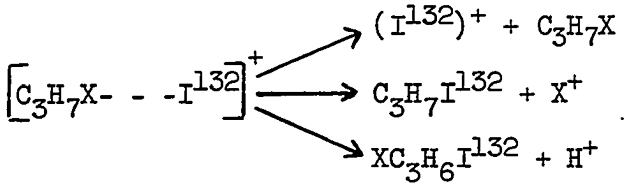
$Te^{131}Cl_4$ due to the effects of the $Te^{130}(n,\gamma)Te^{131}$ reaction, as well as to radiation reactions occurring in the reactor field. Both of these factors may influence the final products. He reasoned, however, that since the covalent bond is nearly always ruptured in the case of dibenzyltelluride(Te^{131}) (71), this should also happen in the case of $Te^{131}Cl_4$. Also, in several experiments solutions of $Te^{132}Cl_4$ (Te^{132}, 77 hr) in toluene were exposed to the reactor gamma radiation field for 20 min, and since the value of the total organic yield of I^{132} was not influenced Halpern inferred that the yield of I^{131} should not be affected.

In 1964 Narayan and Iyer (74) studied the decay of Te^{132} from the chloride complex of tellurium with isopropyl ether as a solution in Ch_3I. Ninety-seven per cent of the activity was organic, 3% of the activity was inorganic, and approximately 3% of the activity was established as methyl iodide. There is a significant difference in the total organic activity of 70% reported by Halpern (73) and in the value of 98% reported by Narayan. However, these two systems are very different.

In the third of a series of papers Halpern (75) described studies on the reactions of I^{132} in liquid mixtures of n-propyl halides and benzene or iodobenzene. The I^{132} was produced by the beta decay of Te^{132} from $Te^{132}Cl_4$. Whereas in previous studies Halpern had accomplished analysis by fractional distillation, in this study he utilized gas chromatography. Because solutions of $TeCl_4$ in alkyl iodides darkened on standing, all solutions were prepared with an iodine concentration of 10^{-2} mole fraction. In these scavenged systems the total organic yield varied only slightly with an average of 20% of the total activity. In the cases of 0.07M

$Te^{132}Cl_4$ in n-C_3H_7I + C_6H_6 and 0.07M $Te^{132}Cl_4$ in n-C_3H_7I + C_6H_5I the only products found were $C_3H_7I^{132}$ and $C_6H_5I^{132}$. However, if C_3H_7Br or C_3H_7Cl was used instead of C_3H_7I, two unidentified peaks were found in addition to the two previously mentioned. I^{132} reacted preferentially with the alipatic halide in all cases and the extent of preference depended on the composition of the organic mixture, i.e., the mole fraction of the C_6H_6 or C_6H_5I.

Halpern suggested that the reaction of the I^{132} with the organic media proceeded through an excited intermediate complex, and that the interaction leading to the complex was ion-dipole in character. Since the dipole moments of n-propyl halides are larger than those of iodobenzene and benzene, the probability of formation of an intermediate complex should be greater in the case of n-propyl halides than for iodobenzene or benzene. This complex would be able to undergo one of three reactions:



The probabilities for the occurrence of the last two reactions would increase with the increasing half life of the intermediate complex, since the longer the complex remains intact the larger the probability of energy (or charge) transfer to surrounding molecules.

The last reported study involving the chemical consequences of beta decay in the tellurium-iodine system in organic media was that of Adloff and Llabador (76). The phase and temperature dependence for $Te^{132}Cl_4$ in benzene and of diphenyltelluride(Te^{132}) was studied. In the case of $TeCl_4$ in benzene a phase dependence was found, while in the second case no phase or temperature dependence was found.

Purpose of Investigation

The ease of separation of the alkyl and aryl tellurides by gas chromatography and the nuclear characteristics of I^{131} make the study of the decay of $Te^{131} \longrightarrow I^{131}$ in organic solutions desirable. Very little research has been done involving the study of the chemical consequences of beta decay from an organotelluride in a hydrocarbon solvent, because of the difficulties encountered in working with organotellurides, particularly those difficulties caused from the high chemical reactivity and the high toxicity of the organotellurides. The only reported study was preliminary in nature.

The purpose of this investigation was to obtain information concerning the chemical consequences of the beta decay of Te^{131} from organotellurides in hydrocarbon solvents in order to add to the present knowledge of the behavior of recoil atoms. The data is treated in terms of possible reaction mechanisms.

EXPERIMENTAL

Chemicals and Materials

The hydrocarbons used in this research were all obtained from the Phillips Petroleum Co. They were all research grade, better than 99.95% purity and were used without further purification.

The column materials used were:

1) Diisodecyl phthalate - Monsanto Chemical Co.
2) SF-96(100), silicone fluid - General Electric, Silicone Products Division.
3) Chromosorb P, 45-60 mesh - F & M Scientific.

The diethyltelluride and di-n-butyltelluride were obtained from City Chemical Corporation. Both were purified by gas-liquid chromatography after they had been irradiated.

The chemicals used for the standardization of the columns were either purchased from Eastman Organic Chemicals, K & K Laboratories, City Chemical Corporation, or Matheson Coleman and Bell.

The labeled methyl iodide-131 was purchased from Volk Radiochemical Company. It had a radiopurity of 99% and a specific activity of 16 mc/mM.

Case A - Results of Beta Decay Following Neutron Activation of Prepared Solutions

Sample preparation

Solutions of diethyltelluride in n-pentane were prepared in two concentrations, 0.1M and 0.5M, to be irradiated under various conditions. The preparation of these solutions was accomplished by micro-pipetting that quantity of diethyltelluride necessary for the desired concentration into a 5 ml volumetric flask and diluting to volume with n-pentane. The volumetric flask was fitted with a rubber septum in order to arrest evaporation of the solvent and slow oxidation of the diethyltelluride while the samples were being prepared. The solution was withdrawn from the flask and transferred to the quartz sample bulblets with a syringe having a 5 in needle. The sample was degassed by the standard freeze-thaw degassing procedure and then the bulblet was sealed.

The quartz sample bulblets consisted of a 9.0 - 9.3 mm diameter bulblet blown onto one end of a 2 mm quartz tube, 6.5 cm in length. The other end of the tube was sealed to a 10/30 standard taper. The quartz bulblets could then be attached to the vacuum manifold by the standard taper. The small diameter of the tube facilitated the sealing process.

Because the organotellurides are highly toxic as well as very volatile, the entire procedure for the sample preparation was done in a low pressure ventilation hood equipped with a plexiglass shield.

Irradiation

The quartz bulblets containing the diethyltelluride were sealed inside a 3/8 in polyethylene tube in order to reduce the probability of breakage during irradiation and to contain the telluride within the polyethylene container should breakage occur. This is shown in Figure 1.

All samples were irradiated at the Ames Laboratory Research Reactor (ALRR). The particular irradiation position used in this study, R-3, received a flux of 4.2 x 10^{13} neutrons/cm^2/sec at a power level of 5 megawatts.

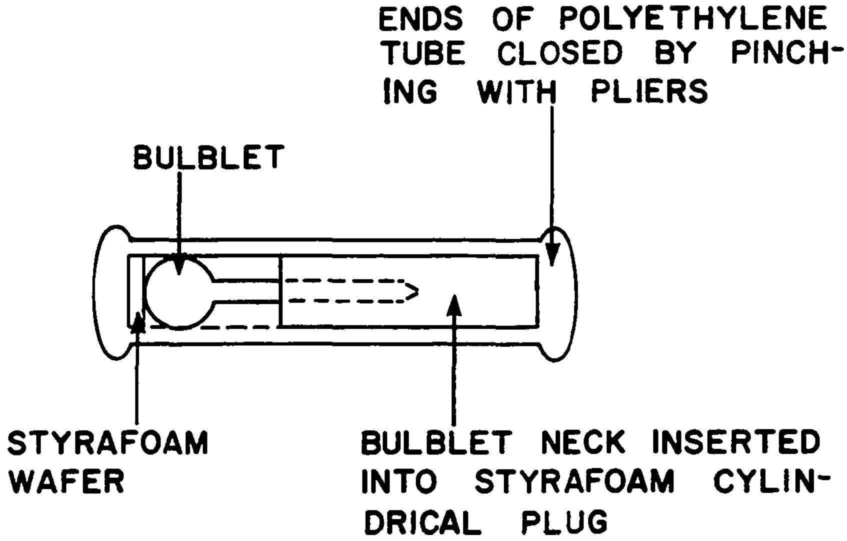


Figure 1. Bulblet packed for irradiation

The irradiations were performed at constant power levels for various time intervals (5 min to 25 min) in order to approach conditions of "zero dose." These irradiations were conducted at two different power levels, 4 and 5 megawatts, at a constant concentration of 0.1M, and were conducted at the two concentrations, 0.1 and 0.5M, at a power level of 4 megawatts.

Analysis

Analyses were performed by the utilization of a radio-gas chromatograph. A diagram of the experimental apparatus is shown in Figure 2. The bulblet was inserted into the breaker specifically designed for the radio-gas chromatograph (Figure 3), and broken. The products, after being separated by the column, passed directly through the detection system, a 3" x 3" Harshaw NaI(Tl) side-hole crystal (Figure 4).

Better separation of products was obtained by temperature programming than by isothermal operation of the chromatograph. Although the hydrocarbon solvent and the higher boiling products dictated the operating conditions for the analysis of the various solutions, usually the temperature programming was begun at 50-60°C and proceeded at a 2 deg/min rate of increase. The maximum temperature depended upon the decay products and the column material used. The flow rate most commonly used was 55 ml/min.

The chromatograph used in this study had previously been used in this research group for low temperature studies. The present study necessitated the complete rebuilding of the chromatograph. Dead space was minimized by attaching the front end of the column directly to the breaker and by attaching the back end of the column directly to the T.C. cell. The copper tubing which had been used previously was replaced with stainless

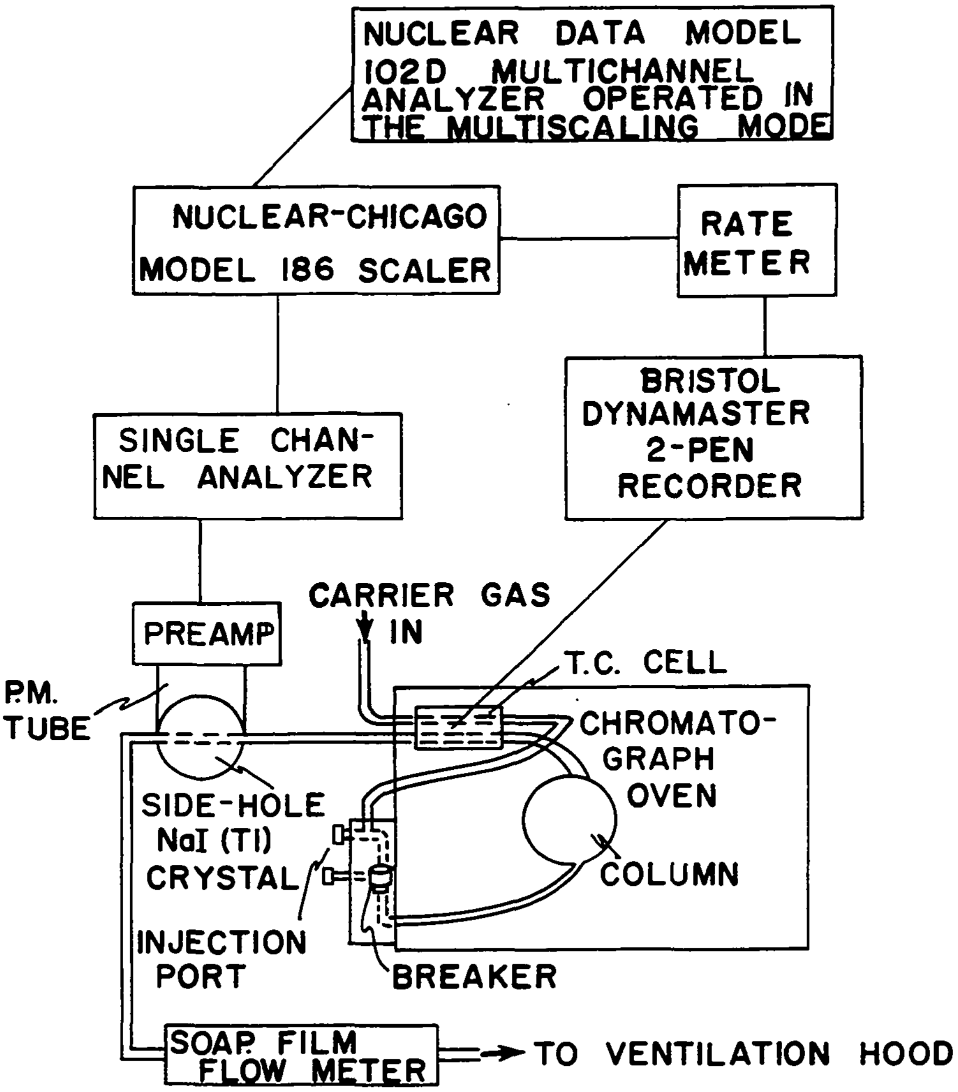


Figure 2. Radio-gas chromatograph

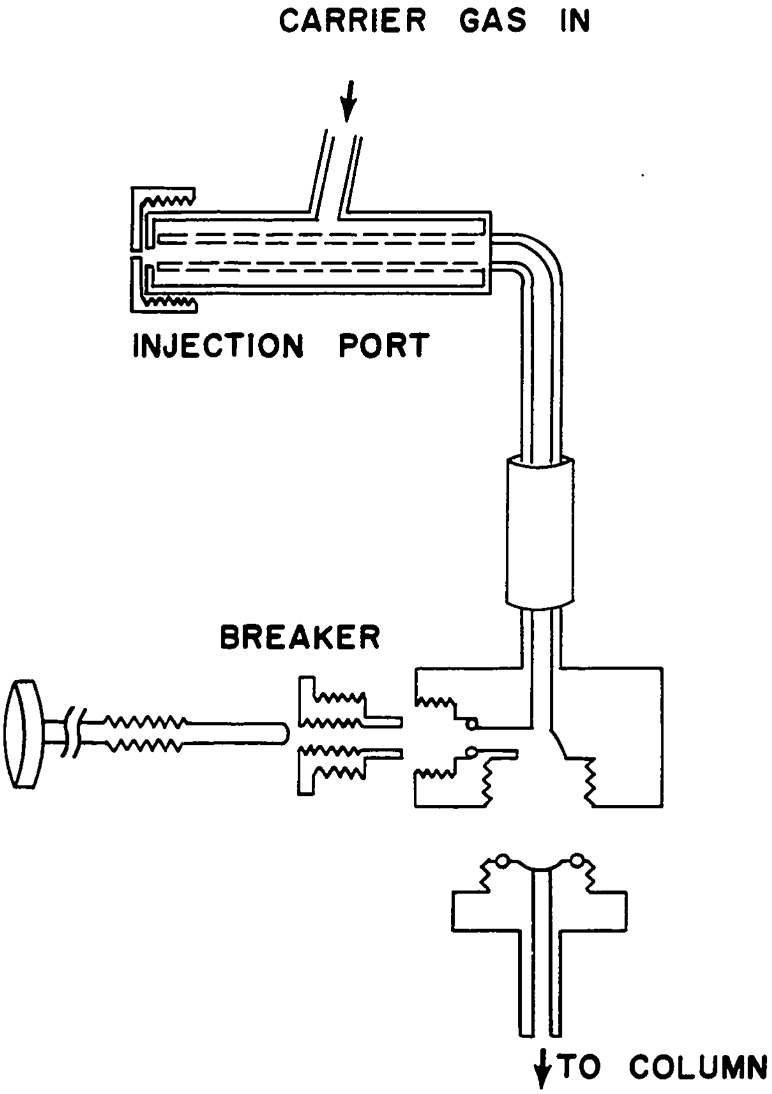


Figure 3. Injection port-breaker system

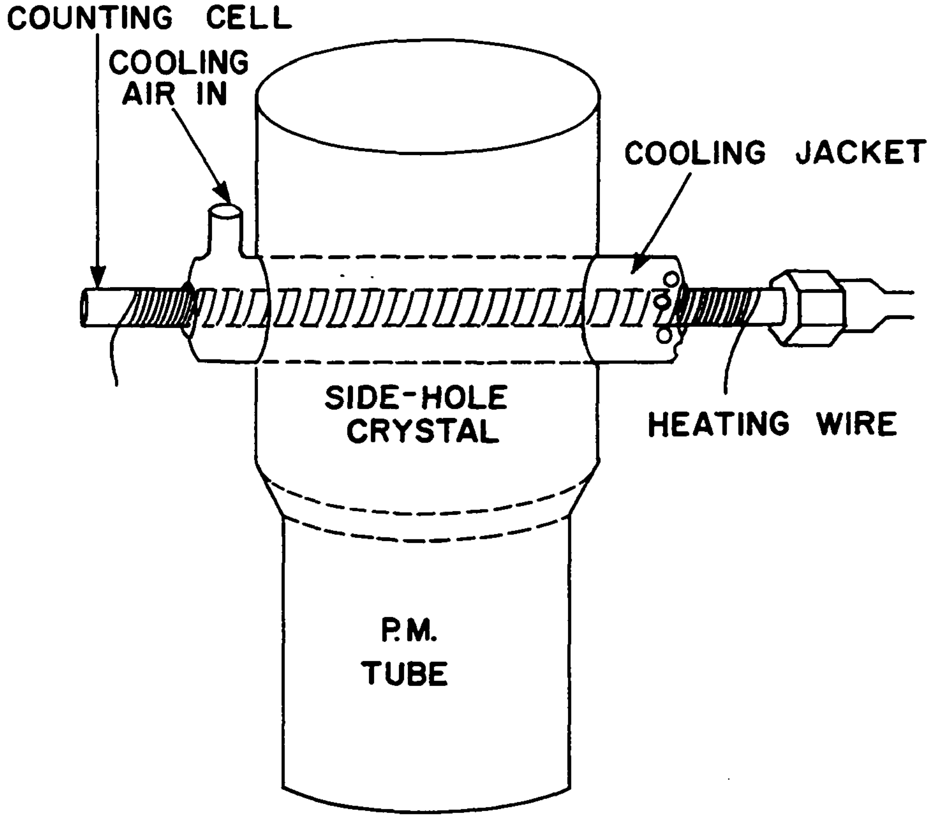


Figure 4. Counting cell arrangement

steel, so that all the chromatograph parts were either pyrex or stainless steel. Auxillary heaters were added to the chromatograph oven in order to reach temperatures in excess of 200°C. Both the T.C. cell and the injection port-breaker system were enclosed in insulated boxes with separate heaters so that their temperature could be independently maintained.

