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Radiation Laboratory

THE RADIATION CHEMISTRY OF THE SYMMETRICAL DICHLOROETHYLENES

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THE RADIATION CHEMISTRY OF THE SYMMETRICAL DICHLOROETHYLENES

Jean H. Futrell
(Thesis)

July, 1958

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THE RADIATION CHEMISTRY OF THE SYMMETRICAL DICHLOROETHYLENES

Contents

Abstract 3
Introduction 5
Experimental Procedures 7
    Purification of Starting Materials 7
    Preparation of Targets 9
    Irradiation Sources 11
    Measurement of Volatile Products 12
    Measurement of Polymer Products 16
Discussion of Results 22
    Treatment of Experimental Data 22
    Effects of Experimental Parameters 23
    Stoichiometry 24
Acknowledgments 30
Appendix 31
Tables 34
Figures 48
References 56

THE RADIATION CHEMISTRY OF THE SYMMETRICAL DICHLOROETHYLENES

Jean H. Futrell

Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

July, 1958

ABSTRACT

Purified, degassed samples of cis- and trans-1,2-dichloroethylene were irradiated in glass cells with 48-Mev helium ions at energy inputs up to 10^{21} ev/cc. The principal volatile radiolysis products are acetylene, hydrogen chloride, chloroacetylene, vinyl chloride, hydrogen, and dichloroacetylene, in order of decreasing yield. The use of a mass spectrometer in conjunction with gas chromatography made possible the identification of several higher-boiling, or "polymer", products as tetrachloroethane, tetrachlorobutene, and pentachlorobutene isomers. However, about half of the higher-boiling material proved to have too low a vapor pressure (b.p. $> 300^{\circ}$) at the highest practicable column temperature for these techniques to yield any clues to its nature. Hence these products were characterized only by yield, average molecular weight, and average composition.

The effect on product yields of the variation of certain kinetic parameters -- total dose, density of initial excitation, and temperature -- was determined in survey experiments. These included irradiation with helium ions at 80° and at room temperature, irradiation with electrons of differing energy distributions provided by a microwave linear accelerator and by a Van de Graaf machine, and irradiation with Co^{60} gamma rays.

There are no significant differences in the radiolytic behavior of the cis- and trans- isomers of 1,2-dichloroethylene, and the nature and yields of radiolysis products are explicable on the basis of a series of free-radical reactions. Primary processes of scission of carbon-chlorine bonds and molecular elimination of hydrogen chloride, followed by reactions deduced from the nature of the reactive fragments, presents a self-consistent

correlation of the experimental data. The yield of disappearance of monomer is of the order of 15 to 20 molecules per hundred electron volts for both isomers, indicating that chain reactions occur. The relatively short chain length and the structural identification of the polymer products that were isolated are in agreement with the postulate that rather unreactive, long-lived polychloro free radicals are formed in these systems.

THE RADIATION CHEMISTRY OF THE SYMMETRICAL DICHLOROETHYLENES

INTRODUCTION

Radiation chemistry, the study of the chemical effects of ionizing radiation, is at present in a state of rapid development. It is a field rather closely related to photochemistry although the energies involved are initially larger by several orders of magnitude. Furthermore, photochemistry as it is customarily studied is a somewhat simpler discipline. The use of monochromatic illumination makes it possible to excite a known species to a single level, and the relatively low concentration of species in the gas phase insures that one studies only the reaction of the excited entities with "normal" molecules.

In liquid phase radiation chemistry,however, the number, nature, and spatial distribution of the excited species are not known with any certainty for systems of interest, nor have the kinetics appropriate to such systems been developed. Ideally, one might hope to know the detailed description of the primary process and to trace the reactions of the ions and excited species through the intermediate free radicals and unstable reactants to the final reaction products for each type of radiation employed. However, such a description must await the development of new experimental techniques and of suitable theoretical concepts.

The present lack of knowledge makes it imperative that much more extensive and reliable information be obtained before one can expect to formulate the general principles of radiation chemistry and to make reasonable predictions. A somewhat pragmatic approach, particularly in the study of the great variety of organic compounds, may be especially useful. The observations and correlations from careful and detailed work may be expected to establish the criteria for a clearer understanding of the physical processes precedent to the chemical reactions.

Only a few systems have been irradiated in the pure state, with the atypical system water receiving the most attention. Among organic substances, hydrocarbons and polymerizable monomers have been investigated to a large extent. Some halides, notably chloroform[1] carbon tetrachloride,[2]

and alkyl bromides and iodides[3,4] have been investigated. Several alcohols[5] and ethers[6] have been studied extensively, and certain carboxylic acids were investigated in connection with API Project 43C on the origin of petroleum.[7-10] For other classes of compounds, only sporadic investigations of a few products from miscellaneous compounds have been pursued.

In this work the radiation chemistry of the cis- and trans-isomers of 1,2-dichloroethylene was investigated. These compounds are of particular interest in two respects. They are perhaps the simplest compounds conveniently available for study containing the functional grouping RCH═CHR in which the phenomenon of long-chain polymerization does not dominate and obscure the other reactions taking place. Secondly they are chlorides, and the chronicling of their behavior under irradiation will contribute to the meager information available on chlorine-containing systems.

There are two general approaches to the experimental study of radiation chemistry. The first is the addition of scavengers such as iodine and diphenylpicrylhydrazyl to a system in order to study the primary processes of the irradiation.[11-13] From the primary effects the ultimate products are deduced from known or postulated reactions of the intermediate excited species and free radicals. Another approach, the approach used in this research, is to measure the ultimate products and infer from them the nature of the primary interactions.

Purified, degassed samples of the dichloroethylene isomers were irradiated in glass cells with 48-Mev helium ions, with 2- to 6-Mev electrons, and with Co^{60} gamma rays. The products were separated by the use of high-vacuum techniques, and were determined quantitatively by means of mass spectrometry and gas chromatography. Certain kinetic parameters -- total dose, denisty of initial ionization and excitation, and temperature -- were varied in an attempt to gain an insight into the nature of the primary events. The data are presented as G values, or "quantum yields", and a mechanism consistent with the data is derived.

EXPERIMENTAL PROCEDURES

Purification of Starting Materials

Method A.

The initial method used for purification was simply the distillation of Eastman White Label chemicals at a reasonably high reflux ratio, typically 10/1, through an adiabatic column packed with glass helices After equilibrium had been established, the product was distilled. Samples taken periodically were used to monitor the distillation, by use of refractive index measurements and mass spectrometer analyses. The middle third was accepted as a "pure" sample, provided the samples of that fraction exhibited a constant refractive index, and provided the mass spectra showed no peaks attributable to impurities.

Method B.

Because of complicating features of working with the trans-isomer, -- the apparent formation of a peroxide and a peroxide polymer in some samples -- a slightly more elaborate procedure was introduced for the purification of trans 1,2-dichloroethylene in subsequent samples. It consisted of the same treatment as Method A, followed by a multiple fractional crystallization procedure. Essentially it was equivalent to four stages of fractional crystallization to the half-frozen point, with a final yield of approximately 65% of the initial input of material from the distillation.

Method C.

With the introduction of gas chromatography* as a supplemental analytical tool, it became evident that neither of the previously described purification methods was adequate. In particular the degree of cross-contamination of the cis- and trans- isomers remained of the order

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*The term "gas chromatography" used in this report refers to the process of gas-liquid partition chromatography described by Keulemans.[14]

of a few percent despite careful distillation and fractional crystallization. Such techniques as selective adsorption, elution chromatography, and azeotropic and steam distillation were tried without effecting significant improvement in separation.

The best approach seemed to be the construction of a fractionating column with plate efficiency equivalent to the best analytical columns, but with high throughput capacity. The column was a vacuum-jacketed tube, 22 mm in inside diameter and 6 feet in length, packed with Podbielniak Helipak No. 3013 stainless steel helices. The efficiency of one model of the column when operated at total reflux was 84 theoretical plates, determined with a n-heptane-methane cyclohexane mixture.[15]

The concurrent acquisition of a Leeds and Northrup recording resistance thermometer made it possible to develop a novel and effective technique for such compounds. The crude materials for distillation (Eastman White Label chemicals, 90 to 98% purity) were chromatogrammed to estimate the initial impurities for material-balance calculations. The column was then operated at total reflux for several minutes to hours until the overhead vapor temperature had reached an equilibrium value. Then a few milliliters of the low-boiling components were removed at total take-off as part of a slop cut, causing the vapor temperature to rise sharply. This process was repeated until the operation no longer produced a significant change in the overhead vapor temperature.

From this point gas chromatography was used to monitor the distillation. The equilibrium product contained, typically, a few tenths of a percent of a lower boiling contaminant — such as the trans- isomer in the distillation of cis-1,2-dichloroethylene — which was easily detectable. These last traces of impurity were then removed by distilling at a very high reflux ratio (about 1000/1). Samples were examined periodically to ascertain when the product was acceptable.

When no contaminant was detectable in the overhead product, the dichloroethylene isomer was distilled rather rapidly. Reflux ratios as low as 5/1 to 6/1 were quite acceptable for this phase, and only occasional gas chromatography purity checks were necessary until the distillation had reached the point at which only 10% or so of the charge liquid remained in

the still pot. Then the reflux ratio was increased to 10/1 to 15/1 for the remainder of the purification, and each 25- to 50- milliliter portion of product was analyzed before being added to the purified sample. Distillation was stopped when any higher boiling contaminant appeared, or when the pot approached dryness.

With this procedure good material balances for the distillation were calculable, and the recovery as pure product was of the order of 90%. The overall boiling range, as indicated by the platinum resistance thermometer, was less than 0.01°, and cryoscopic purity was 99.98 ± 0.02%. Properties of the purified compounds are given in Table I.

Preparation of Targets

The purified liquids were dried by shaking with anhydrous calcium sulfate or with calcium chloride for about an hour. They were degassed by refluxing under vacuum in the manner described by Newton,[16] and were distilled into the desired target for bombardment.

The method of degassing was essentially the same as that for separating volatile radiolysis products, and may be illustrated briefly by reference to Figure 1. The dichloroethylene sample was introduced into the flask, F, which contained a Teflon-enclosed magnetic bar for stirring. A straight manifold, to which the targets could be attached for filling, replaced the illustrated traps A and B. The Dewar flask of the reflux condenser was filled with a trichloroethylene-dry ice slush for degassing cis-1,2-dichloroethylene, or with some suitable -50° mixture for the trans- isomer.

With a liquid nitrogen trap at C and the system connected to vacuum, the stopcock at D was opened slightly to pump off noncondensables in the degassing flask Once the liquid in the flask had begun boiling vigorously, Stopcock D was closed, and the liquid was allowed to reflux for several minutes. Intermittent refluxing and pumping were continued until no pressure rise was noted in the vacuum system after refluxing the liquid for at least 30 minutes.

