I   II   III

The hyperfine interaction with the nitrogen nucleus is presumed to arise by means of σ–π configurational interaction mainly from the contribution of bond eigenfunction I to the ground state wave function. Brovetto and Ferroni[35] and McConnell[36] have shown that not only does the contribution of bond eigenfunctions II and III lead to a positive spin density on the *ortho* and *para* carbon atoms but the cross terms of these bond eigenfunctions results in a *negative* spin density on the meta carbon atoms, the magnitude of which is usually 1/3 to 1/2 that in *ortho* or *para* position.[37] The hyperfine structure does not allow the assignment of the sign of the spin density on the carbon atoms, but we feel that the ratio of the hyperfine coupling constants of the *ortho* and *para* to the *meta* protons is qualitatively in agreement with a valence bond description of the

(35) P. Brovetto and S. Ferroni, *Nuovo Cimento*, **5**, 142 (1957).

(36) H. M. McConnell, *J. Chem. Phys.*, **29**, 244 (1958); **30**, 328 (1959).

(37) The authors are indebted to both referees for pointing this out.

nitrobenzene anion in terms of structures I, II and III. By way of contrast, molecular orbital calculations with reasonable values for coulomb and resonance integrals for the nitro group lead to much too little unpaired electron density in the *meta* π-orbitals.

Several other approaches to electrochemical generation of radicals are available. A continuous flow system from the electrochemical cell into the microwave cavity could be employed, or a sample could be transferred from the cell into a sample tube for measurement. By comparison, the *intra muros* cell technique offers significant advantages in simplicity and convenience. The present cavity design limits the study to reasonably stable anion radicals; eventual development of techniques for observing transient radicals at a mercury electrode will provide a significant tool in the study of electrode processes.

Preliminary work has been done in this Laboratory employing a platinum electrode for generation of radicals by electroöxidation at controlled potential.

| The Radiation Chemistry of the Symmetrical Dichloroethylenes[1] |

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BY JEAN H. FUTRELL AND AMOS S. NEWTON[2]

Purified, degassed liquid samples of *cis*- and *trans*-1,2-dichloroethylenes have been irradiated with helium ions, electrons and gamma-rays. A comparison of the radiolysis products has been made with the products formed in the polymerization of these compounds with benzoyl peroxide. Using a combination of gas chromatography and mass spectrometry, several of the high boiling products (to ~350°) have been characterized as to compound types. The yields of volatile products did not change greatly with changes in linear energy transfer but the yields of polymer products were found to increase markedly with decreasing density of ionization. A mechanism has been proposed to explain the formation of the observed products.

Introduction

As part of a program of investigating the radiation chemistry of organic compounds containing various functional groups, a number of alcohols[3] and ethers[4] have been investigated; the work has now been extended to the study of a simple olefin. The symmetrical dichloroethylenes were chosen for this purpose, as they are perhaps the simplest compounds containing the functional groupings RCH= CHR for which the phenomenon of long-chain polymerization does not dominate and obscure the other reactions taking place. A study of the more complex compound, isopropenyl acetate, has been reported elsewhere.[5] Further, the investigation of

(1) Much of the work presented here is from the dissertation submitted by Jean H. Futrell in partial fulfillment of the requirements for the Ph.D. degree in September, 1958.

(2) Author to whom requests for reprints are to be addressed.

(3) W. R. McDonnel and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

(4) A. S. Newton, *J. Phys. Chem.*, **61**, 1485 (1957).

(5) A. S. Newton and P. O. Strom, *ibid.*, **62**, 24 (1958).

the *cis* and *trans* isomers of 1,2-dichloroethylene permits the comparison of the radiation effects on two compounds differing in their physical properties primarily in that the *cis* isomer has a large dipole moment (1.8 Debye), while the *trans* isomer has no net moment.[6] Because a difference in dielectric constant of the substrate might be expected to have an effect on rates of ionic reactions, this feature is perhaps pertinent to the issue of the importance of ionic processes in the radiation chemistry of condensed phases.[7]

Experimental

Purification of Compounds.—Eastman White Label chemicals were purified by distillation through an 85-plate adiabatic column packed with Podbielniak Helipak No. 3013

(6) G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 138.