Because of the high toxicity of the organotellurides, a low pressure ventilation hood was built above the chromatograph oven. If a leak were to occur somewhere in the system, the telluride could instantaneously be removed by the hood.

The columns were 7 mm diameter pyrex tubing formed into coils, approximately 8" in diameter. Diisodecyl phthalate on Chromosorb P and silicone oil on Chromosorb P were the column materials in general use. In both column materials the resolution times of the iodides were directly related to their boiling points. The maximum attainable temperatures were 150°C for the diisodecyl phthalate column and 250°C for the silicone oil column.

Since it was the chemical consequences of the system $Te^{131} \longrightarrow I^{131}$ that was to be observed, it was necessary to calibrate the single channel analyzer used in conjunction with the radio-gas chromatograph for the purpose of counting I^{131}. The nuclear decay scheme of I^{131} is given in Figure 5. The single channel analyzer was operated in the differential mode with the lower and upper discriminators set so that pulses would be counted between the energy limits shown in Figure 6. A Ba^{133} standard source (4,000 cts/min) was counted before every run to ensure that the detection system had not changed. If more than a 2% deviation in the

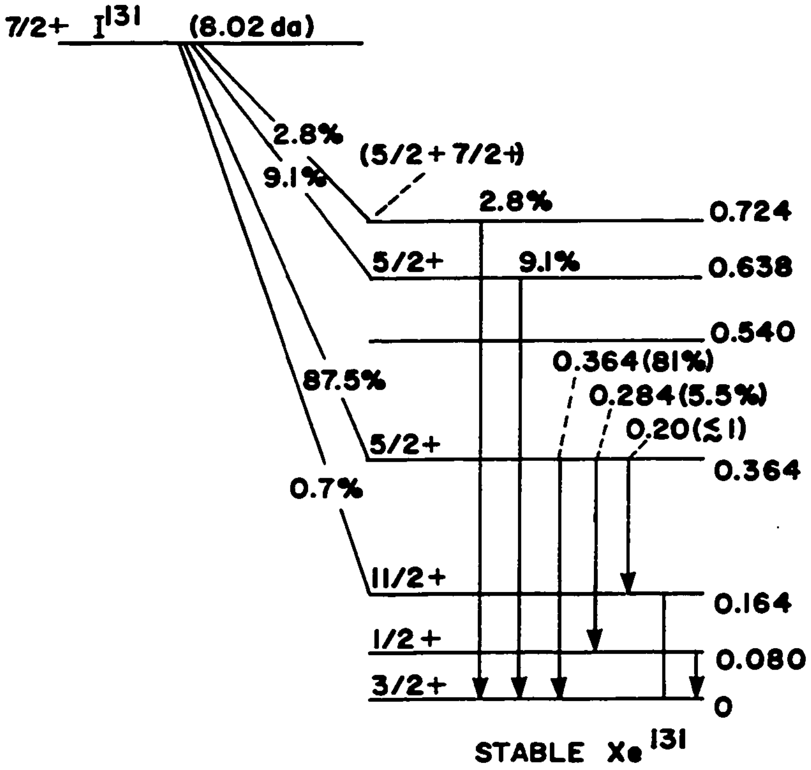


Figure 5. Nuclear decay scheme for I^{131}

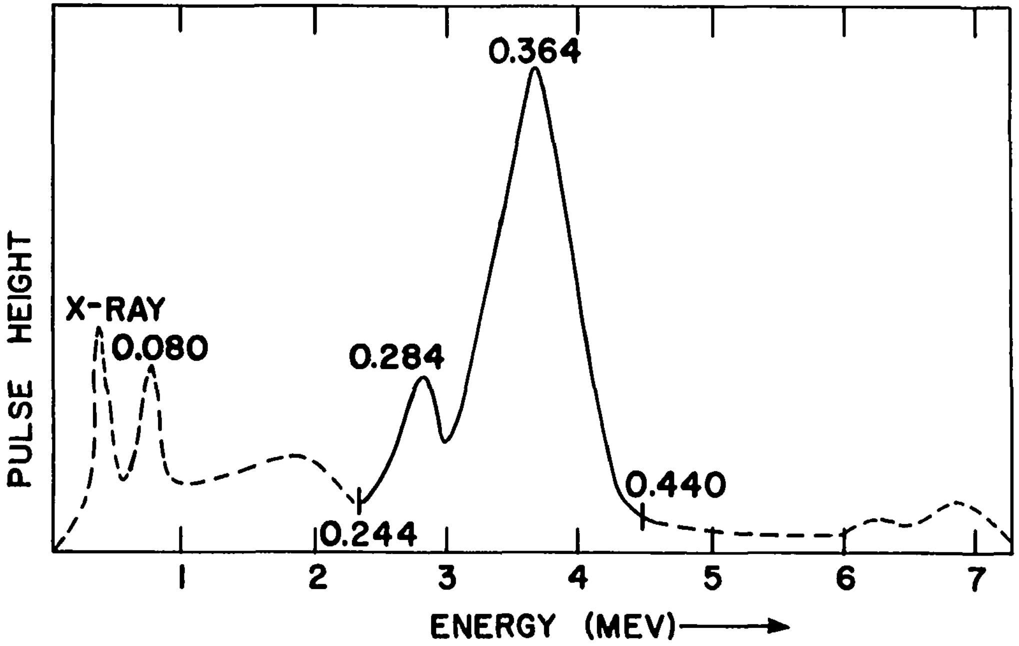


Figure 6. Scintillation spectrum for I^{131}

count rate of the standard Ba^{133} source was noticed, the counting system was recalibrated to the 0.24 Mev - 0.44 Mev window width.

The flow rate during a run was extremely important since for a given activity due to a volatile component the number of counts registered is inversely proportional to the flow rate. Thus, a measure of the activity of a particular product peak can be taken as

$$A_i = N_i f \tag{10}$$

where N_i is the number of counts recorded for a product peak and f is the flow rate. In order to calculate product yields in terms of per cent of the total activity, it was necessary to count each sample on a monitor counter before the sample was analyzed. The relationship between the total counting rate of a sample on the monitor and the measure of the total activity, A, which that same sample produces in the side-hole NaI(Tl) crystal is given by the calibration factor. That is, the calibration factor is that number which results in the number A when multiplied by the monitor count.

$$A = FY, \tag{11}$$

where F is the calibration factor and Y is activity as recorded by the monitor. The yield of a particular product is

$$\frac{A_i}{A} \times 100 = \frac{fN_i}{FY} \times 100 = \% \; . \tag{12}$$

Wolfgang and Rowland (77) were the first to use expressions similar to these in conjunction with a flow-proportional counter.

The calibration factor was obtained by preparing labeled methyl iodide-131 in bulblets identical to those used in preparing samples for irradiation, counting the methyl iodide samples on the monitor, and recording the counts detected by the side-hole crystal after the methyl iodide had passed through the gas chromatograph. The vacuum manifold used to prepare the methyl iodide-131 samples is shown in Figure 7.

The methyl iodide-131 was obtained as 3 mM samples with an activity of 5 mc, sealed inside a pyrex tube, 20 cm long and 0.8 cm in diameter. While one end of the tube was frozen in liquid nitrogen the other end was broken off, and 1.5 ml of triply distilled methyl iodide was added as carrier. A 10/30 St joint was attached to the open end as shown in Figure 7. The tube containing the MeI^{131}, still frozen in liquid nitrogen, was attached at position b, and a bulblet was attached to position a. With the MeI^{131} still frozen stopcock 1 and needle-valves 2 and 3 were opened, and the system evacuated. The needle-value at 3 was closed and the liquid nitrogen was removed from the MeI^{131}. The MeI^{131} was then refrozen and needle value 3 reopened. After the MeI^{131} had been degassed three times, stopcock 1 was closed, needle-valves 2 and 3 opened, and the liquid nitrogen was removed from the tube containing the MeI^{131}. After allowing ample time for the equilibration of the MeI^{131} vapor throughout the closed, evacuated system, the bulblet was sealed off at position c. Needle-valve 2 was then closed, and a new bulblet was placed onto the system at position a. The liquid nitrogen was placed around the tube containing the MeI^{131}, and needle valve 2 and stopcock 1 were opened so that the system would again be evacuated. Stopcock 1 was closed again and needle valve 2 was opened. The liquid nitrogen was again withdrawn, and after the MeI^{131} had again been equilibrated the bulblet was sealed off at position c. The process was repeated for each sample prepared.

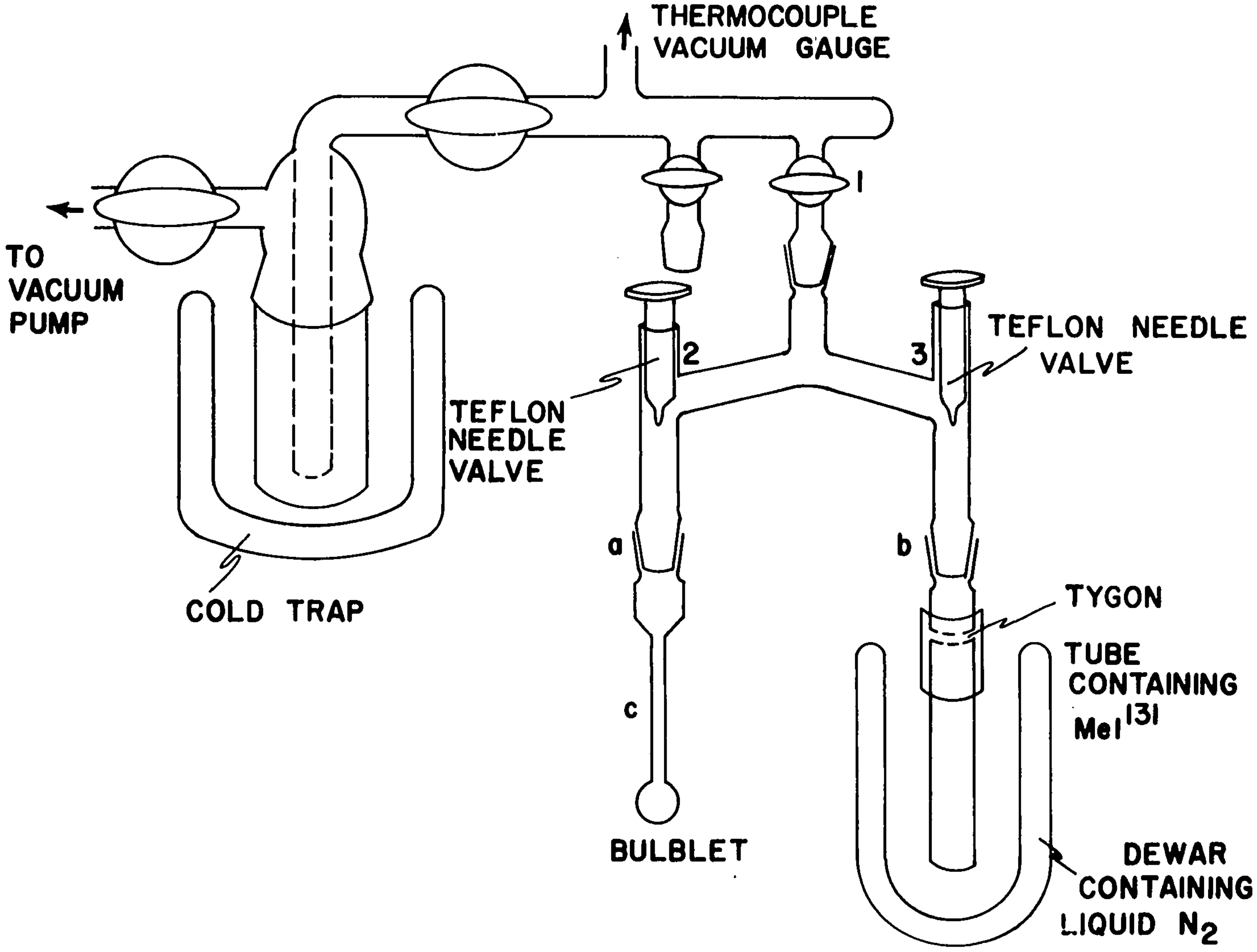


Figure 7. Apparatus for the preparation of MeI^{131} samples

A RIDL model 34-12B 400-channel analyzer was used as a monitor. The counting geometry was constant for all samples, the detector being a 3" x 3" flat NaI(Tl) crystal.

Total iodine-131 activity in the samples must be known in order to calculate product yields, and since the organotellurides used are not enriched in Te^{130}, interfering activities which may be produced during the irradiation must be minimized or eliminated. Table 1 lists the tellurium isotopes, which are activated by thermal neutron irradiation.

The table also lists the (n,γ) reaction products and their pertinent nuclear properties along with the daughter iodine isotopes and their pertinent nuclear properties. The only tellurium activities to be produced in detectable amounts during a 25 min irradiation should be Te^{127} (9.3 hr), Te^{129} (67 min), Te^{131m} (1.2 da), and Te^{131} (25 min). The other isotopes should not produce interfering quantities of activity because of low per cent abundance of the target, small cross section of the target, or long half life of the (n,γ) product with respect to the irradiation time. Since Te^{127} decays to stable I^{127} and Te^{129} decays to 10^7 yr I^{129}, there should be no interfering iodine activity from either of these. The decay of 1.2 da Te^{131m} to I^{131} will be discussed in detail later. It is clear that only Te^{131m} and I^{131} should remain after a period of four days has elapsed from the end of bombardment. This was verified by experiment for a 25 min irradiation. For these analyses the activity of the Te^{131m} was shown to be $\sim 2\%$ of the total. No correction was made since this was within the overall experimental error.

The 400 channel analyzer had to be recalibrated and standardized before each sample series was counted. Only 200 channels were utilized for

Table 1. Nuclear properties of tellurium isotopes and their products[a]

Target			(n,γ) Product			Decay product		
Isotope	Per cent abundance	Cross section (barns)	Isotope	$T_{\frac{1}{2}}$	Radiations (γ-rays)	Isotope	$T_{\frac{1}{2}}$	Radiations
Te^{120}	0.089	2.0	Te^{121m}	150 da	0.082[b], 0.212			
		0.3	Te^{121}	17 da	0.575, 0.506, 0.070	Sb^{121}	Stable	
Te^{122}	2.46	1.0	Te^{123m}	104 da	0.089[b], 0.159[b]	Te^{123}	Stable	
Te^{124}	4.61	2.0	Te^{125m}	58 da	0.110[b], 0.035[b]	Te^{125}	Stable	
Te^{126}	18.71	0.1	Te^{127m}	105 da	0.0887[b]	Te^{127}		
		0.9	Te^{127}	9.3 hr	<1% decay with γ-emission	I^{127}	Stable	
Te^{128}	31.79	0.017	Te^{129m}	33 da	0.1063[b]	Te^{129}		
		0.14	Te^{129}	67 min	0.0268, 0.475, 0.211	I^{129}	1.6 x 10^{7} yr	
Te^{130}	34.48	0.03	Te^{131m}	1.2 da	--[c]	I^{131}	8.02 da	--[d]
						Te^{131} (19%)		
		0.2	Te^{131}	25 min	--[c]	I^{131}	8.02 da	--[d]

[a] Reference 7.