The reflux condenser was then emptied of refrigerant, and the degassed sample was distilled from the pot to the appropriate targets by means of a slush bath slightly above the freezing point of the liquid. When the target had been filled above the level of the beam window, it was sealed under vacuum with pumping at C and was pulled off the manifold.

The basic design of the target vessel used was essentially that described by Garrison, Haymond, and Weeks,[17] and is shown schematically in Figure 2-A. For helium ion irradiations such a flask was mounted in the shaker assembly shown in Figure 3 with a flask attached, and was agitated vigorously during bombardment. The 48.5 Mev ion beam was held at an operating level below 0.3 microampere at all times for an average beam current of 0.1 microampere or less. An air blast was used on the target during irradiation for cooling purposes, and no increase above room temperature was noted for any of the irradiations.

For some of the electron irradiations the same type of target flask was used. No shaker was available for this accelerator, and the energy measurement problem was not resolved satisfactorily. For integration of the current input, the flask was silvered on the outside to give a conducting layer and was grounded to the beam snout, which was electrically isolated from the collimating slits and the microwave cavity. An electrometer lead attached to the target-snout system indicated the integrated beam current during irradiations. Such complications were necessary because the ion density formed in air by electrons was not sufficient to produce a conducting coupling; this problem did not arise with helium ions from the Crocker Laboratory cyclotron.

This type of target was unsatisfactory for several reasons, however, and the slightly different type shown in Figure 2-B was designed for subsequent electron bombardments. The irregular shape of the helium ion targets, coupled with the greater range of the electrons, resulted in the dissipation of an unknown amount of the electron beam energy external to the system. Hence the electron targets were spherical in shape, with sufficient radius to insure that the total impingent electron beam dissipated its energy within the target vessel. To measure the beam more accurately,

a platinum lead was incorporated into the vessel wall for connecting an electrometer lead directly to the irradiation sample. The sidearm was provided simply as a gas space for volatile radiolysis products.

The gamma irradiation cells were cylindrical Pyrex ampoules 1 inch in diameter and 3 inches tall, fitted with break-tip and seal-off tubes. Their size was chosen for convenience in handling, and their capacity was approximately 15 cc of liquid, plus a vapor space.

Irradiation Sources

Helium Ions.

In the helium ion irradiations the external beam of the 60-inch cyclotron of the Crocker Laboratory was used. The range of the beam was 233 mg/cm^2 of aluminum, equivalent to 48.5 Mev. The beam was degraded by passage through the foil in the shaker target, through the air space between the flask and the cyclotron vacuum, and through the glass window of the target itself. The calculated energy of the impingent beam was of the order of 40 to 43 Mev for all helium ion bombardments.

Electrons.

The microwave linear electron accelerator and associated equipment described by Lemmon and Mosier[18] was used for the several survey experiments. In early work the total beam, of 3.5 Mev mean energy, was used directly. A low rate of energy input, in the neighborhood of 30 microcoulombs per minute, was used to minimize thermal effects, as there was no method of either cooling or agitating the sample during irradiation. In later experiments the beam was passed through a magnetic field and collimated to select the peak energy component at 4.6 ± 0.1 Mev.

In two experiments the 2-Mev Van de Graaf accelerator at the California Research Corporation was used. No precise beam monitoring equipment was available, but the lowest stable operating current of 2 to 3 microamperes (indicated) was utilized with air-blast cooling of the target.

Gamma Source.

The 2000-curie Co^{60} source described by Tolbert, Nielson, Edwards, Whittemore, and Garden[19] was used for the gamma irradiations. The hydrogen yield from a concurrently irradiated sample of cyclohexane was used as a dosimeter, assuming $G(H_2) = 5.6$.[20]

Measurement of Volatile Products

The apparatus for determining the volatile radiolysis products is shown schematically in Figure 1. With the system evacuated and with the reflux Dewar filled with a suitable slush bath at or near the freezing point of the irradiated compound, stopcock D was closed. The iron hammer indicated was then used to open the break seal, permitting the contents of the target to drain into the Flask F.

With liquid nitrogen traps at A and B, a procedure analogous to that described for degassing the liquids prior to irradiation was followed, the semi-automatic Toepler pump replacing the vacuum pump for this operation. When no more gas could be pumped through the traps, the pressure and volume at 25° were measured in the gas burette, and this fraction was pushed into the detachable bulb indicated for subsequent analysis. A Consolidated Engineering Corporation model 21-103A mass spectrometer was used to analyze all the fractions collected.*

Because HCl was a major radiolysis product, and because adsorption problems with hydrogen halides preclude accurate mass spectrometer analyses of such samples, the separation procedure for subsequent gas fractions changed somewhat in the course of experimentation. The various schemes devised are quite similar in principle, so only the most recent method is described here.

The condensable gases in Trap A were further fractionated by pumping them through an ethyl bromide slush (-125°) at Trap B by means

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*This is a standard analytical instrument of the 180° Dempster type, with a room-temperature expansion volume. The usual procedures were followed in the analyses.[21]

of a liquid nitrogen trap at C.[22] Stopcock E was then closed, the Dewar on C was removed, and the contents of Trap C were pumped into the gas burette. Meanwhile the condensed gas in Trap B could be transferred back to A, so that the separation cycle might be repeated a sufficient number of times to insure the removal of all gases volatile at -125°. Occasionally during the operation of transferring distilled gases back into Trap A, Stopcock D would be opened briefly — thus pumping over any products that had refluxed out of the residual liquid in F.

The sample bulb for the ethyl bromide fraction was a special design, with a detachable sidearm containing some 10 grams of pelleted potassium hydroxide. Once all the gases that could be pumped through the ethyl bromide trap had been pushed into the sample bulb, it was removed and placed in a hood. The KOH pellets were shaken from the sidearm into the bulb, and the bulb was shaken vigorously to insure that all the gas came in contact with the pellets. It was then set aside until the remaining separation procedures had been completed.

A third gas fraction was separated in the same manner as the ethyl bromide fraction, usually with a dry ice-trichloroethylene slurry (-80°) as a refrigerant.[22] Because the dichloroethylenes had a measurable vapor pressure at this temperature, the multiple-pass fractionation technique was continued only until a constant amount of gas was collected in the gas burette with each transfer operation.

The liquid distilled into Trap A during the separation procedure was transferred to a graduated receiver and analyzed as an additional fraction with the mass spectrometer. In later experiments gas chromatography was used to guarantee that separation of the volatile products was complete. After removal of the distilled liquid, a small amount of the vapor at the top of the reflux condenser was distilled into a special receiver for chromatographic examination. Only if both this sample and the distilled liquid sample showed less than 0.5% of low boiling constituents would the separation be considered satisfactory; otherwise the separation cycle was repeated until this criterion was satisfied.

For the third gas fraction, refrigerants other than carbon dioxide were sometimes desirable. The appreciable vapor pressures of the dichloro-

ethylenes at this temperature and the long pumping times necessary to recover certain volatile products caused this fraction to contain a high concentration of dichloroethylene for the longer irradiations. Since a high concentration of dichloroethylene interferes with mass spectrometer analyses, a trichloroethylene slush (-90°) or isopropyl benzene slush (-100°) was more practicable in such experiments. Furthermore, the purpose of taking an ethyl bromide fraction was to remove chiefly acetylene and HCl, so that the additional difficulty of this operation seemed unjustified for some of these experiments. Consequently only two gas samples, a liquid nitrogen fraction and a trichloroethylene fraction, were separated from these targets.

The ethyl bromide transfer bulb in the general procedure was then reattached to the vacuum manifold; and its contents, less the HCl, were removed for analysis. They were pumped through a dry ice trap to prevent the transfer from the bulb into the gas burette of water formed in the reaction. It was shown by use of carbon tetrafluoride as an internal standard that only the HCl in the mixture would normally react over a period of 2 or 3 hours, so that the change in the amount of gas in this fraction was a measure of the yield of HCl. Gravimetric analysis for chloride confirmed that the method determined HCl quantitatively. Although these relationships held for each case tested, blackening of KOH pellets in some experiments indicated that other consitiuents had reacted. When the extent of this reaction seemed appreciable, or when the pressure decrease accompanying this carbon deposition was excessive, the results were not reported.

Also reported in Tables II and III as a volatile product are the apparent yields of CO for each experiment. This value is a measure of the amount of oxygen incorporated in the target during irradiation, and could arise from the presence of air, water, or a volatile peroxide. In general there was insufficient nitrogen to account for the CO as air contamination, so that adsorbed and dissolved water appears a likely explanation. In cases of large CO yields, the possibility that a small amount of a peroxide was irradiated with the dichloroethylenes must be

considered. In any event, the measured yields of CO are quite small, indicating that the extent of contamination by an oxygenated compound was negligible.

In two experiments the helium ion cells were modified by installing a bubble tube through which helium could be swept and an outlet tube which could be sealed to a potassium iodide solution absorption train. After irradiation, the cis-1,2-dichloroethylene target was attached to the system, and the break-tip seals were opened, allowing the helium stream to sweep out the volatile products. The addition of starch to the KI flask caused no coloration after thirty minutes' sweeping, implying a yield of chlorine corresponding to no more than 0.0005 molecules per 100 ev. Repetition of the experiment with the trans-isomer yielded an identical result.

The most consistently reproducible results in these experiments were the yield data for hydrogen and acetylene. Because of combined effects of high reactivity and high solubility, the chloroacetylene and vinyl chloride yields were erratically low in some experiments. Whenever there was evidence of decomposition or of incomplete separation of these products from the residual liquids, the measured values were not reported with the other yield data.

The reactivity and solubility arguments, coupled with a low yield, are even more severely applicable to dichloroacetylene. Hence the experimental results scatter widely, and the mean yield is probably reliable to no better than ± 50%.

Considerable difficulty was encountered in measuring yields of HCl. Passing the appropriate gas fraction repeatedly through a KOH absorption tube gave erratic results; in some experiments two passes sufficed -- in others, ten passes would not remove all the HCl. Even in the technique using a sidearm transfer bulb, usually quite reliable, traces of HCl occasionally remained. In certain experiments blackening of some of the KOH pellets indicated that gas fraction constituents other than HCl had reacted. Hence yields clearly incompatible with the majority of the data were not reported.

With the exception of dichloroacetylene, there are reproducible data for the volatile products over the range of dosages studied. The measurement of the amounts of volatile products with a gas burette, the refluxing under vacuum as a separation method, and the use of a mass spectrometer as an analytical tool combined to make the determination of the yields of these products rather precise. The determination of higher boiling or "polymer" products was much less satisfactory, and these results are discussed separately.