(7) M. Burton in "Hearings on Physical Research Program as it Relates to the Field of Atomic Energy," Subcommittee on Research and Development of the Joint Committee on Atomic Energy, Eighty fifth Congress, Second Session (United States Government Printing Office, Washington 25, D. C., 1958), p. 110.

stainless steel helices. Gas chromatography and mass spectrometric analysis were used to monitor the distillation, and the purified product was distilled with a boiling range of less than 0.01° and with a purity of 99.98 ± 0.02% as determined by cryoscopic methods. The properties of the purified isomers are listed in Table I.

Preparation of Targets.—Pyrex glass cells of the type described by Garrison, Haymond and Weeks[8] were used for the helium-ion irradiations and for some of the electron irradiations. In other electron irradiations the cell design was modified to consist of a spherical body rather than an Erlenmeyer shape (so that all electrons would be stopped within the vessel), and a platinum lead was sealed into the glass wall for more effective beam monitoring. These cells accommodated from 115 to 140 ml. of liquid, depending on the construction. Gamma-irradiation cells were cylindrical glass ampoules 1 inch in diameter and 3 inches tall, fitted with break-tip and seal-off tubes. These contained 15 ml. of liquid and an equal volume of gas space.

The purified dichloroethylene isomers were degassed by refluxing under vacuum[9] and were distilled and sealed in the appropriate target vessels under vacuum.

Irradiation Procedures.—The helium-ion irradiations were made with the external beam of the 60-inch Crocker Laboratory cyclotron with 40 to 43 mev. ions incident on the liquids at beam currents of the order of 0.1 to 0.2 μamp. The irradiations were conducted at room temperature (approximately 25°) and the temperature was roughly controlled by an air blast against the target. The target was shaken vigorously during the irradiation. One sample of cis-1,2-dichloroethylene was irradiated at approximately 80° while heated remotely by an infrared lamp in a manner described previously.[10] The local dose rate in the area of helium ion absorption was about 2 × 10²² ev./g./min.

Electron irradiations were conducted with the microwave linear electron accelerator which has been described by Lemmon and Mosier.[11] In other experiments the 2-mev. Van de Graaff accelerator at the California Research Corporation was employed. The lowest practicable rates of irradiation were used, with air-blast cooling, to keep the targets at or near room temperature. In the Van de Graaff experiments the local dose rate was very approximately 3 × 10²⁰ ev./g./min.

Gamma radiolyses were conducted in a 2000-curie Co⁶⁰ source[12] and were monitored by means of oxygen saturated Fricke dosimeters [$G(Fe^{+++}) = 15.5$]. The dose rate to the dosimeter was 2.19 × 10¹⁸ ev./g./min. Use of a cyclohexane dosimeter, assuming $G(H_2) = 5.4$[13] gave the same value of the radiation intensity as the Fricke dosimeters. Corrections were made for differences in electron density between the calibrating material and the samples, yielding a dose rate of 1.96 × 10¹⁸ ev./g./min. for the dichloroethylenes.

(8) W. M. Garrison, H. R. Haymond and B. M. Weeks Radiation Research, 1, 97 (1954).

(9) A. S. Newton, Anal. Chem., 28, 1214 (1956).

(10) A. S. Newton, J. Phys. Chem., 61, 1490 (1957).

(11) R. M. Lemmon and D. F. Mosier, Radiation Research, 4, 373 (1956).

(12) B. M. Tolbert, G. Nielsen, G. Edwards, I. M. Whittemore and N. B. Garden, "A High-Intensity Cobalt-60 Source," in Chemistry Division Quarterly Report, UCRL-3710, Feb. 1957, p. 72.