[b] Isomeric transition.

[c] See Table 8.

[d] Decay scheme shown on page 34.

counting and the analyzer was calibrated so that the 200 channels corresponded to an energy range of 0-0.81 Mev. However, the analyzer was operated in the differential mode, and the discriminators were set for the limits shown in Figure 6. The gain stabilizers were set for channel 16 and for the center of the 0.36 Mev peak of I^{131}. The center of the 0.36 Mev peak was always placed in channel 92 and the counts recorded between channels 64 and 110. A Ba^{133} standard source (157,000 cts/min) was counted after each calibration, and the counting rate of the standard varied less than ± 1% for all experiments.

Case B - Results of the Beta Decay of Purified Organotellurides(Te^{131}) in Solution

Sample preparation

Diethyltelluride and di-n-butyltelluride samples were prepared for irradiation by pipetting the telluride into quartz bulblets, degassing the samples by the freeze-thaw method, sealing the bulblets, and packing them in a polyethylene container. The bulblets have previously been described, and the bulblet ready for irradiation is shown in Figure 1.

Irradiation

All samples were irradiated in "rabbit" R-5 at the ALRR. This irradiation position received a flux of 3.5×10^{13} neutrons cm^2/sec at a power level of 5 megawatts. A pneumatic tube carried the samples between the "hot" laboratory where the solutions were prepared, and the irradiation position in the reactor.

All irradiations were for a time duration of 25 min and were performed at full power.

Solution preparation

After irradiation the organotelluride was separated by gas chromatography from various products formed by recoil and radiation damage during the irradiation. The gas chromatograph used in this procedure was built from laboratory spare parts. A Sargent Laboratory Oven (no. S-63995) was used as the chromatograph oven. The detection unit consisted of stainless steel conductivity elements obtained from Gow-Mac Instrument Company and inserted into a thermo-conductivity cell block, which had been constructed by the Ames Laboratory machine shop. The 7 mm pyrex column and the T.C. cell were placed in the chromatograph as shown in Figure 8. The temperature of the column and T.C. cell were maintained at the same temperature as the chromatograph oven, which was operated isothermally. The breaker-injection port system was identical to that shown in Figure 3 and was contained in an insulated box attached to the top of the oven. The output from the T.C. cell was registered by a Sargent strip-chart recorder, model MR. A bubbler containing mineral oil was used for leak detection in the place of a commercial rotameter.

The chromatograph and the vacuum manifold used for degassing the samples were placed in a large walk-in hood in the hot laboratory. A smaller hood equipped as a glove box and located directly across the laboratory from the walk-in hood was used for the preparation of the solutions and handling of the organotellurides.

The procedure followed for the preparation of the solutions following irradiation of the organotelluride is given below.

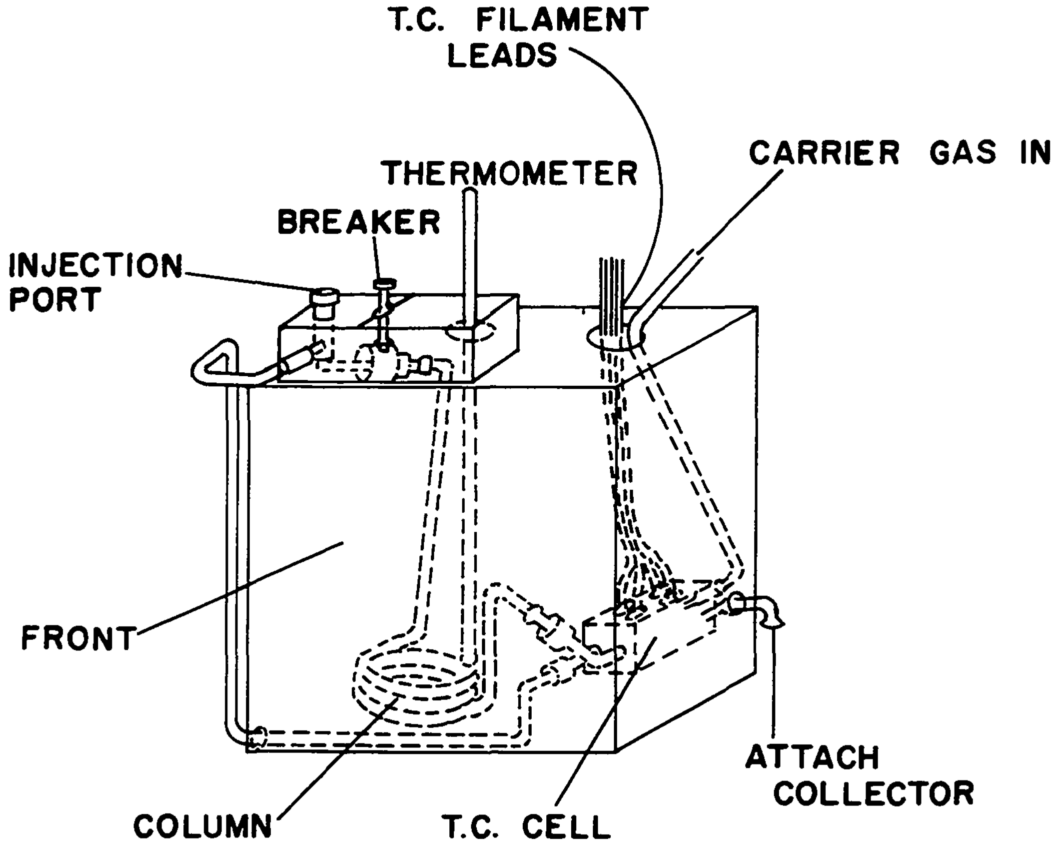


Figure 8. Prep chromatograph for purification of organotellurides

1) Immediately after irradiation the sample was transferred from the receiver to the small hood, where the quartz bulblet was removed from the irradiation capsule.

2) The quartz bulblet was inserted into the chromatograph breaker. After the system had been closed off and the bridge power and recorder turned on, the bulblet was broken.

   Average time from end of irradiation: 3 min.

3) Sample collection was begun about 30 sec after elution of the organotelluride began and stopped about 30 sec before elution of the telluride ended. Examples of chromatograms for the organotellurides are given in Figures 9 and 10. The fraction of the peak collected is indicated. The average time for elution was 6 min for diethyltelluride and 13 min for di-n-butyltelluride. The longer time necessary for elution of di-n-butyltelluride was probably due to the slow diffusion of the telluride from the broken bulblet into the stream of carrier gas. The chromatograph was operated at a temperature of 180°C, the highest temperature attainable, while the boiling point of di-n-butyltelluride at 760 mm is well above 200°C. The value obtained from the literature is 132-135°C at 99 mm (19).

4) The collector was sealed off and transferred to the small hood. The organotelluride was pipetted from the collector into a special 5 ml volumetric flask (Figure 11) containing approximately 2 ml of hydrocarbon solvent. After addition of the organotelluride, the flask was filled to volume with the same hydrocarbon. The solution preparation was considered complete at this point.

Figure 9. Chromatograms of diethyltelluride

a. Before irradiation

b. After irradiation

Operating conditions --

Oven temp: 145°C

Flow rate: 10 sec/10 ml

Column: 20% diisodecylphthalate on Chromosorb P, 10 ft long, 7 mm diameter

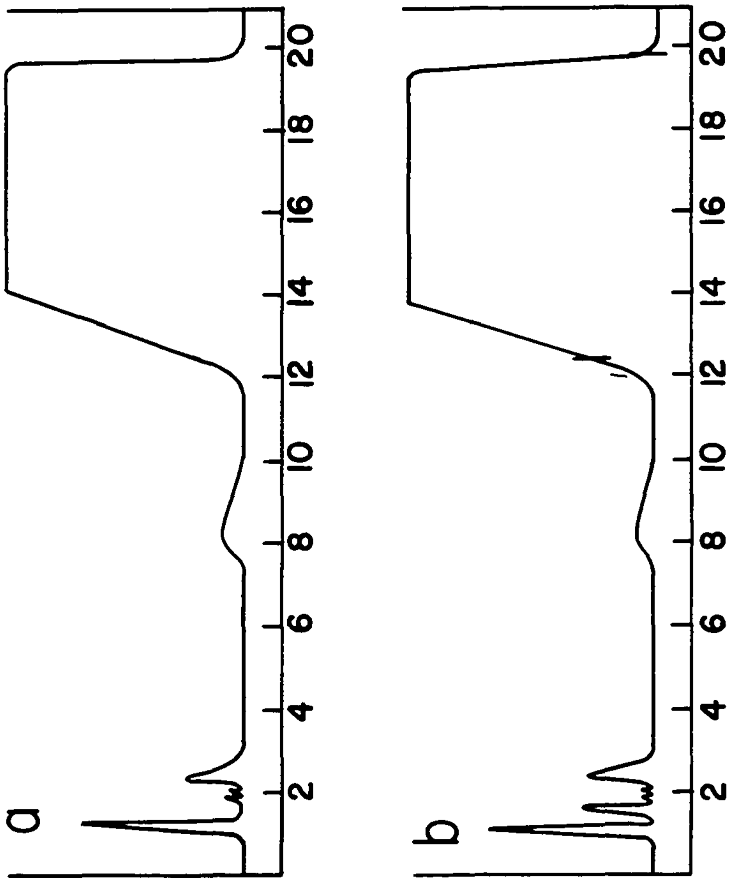

a
b
2
4
6
8
10
12
14
16
18
20

Figure 10. Chromatograms of di-n-butyltelluride

a. Before irradiation

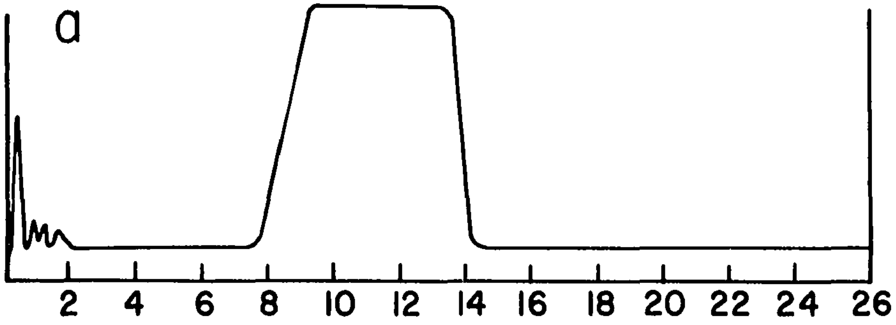
b. After irradiation

Operating conditions --

Oven temp: 180°C

Flow rate: 8 sec/10 ml

Column: 20% silicone oil on Chromosorb P, 10 ft long, 7 mm diameter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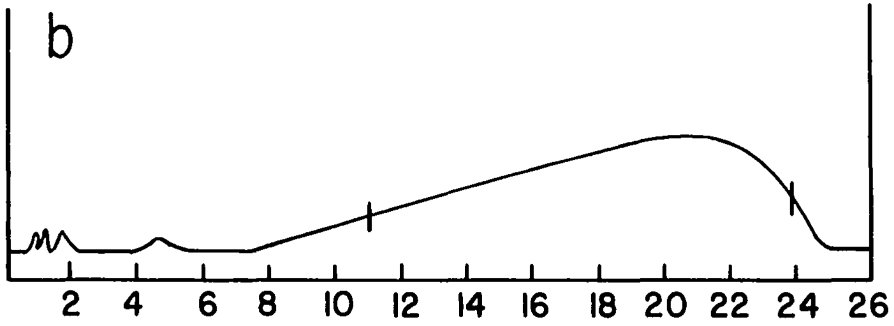
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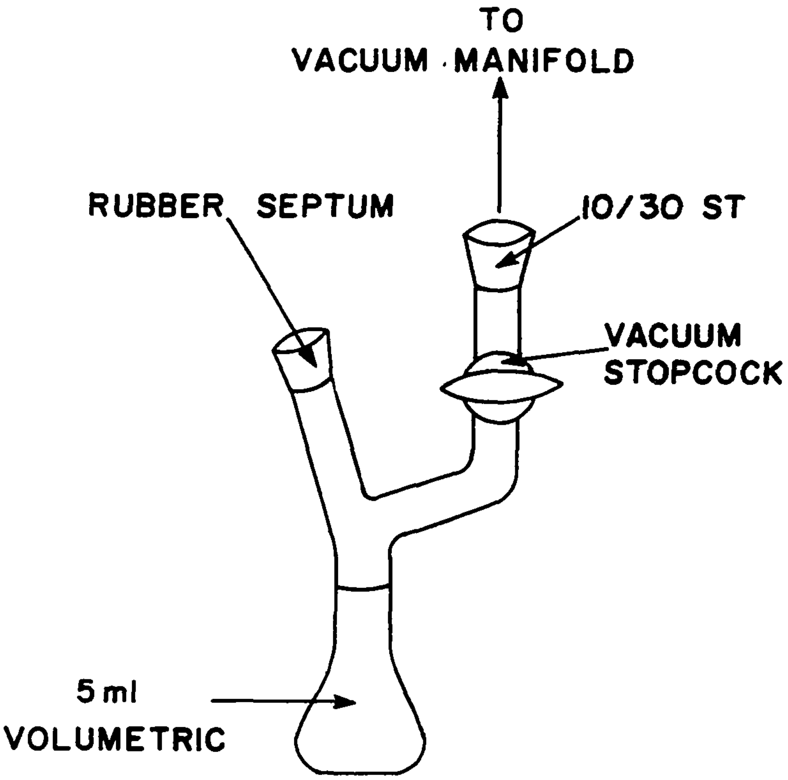


Figure 11. Special flask for preparation of solutions

The time required to prepare the solution after collecting had stopped was approximately one min.

5) The flask containing the solution was placed onto the vacuum manifold, and the solution was degassed by the freeze-thaw technique. The time required for the degassing procedure was approximately 10 min.
6) After the solution had been degassed, the stopcock on the flask was closed and the flask removed from the vacuum manifold, wrapped in black tape and allowed to stand for approximately 5 hr, 12 half lives of the Te^{131}.
7) At this time pyrex bulblets were filled with the solution from the flask and the samples were degassed by the freeze-thaw technique. The special flask was used in order to eliminate oxidation of the organotelluride while this step was being accomplished.