Measurement of Polymer Products

The solution of the purity problem in the case of the trans-isomer introduced a complicating factor of considerably greater magnitude in the study of polymer products. The purified trans-1,2-dichloroethylene was observed to undergo a polymerization reaction in the presence of air and the fluorescent lighting of the laboratory to form a flocculent white precipitate. This phenomenon was interpreted as the light-catalyzed formation of a peroxide which induced polymerization to a relatively high molecular weight substance. A sample of freshly distilled trans- isomer placed in a desk drawer for three months showed no evidence of polymer formation; neither did a sample which was degassed and sealed in an ampoule and left in the laboratory under bright illumination. Samples stored in glass-stoppered bottles in the laboratory formed a white precipitate within a week after distillation.

Microanalysis of the white residue obtained upon evaporation of the dichloroethylene corresponded to the composition $(CHCl)_x$. The fact that the amount of oxygen incorporated into the polymer was undetectable suggested a high molecular weight, as did the low solubility in monomer or in other solvents tried. It seems likely that the trans-1,2-dichloroethylene, when obtained, originally contained some inhibitor with approximately the same volatility characteristics. Hence it was not removed completely by the original purification techniques employed, and the problem became apparent only with the development of the high-efficiency distillation technique.

Thus the measured polymer yield from the trans- isomer probably includes an unknown amount of "background" polymerization. Consequently it is certain that the characterization of a "high polymer" product from the trans- isomer is weighted by the presence of the peroxide polymer, and possibly there is a contribution to the yield of lower boiling polymers.

Most investigations of the radiation chemistry of organic substances to date have included reporting the formation of "polymer", which may include a number of products for which analyses could not be made, quite analogous to the "tar" formed in many organic synthesis; its composition, if reported at all, is usually derived from material balance considerations.

The techniques of gas chromatography offered hope of accomplishing a more satisfactory determination of polymer products, and considerable effort was devoted to developing a suitable method. The complicating factor that the chlorinated polymers reacted with copper and brass at high temperatures made the use of a conventional metal system impractical. However, an all glass system containing a column constructed from 5-mm Pyrex tubing 2 meters in length afforded considerably more success. Several column packings, such as General Electric silicone fluid 9640, dinonyl phthalate, Fluorolube HG 1200, and squalane, adsorbed on 40-60-mesh Sil-O-Cel firebrick, were tried as stationary phases. In each case maximum operating temperatures somewhat lower than those reported for these packings were imposed by the operating criteria. For the silicone column, 153° proved to be the maximum temperature, as at higher temperatures mass spectra of the column effluent exhibited a background of peaks attributable to the column packing. Since it was planned that the mass spectrometer be used to identify polymer constituents, this established the upper temperature limit for this column. The other packings investigated in this regard exhibited even lower maxima; consequently the silicone column was adopted for the identification of high boiling products.

Since the residual liquid from an irradiation was a fairly dilute solution of polymer products in dichloroethylene, it was necessary to

reduce the volume of solvent considerably before any high boiling product could be observed. The ideal solution to this problem would be a high-efficiency analytical distillation apparatus with no liquid holdup, and the best operating compromise available was a Vigreaux column with an estimated separation efficiency of two to four theoretical plates. With it the volume of residual liquid could be reduced to the order of 2 to 3 cc without distilling a significant amount of the higher boilers. This pot liquid was then further subdivided by means of a molecular distillation, from which three fractions were obtained: (1) a vacuum-distilled fraction, (2) a molecularly distilled fraction, and (3) residuum.

Samples of these fractions were injected into the silicone column operated at different temperatures and helium flow rates up to the maximum of 76 cc/min of helium at 153°. Composite chromatograms of polymers from cis-1,2-dichloroethylene are shown in Figure 6 and from trans-1,2-dichloroethylene in Figure 7. These chart facsimiles represent the situation if polymer analyses are conducted immediately after separation of the volatile products. When the trans- isomer residual liquid is exposed to oxygen prior to the investigation for polymers, two additional chromatogram peaks appear. These are the cis- and trans-1,2-dichloroethylene oxides, whose discovery and characterization are reported in the Appendix. Although their identification resulted from the approach described in this section, they are in a sense secondary products and are therefore not considered explicitly as polymer products.

After the emergence times for the several components had been determined, samples of the individual components were collected for mass spectrometer analysis by attaching a removable trap to the effluent line of the thermal conductivity cell while each respective peak was emerging. With the sample frozen in the trap, the helium and noncondensables were pumped out by means of the mass spectrometer inlet vacuum system. After warming, the remaining contents of the trap were flashed into the analyzer section of the mass spectrometer.

Since very little information is available on the mass spectral fragmentation patterns of chlorinated hydrocarbons, it was necessary to obtain basic correlations between structure and pattern for several types

of compounds. Samples of commerically available polychlorinated hydrocarbons, both saturated and unsaturated, and containing chlorines distributed in various ways along the carbon skeleton, were obtained for study. In addition to serving as sources of information for the mass spectral study, several of these were injected into the chromatography column to establish the sensitivity parameters given in Table VII.

With these data it was possible to make tentative structural assignments to several of the products. Knowledge of the isotopic abundances of chlorine made it possible by simple statistics to establish the empirical formula in almost every case for the positive ions contributing to each m/q in the mass spectra. With the basic assumptions, supported by the correlations, that peaks representing chlorine atom migration are small and that successive hydrogen atom migration is unlikely, one can construct the probable structure of the species from its fragmentation pattern. For several chromatogram constituents the identification in this manner was reasonably certain; for others it was less so; and for some it was impossible because of the small amount formed, because of probable cross-contamination of components, or because of peculiarities in the spectra. These are all indicated in Tables VIII and IX.

The correlation of column emergence times versus boiling points of the chlorinated compounds investigated, given in Figure 8, was used to estimate the boiling points of polymer constituents. These estimated boiling points are reported for possible later use in establishing the postulated structures if authentic samples of the indicated compounds should become available.

Roughly half of the composite polymer proved to have too low a vapor pressure at 153° to be eluted from the column as a discrete component. Moreover, the second pentachlorobutene isomer observed had so low a vapor pressure (of the order of a micron) at room temperature that a mass spectral pattern could be obtained only with considerably difficulty. An attempt was made to obtain a spectrum using the heated-inlet-system mass spectrometer at California Research Corporation, but, unfortunately, the chlorinated polymers reacted with the gallium metal in the introduction system. It would therefore be impossible, with the presently

available equipment and techniques, to identify any higher boiling components if they could be isolated.

The possibility of cyclization of the polymer at the trimer stage was investigated by comparing the infrared spectra of the residuum fractions with the spectra of the α, β, γ, δ, and ϵ isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane as reported by Daasch.[23] The complexity of the polymer spectra made is impossible to rule out the presence of trace quantities of the α, β, and γ isomers, but there was no evidence for the presence of even minute quantities of the δ and ϵ isomers. Therefore the possibility of termination of a large reaction of the polymer chains by cyclization may be eliminated.

These higher boiling constituents were characterized then only by their average molecular weight and composition. The molecular weight was determined by measurement of the freezing point depression of a benzene solution of the molecular distillation residuum. This measured average molecular weight was corrected for the molecular weight contribution of the identified polymers present in this fraction, and the resulting values are reported in Tables VIII and IX. Similar corrections were applied to the results from microanalyses for carbon, hydrogen, chlorine, and oxygen. It has already been suggested that some unknown contribution to the polymer from the trans- isomer is from a background degradation, and that the derived G values for polymerization must represent an upper limit. Probably the true values are of the same order as those for the cis- isomer.

The yields reported for the polymer constituents were calculated on the basis of several assumptions. For each compound the specific response of the gas chromatography detector may be expressed as a sensitivity, measured in this case as the displayed peak area per microliter injected [peak height in chart deviations times half-width (in minutes) per microliter]. An average of 14.3 taken from Table VII was used to calculate the volume present in the composite liquid. On the assumption of an average density of 1.5 and by use of the appropriate molecular weight, the number of millimoles formed was calculated.

The residual liquid from an irradiation of 1,2-dichloroethane was analyzed in the same manner. Since this was a saturated compound, no chain reaction was observed. No high polymers were formed, and all the major polymer constituents were identified.

Residual liquids from gamma bombardments of the dichloroethylenes were analyzed in like fashion. Because of the rather small dosages that could be given in a short time, only a few of the major components could be observed. These fragmentary data are reported in Table VI.

Only two samples of residual liquid from trans-1,2-dichloroethylene and one from the cis- isomer were examined in the detail indicated in this discussion. The several assumptions required in deriving yield data and the lack of precision indicated that a more thorough investigation, such as that pursued for the volatile products, would not be profitable at this time. Probably the reported results are reliable to ± 50%.

DISCUSSION OF RESULTS

Treatment of Experimental Data

The yields of the various products are reported as G values, the number of molecules of the product per hundred electron volts energy imparted to the system. The particle energy, corrected for energy degraded in target foils, in the air path, and in the glass window,[24] when multiplied by the measured microampere hours or microcoulombs and by the proper conversion factors,[25] gives the energy input directly. This is used to calculate a factor g_f, which, when multiplied by the yield in millimoles, gives the G of the product. Thus we have

$$g_f = \frac{6.02 \times 10^{20} \times 100}{E_{input,\ ev}}$$

The yields in millimoles of volatile products were calculated from the measured PV product, assuming additivity of partial pressures and the applicability of the perfect gas law for the low pressures attained; the yields in millimoles of polymer products were derived from estimated gas chromatography sensitivities. Both g_f and G values are reported in the tables.

The radiolysis yields of volatile products from the cis- and trans- isomers were so similar that the cross-contamination present in early irradiations were undetectable in the yield data. Thus Tables II and III contain the results from irradiation of compounds purified by all three of the procedures described.

For the cyclotron irradiations the error in the determination of the integrated dosage, representing both the error in circuitry and the uncertainty in beam energy, is estimated as approximately 5%. The hydrogen yield is subject to the least experimental error in the separation and analysis procedures, and the scatter in $G(H_2)$ is in part a measure of this uncertainty in the energy input measurement. Hence an attempt to normalize out this effect was made in the presentation of the data. The yield of each radiolysis product in a given experiment was multiplied by the ratio of the measured hydrogen yield to the mean hydrogen yield for all radiolyses

of that isomer. Thus the values presented in Tables II and III are the experimentally measured yields of hydrogen and the corrected yields of the other products. The mean hydrogen yields taken as the "best" values, were $G(H_2)_{cis} = 0.028$ and $G(H_2)_{trans} = 0.040$.

Problems in monitoring electron irradiations made the apparent G values rather erratic, yielding values both somewhat higher and somewhat lower than the helium ion results. Hence the electron yields were normalized to the same hydrogen yields as the cyclotron irradiations, and are presented in this form in Tables IV and V. The similarity of the hydrogen results (in fact, of all the volatile products) from the helium ion and gamma radiolyses corroborate the assumption that this yield is independent of irradiation intensity.