(13) R. H. Schuler, J. Phys. Chem., 61, 1472 (1957); M. Burton and S. Lipsky, ibid., 1461 (1957), gives G(H₂) as 5.9.

Benzoyl Peroxide Experiments.—Comparisons were made with the products observed when benzoyl peroxide was decomposed in the presence of excess of each of the respective 1,2-dichloroethylenes. One mmole of benzoyl peroxide (Monomer–Polymer Corporation, analysis, 96% active), was weighed into a flask fitted with a break seal. This was evacuated and 50 ml. of the purified and degassed compound added by vacuum transfer. The flask was sealed and heated at 70° for 100 hr.,[14] after which the products were analyzed as described below except the KOH treatment of the gas was eliminated. It was established that only traces of HCl were formed in the reaction. Washing the gas with water and testing with silver nitrate yielded only a faint turbidity.

Volatile Products.—After irradiation the target vessel was sealed into a vacuum system and opened under vacuum in such a manner that its contents drained into a flask for refluxing under vacuum. Gaseous and low-boiling products evolved from the liquid in this process were pumped through refrigerated traps with an automatic Toepler pump.[9] Fractions volatile at −196, −125 and −80° were separated and were analyzed with a Consolidated Engineering Corporation model 21-103 mass spectrometer. Because analyses for HCl are erratic with this mass spectrometer, the constituents in the gas fraction volatile at −125° were contacted with KOH pellets prior to analysis in order to remove this component. The HCl yield was determined by both the decrease in gas volume and by gravimetric determination of chloride in the KOH scrubbing pellets. The two methods agreed quite satisfactorily. No HCl was observed in the residual gas and no trend was observed in the HCl yields with total dose indicating HCl absorption effects on the collection apparatus to be negligible for the dose range studied.

Polymer Products.—Various techniques involving concentration of the polymer products, separation of the high boiling constituents by gas chromatography, and identification of the individual components by mass spectrometry were used to study the polymer products. In some cases the residual liquid after separation of the low boiling products was concentrated in a small Vigreux column. In others the bulk dichloroethylenes were removed by vacuum evaporation. The density and weight of the residual material was used to calculate the volume where complete recovery was impossible. In some cases a semi-micro molecular distillation was run on the high boiling products.

All fractions were analyzed by gas chromatography using 5 mm. i.d. glass columns 2 m. in length with stationary phases of General Electric Silicone Fluid 96–40 or Fluorolube HG-1200 (Hooker Electrochemical Co.) adsorbed on 40 to 60 mesh Sil-O-Cell Firebrick. Temperatures up to 153° were used without bleeding. At higher column temperatures, continuous elution of the stationary phase interfered with the mass spectrometer identification of the components.

Samples were injected into the column to determine the emergence times of the principal constituents. This was followed by a second injection in which each respective component was collected from the column effluent as a discrete sample in refrigerated traps attached at the proper emergence time. These separated components were then characterized by their mass spectrometer fragmentation patterns. Mass spectrometer fragmentation patterns of available chlorinated hydrocarbons were used to obtain correlations between molecular structure and fragmentation patterns for polychloro compounds. These same commercial compounds were used in the gas chromatography runs to establish the response per μl. liquid injected and the correlation between boiling point and emergence times. In this way the volume fraction of various components was determined from the gas chromatographic peak areas and calibrations. The unaccounted peak area in a given fraction was ascribed to compounds boiling too high to be detected at the column temperature used, the highest useful limit being a boiling point of 350° using the Fluorolube HG-1200 column. Details on these procedures are available elsewhere.[15]

The residual material from molecular distillation of the "polymer" consisted of material having a vapor pressure too low for these techniques to yield useful information. Where possible, this was characterized by average mol. wt. (f.p. depression in benzene) and composition. One or more

(14) C. E. Frank and A. U. Blackman, THIS JOURNAL, 72, 3283 (1950).