Analysis

The equipment and procedures used for analysis were the same as those previously described. However, in this series of experiments 4.1% of the total activity was found to have the same resolution time as the organotelluride. In order to prove that this activity was that of radiotelluride and not an organoiodide(I^{131}) possessing the same resolution time, the organotelluride fraction was collected after passing through the sidehole crystal, and a spectrum was recorded. The spectrum is shown in Figure 12. It clearly is not that of I^{131} and must be due to longer lived tellurium isotopes. The spectrum is probably the result of at least three

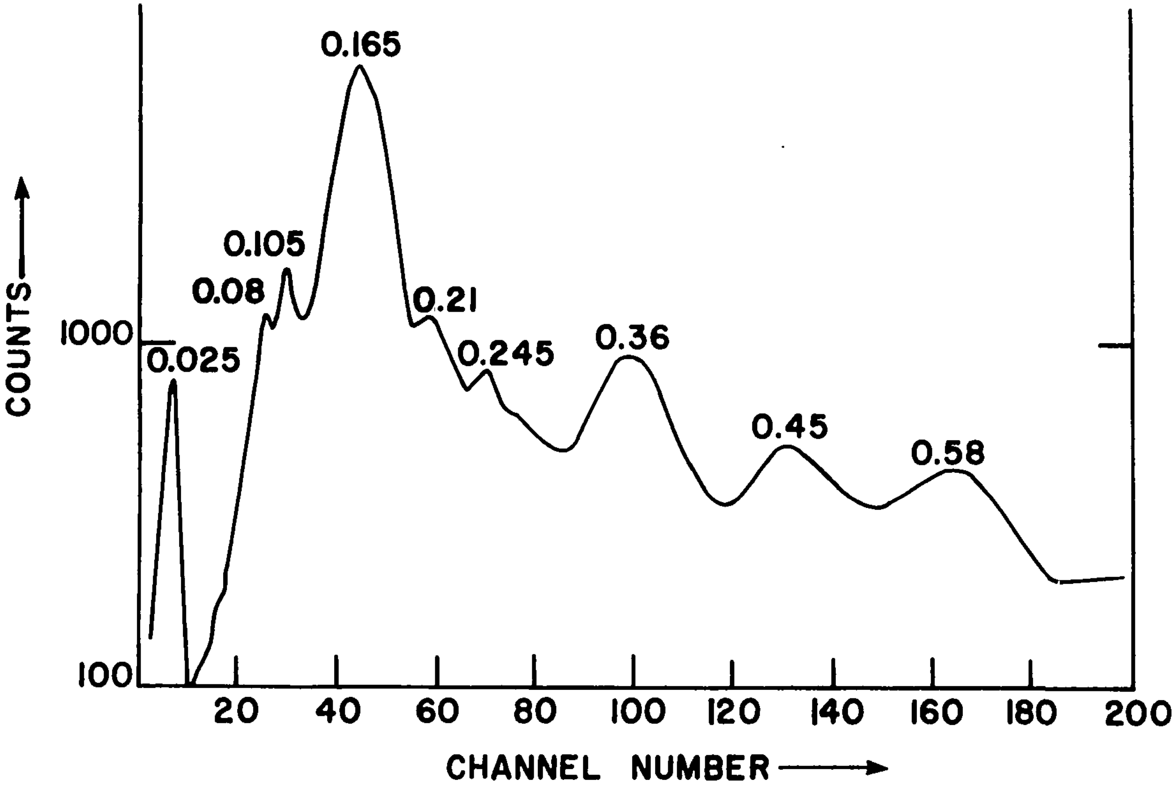


Figure 12. Spectrum of organotelluride fraction

tellurium isotopes: Te^{131m} (1.2 da), Te^{129m} (33 da), and Te^{129} (67 min, resulting from the decay of Te^{129m}). Thus the measure of the total activity for this set of experiments was not given by Equation 11; it was given by

$$A' = 0.959\ A \tag{13}$$

Only a small fraction of the long lived tellurium activities detected in the organotelluride fraction at the time of analysis would have decayed before the chromatographic separation following the irradiation of the telluride, while nearly one-third of the Te^{131} would have decayed by that time. That is, because of the purification of the telluride following irradiation, the specific activity of the I^{131} in the solution was about one-third of that in the first series of experiments, but the specific activity of the long lived radiotelluride was approximately the same.

RESULTS

Case A - Results of Beta Decay Following Neutron Activation of Prepared Solutions

The results of the preliminary experiments, in which the solutions were irradiated after preparation, are shown in graphic form in Figures 13-21. These graphs show the effect of dose on the product distribution. The γ-flux through the sample during irradiation is uniform; therefore, every part of the sample receives the same dose. If the γ-flux and the sample size are constant for each irradiation at a particular power level and irradiation position, the irradiation time can be used as a measure of the dose received. For this reason, the yield of each product has been plotted versus the irradiation time.

Treatment of error

The yields recorded on the graphs are expressed in terms of per cent of the total organic activity. Least square analyses were performed for all product yields, and the yields at "zero" dose are reported in Tables 2-4. The error reported is the standard deviation of the intercept resulting from the least square analysis.

Discussion of results

A larger dose effect resulted at 5 megawatts than at 4 megawatts as was expected. This is evidenced by the larger slopes resulting from the dose effect at 5 megawatts. However, comparison of Tables 2 and 3 show that the yield at zero dose is the same for products at the two power levels if other conditions are unchanged. That is, the only difference in these two series of experiments was the increased slope at 5 megawatts.

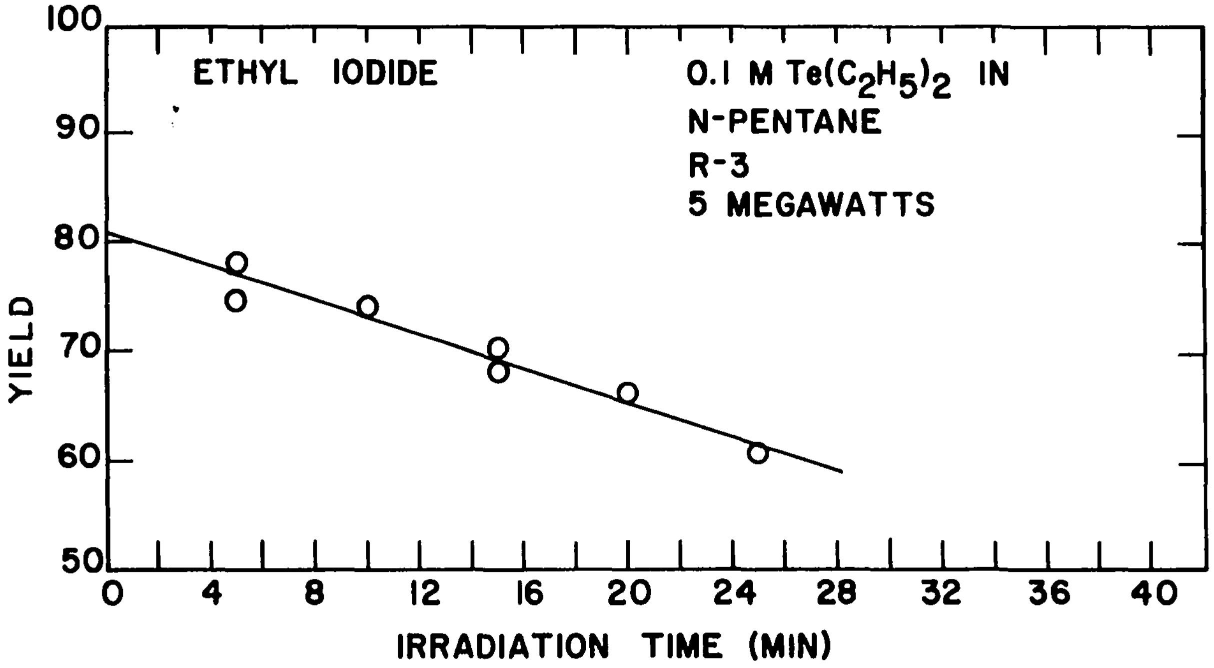


Figure 13. Effect of dose on the yield expressed as per cent of the total organic activity

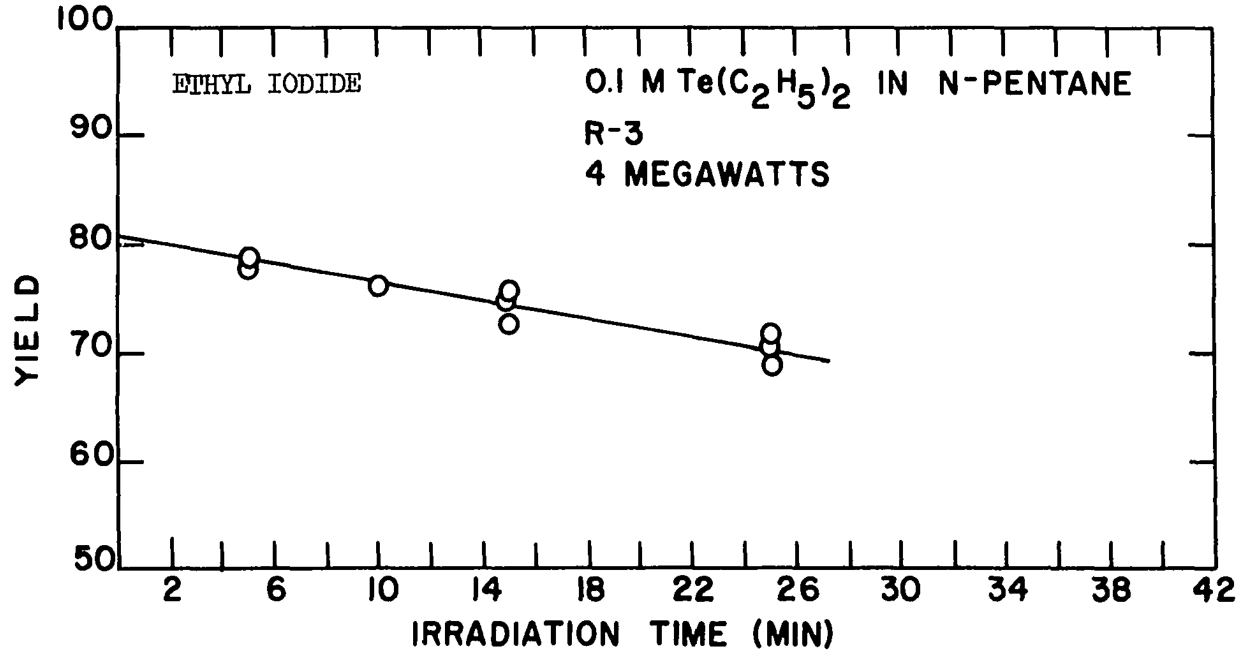


Figure 14. Effect of dose on the yield expressed as per cent of the total organic activity

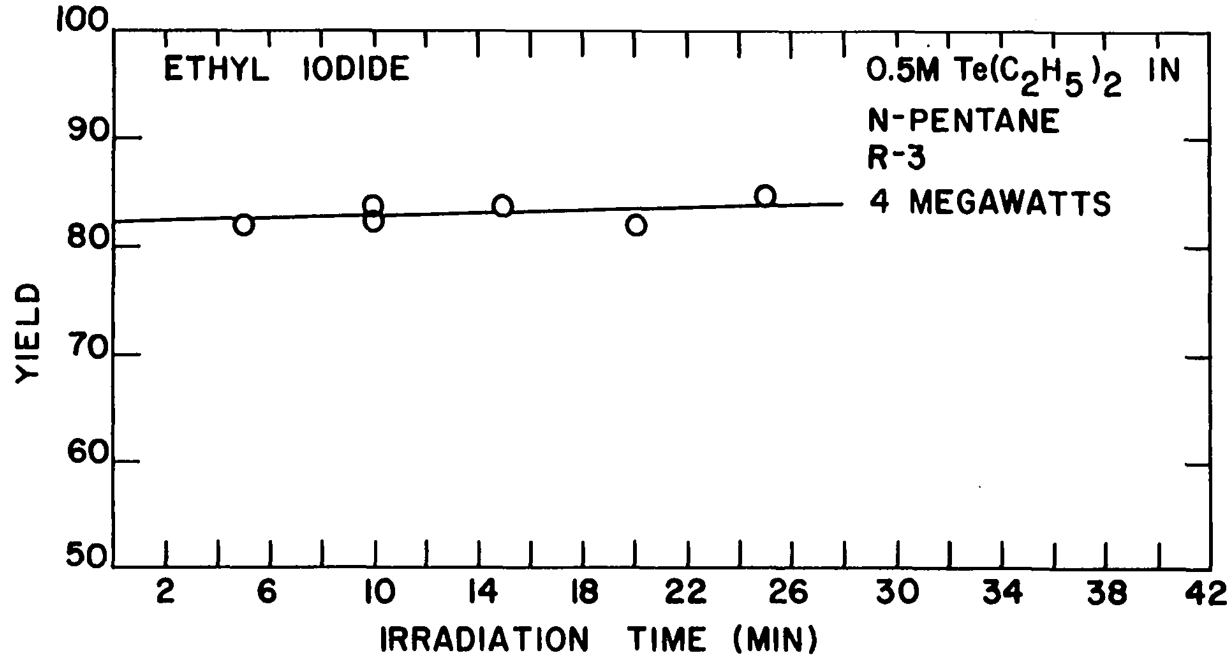


Figure 15. Effect of dose on the yield expressed as per cent of the total organic activity

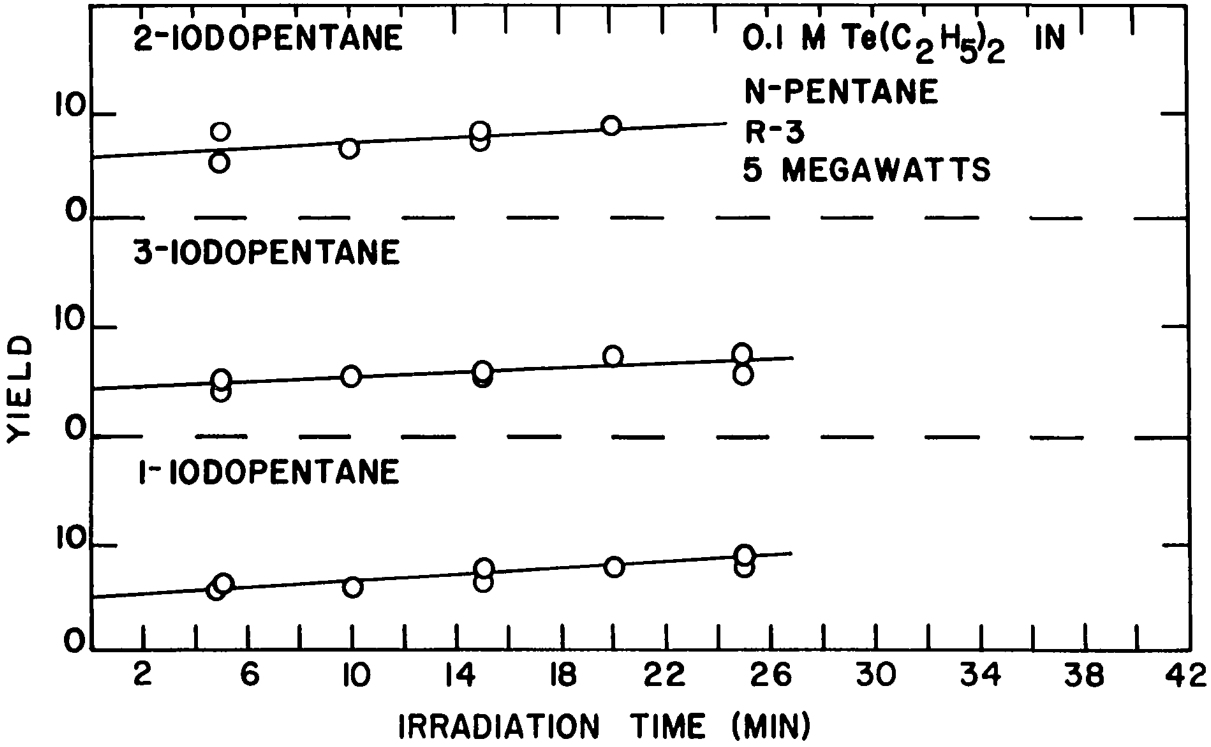


Figure 16. Effect of dose on the yield expressed as per cent of the total organic activity

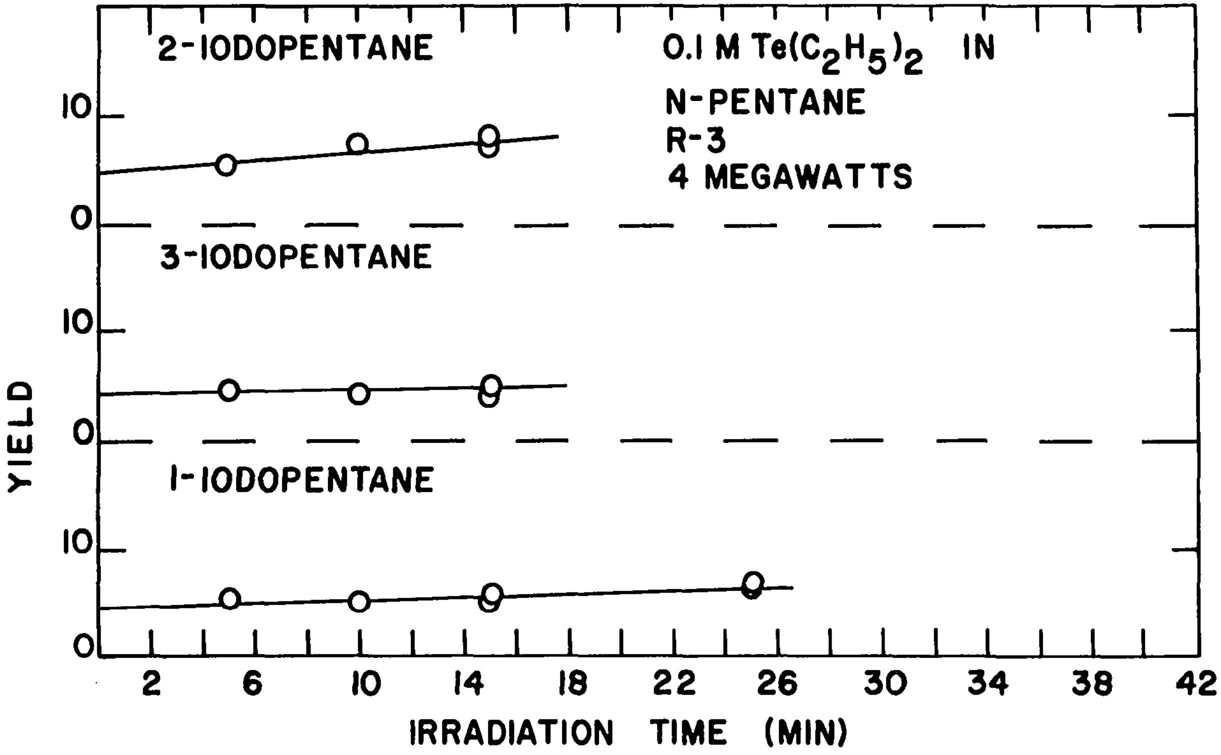


Figure 17. Effect of dose on the yield expressed as per cent of the total organic activity