Effect of Experimental Parameters

The directly measurable quantities to be determined from a study of the radiation chemistry of a system such as dichloroethylene are the G values for all primary products. The very large effects of the presence of small amounts of products on the radiolysis of several systems[26] require that the initial rates of formation of the radiolysis products be determined. In an experimental sense this involves a study of the radiolytic yields as a function of energy input in order to make the extrapolation to zero dose. Such an extrapolation is given for cis-1,2-dichloroethylene in Figure 4 and for trans-1,2-dichloroethylene in Figure 5. Over the range of measurement the data are fitted best by a straight line of zero slope showing that the yield of volatile products is directly proportional to the energy input and that secondary processes are not important in the range of dosages studied. The G values for each product differ slightly for the two isomers, but their radiolytic behavior is quite similar.

The response of the dichloroethylenes under conditions of different initial distributions of excited species was determined by varying the irradiation sources. The electron experiments, whose results are reported in Tables IV and V, represent in themselves three different distributions of energy deposition. The irradiations utilizing the total

beam from the microwave electron accelerator represent electrons with energies from thermal to about 6 Mev, with a skewed maximum near the mean energy of 3.5 Mev, while in experiments with the magnet spectrometer electrons of 4.6 ± 0.1 Mev were selected. The electrons delivered by this accelerator were pulses of 2 microseconds duration, occurring 15 times per second, of very high current density (up to 100 milliamperes). The Van de Graaff, however, delivers a continuous beam of monoenergetic 2 Mev electrons during irradiation.

Comparison of the yields of volatile products for the helium ion, electron, and gamma radiolyses in Tables IV, V, and VI shows no significant change in the G values, implying the absence of track effects in events leading to the formation of these products. However, there is a striking difference in the ratios of polymer products; the yield of dimer is somewhat higher for the gamma radiolyses. The polymer G values are doubtless incorrect in magnitude because of the inaccuracies of measuring the small yields produced with the gamma source available. Nevertheless, the ratio of dimer to s-tetrachloroethane is significantly higher, consistent with the mechanism suggested for their production.

A third experimental parameter, temperature, was varied in the survey experiment reported in Table XIV. The sample of cis-1,2-dichloroethylene was irradiated at approximately 80° as described by Newton.[22] The yields of all products increased generally as a result of the increase in temperature, probably because of the decreased viscosity of the medium. Thus diffusion of radical fragments out of the cage of solvent molecules was facilitated, reducing the extent of primary recombination. However, no readily interpretable kinetic information was obtained, and this line of investigation was not pursued further.

Stoichiometry

Samples of 1,2-dichloroethane were irradiated in order to establish the radiolysis behavior of the saturated analog of the symmetrical dichloroethylenes, giving the results shown in Table X. The

stoichiometry of the radiolysis reactions were analyzed to ascertain whether any products had been overlooked. The results of this study are reported in Table XI.

With this information available it became more meaningful to examine the stoichiometry of the radiolysis of the dichloroethylenes. The results are shown in Tables XII and XIII, again omitting the dichloroethylene oxides. The agreement of the summations of carbon, hydrogen, and chlorine is deemed adequate to establish the $G(-C_2H_2Cl_2)$ values quoted. Concurrently, the summation presents a measure of the completeness of the analytical detection and measurement of all the products formed.

Since the hundred electron volt yield for disappearance of monomer for the dichloroethylenes is 2 to 4 times as large as that of the saturated analog, it is apparent that chain reactions occur. Both this fact and the fact that the chains are relatively short are consistent with the supposition that relatively unreactive polychloro free radicals are formed in these systems.

Reaction Mechanisms

The measurement of the ultimate products in experiments such as these does not permit the determination of a unique reaction mechanism. However, the simplest mechanism adequate to explain the data is a free radical reaction sequence similar to that proposed by Willard and Hanrahan for alkyl iodides.[27]

The principal primary act in the radiolysis system is postulated as the scission of the C—Cl bond,

$$C_2H_2Cl_2 \longrightarrow CHCl{=}CH\cdot + Cl\cdot \qquad (1)$$

This is consistent with the mass spectral fragmentation patterns of the dichloroethylenes,[28] in which the base peak of the spectra represents a scission of the molecule ion. Furthermore, the primary act on photolysis of the two isomers with 1980 to 1860 Å radiation was established by Mahncke and Noyes as the breaking of a C—Cl bond.[29]

A large share of the $C_2H_2Cl\cdot$ fragments formed must have sufficient energy to split off another atom of chlorine in order to explain the high yield of acetylene:

$$CHCl{=}CH\cdot \longrightarrow HC{\equiv}CH + Cl\cdot \qquad (2)$$

The alternative decomposition sequence

$$C_2H_2Cl_2 \longrightarrow HC{\equiv}CH + Cl_2 \qquad (2a)$$

may be postulated, but no Cl_2 was detected as a product, and steps to remove the Cl_2 by reactions such as $R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$ would be required. An activation energy of the order of 3 kcal for such a reaction[30] is probably adequate to prevent total consumption of Cl_2; hence the simpler mechanism is preferable.

The production of vinyl chloride may not be presented as a hydrogen abstraction reaction:

$$CHCl{=}CH\cdot + C_2H_2Cl_2 \longrightarrow CH_2{=}CHCl + CHCl{=}CCl\cdot \qquad (3)$$

The resulting radical would be expected to decompose,

$$CHCl{=}CCl\cdot \longrightarrow HC{\equiv}CCl + Cl\cdot \qquad (4)$$

analogous to the production of vinyl chloride from $CH_2Cl\ CHCl\cdot$ radicals postulated by Barton.[31]

The remaining chloroacetylene produced in the radiolysis can best be explained by the unimolecular primary elimination of HCl:

$$C_2H_2Cl_2 \longrightarrow HC{\equiv}CCl + HCl \qquad (5)$$

The alternative process involving splitting off H and Cl atoms would be acceptable except for the fact that insufficient hydrogen-excess products were observed. The only hydrogen "sink" available is the "high" polymer, and it seems unlikely that hydrogen addition to radicals would produce no compounds boiling under 300°.

By analogy to Reaction (5) the production of dichloroethylene may be written

$$C_2H_2Cl_2 \longrightarrow ClC{\equiv}CCl + H_2 \text{ or } 2\ H\cdot \qquad (6)$$

and the production of hydrogen by the subsequent reaction

$$H\cdot + C_2H_2Cl_2 \longrightarrow H_2 + CHCl{=}CCl\cdot \qquad (7)$$

Because of the relative ease with which a hydrogen atom can escape the Franck-Rabinowitch cage, both the molecular and atomic mechanisms would be essentially independent of density of excitation. The nonequivalence of the dichloroacetylene and hydrogen yields suggests that the atomic process contributes to the hydrogen production. There must be an additional source for hydrogen atoms, such as Reaction (5) going by the alternative radical process to a very slight extent, to account for this difference. Because of the small relative magnitude of the hydrogen yield, this additional source cannot be specified explicitly.

The higher hydrogen yield from the trans- isomer and the mechanism for hydrogen production are partially substantiated by the mass spectral fragmentation patterns.[27] The m/q 95 and 94 peaks in the trans- fragmentation pattern, representing loss of one and two hydrogens, respectively, are higher by a factor of 1.6 than the corresponding peaks in the cis- isomer pattern.

The primary processes postulated and their subsequent rearrangements result in the production of a large number of chlorine atoms in the system. In a succession of steps they are responsible for the formation of polymer products:

$$Cl\cdot + C_2H_2Cl_2 \longrightarrow CHCl_2\ CHCl\cdot \qquad (8)$$

$$CHCl_2\ CHCl\cdot + Cl\cdot \longrightarrow CHCl_2\ CHCl_2 \qquad (9)$$

$$CHCl_2\ CHCl\cdot + C_2H_2Cl_2 \longrightarrow CHCl_2\ CHCl\ CHCl\ CHCl\cdot \qquad (10)$$

$$CHCl_2\ CHCl\ CHCl\ CHCl\cdot \longrightarrow CHCl_2\ CHCl\ CH{=}CHCl + Cl\cdot \qquad (11)$$

Reactions (8), (10), and (11) are those considered responsible for the free-radical-induced dimerization of dichloroethylene reported

by Bauer.[32] A number of such reaction sequences involving intermediate polyhalo radicals of relatively low reactivity have been characterized.[33] The structure of the major dimer product, and hence the mechanism for its production, were substantiated by comparison with an authentic sample prepared by Dr. Amos S. Newton by means of the benzoyl peroxide-induced dimerization of dichloroethylene.

Several reaction sequences could be written for the production of pentachlorobutenes, the simplest being

$$CHCl_2\ CHCl\ CHC\ CHCl\cdot + Cl\cdot \longrightarrow CHCl_2\ CHCl\ C\ Cl{=}CHCl + HCl \qquad (12)$$

However, the production of a specific structure is difficult to reconcile with this hypothesis. One could explain the difficulty by the assumption that other pentachlorobutenes are produced but were undetectable because of lower vapor pressures; or one might argue that the structural assignment derived for these products is meaningless. Perhaps a better explanation is the production of a hexachlorobutane by the reaction

$$2\ CHCl_2\ CHCl\cdot \longrightarrow CHCl_2\ CHCl\ CHCl\ CHCl_2 \qquad (13)$$

followed by dehydrohalogenation.

$$CHCl_2\ CHCl\ CHCl\ CHCl_2 \longrightarrow CHCl_2\ CHCl\ CCl{=}CHCl + HCl \qquad (14)$$

The dehydrohalogenation could, of course, occur by hydrogen abstraction by chlorine atoms, followed by splitting off a Cl atom from the polychloro free radical. The structural specificity of the direct dehydrohalogenation stems from the reasonable presumption that HCl elimination removes Cl from a carbon containing two halogens; in the radical formulation the specificity is maintained by the greatly lowered reactivity of alpha hydrogens in chlorine substituted systems.[34]

It should be noted that the reaction sequence outlined leads to a calculated yield of HCl in excess of the measured G value. It can only be argued that this result is an artifact resulting from the inaccuracy in determining the pentachlorobutene yields. Lowering the G of pentachlorobutene by an appropriate amount worsens the chlorine balance of the

stoichiometry results; however, the probable error of the chlorine microanalyses of the polymer fractions makes it impossible to judge whether this is a significant objection to the mechanism.

The "high" polymer probably results from the addition of successive monomer units to the dimer radical:

$$CHCl_2\ CHCl\ CHCl\ CHCl\cdot + C_2H_2Cl_2 \longrightarrow \text{high polymer} \qquad (15)$$

The chains presumably terminate by radical-radical reactions or by splitting off Cl atoms, as is the case for the lower molecular weight condensation products.