(15) Jean H. Futrell, University of California Radiation Laboratory Report UCRL-8362, July, 1958.

TABLE II

YIELDS[a] OF VOLATILE PRODUCTS FROM cis- AND trans-1,2-DICHLOROETHYLENE IRRADIATED WITH He^{++}, e^- AND γ-RAYS

Product	Cis-1,2 DCE			trans-1,2 DCE			He^{++} (80°)
	He^{++}	e^{-b}	γ	He^{++}	e^{-b}	γ	
H_2	0.027	0.027	0.018	0.040	0.040	0.035	0.049
HC≡CH	1.83	2.08	1.9	1.59	1.50	1.6	2.0
HC≡CCl	1.02	0.90	1.05	0.83	0.82	0.8	1.0
Cl—C≡CCl	0.006	.003	0.009	.004	.002	.003	...
CH_2=CHCl	0.34	.33	0.36	.25	.26	.25	0.24
HCl	1.35	1.5	1.0	1.21	...	1.2	1.4
Isomerization	≤3.1	...	4.0	1.8	...	3.1	
CHCl=CCl_2	≤0.25	...	0.2	0.12	...	0.06	

[a] Extrapolated values at zero time of irradiation. Irradiation at 25° except as noted. [b] 2 mev. electrons from Van de Graaff generator. (Values normalized to H_2 yield equal to that in He^{++} irradiation.)

components of this high boiling material absorb oxygen from the air but this reaction was not specifically investigated. Care was taken to avoid exposure to air except as necessary for handling the analytical samples.

Experimental Results

Volatile Products.—The yields of volatile products formed in the irradiation of the respective dichloroethylene isomers are shown in Table II. In helium ion irradiations there was no effect of total irradiation dose on the product yields in the energy input range from 10^{20} to 10^{21} ev./ml. Experimental difficulties in monitoring electron irradiations led to rather erratic G values from those irradiations. the values found being both higher and lower than the helium ion results. The yields from electron irradiations were normalized to the same hydrogen yield as found in the helium ion results. This assumes an independence of hydrogen yield on linear energy-transfer similar to that found by Schuler and Allen for cyclohexane.[16] This assumption is not strictly true as shown by the gamma-ray results for cis-1,2-dichloroethylene. In gamma-ray irradiations in the same energy input range an effect of total energy input was observed on the volatile product yields. especially HCl. chloro acetylene and acetylene. This effect is ascribed to irradiation of the gas phase leading to secondary reactions which decrease the observed yields of these products. In the Co^{60} source used. it was not feasible to isolate the gas phase from the radiation field. The observed change in gaseous product yields with increasing dose in the gamma ray irradiation must result from the irradiation of the gas phase. The mechanism of the reactions leading to decreased gaseous product yields was not investigated. The G values for gaseous products from irradiations listed in Table II are those obtained by extrapolation to zero time of irradiation. The precision of these values is probably not over 10 to 20% in the gamma-ray radiolyses. while the products in helium ion irradiation were found reproducible to within 5%. Dichloroacetylene yields in all cases are much less precise owing to its low abundance and to the difficulties of determining it in small amounts in the presence of dichloroethylene found in the same fraction.

Effect of Temperature.—In Table II product yields obtained by helium ion irradiation of trans-1,2-dichloroethylene at 25 and 80° are shown. The temperature coefficient of product yields (a 55° rise increased the respective yields by about 25%)

(16) R. H. Schuler and A. O. Allen, THIS JOURNAL, 77, 507 (1955).

is low enough to insure that the control of temperature used was sufficient for the 25° experiments. An analysis of this effect of temperature is not feasible without a more extensive study and is outside the scope of the present paper.