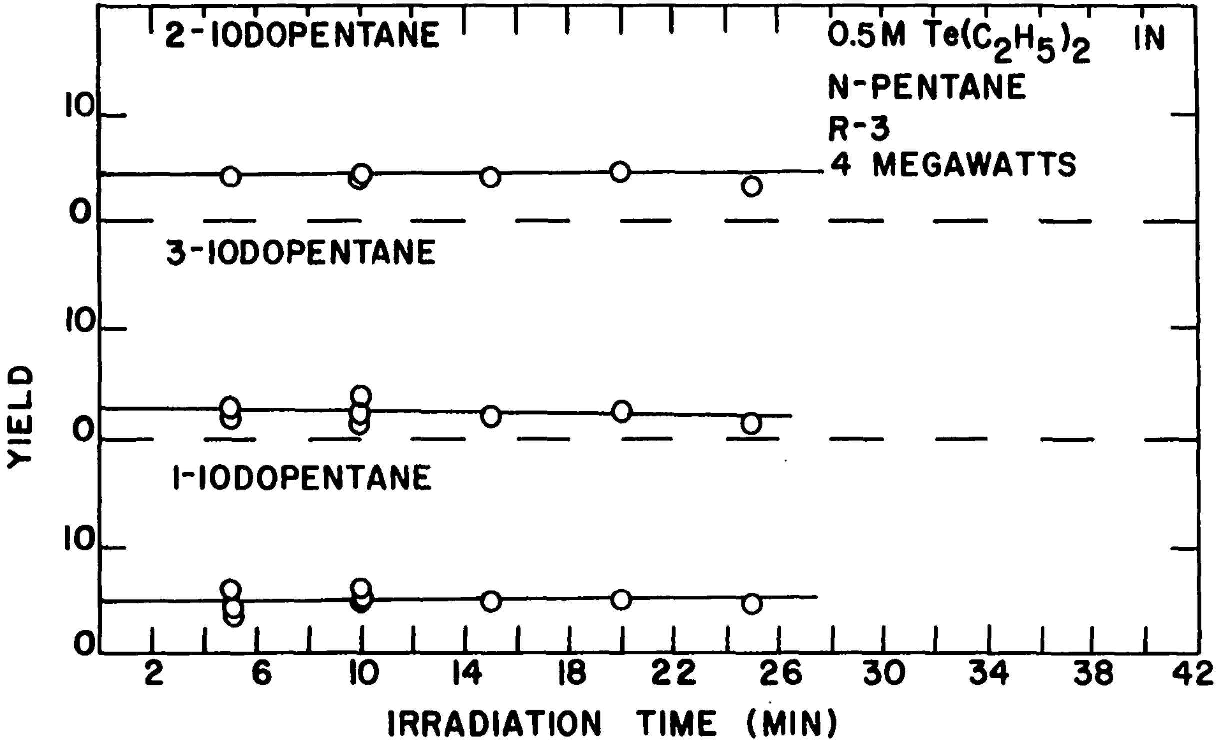


Figure 18. Effect of dose on the yield expressed as per cent of the total organic activity

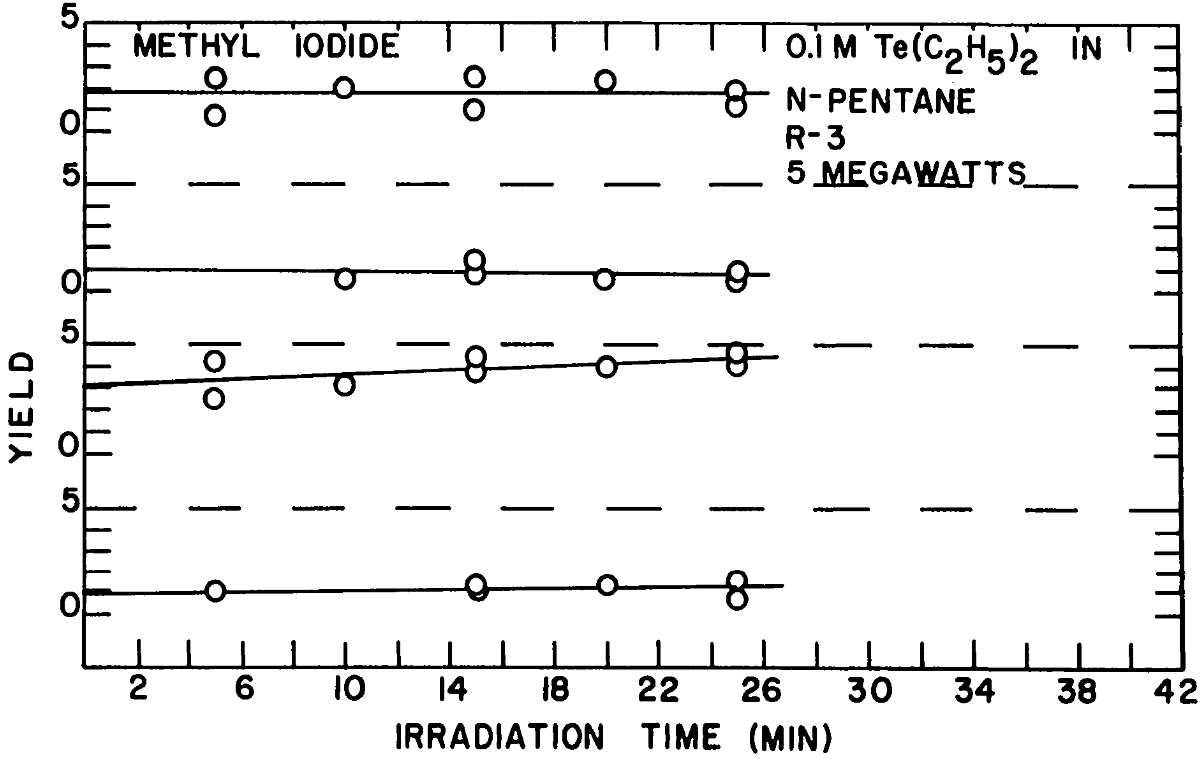


Figure 19. Effect of dose on the yield expressed as per cent of the total organic activity

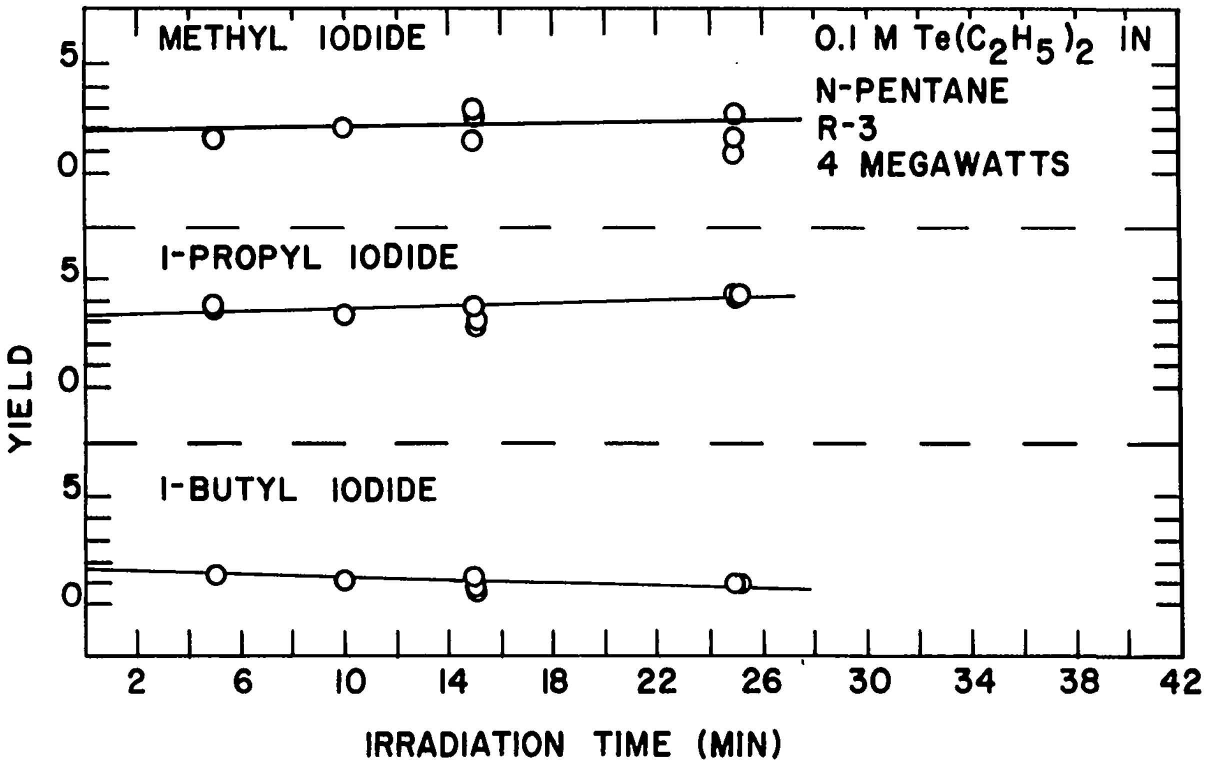


Figure 20. Effect of dose on the yield expressed as per cent of the total organic activity

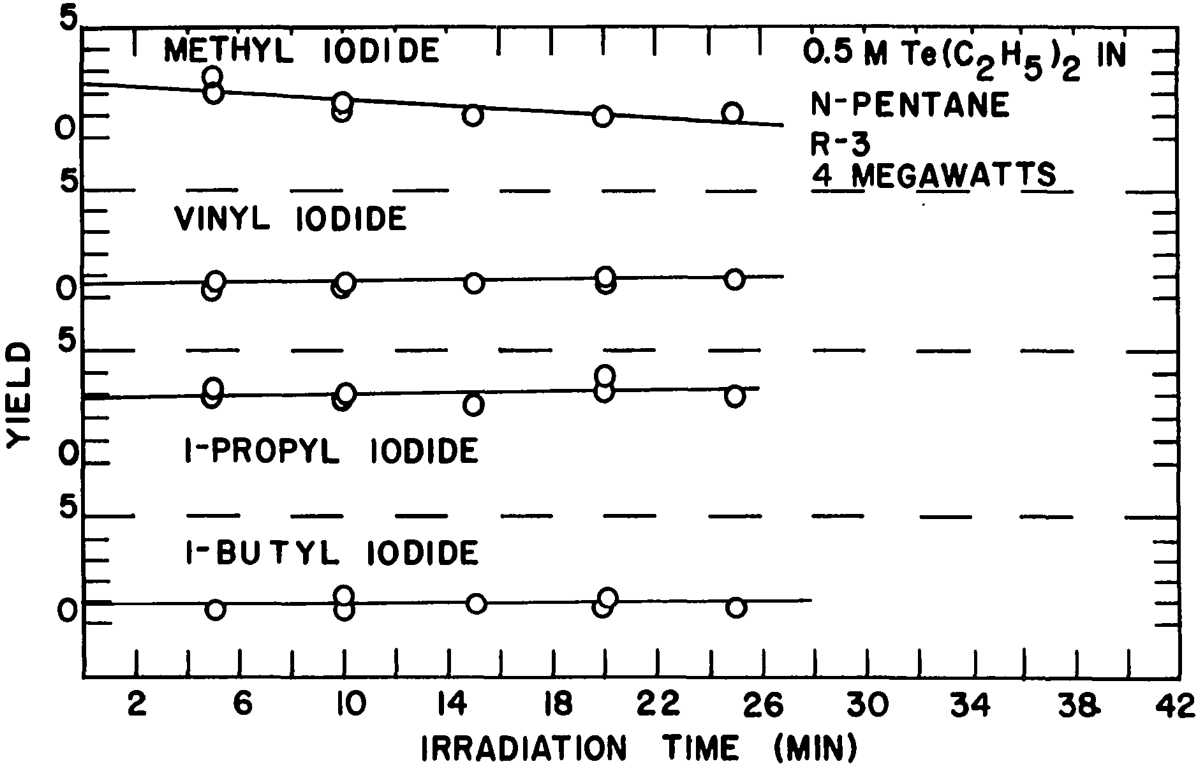


Figure 21. Effect of dose on the yield expressed as per cent of the total organic activity

Table 2. Product distribution from dose studies I. 0.1 M $Te(C_2H_5)_2$ in n-pentane[a]

Product	Yield (% total organic activity)	Yield[b] (% total activity)
Iodomethane	1.89 ± 0.76	1.64
Vinyl iodide[c]		
Iodoethane	80.82 ± 1.31	70.20
1-Iodopropane	3.08 ± 0.36	2.68
1-Iodobutane	1.52 ± 0.37	1.32
2-Iodopentane	4.78 ± 0.93	4.16
3-Iodopentane	4.26 ± 0.17	3.70
1-Iodopentane	4.66 ± 0.35	4.04

[a] Irradiation position: R-3 at ALRR.
Power level: 4 megawatts.

[b] Per cent activity in organic phase: 86.89 ± 6.14.

[c] Poor resolution of peak did not permit recording of data for this product from this series of runs.

Table 3. Product distribution from dose studies II. 0.1 M $Te(C_2H_5)_2$ in n-pentane[a]

Product	Yield (% total organic activity)	Yield[b] (% total activity)
Iodomethane	1.79 ± 0.60	1.55
Vinyl iodide	0.97 ± 0.51	0.84
Iodoethane	81.03 ± 1.25	70.30
1-Iodopropane	3.04 ± 0.49	2.64
1-Iodobutane	0.83 ± 0.44	0.72
2-Iodopentane	5.76 ± 0.26	5.00
3-Iodopentane	4.34 ± 0.57	3.77
1-Iodopentane	5.00 ± 0.45	4.34

[a] Irradiation position: R-3 at ALRR.
Power level: 5 megawatts.

[b] Per cent activity in organic phase: 86.89 ± 6.14.

Table 4. Product distribution from dose studies III. 0.5 M $Te(C_2H_5)_2$ in n-pentane[a]

Product	Yield (% total organic activity)	Yield[b] (% total activity)
Iodomethane	2.41 ± 0.41	2.09
Vinyl iodide	0.58 ± 0.14	0.50
Iodoethane	82.09 ± 1.02	71.30
1-Iodopropane	2.84 ± 0.24	2.46
1-Iodobutane	0.87 ± 0.27	0.76
2-Iodopentane	4.50 ± 0.49	3.91
3-Iodopentane	2.65 ± 0.56	2.30
1-Iodopentane	4.88 ± 0.52	4.23

[a] Irradiation position: R-3 at ALRR.
Power level: 4 megawatts.

[b] Per cent activity in organic phase: 86.89 ± 6.14.

Comparison of the results of Tables 3 and 4 show, that with the exception of iodomethane and 3-iodopentane, the yield of the various products in 0.5 M $Te(C_2H_5)_2$ in n-pentane at 4 megawatts is within experimental error of their yields in 0.1 M $Te(C_2H_5)_2$ in n-pentane at 4 megawatts.

Several samples of 0.1 M $Te(C_2H_5)_2$ in n-pentane solutions were irradiated at 5 megawatts for various time intervals in order to determine the total organic yield resulting from these irradiations. The value found for the per cent activity in the organic phase was 86.89 ± 6.14. The yield of each product was calculated in terms of per cent of the total activity and is reported in the second column of Tables 2-4.

Case B - Results of the Beta Decay of Purified Organotellurides(Te^{131}) in Solution

The results of these experiments are given in Tables 5 and 6.