The initiator radical postulated in Reaction (1) of the Appendix as responsible for the synthesis of the dichloroethylene oxides may be accounted for by (a) the persistence of a long-lived free radical until the system is opened to air, or (b) the formation of an unstable peroxide by some of the polyhalogenated products. The latter appears more attractive in terms of present concepts both of radical lifetimes and of the properties of polychloro systems. The fact that the trans- isomer forms a peroxide polymer on standing has been discussed, and some recent experiments indicate that the pure monomer also forms the dichloroethylene oxides under suitable conditions. Thus it seems quite plausible that certain polymer products would be less stable than the monomer itself and would undergo the reaction more readily. Peak E in the chromatograms of the trans-1,2-dichloroethylene residual liquid appears to be such a peroxide product.

In summary, the radiolysis products from the symmetrical dichloroethylenes are compatible with a series of free radical reactions. Primary interaction resulting partly in C–Cl bond clevage and partly in elimination of HCl, followed by a series of steps deduced from the nature of the reactive fragments, presents a self-consistent explanation of the experimental data. No products were observed which required the postulation of radiation specific reactions, and the radiolytic behavior is somewhat simpler than might have been expected for such compounds.

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APPENDIX

The Radiolytic Synthesis of the Cis- and Trans- Isomers of 1,2-Dichloroethylene Oxide

Among the suggested means of utilization of radioactive wastes from atomic energy plants is the synthesis of new compounds which cannot be made efficiently by ordinary chemical methods. An example of such a synthesis is the radiolytic preparation of heptadecene-8 described by Burton and Breger.[1] In the course of some investigations of the radiation chemistry of the symmetrical dichloroethylenes, the cis- and trans- forms of 1,2-dichloroethylene oxide have been produced. These compounds have not been previously reported, and in view of the current interest in radiation utilization, we are presenting preliminary data on the radiolytic synthesis and physical properties of these compounds.

The cis- and trans- forms of 1,2-dichloroethylene were irradiated in glass cells[2] in vacuo with 40 Mev helium ions inpingent on the liquid. After irradiation, the low-boiling and gaseous products were separated by vacuum techniques.[3] The residual high-boiling products plus the bulk of the 1,2-dichloroethylene were stored in glass-stoppered bottles in the presence of air after preliminary analysis for high-boiling products. In samples that had stood several months, two peaks were found in GLP chromatograms (nonyl phthalate column) that were not present in samples chromatogrammed immediately after irradiation. These peaks were concentrated in the pot liquid by distillation through a small Vigreaux column and were further concentrated and purified by running repeated GLP chromatograms of the pot liquid, collecting the respective peaks each time. By this means samples of 1 gm and 0.2 gm of the two respective peak materials were isolated in relatively pure form. These were further purified by use of a Silicone oil (G.E. 96-40) column with collection of the respective components. These are referred to as dichloroethylene oxide I and dichloroethylene oxide II according to their respective GLP chromatographic emergence times.

The relative yields of oxide I to oxide II from trans- 1,2-dichloroethylene was about 4.6 : 1. The ratio from irradiated cis- 1,2-dichloroethylene was smaller but has not been well determined because of the much lower yield from this isomer.

The compounds isolated have been characterized as the cis- and trans- isomers of 1,2-dichloroethylene oxide by mass-spectrometer spectral patterns and by comparison of the infrared spectra with the spectra of the cis- and trans- forms of 2,3-epoxybutane. All the compounds have the CH band in the region 2950 to 3050 wave numbers which Henbest, Meakins, Nicholls, and Taylor have suggested as being characteristic of the substituted oxirane ring,[4] and all exhibit bands in the three regions where Patterson[5] and others have assigned the C—O—C skeletal motions.[5] The mass spectra, with parent masses at 112 to 117 mass units, give the empirical formula $C_2H_2Cl_2O$ from isotope ratio arguments. Chemical analysis for C, H, and Cl yielded 21.2%, 1.97%, and 63.5% for oxide I; and 21.2%, 1.92%, and 63.6% for oxide II. The calculated values for $C_2H_2Cl_2O$ are 21.27%, 1.78%, and 62.78%.

Known compounds of this composition, dichloroacetaldehyde and chloroacetylchloride, were shown to differ from oxide I and oxide II in both mass spectrometer ionization patterns and GLP chromatographic retention times.

Some physical properties of these two compounds are listed in Table I. It has not been possible to decide unequivocally which compound is the cis- form and which is the trans- form. An argument can be made from the comparison of the infrared spectra of oxides I and II with the spectra of the 2,3-epoxybutanes that oxide I is the cis- form and oxide II the trans- form.

Table I

Physical Properties of 1,2-dichloroethylene oxides

	Compound I	Compound II
boiling point	80-81°	111-112°
melting point	-43°	-63°
$D^{25/4}$	1.405	1.470
n_D^{25}	1.438	1.452
M.W. (cryoscopic)	115.6	
M.W. (M.S. inlet pressure)	113.2	115.2

At present one can only speculate as to the origin of these compounds. Yields of oxide I as high as G = 9 were found in old samples of irradiated trans- 1,2-dichloroethylene. As this is as large as the total yield of "polymer" determined immediately after irradiation, a chain reaction for the formation of the oxides is indicated. An attractive possibility is an auto-oxidation reaction[6] using a long-lived free radical present in very low concentration as the intermediate.

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (1)$$

$$ROO\cdot + C_2H_2Cl_2 \longrightarrow ROOC_2H_2Cl_2\cdot \qquad (2)$$

$$ROOC_2H_2Cl_2\cdot \longrightarrow RO\cdot + HClC\overset{O}{\frown}CHCl \qquad (3)$$

$$RO\cdot + C_2H_2Cl_2 \longrightarrow ROC_2H_2Cl_2\cdot \qquad (4)$$

$$ROC_2H_2Cl_2\cdot \longrightarrow R\cdot + HClC\overset{O}{\frown}CHCl \qquad (5)$$

Preliminary tests with other sources of radicals (benzoyl peroxide) in the presence of oxygen showed that small yields of both the dichloroethylene oxides are formed from both cis- and trans- 1,2-dichloroethylenes.

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Table I

Physical Properties of the Dichloroethylenes

Property	Cis- isomer Measured	Cis- isomer Literature[a]	Trans- isomer Measured	Trans- isomer Literature[a]
n_D^{25}	1.4426	1.4428	1.4395	1.4397
d_4^{25}	1.2698	1.2736	1.2420	1.2489
B.P. (760 mm)	60.36°	60.36°	47.66°	47.67°
F.P.	-81.52°	-80.0°	-49.36°	-49.8°

(a) A. Weissberger, Editor, "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y. Vol. VII; J. A. Reddick and E. E. Toops, "Organic Solvents," 2nd Ed., 1955, pp. 204-205.

Table II

Hundred Electron Volt Yields of Volatile Products from Helium Ion Irradiation of Cis-1,2-Dichloroethylene

Product	Microampere-hours of Bombardment									
	0.03	0.10	0.05	0.07	0.07	0.15	0.20[b]	0.03	0.12	0.30
H_2[a]	0.026	0.025	0.023	0.029	0.030	0.032	0.030	0.027	0.025	0.029
CO	0.0014	0.0004	0.0007	0.0006	0.007	0.008	0.0007	0.0011	0.0005	0.0008
CH_2=CHCl	0.34	0.32	0.33		0.26	0.31	0.19	0.26	0.40	0.46
ClC≡CH	1.18	1.00	1.14		0.90	0.84	0.81	1.04	1.03	1.02
ClC≡CCl	0.003	0.006	0.015		0.005	0.006	0.001	0.002	0.011	0.003
HC≡CH	1.99	1.92	2.06	1.71	1.96	1.66	1.63	1.77	1.84	1.75
HCl		1.23		1.34	1.40	1.25		1.34	1.37	1.55
ev x 10^{-22}	1.45	4.80	2.40	2.91	2.91	6.24	9.04	1.45	5.76	13.57
Vol. in cc.	146.9	128.4	138.7	135.4	132.8	131.1	142.8	127.2	132.1	124.8
ev/cc. x 10^{-20}	0.99	3.73	1.73	2.15	2.19	4.76	6.33	1.14	4.36	10.86
g_f	4.28	1.26	2.51	2.07	2.07	0.96	0.67	4.14	1.05	0.44

(a) Measured value, all others multiplied by ratio $(G(H_2)_{avg.}/G(H_2)_{meas.}$

(b) Residual liquid from this experiment used in polymer study.

Table III

Hundred Electron Volt Yields of Volatile Products from Helium Ion Irradiation of Trans-1,2-Dichloroethylene

	Microampere-hours of Bombardment										
Product	0.03	0.08	0.07	0.20[b]	0.15[b]	0.05	0.13	0.10	0.03	0.30	0.10
H_2[a]	0.038	0.036	0.046	0.040	0.040	0.038	0.039	0.042	0.043	0.043	0.038
CO	0.003	0.002	0.001	0.0007	0.004	0.0005	0.0007		0.0007	0.0003	0.0002
CH_2=CHCl	0.22	0.25	0.22					0.29	0.27	0.28	0.22
ClC≡CH	0.86	0.88	0.80					0.85	0.85	0.79	0.78
ClC≡CCl	0.001	0.006	0.003	0.003	0.001	0.004	0.001	0.010	0.007	0.005	0.001
HC≡CH	1.71	1.52	1.59	1.61	1.61	1.65	1.65	1.52	1.46	1.54	1.64
HCl				1.23	1.21		1.28	1.16	1.05	1.22	1.32
ev x 10^{-22}	1.44	3.84	3.16	9.69	7.20	2.51	6.03	4.80	1.36	12.48	4.64
Vol. in cc.	142.0	128.4	150.4	142.5	133.1	132.1	119.6	110.1	146.6	120.4	116.6
ev/cc. x 10^{-20}	1.01	2.99	2.10	6.80	5.41	1.90	5.04	4.36	0.93	10.36	3.98
g_f	4.30	1.55	1.90	0.62	0.84	2.51	1.00	1.25	4.43	0.48	1.30

(a) Measured value, all others multiplied by ratio $G(H_2)_{avg.}/G(H_2)_{meas.}$

(b) Residual liquid from this experiment used in polymer study.