Polymer Products.—The yields of major polymer products shown in Table III. determined as described previously. were reproducible to better than 10%. No large effect of total radiation dose was noted on these products either in the helium ion or gamma-ray irradiations. Polymer yield values from the trans-isomer were more difficult to determine than from the cis-isomer owing to precipitation of an insoluble polymer in the irradiation of this isomer. This effect was especially pronounced in gamma-irradiations where the amount of high molecular weight polymer was large and precipitation occurred during the irradiation.

In Table III material reported as "non-volatile" polymer is material with too low a vapor pressure to be characterized by gas chromatography and mass spectrometry. This material could not be molecularly distilled at 50°. A microanalysis of this polymer showed a composition $C_{2.00}H_{2.10}Cl_{2.01}$ for the non-volatile polymer from trans-1,2-dichloroethylene and a composition of $C_{2.00}H_{2.35}Cl_{1.99}$ from the cis-dichloroethylene. From helium ion irradiations where insoluble polymer from the trans-isomer did not interfere. molecular weights of 303 and 376 were found for the non-volatile polymer from cis- and trans-1,2-dichloroethylenes. respectively. These values include the hexachlorohexene components of these polymers.

Other Products.—A search was made for some compounds which could conceivably be formed in the radiolysis. To test for free chlorine. the targets were modified so that dry N_2 could be bubbled through them after irradiation. The effluent gases were passed through an absorption flask containing potassium iodide solution. No iodine could be detected after 30 minutes sweeping and a detection limit of <0.0005 was set for G (Cl_2) production from either isomer. Similarly. a search by infrared spectral analysis for absorptions attributable to isomers of 1,2,3,4,5,6-hexachlorocyclohexane yielded negative results.[17,18] The δ and ε isomers were undetectable and no more than trace quantities of the α, β or γ isomers could

(18) L. W. Daasch, Anal. Chem., 19, 779 (1947).

TABLE III

YIELDS OF POLYMER PRODUCTS FROM cis- AND trans-1,2-DICHLOROETHYLENES IRRADIATED WITH He^{++}, γ-RAYS AND BENZOYL PEROXIDE INITIATION

Product	Est. b.p.	$G(He^{++})$	$G(\gamma\text{-ray})$	Benzoyl peroxide,[c] 70°	$G(He^{++})$	$G(\gamma\text{-ray})$	Benzoyl peroxide,[c] 70°
		Cis-1,2-dichloroethylene			Trans-1,2-dichloroethylene		
CO_2 (from peroxide only)				0.52			0.90
Isomerization		<3.1	4.0	14.7	1.8	3.1	24.2
1,1,2,2-Tetrachloroethane		0.4	<0.3	<0.005	0.4	0.15	<0.005
1,3,4,4-Tetrachlorobutene-1[a] (2 compds.)	187–203°	1.3	11.0	68.0	0.8	5.5	77.3
Tetrachlorobutenes[b] (3 compds.)	215–228°	0.3	0.3	≤0.1	0.1	~0.1	<0.1
1,2,3,4,4-Pentachlorobutene-1[a] (3 compds.)	250–265°	1.5	0.5	<0.1	1.1	0.34	<0.1
Hexachlorohexenes[b] (4 compds.)	295–320°	1.2	3.0	9.2	0.6	3.0	27.7
Non-volatile polymer as $(C_2H_2Cl_2)_n$	>350°	4.7	1.4	13.5	5.5	120	23.6
Total polymer as $(C_2H_2Cl_2)_n$		14.5	51	177	11.7	140	271

[a] Structure probable, compound type certain. [b] Compound type identification probable. No structure assignment possible. [c] Expressed as molecules of product per molecule of benzoyl peroxide added.

have been present. It was concluded that cyclization of the polymer at the trimer stage is not an important feature of the radiolysis mechanism.
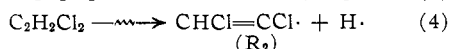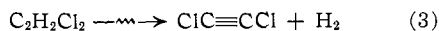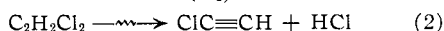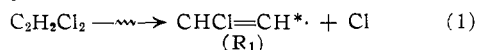
Discussion