Table 5. Yields of products resulting from the fragmentation of the organotelluride (%)

Products		Solvents				
		n-pentane	n-hexane	Cyclopentane	Benzene	Toluene
Iodomethane						
	a	0.90 ± 0.21	0.67 ± 0.16	0.0	0.36 ± 0.14	0.0
	b	0.91 ± 0.12	0.86 ± 0.17	0.38 ± 0.04	0.0	0.0
Vinyl iodide						
	a	1.05 ± 0.09	0.48 ± 0.17	0.71 ± 0.22	0.82 ± 0.26	0.82 ± 0.20
	b	0.41 ± 0.09	0.52 ± 0.10	0.49 ± 0.11	0.0	
Iodoethane						
	a	88.34 ± 2.83	94.67 ± 0.12	91.43 ± 1.18	91.67 ± 3.29	82.21 ± 2.50
	b	1.58 ± 0.24	1.28 ± 0.32	1.83 ± 0.36	0.52 ± 0.22	1.01 ± 0.42
1-Iodopropane						
	a	0.76 ± 0.11	0.65 ± 0.32	0.0	0.0	0.0
	b	0.60 ± 0.11	0.69 ± 0.06	0.0	0.0	0.0
1-Iodobutane						
	a	0.88 ± 0.21	0.62 ± 0.40	0.57 ± 0.14	1.38 ± 0.10	1.51 ± 0.31
	b	69.95 ± 2.18	79.47 ± 2.69	78.05 ± 2.17	64.09 ± 2.61	69.00 ± 2.88
2-Iodobutane						
	a	0.0	0.0	0.0	0.0	0.0
	b	1.46 ± 0.14	2.08 ± 0.16	2.10 ± 0.16	0.89 ± 0.30	---

[a] Diethyltelluride.

[b] Di-n-butyltelluride.

Table 6. Yields of products from reactions of I· with solvent molecules

Solvent	Product	Organotelluride Diethyltelluride	 Di-n-butyltelluride
n-pentane			
	2-Iodopentane	1.87 ± 0.32	1.84 ± 0.32
	3-Iodopentane	0.98 ± 0.21	0.81 ± 0.06
	1-Iodopentane	1.83 ± 0.39	1.54 ± 0.23
n-hexane			
	2- and 3-Iodohexane	3.34 ± 0.16	3.36 ± 0.41
	1-Iodohexane	1.83 ± 0.59	2.67 ± 0.62
Cyclopentane			
	1-Iodopentane	1.39 ± 0.30	2.05 ± 0.33
	Iodocyclopentane	4.02 ± 0.38	3.80 ± 0.34
Benzene			
	Iodobenzene	1.87 ± 0.15	1.76 ± 0.27
Toluene			
	o- and p-Iodotoluene	1.40 ± 0.13	1.51 ± 0.32

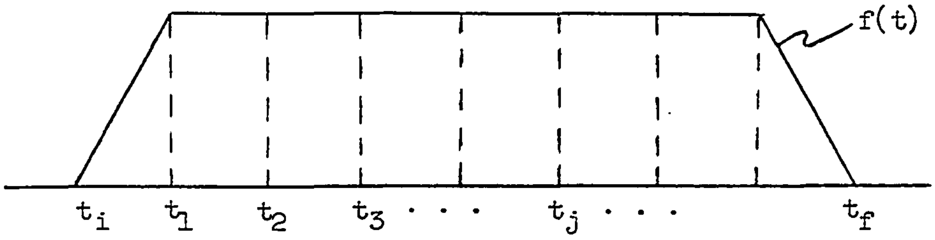
Treatment of error

Each number reported in Table 5 is the average of three to seven values. The error reported is the standard deviation of a single measurement.

Decay of Te^{131} before the solution was prepared

An equation has been derived for calculating the fraction of Te^{131} decays occurring before solution, i.e., before each organotelluride molecule is surrounded by hydrocarbon molecules. It is assumed that no I^{131} containing species are present as elution of the organotelluride begins. A function is assumed which closely approximates the elution curve of the telluride.

Consider the following elution curve:



If f(t) describes the curve, the fraction of the organotelluride eluted in a given time interval is given by

$$\frac{\int_{t_j}^{t_{j+1}} f(t)\, dt}{\int_{t_i}^{t_f} f(t)\, dt} = A_j \tag{13}$$

The number of radioactive organotelluride molecules at any particular time, t_j, is

$$N = \frac{\phi \sigma V \rho N_o}{\lambda M} (1 - e^{-\lambda t_o})\, e^{-\lambda t_j} \tag{14}$$

where

t_o = irradiation time

V = volume of the organotelluride in ml

ρ = density of the organotelluride

N_o = Avogadro's number

M = molecular weight of the organotelluride

ϕ = neutron flux

σ = cross section of the reaction $Te^{130}(n,\gamma)Te^{131}$

λ = decay constant for Te^{131}

For any particular elution fraction the number of telluride molecules undergoing decay between t_j and T_o is

$$PA_j\ (1 - e^{-\lambda t_o}) \left[e^{-\lambda t_j} - e^{-\lambda T_o}\right] \qquad (15)$$

where

T_o = time period between the end of irradiation and the time when the solution was prepared, and

$P = \dfrac{\phi\sigma V\rho N_o}{\lambda M}$

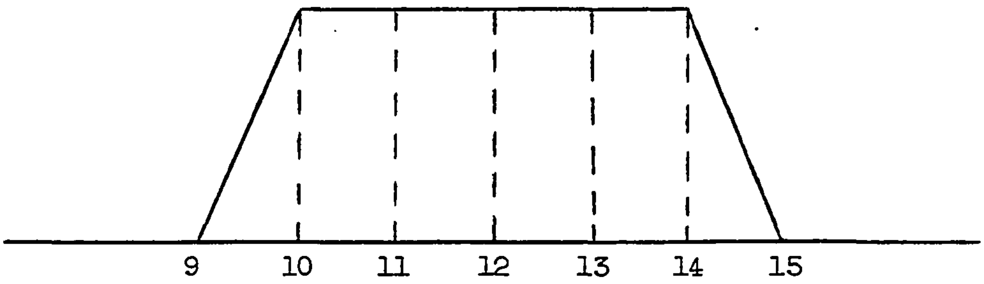
Therefore, the fraction of organotelluride decaying between elution and the solution preparation is given by:

$$F = \frac{P(1-e^{-\lambda t_o}) \left[A_1(e^{-\lambda t_1} - e^{-\lambda T_o}) + A_2(e^{-\lambda t_2} - e^{-\lambda T_o}) \ldots\right]}{P(1-e^{-\lambda t_o})\, e^{-\lambda T_o}}$$

or

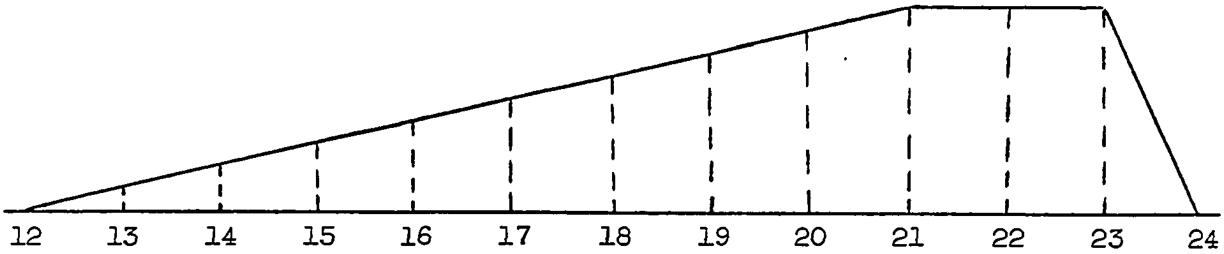
$$F = \frac{\sum\limits_{j=1} A_j(e^{-\lambda t_j} - e^{-\lambda T_o})}{e^{-\lambda T_o}} \qquad (16)$$

An approximation to the average elution curve for diethyltelluride is sketched below:



If the total area is normalized to 1 and if T_o is 16 min, the fraction of diethyltelluride molecules decaying before solution is calculated from Equation 16 to be 12.5%.

The average elution curve for di-n-butyltelluride is approximated below:



If the total area is normalized to 1 and if T_0 is 25 min, the fraction of di-n-butyltelluride molecules decaying before the solution has been prepared is calculated from Equation 16 to be 14.8%.

Scavenger studies

Scavenger studies were attempted; however, difficulties were encountered. The scavenger most commonly used because of its desirable properties, such as low activation energy for its reaction with radicals, is I_2. Upon the addition of I_2 to solutions of dialkyltellurides a flocculent precipitate, R_2TeI_2, is formed thereby decreasing the I_2 concentration. It was not certain that the scavenging action of the I_2 had not been hindered. The use of 2,2-diphenyl-1-picrylhydrazyl, DPPH, as a scavenger was also tried. However, DPPH is a bulky, stable free radical and its scavenging action is not clearly understood (78). In solutions of DPPH + diethyltelluride in n-pentane and in n-hexane, the yields of all products were within experimental error of the same product products when no scavenger was present.

Discussion of results

The data for the results of the beta decay of di-n-butyltelluride in toluene are incomplete in that 1) the value for 1-iodobutane may be doubtful and 2) no value is reported for 2-iodobutane.

The yields reported are all in terms of per cent of the total activity.

The activity in most experiments was on the order of 100-500 counts in the peaks of those products produced in small yields. The separations had to be particularly good in order to achieve results with acceptable standard deviations. The large standard deviations were probably due to the low activity of the samples. The number of I^{131} atoms present at the time of analysis was calculated to be 4.88×10^{10}. The following assumptions were made: 1) the period of irradiation is 20 min, 2) only 60% of the Te^{131} produced is in the form of the dialkyltelluride in question due to (n,γ) recoil effects, 3) 90% of the dialkyltelluride-131 is recovered from the chromatographic separation, 4) the purified dialkyltelluride sample is diluted to 5 ml and 0.3 ml samples of this solution are prepared for analysis, and 5) analysis is performed four days after irradiation ceases.

DISCUSSION

Effect of Neutron Activation on Results

In studying the effects of beta decay in these systems it is important to know that the products observed have been produced by mechanisms initiated by beta decay from the particular organotelluride-131 in question. If the system is clouded by (n,γ) recoil effects or radiation damage, it becomes quite complex. Related to this subject is a study by Halpern (73), in which he compared the results of the beta decay of $Te^{131}Cl_4$ and $Te^{132}Cl_4$ in toluene. He prepared the $Te^{132}Cl_4$ from metallic tellurium(Te^{132}) (78 hr half life) and dissolved it in toluene. The short half life (25 min) of Te^{131} did not permit the preparation of $Te^{131}Cl_4$ before dissolving in toluene; therefore he had to irradiate a toluene solution in which $TeCl_4$ had previously been dissolved. In the comparison of the decay of the two isotopes the methods by which the solutions were prepared must be considered. It cannot be assumed that all of the Te^{131} formed is in the form of $Te^{131}Cl_4$ due to recoil effects from the $Te^{130}(n,\gamma)Te^{131}$ reaction and radiation effects from the reactor radiation field. In an earlier study Halpern (71) found that the covalent bond, in the case of dibenzyltelluride(Te^{131}), always breaks in the $Te^{131} \longrightarrow I^{131}$ transformation. Hence he suggested that bonds will break in $TeCl_4$ as a result of the beta decay, freeing the I^{131} atom and negating any effect by the $Te^{130}(n,\gamma)Te^{131}$ reaction. He also placed a solution of $Te^{132}Cl_4$ in toluene in the reactor radiation field for 20 min, and no effect was noticed on the product distribution. Thus Halpern reasoned that the activation and radiation effects were negligible, and that the yields were a direct result of the chemical consequences of the beta decay of $Te^{131}Cl_4$.

First, it cannot be assumed that because a covalent bond breaks as a result of the beta decay of a particular isotope in one compound, it will do so in other compounds (50,51,52,53,55). Bond rupture depends on many factors, such as structure, bond distance, and bond energy. Secondly, placing Te^{132} (half life 78 hr) in a radiation field for 20 min is not going to have the same effect on product yields as placing Te^{131} (half life 25 min) in a radiation field for 20 min. In the case of $Te^{131}Cl_4$ nearly one-half of the I^{131} present at the time of the analysis was born in the radiation field of the reactor, whereas in the case of Te^{132} only a very small fraction of the Te^{132} atoms would undergo decay in the 20 min irradiation period.

In preliminary experiments solutions of diethyltelluride in n-pentane were prepared and irradiated as discussed in the experimental section. Figures 13, 14, 16, 17, 19, and 20 show the dose effect at two different power levels (or two different radiation field intensities) on the product distribution of 0.1 M $Te(C_2H_5)_2$ in n-pentane. The radicals surrounding the $Te^{131}(C_2H_5)_2$ at the time of decay and resulting from the radiation field apparently influence the product distribution. Some products are affected to a larger extent than are others, which is probably a result of a higher G value for the production of some radical precursors. It is highly probable that a radiation effect was also experienced by the $Te^{131}Cl_4$ in toluene solution.

In order to determine if there is an effect resulting from the $Te^{130}(n,\gamma)Te^{131}$ reaction, the "zero" dose product distribution resulting from the irradiation of a solution of diethyltelluride in n-pentane (n,γ + beta decay processes) can be compared to that of a solution of diethyltelluride-131 in n-pentane (beta decay only). This is done in Table 7. There are several large differences which may be attributed in all or part to the effect of the $Te^{130}(n,\gamma)Te^{131}$ reaction.

1) The yield of iodoethane is 18% less in the solution irradiated to produce the Te^{131}.
2) The yields of 2-, 3-, and 1-iodopentane are 3.13%, 2.79%, and 2.51% higher in the solutions irradiated to produce the Te^{131}.
3) The total organic yield is ~10% less in the solutions irradiated to produce the Te^{131}.

Table 7. $Te^{130}(n,\gamma)Te^{131}$ effect

Product	Yield[a] (% total activity)	Yield[b] (% total activity)
Iodomethane	1.55	0.90
Vinyl iodide	0.84	1.05
Iodoethane	70.30	88.34
1-Iodopropane	2.64	0.76
1-Iodobutane	0.72	0.88
2-Iodopentane	5.00	1.87
3-Iodopentane	3.77	0.98
1-Iodopentane	4.34	1.83

[a] Irradiation of solution of diethyltelluride in n-pentane. Data are those of Table 3, since the product distribution in Table 2 is within experimental error of that in Table 3.

[b] Diethyltelluride(Te^{131}) separated after irradiation and dissolved in n-pentane.

As a result of the (n,γ) recoil both C-Te bonds may rupture, and the Te^{131} may stabilize in solution as a neutral uncombined species. In view of the fact that in case B such a large percentage of the beta decays result in an unexcited I^{131} as evidenced by the ~90% yield of ethyl iodide-131, it is possible that the decay of a large fraction of a neutral Te^{131} species in solution would result in a thermalized I^{131} atom. Such an I^{131} atom would in the absence of radicals react with another iodine atom yielding molecular iodine, thereby decreasing the organic yield in case A. The fact that the total organic yield was 10% less in case A may also be due to the reaction of products resulting from the beta decay of Te^{131} during the period of irradiation with either the radiation field itself or with radiation products to produce high boiling polymers. These high boiling products would not be detected since they would remain behind on the chromatographic column during an analysis.

In a high percentage of the $Te^{130}(n,\gamma)Te^{131}$ reactions one or both of the C-Te bonds are ruptured. The recoil atom can recombine to form diethyltelluride or it can react with the pentane solvent to form any of a number of alkyltellurides, e.g., diamyltelluride(Te^{131}) or ethylamyltelluride(Te^{131}). Beta decay from diamyltelluride or ethylamyltelluride would most likely result in an iodopentane product. The higher yields of iodopentanes may be due to such a phenomenon.

The yield of iodoethane is 18% less, whereas the yields of the iodopentanes have increased ~8%. Probably 8% of the decrease in the iodoethane yield is caused by the process leading to the increase in the iodopentane yields, as discussed. The other 10% reduction in the iodoethane yield is equal to the decrease in the total organic yield.

It is highly probable that an (n,γ) recoil effect was also experienced by the $Te^{131}Cl_4$ in toluene solution. Hence it appears Halpern's comparison of the chemical reactivity of I^{131} to that of I^{132} was invalid because of the applied experimental conditions.

Nuclear Decay Properties

As previously mentioned both Te^{131m} and Te^{131g} decay to I^{131}. However, 81% of Te^{131m} decays by beta emission to I^{131}, while the other 19% proceed by isomeric transition to Te^{131g}, which decays to I^{131}. Calculations show that 4 days after irradiation the I^{131} activity resulting from the decay of 1.2 da Te^{131m} produced during the 25 min irradiation is 8.38×10^3 dps, while that resulting from 25 min Te^{131g} is 3.99×10^4 dps. Thus 21% of the observed products result from the decay of Te^{131m}.