Table IV

Relative Yields of Volatile Products from Electron Irradiation of Cis-1,2-Dichloroethylene[a]

Product	He^{++}(b)	G, Molecules/100 ev e^-(c)	e^-(d)	e^-(d)	e^-(e)
H_2	0.028	0.028	0.028	0.028	0.028
CH_2=CHCl	0.34	0.50	0.28	0.30	0.24
ClC≡CH	1.02	0.93	1.09	0.87	0.70
ClC≡CCl	0.006	0.007	0.002	0.001	0.002
HC≡CH	1.83	2.06	2.42	2.24	1.60
HCl	1.36	1.09	1.92	1.40	1.56
ev x 10^{-22}		14.04	2.23	5.14	5.66
Vol. in cc.		145.0	127.9	118.4	164.8
ev/cc. x 10^{-20}		9.68	1.74	4.34	3.43

(a) Electron yields are normalized to same hydrogen yield as He^{++} irradiations.

(b) Averages of 10 experiments.

(c) Total beam from microwave linear electron accelerator with mean energy of 3.5 Mev.

(d) Monoenergetic 4.6 Mev electrons from microwave linear electron accelerator.

(e) Monoenergetic 2 Mev electrons from Van de Graaff.

Table V

Relative Yields of Volatile Products from Electron Irradiation of Trans-1,2-Dichloroethylene[a]

Product	G, Molecules/100 ev		
	He^{++}[b]	e^-[c]	e^-[d]
H_2	0.040	0.040	0.040
$CH_2=CHCl$	0.25	0.33	0.26
$ClC\equiv CH$	0.82	0.50	0.82
$ClC\equiv CCl$	0.004	0.003	0.002
$HC\equiv CH$	1.59	0.90	1.50
HCl	1.21		1.86
ev x 10^{-22}		13.52	5.66
Vol. in cc.		127.0	159.3
ev/cc. x 10^{-20}		10.64	3.55

(a) Electron yields are normalized to same hydrogen yield as He^{++} irradiations.

(b) Averages of 11 experiments.

(c) Total beam from microwave linear electron accelerator with mean energy of 3.5 Mev.

(d) Monoenergetic 2 Mev electrons from Van de Graaff.

Table VI

Comparison of Hundred Electron Volt Yields from Helium Ion and Gamma Radiolyses

Product	Cis-$C_2H_2Cl_2$ He^{++}(a)	Cis-$C_2H_2Cl_2$ γ(b)	Trans-$C_2H_2Cl_2$ He^{++}(c)	Trans-$C_2H_2Cl_2$ γ(b)
H_2	0.028	0.018	0.040	0.033
$CH_2{=}CHCl$	0.34	0.32	0.25	0.45
$ClC{\equiv}CH$	1.02	0.98	0.82	0.90
$ClC{\equiv}CCl$	0.006	0.009	0.004	0.003
$HC{\equiv}CH$	1.83	1.85	1.59	1.85
HCl	1.31		1.21	0.9
$CHCl_2CHCl_2$	0.4	0.6	0.4	0.2
$C_4H_4Cl_4$	1.0	13.6	1.0	3.8
$C_4H_3Cl_5$	1.4	0.5	1.1	0.4
ev x 10^{-22}		0.014		0.014
Vol. in cc.		15.0		15.0
ev/cc. x 10^{-20}		0.009		0.009
g_f		43.6		436.

(a) Averages of 10 experiments.

(b) Cobalt sixty gamma source.

(c) Averages of 11 experiments.

Table VII

Boiling Point-Emergence Time Correlation for Chlorinated Hydrocarbons

Compound	Normal boiling point[a] °C	Emergence time, min. (after air)	Sensitivity[b] arbitrary units
Tetrachloroethylene	121	4.65	15.3
uns-tetrachloroethane	130	5.35	13.9
sym-tetrachloroethane	145	7.05	14.5
Pentachloroethane	162	10.98	14.2
Hexachloroethane	185	18.47	--
Hexachlorobutadiene-1,3	215	30.6	13.4
2,3-Dichloropropene-1	94	2.33	14.8
1,2-Dichloropropane	97	2.30	14.2
1,1,2,3,3-Pentachloropropane	200	20.95	13.4
1,1,2-Trichloroethane	114	2.86	14.7
1-Chloroheptane	160	9.4	--
1-Chlorooctane	183	15.9	--
1,2,3-Trichloropropane	156	7.5	15.8
1,2-Dichloropropane	155	7.0	12.7
Average sensitivity			14.3

(a) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(b) Defined on p. 20.

Table VIII

Polymer Products from Helium Ion Irradiation of Cis-1,2-Dichloroethylene

Product	Est. normal boiling point °C	Approximate G value 0.20 μah
Tetrachlorobutene[c] isomer	134	0.02
1,1,2,2-tetrachloroethane[a]	146	0.43
Tetrachlorobutene-1[a] 1,3,4,4-isomer	195	0.77
Tetrachlorobutene-1[b] 1,3,4,4-isomer	223	0.17
Pentachlorobutene-1[b] 1,2,3,4,4-isomer	241	0.73
Pentachlorobutene-1[b] 1,2,3,4,4-isomer	256	0.73
"High" Polymer	>300	
G value		2.21
Mol. Wt.		303
Composition		$(CHCl)_{6.4}$
ev/cc. x 10^{-20}		10.86
g_f		0.44

(a) Structure well established.

(b) Probable structure.

(c) Structure uncertain.

Table IX

Polymer Products from Helium Ion Irradiation of Trans-1,2-Dichloroethylene

Product	Est. Normal boiling point °C	Approximate G values 0.20 μah	0.15 μah
Tetrachlorobutene[c] isomer	134	0.07	--
1,1,2,2-tetrachloroethane[a]	146	0.5	0.35
Peak E, peroxide[c] 1,2,3,4-tetrachlorobutene peroxide	159	0.3	0.5
Tetrachlorobutene-1[a] 1,3,4,4-isomer	195	0.9	0.85
Pentachlorobutene-1[b] 1,2,3,4,4-isomer	241	0.45	0.56
Pentachlorobutene-1[b] 1,2,3,4,4-isomer	256	0.45	0.56
"High" Polymer	>300		
G value		3.4	6.7
Mol. Wt.		353	399
Composition		$(CHClO_{.12})_7$	$(CHClO_{.06})_8$
ev/cc. x 10^{-20}		6.80	5.41
g_f		0.62	0.84

(a) Structure well established.

(b) Probable structure.

(c) Structure uncertain.

Table X

Hundred Electron Volt Yields from Helium Ion Irradiation of 1,2-Dichloroethane

Product	0.05 μah	0.07 μah
Hydrogen	0.27	0.27
Methane	0.0015	0.0014
Methyl chloride	0.013	0.013
Acetylene	0.137	0.137
Ethylene	0.78	0.76
Chloroacetylene	0.018	0.018
Dichloroacetylene	0.0011	0.0006
Vinyl chloride	1.18	0.96
Ethyl chloride	0.70	0.51
Methylene chloride	0.013	0.005
1,1-Dichloroethane	0.040	0.010
1,2-Dichloroethylene	0.021	0.007
HCl	4.62	4.38
1,1,2-Trichloroethane		0.7
1,4-Dichlorobutane		0.3
1,2,4-Trichlorobutane		0.48
1,2,3,4-Tetrachlorobutane (I)		0.26
1,2,3,4-Tetrachlorobutane (II)		0.23
"High" Polymer		0
ev x 10^{-22}	2.42	3.38
Vol. in cc.	145.4	125.5
ev/cc. x 10^{-20}	1.67	2.69

Table XI

Stoichiometry of Helium Ion Radiolysis of 1,2-Dichloroethane

Product	Best G value	Atom Balance C	H	Cl
Hydrogen	0.27		0.54	
Methane	0.0015	0.0015	0.006	
Methyl chloride	0.013	0.013	0.039	0.013
Methylene chloride	0.009	0.009	0.018	0.018
Acetylene	0.137	0.274	0.274	
Ethylene	0.77	1.54	3.08	
Vinyl chloride	1.07	2.14	3.21	1.07
Ethyl chloride	0.60	1.20	3.0	0.6
1,1-Dichloroethane	0.02	0.04	0.08	0.04
Dichloroethylene	0.01	0.02	0.02	0.02
Hydrogen chloride	4.5		4.5	4.5
1,1,2-Trichloroethane	0.7	1.4	2.1	2.1
1,4-Dichlorobutane	0.3	1.2	2.4	0.6
1,2,4-Trichlorobutane	0.5	2.0	3.5	1.5
1,2,3,4-Tetrachlorobutanes	0.5	2.0	3.0	2.0
	Σ	11.8	25.8	12.4
G ($-C_2H_2Cl_2$)	6.2			

Table XII

Stoichiometry of Helium Ion Radiolysis of Cis-1,2-Dichloroethylene

Product	Best G Value	Atom Balance C	H	Cl
Hydrogen	0.028		0.056	
Vinyl chloride	0.34	0.68	1.02	0.34
Chloroacetylene	1.02	2.04	1.02	1.02
Dichloroacetylene	0.006	0.012		0.012
Acetylene	1.83	3.66	3.66	
Hydrogen chloride	1.36		1.36	1.36
1,1,2,2-Tetrachloroethane	0.4	0.8	0.8	1.6
Tetrachlorobutenes	1	4	4	4
Pentachlorobutenes	1.4	5.6	4.2	7
"High" Polymer	2.21	14.1	14.1	14.1
	Σ	30.9	30.2	29.4
G ($-C_2H_2Cl_2$)	15.1			

Table XIII

Stoichiometry of Helium Ion Radiolysis of Trans- 1,2-Dichloroethylene

Product	Best G value	Atom Balance C	H	Cl
Hydrogen	0.040		0.08	
Vinyl chloride	0.25	0.50	0.75	0.25
Chloroacetylene	0.83	1.66	0.83	0.83
Dichloroacetylene	0.004	0.008		0.008
Acetylene	1.59	3.18	3.18	
Hydrogen chloride	1.21		1.21	1.21
1,1,2,2-Tetrachloroethane	0.4	0.8	0.8	1.6
E, peroxide	0.4	1.6	1.6	1.6
Tetrachlorobutenes	0.9	3.6	3.6	3.6
Pentachlorobutenes	1	4	3	5
"High" Polymer	5	37.5	37.5	37.5
	Σ	52.8	52.6	51.6
G $(-C_2H_2Cl_2)$	26.1			

Table XIV

Effect of Temperature on Helium Ion Yields of Volatile Products

Product	G Values from Trans-$C_2H_2Cl_2$ $25^{o(a)}$	80°
H_2	0.040	0.049
$CH_2 = CHCl$	0.25	0.24
$ClC \equiv CH$	0.82	1.0
$ClC \equiv CCl$	0.004	--
$HC \equiv CH$	1.59	2.0
HCl	1.21	1.4
ev x 10^{-22}		4.16
Vol. in cc.		127.0
ev/cc. x 10^{-20}		3.28

(a) Averages for 11 experiments.