An examination of Table II reveals the respective volatile products from the two isomers to differ only slightly in yield. The yield of H_2 is lower from cis-1,2-dichloroethylene than from the trans isomer. while the yields of other volatile products are slightly higher from the cis compound. This latter difference is consistent with the suggestion that the decomposition of the cis form of ethylenic compounds is more extensive than the trans form,[19,20] while the trans- form is more readily polymerized.[21] No effects were observed which suggest ionic mechanisms to be responsible for the products observed and the present data can be interpreted in terms of uncharged species.

As the observed products are the same for both isomers. differences in yields of products are attributed to differences in activation energies of various reactions for the two species involved. The same basic mechanism is assumed operative for both isomers. The simplest over-all mechanism is a combination of molecular dissociations and free radical processes. Processes involving triplet state molecules have not been postulated though such excited molecules may be formed in the irradiation process. Some of the propo ed molecular dissociation processes may proceed through triplet states or ionic processes.

The experiments with benzoyl peroxide yielded no HCl. acetylene. chloroacetylene or vinyl chloride. so these products are not pertinent to the chain reaction sequence leading to high molecular weight products.

Primary Processes

$$C_2H_2Cl_2 \xrightarrow{\quad} CHCl{=}CH^* \cdot + Cl \quad (1)$$
$$(R_1)$$

$$C_2H_2Cl_2 \xrightarrow{\quad} ClC{\equiv}CH + HCl \quad (2)$$

$$C_2H_2Cl_2 \xrightarrow{\quad} ClC{\equiv}CCl + H_2 \quad (3)$$

$$C_2H_2Cl_2 \xrightarrow{\quad} CHCl{=}CCl \cdot + H \cdot \quad (4)$$
$$(R_2)$$

The principal primary act in the radiolysis is
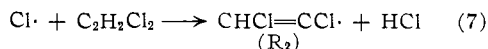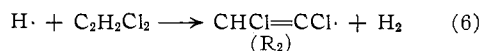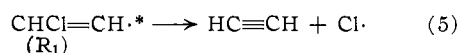
(19) M. Pahl. Z. Naturforsch., 9B, 188 (1954).
(20) R. Viallard and M. Magat, Compt. rend., 228, 1118 (1949).
(21) Cheves Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 128–130.

postulated to be the absorption of energy followed by scission of a C–Cl bond as in reaction 1. Mahncke and Noyes[22] concluded that the primary act of photolysis at 1980 to 1860 Å. of the two dichloroethylene isomers is the breaking of a C–Cl bond. This is consistent with the mass spectrometric fragmentation patterns of the dichloroethylenes in which the largest peak represents such a scission in the molecule ion.[23]

The major part of the chloroacetylene and HCl produced can be ascribed to a direct molecular rearrangement of the excited molecule as shown in reaction 2. This mechanism is consistent with the absence of an effect of change in linear energy transfer on the chloroacetylene yield. Inaccuracies in analysis for dichloroacetylene are such that. while it is probable there is little effect of linear energy transfer. this cannot be proved or disproved from the present experiments. Reaction 3 is postulated as the source of the dichloroacetylene and part of the hydrogen. The remaining hydrogen must come from a process such as reaction 4.

Secondary Processes.—Subsequent reactions of these intermediate species are postulated to account for the rest of the volatile products

$$CHCl{=}CH \cdot^* \longrightarrow HC{\equiv}CH + Cl \cdot \quad (5)$$
$$(R_1)$$

$$H \cdot + C_2H_2Cl_2 \longrightarrow CHCl{=}CCl \cdot + H_2 \quad (6)$$
$$(R_2)$$

$$Cl \cdot + C_2H_2Cl_2 \longrightarrow CHCl{=}CCl \cdot + HCl \quad (7)$$
$$(R_2)$$