The radiations accompanying the decay of Te^{131g} and Te^{131m} are listed in Table 8. If the per cent of a transition internally converted is known, it is also listed.

Excitation due to recoil

Only part of the recoil energy is converted to internal energy as approximated by Equation 7. It was previously calculated for the 2.4 Mev beta of Te^{131} that E_i = 4.9 ev if the recoil atom, I^{131}, were a constituent of ethyl iodide, and E_i = 8.2 ev if the recoil atom were a constituent of butyl iodide. However, these are maximum values for E_i and the average value is approximately one-half of the maximum value (55). Since the C-I bond energy is ~2 ev there should be sufficient energy present due to recoil in a good number of the transitions to rupture the bond. In a diatomic molecule the bond must rupture in the time of one

Table 8. Nuclear properties of the Te^{131m} - Te^{131g} system

Isotope	Energies (Mev)	Abundance (%)	Energies (Mev)	Abundance (%)	Fraction Decaying by I.C. (%)
Te^{131g}	2.14	60	0.145	80	20.6[a]
(25 min)	1.68	25	0.454	20	---
	1.15	10	1.13	10	---
	1.36	5	0.60	5	---
			0.92	5	---
			0.985	--	---
Te^{131m}	0.420	43	0.1817[b]	19	100
(1.2 da)	0.570	31	0.780	80	---
	2.457	3.8	0.840	40	---
	0.215	3.6	1.140	25	---
			1.220	17	---
			0.335	16	---
			0.100	8	---
			0.200	8	---
			1.080	5	---
			0.920	5	---
			0.080	4	---
			2.000	4	---
			1.620	3	---
			0.240	3	---
			1.920	2	---
			2.240	0.6	---

[a] Reference 79.

[b] Isomeric transition.

vibration if there is sufficient energy; however, in a polyatomic molecule a concentration of vibrational energy in the appropriate mode is necessary before dissociation can occur.

It is also possible for γ-rays emitted in cascade following beta emission to impart their full recoil energy to the daughter nucleus, rather than vectorially add their recoil momenta, if the half lives of the γ-rays are long compared to the time for a molecular vibration, 10^{-14} sec.

In solutions of diethyltelluride(Te^{131}) the yield of ethyl iodide was ~90% of the total activity in each of the five solutions studied, while in solutions of di-n-butyltelluride(Te^{131}) the yield of n-butyl iodide was ~70-79%. The excitation phenomena, such as the shaking effect, internal conversion, and recoil of the emitted beta particles, are the same whether Te^{131} decays from diethyltelluride or di-n-butyltelluride. Since the C-I bond energies in ethyl iodide and in n-butyl iodide are within a few Kcal of each other (80), the increased bond rupture in case of n-butyl iodide must be due to the increase in recoil energy converted into internal energy. Carlson and White (53,55) experienced a similar phenomenon in studies on CH_3I^{131} and $C_2H_5I^{131}$ by mass spectrometric analyses. They found an abundance of 69.4% for CH_3Xe^+ and 1.4% for $C_2H_5Xe^+$.

Excitation due to internal conversion

It has been shown that internal conversion, the release of an orbital electron rather than emission of a gamma ray, in an atom which is a constituent of a molecule results in the rapid redistribution of the charge throughout the molecule, thereby producing multiple coulombic repulsions (81). This internal charge transfer is an extremely rapid process leading to extensive molecular breakdown. The 0.145 Mev gamma is the only γ-ray in the decay of Te^{131g} for which an internal conversion coefficient has been reported; internal conversion occurs in 20.6% of transitions. Since 79% of the I^{131} atoms present at the time of analysis are formed from the decay of Te^{131g}, 13.1% have undergone internal conversion due to the 0.145 Mev transition. Of the I^{131} atoms present at the time of analysis 4% have been formed as a result of the decay of Te^{131m} to Te^{131g} by isomeric transition, the Te^{131g} in turn decaying by beta emission to I^{131}. It is difficult to surmise the result of such a transition.

If the bond were ruptured due to multicentered coulombic repulsions, the result would be an iodine ion possessing a high charge. It is almost certain the iodine ion will not react while its charge is >1. Within a few collisional interactions the charge of the iodine ion will be reduced to at least +1. With the exception of n-pentane and cyclopentane, the ionization potential of each solvent studied is lower than that of an iodine atom, and thus charge transfer will probably occur producing a neutral iodine atom. If the I^+ ion should be electronically excited, sufficient energy is available even in the lowest excited state ($^3P_0$, 0.800 ev) (82), so that charge transfer would likely occur in all the solvents studied. Any excess energy would be absorbed by the solvent molecule, which could result in further fragmentation. The reactions would then be those of an iodine radical in solution.

Excitation due to the shaking phenomenon

Bond rupture can also occur as a result of the shaking effect. If the beta emission is adiabatic, the beta particle removes all of the excess excitation energy and the electronic cloud contracts about the new nucleus to form an ion in its ground electronic state. If, however, the transition is nonadiabatic, excitation energy is available and the result is a Frank-Condon transition to an electronically excited state. If the transition is to a repulsive state or to a vibrational level above the dissociation limit of an excited bound state, dissociation results with the excess energy being distributed as translational energy of the fragments. The transition may also occur to an excited bound state which may undergo any of the many available routes of de-excitation. The most probable mode of electronic de-excitation, if predissociation does not occur, is collisional deactivation. Half lives for nonradiative processes, such as internal conversion, inter-system crossing, etc., are substantially longer than the time of a collisional process in the liquid phase, 10^{-13}-10^{-14} sec.

In the beta decay studies by Wexler (50,51,52) and Carlson and White (53,55) a large number of different fragments were observed. Their studies were all performed in a mass spectrometer with samples necessarily at very low pressures, on the order of 10^{-6} mm. Collisional times at this pressure are on the order of 10^{-1} sec, and if a molecule survives bond rupture from available recoil energy due to fast redistribution of vibrational energy, the electronic energy may be converted to vibrational energy of a lower electronic level by a nonradiative transition. This vibrational energy may then be distributed throughout the whole molecule.

Molecules as simple as ethane have an extremely large number of electronic levels, spaced only a few millivolts apart, which facilitate nonradiative transitions. This vibrational energy converted from electronic excitation is available for fragmentation.

In contrast to the large variety of fragments observed by Wexler and Carlson, only a small number of products were observed in this study. The fact that the yield of ethyl iodide is ~90% in the case of diethyltelluride(Te^{131}) solutions, means that either:

1) The largest part of transitions are to the bound ground state and the vibrational energy resulting from the recoil is distributed about the vibrational modes of the molecule such that bond rupture does not occur,
2) The excited electronic levels reached are bound and are collisionally de-excited so that bond rupture does not occur, or
3) A recombination process occurs to produce C_2H_5I if bond rupture has resulted from the shaking effect.

Reaction Mechanisms

Rupture of the newly formed C-I bond out of the remains of two C-Te bonds is evident in only about 10% of the beta transformations. However, the reactions of these recoil atoms are quite interesting.

It is suggested that these products (other than the stable daughter molecule) resulted from:

1) The reaction of an iodine atom after internal conversion with radicals or molecular-ions. These could result from either the

coulombic decomposition of the telluride molecule or from the fragmentation of the solvent molecule participating in the charge transfer, or

2) The reaction of an iodine atom, freed by the shaking effect, with radicals resulting from the decomposition of the hydrocarbon fragment of the organotelluride, or

3) The reaction of an iodine atom with a hydrocarbon solvent molecule.

It may also be possible for a product to result from the rupture of a bond other than the C-I bond, i.e., C-C or C-H. However, the C-I bond is much weaker than either the C-C or C-H bond. There is not sufficient evidence from this study to pin down whether the fragmentation products resulted from 1) or 2), but it is clear which products resulted from the reaction of the I^{131} atom with the solvent.

Consider the case in which internal conversion does not occur. The initial result of the beta decay of Te^{131} from a dialkyltelluride is an intermediate complex, which upon breakup yields an alkyl iodide molecule and a hydrocarbon fragment. Because of the change in atomic number the system lacks one electron for neutrality. The resulting positive charge is accepted by the hydrocarbon fragment, because the ionization potential of the hydrocarbon fragment is lower than that of the alkyl iodides. (See Appendix A.)

Example:

$$\begin{array}{c} C_2H_5\text{-Te}^*\text{-}C_2H_5 \longrightarrow \left[C_2H_5\text{---I}^*\text{-}C_2H_5\right]^+ \\ \big\downarrow \text{0 Kcal} \\ C_2H_5{}^+ + I^*C_2H_5 \\ \text{(IP: 8.72 ev)} \quad \text{(IP: 9.47 ev)} \end{array} \tag{17}$$

If the beta emission is nonadiabatic, excitation results, and the $C_2H_5I^*$ may dissociate to $C_2H_5\cdot + \cdot I^*$ by one of many processes. In order for the hydrocarbon fragment of the daughter molecule to decompose further the C-I bond must survive long enough for electronic cooling and the redistribution of the resulting vibrational energy throughout the daughter molecule.

The most feasible reaction mechanisms leading to the products in the cases of both studies, diethyltelluride and di-n-butyltelluride, are listed in Figures 23 and 24. These mechanisms are based upon reactions initiated by excitation due to the shaking effect. The original hydrocarbon solvent is the precursor of the other fragments.

It is interesting to note in Table 5 that in the case of beta decay from both diethyltelluride and di-n-butyltelluride the yield for a particular product tends to be approximately constant for the two aliphatics and cyclopentane but different for the two aromatics studied. In studies on aliphatic-aromatic mixtures radiation products have been explained on the basis that the aromatic is an "energy sink" (83,84). That is, there is a high probability of energy transfer upon a collisional interaction from the aliphatic to the aromatic molecule.

Something may be learned about the feasibility of these mechanisms by calculating the minimum excitation energy that must be present in the initial daughter molecule and comparing that value with product yields. In order to calculate the minimum initial excitation energy of the daughter molecule complete randomization of the excess internal energy in each radical or ion in the chain of decompositions must be assumed. The fraction of the excess internal energy found in a fragment is $(3N_2-6)/(3N_1-6)$, where N_1 is the number of atoms in the decomposing radical or ion and N_2 is the number in the product fragment. Consider as an example the following fragmentation pattern:

$$A_1 \xrightarrow{\Delta H_1} A_2 + A_2'$$

$$A_2 \xrightarrow{\Delta H_2} A_3 + A_3' \qquad (18)$$

$$A_3 \xrightarrow{\Delta H_3} A_4 + A_4'$$

If E_i is the internal energy aquired by the fragment and $E_i{}'$ is the excess internal energy of fragmentation over the H_i for fragmentation,

$$E_T = \Delta H_1 + E_1{}' \quad , \qquad (19)$$

$$E_2 - \Delta H_2 = E_2{}' \quad , \qquad (20)$$

$$E_3 - \Delta H_3 = E_3{}' \quad , \qquad (21)$$

$$\frac{(3N_2-6)}{(3N_1-6)} E_1{}' = E_2 \ , \qquad (22)$$

$$\frac{(3N_3-6)}{(3N_2-6)} E_2{}' = E_3 \ , \qquad (23)$$

$$\frac{(3N_4-6)}{(3N_3-6)} E_3{}' = E_4 \ . \qquad (24)$$

By working backward from Equation 24 and applying the necessary algebra the minimum excitation energy A_1 must have in order for the fragment A_4 to be produced, assuming Equation 18 is the correct mechanism, is given by

$$E_T = \Delta H_1 + \frac{(3N_1-6)}{(3N_2-6)}\left[\Delta H_2 + \frac{(3N_2-6)}{(3N_3-6)}\Delta H_3\right] \qquad (25)$$

This expression, or ones similarly derived for the appropriate cases, will be applied in the following discussions of diethyl- and di-n-butyltelluride.

Diethyltelluride

It is suggested that the products iodomethane, vinyl iodide, iodoethane (in part), 1-iodopropane, and 1-iodobutane result from the reaction of the freed recoil I^{131} atom with a fragment resulting from the decomposition of the daughter molecule. The proposed mechanism leading to the product spectrum resulting from the beta decay of diethyltelluride in liquid solution is given in Figure 23.

The energy necessary to break the C-I bond in ethyl iodide is 53 Kcal (80). The overall process leading to $C_4H_{10}^+$, after the initial rupture of the C-I bond in ethyl iodide, is exoergic. This mechanism (I, Figure 23) assumes that the $C_2H_5^+$ molecular-ion resulting from the decomposition of the beta decay intermediate complex exists long enough for reaction with the ethyl radical. Since the ionization potential for the ethyl radical (8.72 ev) is lower than that for any of the solvents examined, it is likely this assumption is valid. If the ionization potential of the solvent is less than that of C_4H_9I (9.32 ev), C_4H_9I will be stabilized; otherwise the $C_4H_9I^+$ will decompose. Evidence that this mechanism may be valid is given in Table 5. The ionization potentials for n-pentane, n-hexane, and cyclopentane (10.55, 9.59, and 11.1 ev) are higher than that for iodobutane, whereas the ionization potentials for benzene and

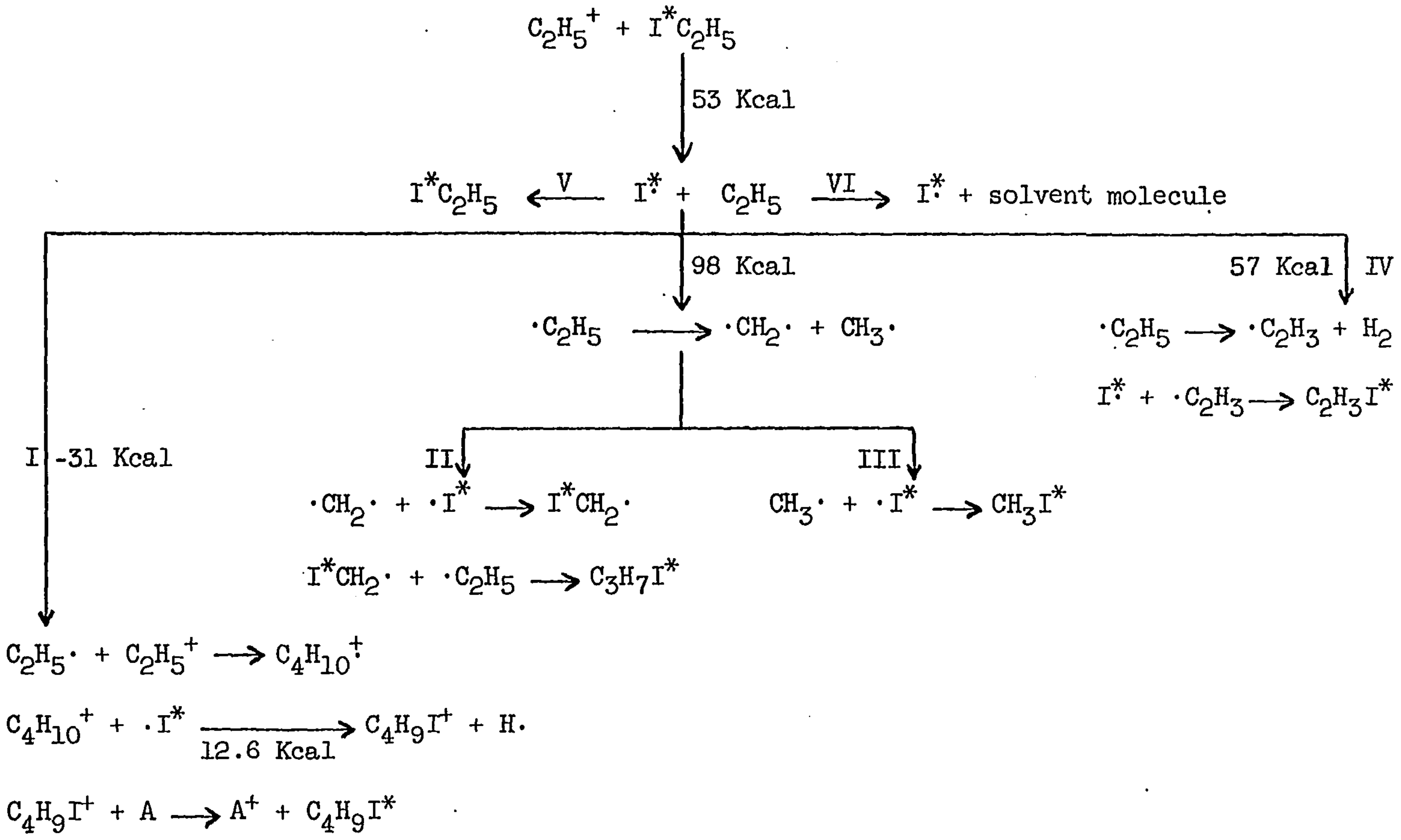


Figure 23. Reaction mechanisms for products resulting from reaction of the iodine radical with fragments of the original diethyltelluride molecule

toluene (9.21 and 8.82 ev) are lower. Approximately 0.70% is probably formed by this mechanism in the benzene and toluene solutions. Approximately 0.70% is formed by some other process, possibly initiated by internal conversion.