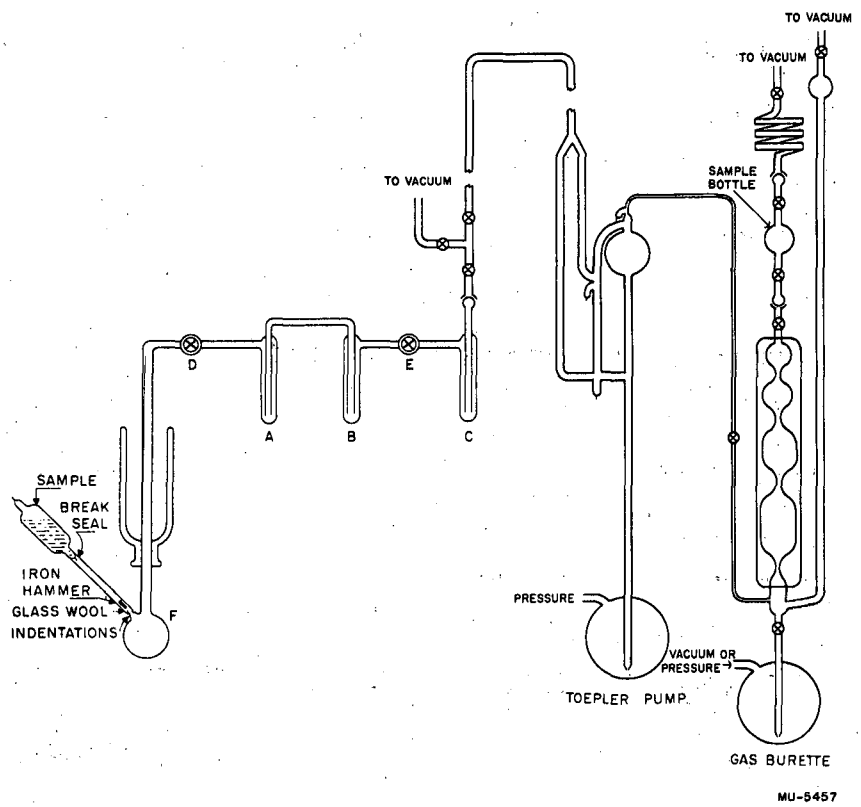
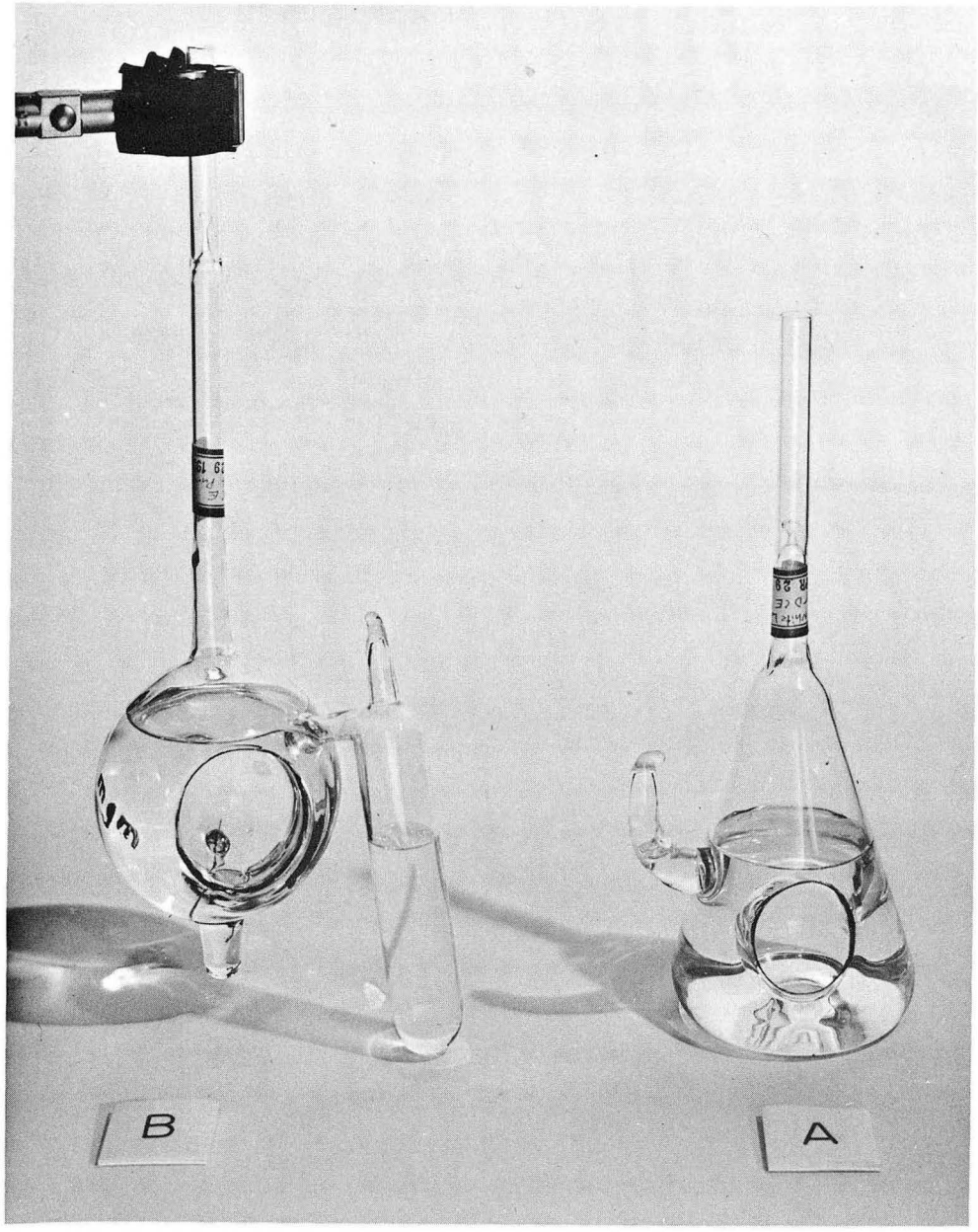
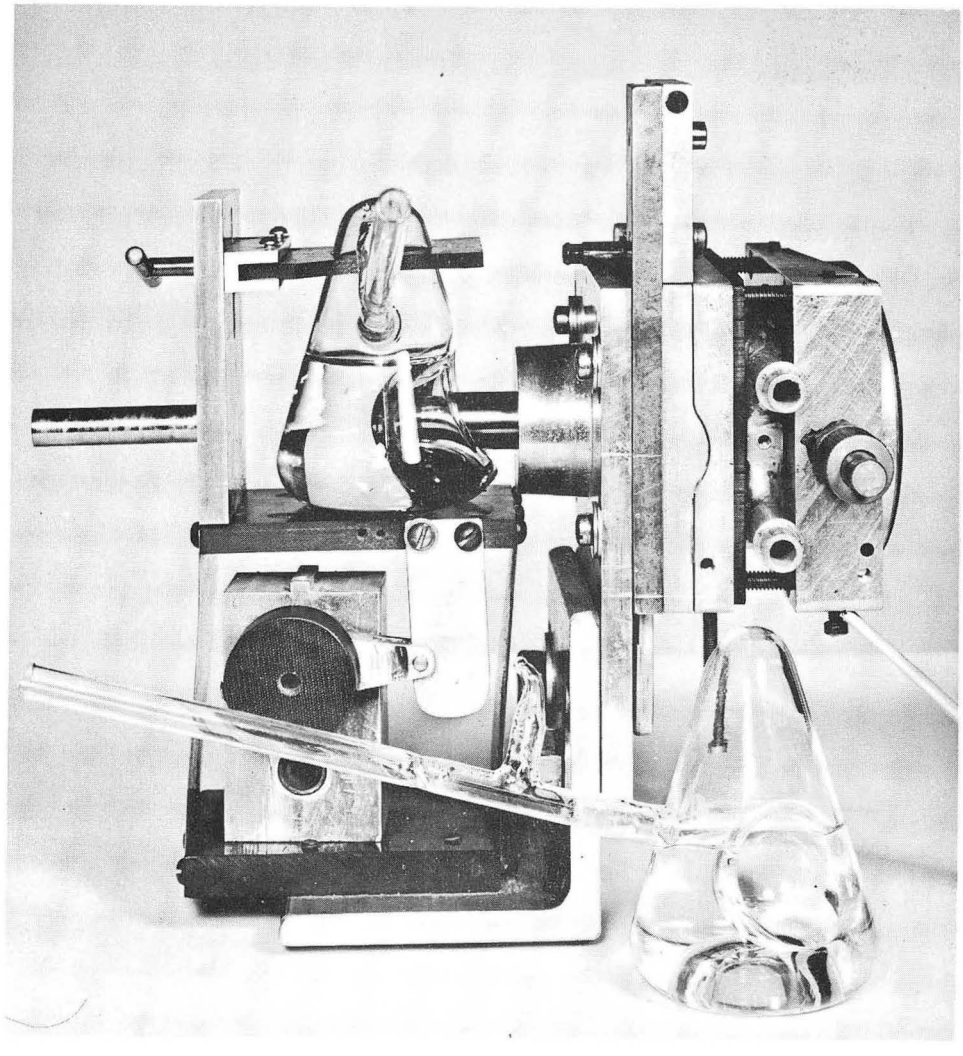


Fig. 1. Apparatus for separating volatile products.



ZN-1970

Fig. 2. (a) Helium ion irradiation cell.
(b) Electron irradiation cell.



ZN-1971

Fig. 3. Shaker target assembly for cyclotron irradiations.

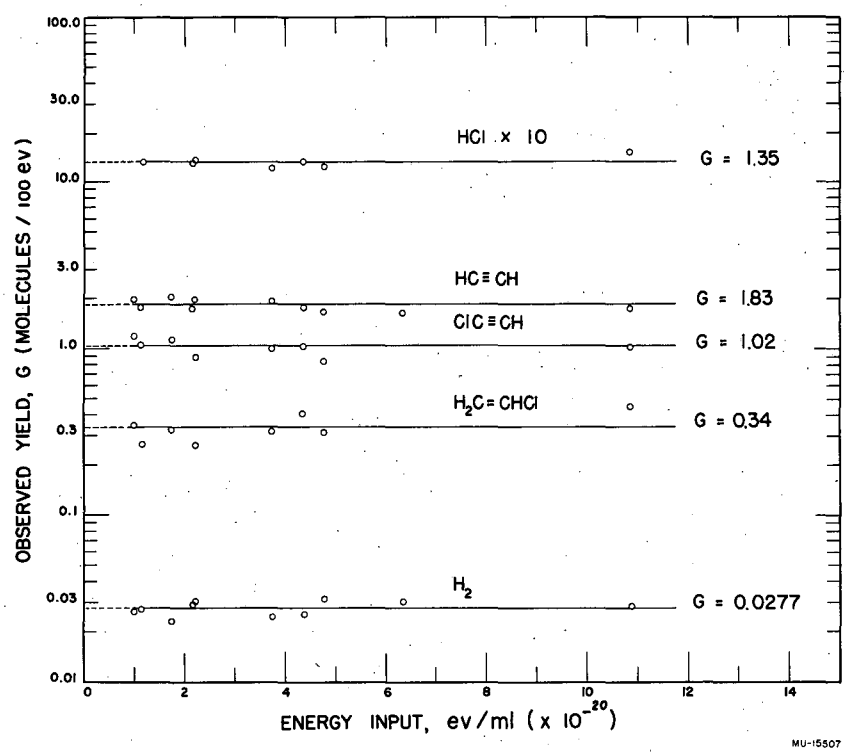


Fig. 4. Yields of volatile products from helium ion irradiation of cis-1,2-dichloroethylene.

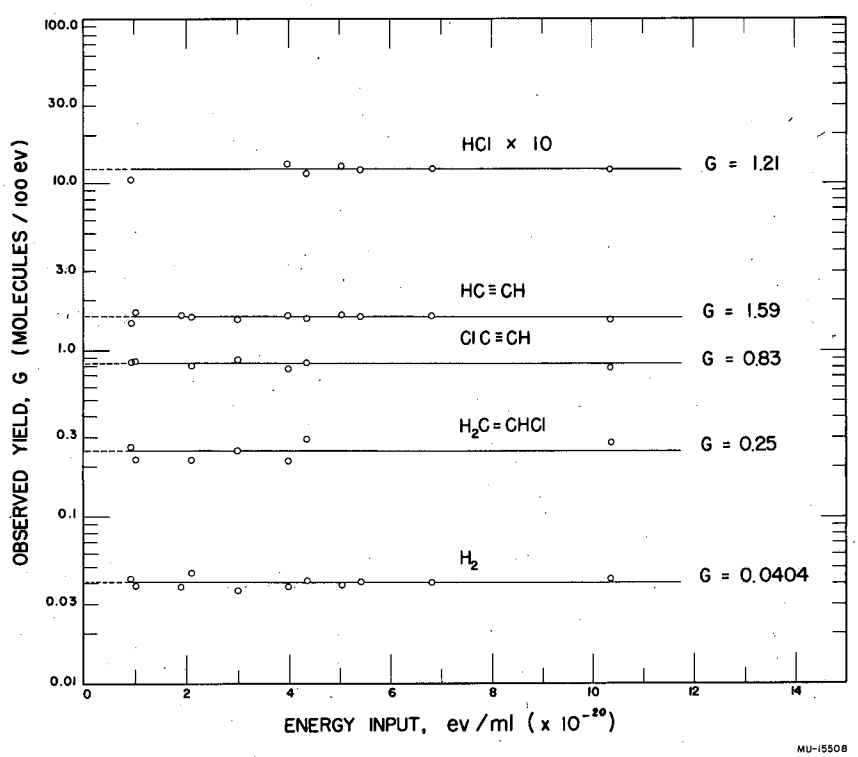


Fig. 5. Yields of volatile products from helium ion irradiation of trans-1,2-dichloroethylele.

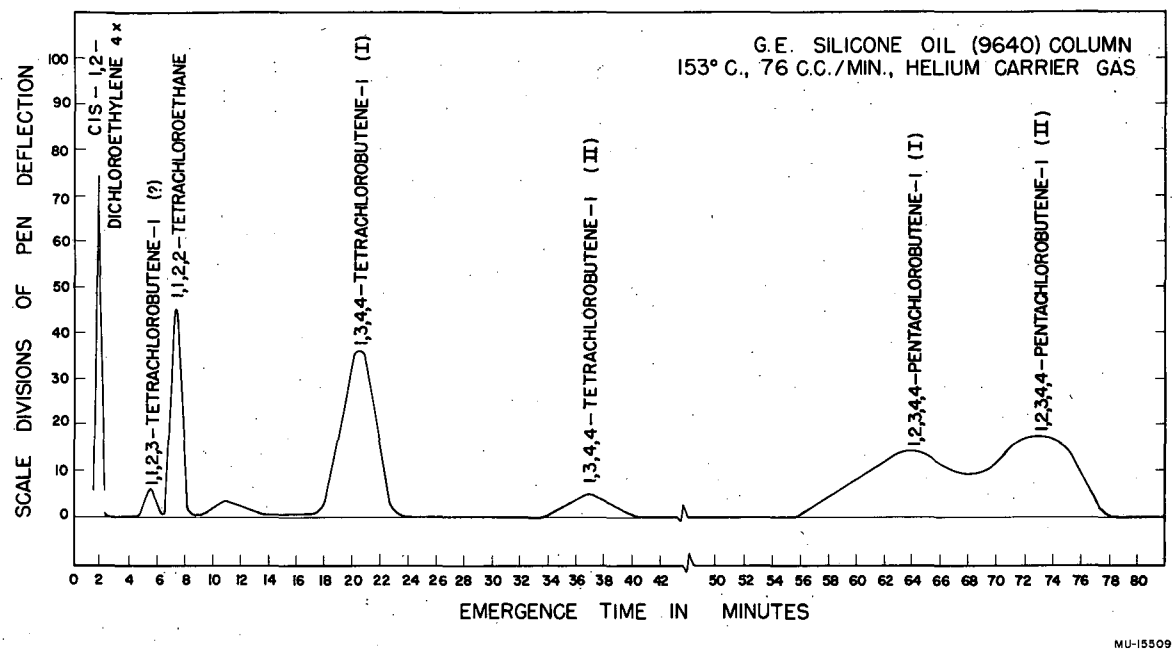


Fig. 6. Composite chromatogram of 60λ of polymer fraction from cis-1,2-dichloroethylene.

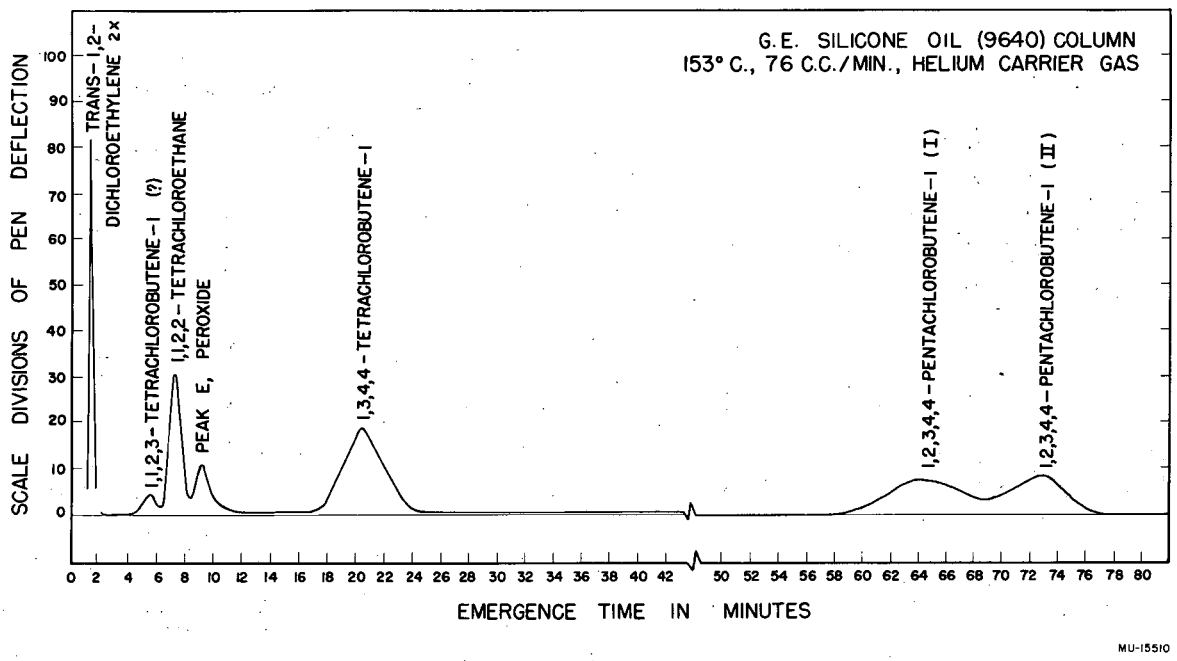


Fig. 7. Composite chromatogram of 50λ of polymer fraction from trans-1,2-dichloroethylene.

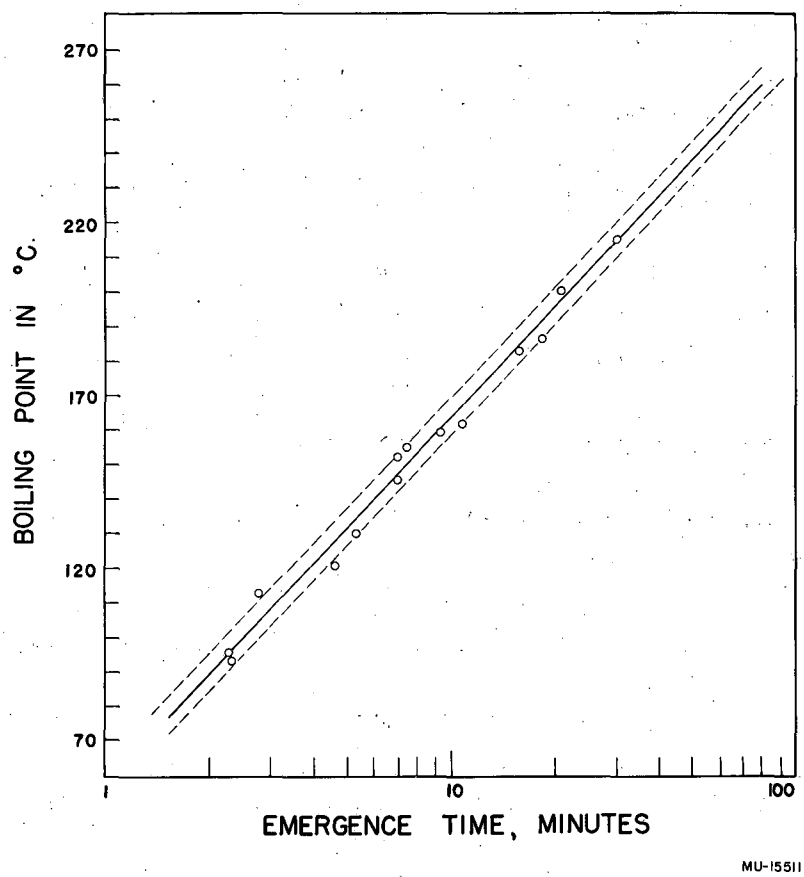


Fig. 8. Boiling point — emergence time correlation for chlorinated hydrocarbons.

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