The ethyl radical can fragment to yield a methylene and a methyl radical. These two radicals compete for the iodine atom, the result being 1-iodopropane in the former case (II, Figure 23) or iodomethane (III) in the latter. The yields of both iodomethane (E_T = 170.6 Kcal/mole) and 1-iodopropane (E_T = 170.6 Kcal/mole) are ~0.70% in the aliphatic solvents and zero in cyclopentane, benzene, and toluene. Energy transfer apparently occurs from the $C_2H_5^*$ to the aromatic solvent so that the ethyl radical either reacts with the $C_2H_5^+$ molecule-ion leading to a 1-iodobutane molecule or with a solvent molecule. In the latter case the product would be undetected.

Figure 23 also shows a mechanism for the formation of vinyl iodide (IV) (E_T = 121.6 Kcal/mole). It is interesting to note that the yield of vinyl iodide resulting from the beta decay of diethyltelluride is approximately constant in all five solvents, while the yields of iodomethane and 1-iodopropane (E_T = 170.6 Kcal/mole for both) vanish in cyclopentane, benzene, and toluene. These results suggest one mechanism for each of these products.

If the recoil I^{131} atom survives the bond rupture with enough translational energy to break out of its "cage," it finds itself surrounded by solvent molecules. Studies have shown that iodine atoms will not abstract hydrogen from organic molecules (85), but they will displace hydrogen from organic molecules (86). Hydrogen displacement reactions are proposed for the reactions that lead to the products listed in Table 6. These reactions and their estimated ΔH_r are given in Table 9.

Table 9. Solvent reactions

Solvent	Reaction	ΔH_r[a] (Kcal/mole)
N-pentane	$I\cdot + C_5H_{12} \longrightarrow 1\text{-}C_5H_{11}I + H\cdot$	45.4
	$\longrightarrow 2\text{-}C_5H_{11}I + H\cdot$	
	$\longrightarrow 3\text{-}C_5H_{11}I + H\cdot$	
N-hexane	$I\cdot + C_6H_{14} \longrightarrow 1\text{-}C_6H_{13}I + H\cdot$	45.5
	$\longrightarrow 2\text{-}C_6H_{13}I + H\cdot$	
	$\longrightarrow 3\text{-}C_6H_{13}I + H\cdot$	
Cyclopentane	$I\cdot + C_5H_{10} \longrightarrow C_5H_9I + H\cdot$	39.3
Benzene	$I\cdot + C_6H_6 \longrightarrow C_6H_5I + H\cdot$	38.0
Toluene	$I\cdot + C_7H_8 \longrightarrow o\text{-}C_7H_7I$	38.6
	$\longrightarrow p\text{-}C_7H_7I$	

[a] See Appendix B.

These values for ΔH_r probably are in error because of the method of estimation of heats of formation. If they were to be considered correct for a moment, however, and compared with the yields of products in question, one could conclude information (relative) about activation energies for the hydrogen displacement reactions. It is also possible that intermolecular energy transfer has occurred between the I^{131} atom and the aromatic solvents, thereby decreasing the number of solvent reactions in the aromatic solutions. The total yield of products resulting from solvent reactions is ~5.0% in the two aliphatic solvents and cyclopentane but decreases to ~1.6% in the aromatic solvents. (See Table 6.)

Iodine-131 atoms that have become thermalized and break free from their cage are relatively stable and in the absence of radicals only react with other iodine atoms to yield I_2 (85).

Di-n-butyltelluride

The products iodomethane, vinyl iodide, iodoethane, 1-iodopropane, 2-iodobutane, and 1-iodobutane (in part), are suggested to result from the reaction of the I^{131} atom with a fragment resulting from the decomposition of the daughter molecule. The proposed mechanism leading to the product spectrum resulting from the beta decay of di-n-butyltelluride in liquid solution is given in Figure 24.

The yields of iodomethane (E_T = 151 Kcal/mole) and 1-iodopropane (E_T = 149 Kcal/mole) were ~0.90% and 0.70% in both aliphatic solvents studied. The above E_T's were calculated assuming mechanisms VII and I. The yields of both vanish in benzene and toluene solvents as expected, but iodomethane in cyclopentane has decreased from 0.90% to 0.40% and 1-iodopropane did not exist as a product in cyclopentane. From the other product distributions in the solvents studied one would not expect

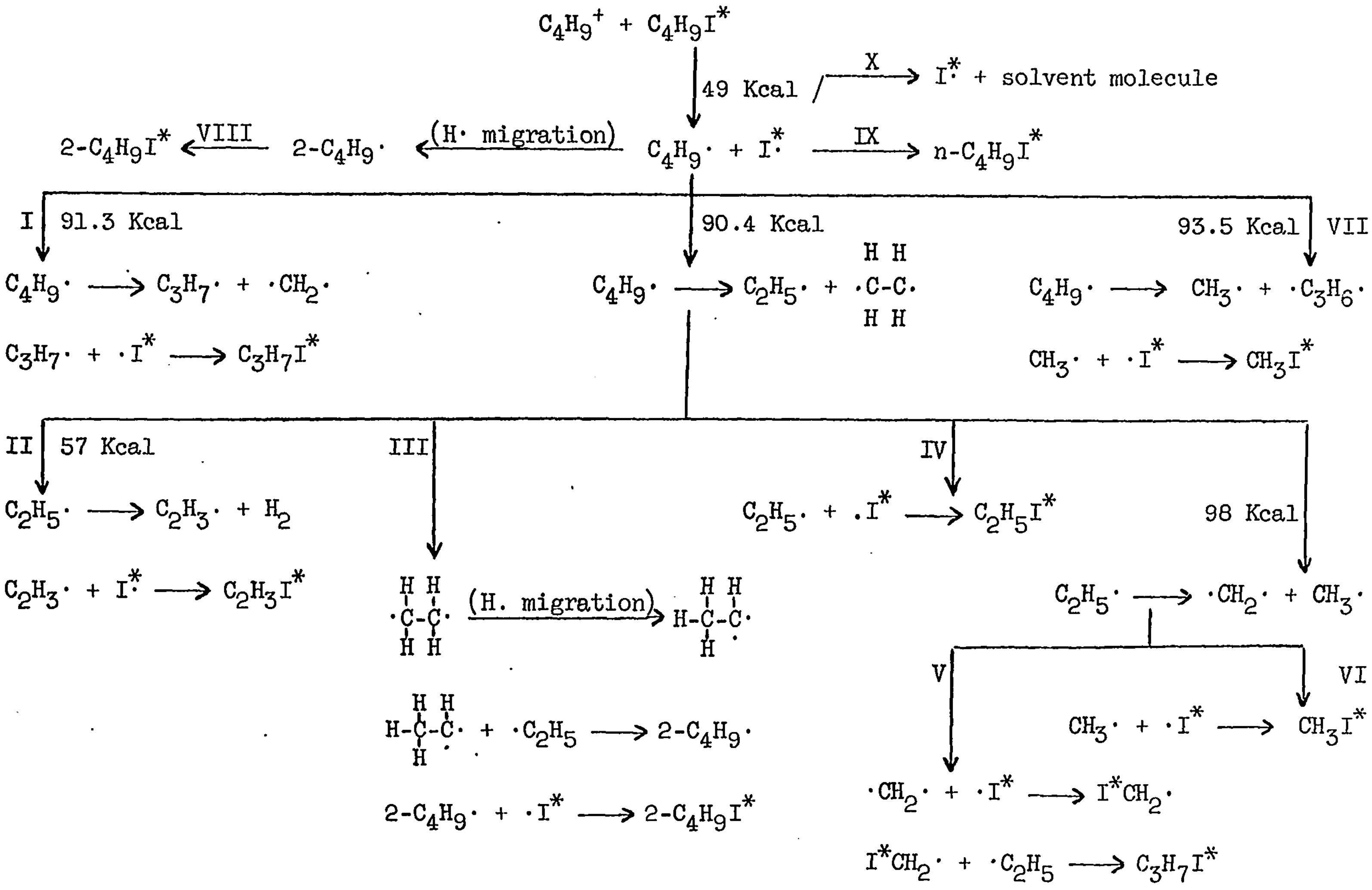


Figure 24. Reaction mechanisms for products resulting from reaction of the iodine radical with fragments of the original di-n-butyltelluride molecule.

cyclopentane to be an energy acceptor as are benzene and toluene; therefore, two mechanisms may be suggested.

The yield of vinyl iodide was found to be ~0.45% in the two aliphatics and in cyclopentane and to vanish in benzene and toluene. This would be consistent with mechanism II for which E_T = 284 Kcal/mole.

The decrease in the yields of iodoethane and 2-iodobutane in the aromatic solvents suggests that ~1% of these products are formed via mechanisms IV and III, respectively. E_T = 148 Kcal/mole for both mechanisms. However, the fact that neither vanishes in the aromatic solvents means that there must be another mechanism resulting in their production. 2-iodobutane may also be formed by mechanism VIII.

It is improbable that there are mechanisms requiring higher E_T's leading to these products which contribute to their yields, unless they are kinetically more desirable. Mechanisms V and VI for the production of 1-iodopropane and iodomethane are offered as examples of possible mechanisms requiring larger E_T's (226 Kcal/mole) than the mechanisms that were discussed.

E_T is the minimum energy necessary for a product to result via a particular mechanism. That is, it is the minimum energy that must be available in the daughter molecule resulting from the beta decay to produce the product. There may also be an activation energy in some of the rate determining steps of the mechanism. In comparing the product yields and E_T's for both the beta decay of diethyltelluride and di-n-butyltelluride it was observed that the yields of the products proceeding by mechanisms for which $E_T \gtrsim 140$ Kcal/mole are quenched in the aromatic solvents, while those proceeding by mechanisms for which $E_T \lesssim 125$ Kcal/mole are not influenced.

The yields of the products resulting from hydrogen abstraction reactions resulting from the beta decay of di-n-butyltelluride in all the solvents studied were within experimental error of those resulting from the beta decay of diethyltelluride and were discussed in the previous section.

The mechanisms given in Tables 23 and 24 and leading to observed products must be initiated by excitation energy resulting from a combination of recoil and the shaking effect (see Equation 17). These mechanisms explain the results obtained very well. However, there are a few anomalies, those being the products iodomethane and 1-iodopropane resulting from the decay of both diethyltelluride(Te^{131}) and di-n-butyltelluride(Te^{131}) in the solvent cyclopentane. Cyclopentane has an ionization potential larger than the iodine atom, which may in some way be the cause of these anomalies. It is also possible that these anomalies are the result of internal conversion processes, which is not well understood beyond the fact that "explosion" of the molecule occurs. It is difficult to say that internal conversion may not be the direct cause of many of the products observed.

CONCLUSIONS

In solutions of diethyltelluride the ethyl iodide yield was ~90%, while in those of di-n-butyltelluride the 1-iodobutane yield was ~70-79%. It is suggested that the increased bond rupture resulting from the beta decay of di-n-butyltelluride-131 was due to the added recoil energy converted into internal energy of the daughter molecule, 1-iodobutane.

The other products observed are proposed to result from three general types of reactions. 1) An iodine atom or ion after internal conversion may react with a radical or molecule-ion. 2) An iodine atom may be produced by bond rupture of the C-I bond in the daughter molecule as a direct result of the nonadiabatic perturbation of atomic electrons resulting from the sudden change in the charge of the nucleus. The iodine atom can react with fragments of the original organotelluride. 3) An iodine atom once freed may also react with a solvent molecule.

Since the beta particle leaves the vicinity of the nucleus in a time short compared to orbital electron motion, the electrons may undergo a nonadiabatic "shaking" resulting in electronic excitation. The result is a Frank-Condon transition to an excited electronic state. The C-I bond may be ruptured by one of many processes. The excess vibrational energy is distributed among the vibrational degrees of freedom of the hydrocarbon fragment, which is the precursor of the other fragments entering into reactions leading to observed products. Mechanisms initiated by this process and yielding the observed products have been proposed.

The data can be explained by considering the intermolecular energy transfer properties of the solutions and the suggested reaction mechanisms. However, it is impossible from the present data to determine whether any, or indeed all, of the products other than the daughter molecule were the result of internal conversion.

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APPENDIX A

Table 10. Ionization potentials of various species of interest in this thesis

Molecule or radical	Ionization potential (ev)[a]
n-pentane	10.55
n-hexane	9.59
Cyclopentane	11.1
Benzene	9.21
Toluene	8.82
Iodoethane	9.47
1-Iodobutane	9.32
Iodine (I_2)	9.41
Methyl radical	9.9
Ethyl radical	8.72
1-Butyl radical	8.47
Iodine atom	10.44

[a] Reference 87.

APPENDIX B

Heats of Reaction

The heats of reaction, ΔH, given for the proposed mechanisms were calculated from heats of formation. Were ΔH_f for a given species not obtainable from literature, it was estimated using partial bond contributions for ΔH_f (Benson). ΔH_f was estimated by this method for many radicals and molecules for which literature values were obtainable in order to determine how accurate the estimations were.

Table 11. Heats of formation I. Molecule-ions

Molecule-ions	ΔH_f Observed	ΔH_f Calculated	Reference for observed value
$C_4H_{10}^+$	219		(87)
$C_2H_5^+$	224		(87)
$C_2H_4^+$	255		(87)
$C_4H_9I^+$	205		(87)

Table 12. Heats of formation II. Molecules

Molecules	ΔH_f Observed	ΔH_f Calculated	Reference for observed value
C_2H_4	12.5	12.8	(88)
C_2H_6	-20.2	-20.25	(88)
$n\text{-}C_4H_{10}$	-30.1	-30.1	(88)
$i\text{-}C_4H_{10}$	-32.1	-30.1	(88)
$1\text{-}C_4H_8$	0.0	0.08	(88)
$c\text{-}C_5H_{10}$	-18.5	-24.65	(88)
C_6H_6	19.8	19.5	(88)
$C_6H_5CH_3$	12.0	12.0	(88)
$CH_3\text{-}CH{=}CH_2$	4.9	4.8	(88)
CH_4	-17.9	-15.3	(80)
$n\text{-}C_5H_{12}$		-35.04	
$n\text{-}C_6H_{14}$		-39.97	
CH_3I	3.3	3.5	(80)
CH_2I_2	26.0	22.3	(80)
C_2H_5I	- 2.1	- 1.4	(80)
$n\text{-}C_3H_7I$		- 6.35	
$n\text{-}C_4H_9I$		-11.3	
C_2H_3I		32.2	
$n\text{-}C_5H_{11}I$		-16.2	
$n\text{-}C_6H_{13}I$		-21.1	
$c\text{-}C_5H_9I$		- 5.8	
C_6H_5I		31.25[a]	
o- and $p\text{-}C_6H_4ICH_3$		24.0	

[a] Calculated using $DH^{\circ}(C_6H_5\text{-}I)$ = 57 Kcal/mole.

Table 13. Heats of formation III. Radicals

Radicals	ΔH_f Observed	ΔH_f Calculated	Reference for observed value
$CH_3\cdot$	34.0 ± 1	35.5[a]	(80)
$C_2H_5\cdot$	26.0 ± 1	30.6[a]	(80)
$i\text{-}C_3H_7\cdot$	17.6 ± 1	25.6[a]	(80)
$C_6H_5\cdot$	71.0 ± 2	63.2[a]	(80)
$n\text{-}C_4H_9\cdot$	17.0 ± 2	20.7	(89)
$\cdot CH_2\cdot$	90.0 ± 4	86.3	(89)
$C_2H_3\cdot$	83.0		(87)
$\cdot C_2H_4\cdot$		81.4	
$n\text{-}C_3H_7\cdot$	22.0		(87)
$H\cdot$	52.1		(87)
$I\cdot$	25.5		(87)
$IC_2H_4\cdot$		49.4	
$ICH_2\cdot$		54.3	

[a] $\Delta H_f(C\cdot)$ was calculated from the literature value to be used for other estimations, $\Delta H_f(C\cdot) = 47.0 \pm 8$ Kcal.