A large fraction of the radical species R_1 formed by reaction 1 must have sufficient energy to lose an additional chlorine atom to form acetylene. An alternate sequence involving direct elimination of molecular chlorine from an excited dichloroethylene and subsequent disappearance of Cl_2 by reaction with other radicals leads to the same stoichiometry. As no Cl_2 was observed as a product. the simpler two step sequence is preferred. Reactions 6 and 7 are postulated as the sources of the remaining H_2 and HCl not accounted for in the primary process. As these reactions may be

(22) H. E. Mahncke and W. A. Noyes, Jr., THIS JOURNAL, 58, 932 (1936).
(23) "Catalog of Mass Spectral Data." API Project 44, Carnegie Institute of Technology, Pittsburgh. F. D. Rossini, Editor, Serials 280, 281. contributed by National Bureau of Standards, April 30, 1949.

slightly endothermic, the atoms involved must have excess kinetic energy.

Vinyl chloride, which shows virtually no change in yields with change in linear energy transfer is difficult to interpret in terms of molecular processes. Several reactions are conceivable and it is possible that all contribute to the over-all yield of vinyl chloride, but the hydrogen abstraction reaction, (8), is postulated as the most probable mechanism
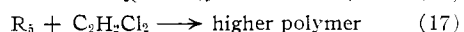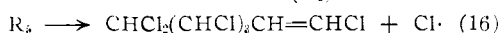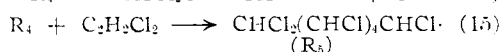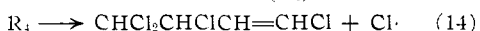
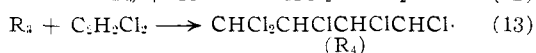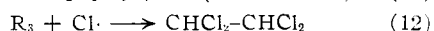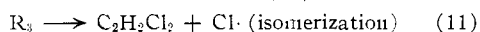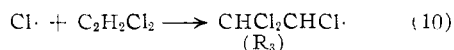$$R_1{}^* + C_2H_2Cl_2 \longrightarrow C_2H_3Cl + C_2HCl_2 \cdot \quad (8)$$
$$(R_2)$$
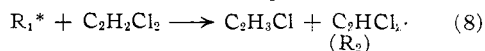
for the very compelling reason that it is the one reaction for which a sufficient quantity of the reactive species is available or for which other compounds that are not observed as products would also not be expected. Reaction 8 is not energetically favorable (it is probably endothermic) and must have a moderately high activation energy. However, if some of the radicals R_1 possess excess energy, this reaction can occur on collision with a molecule. Thus reaction 8 represents a competition with reaction 5 in regard to the fate of excited R_1 radicals. Both reactions 5 and 8, occurring in a fast time sequence after reaction 1, are independent of linear energy transfer.

Small amounts of trichloroethylene are observed and these can be formed by reaction 9. This product shows a dependence on linear energy transfer.

$$R_2 \cdot + Cl \cdot \longrightarrow C_2HCl_3 \quad (9)$$
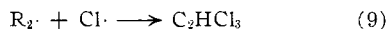
Polymer Sequence.—These primary processes and their subsequent reactions result in the production of a large number of chlorine atoms in the system. In a succession of steps, these chlorine radicals account for the "polymer" products by a series of reactions similar to those which have been proposed for the free radical induced dimerization of such monomer molecules.

$$Cl \cdot + C_2H_2Cl_2 \longrightarrow CHCl_2CHCl \cdot \quad (10)$$
$$(R_3)$$

$$R_3 \longrightarrow C_2H_2Cl_2 + Cl \cdot \text{ (isomerization)} \quad (11)$$

$$R_3 + Cl \cdot \longrightarrow CHCl_2 - CHCl_2 \quad (12)$$

$$R_3 + C_2H_2Cl_2 \longrightarrow CHCl_2CHClCHClCHCl \cdot \quad (13)$$
$$(R_4)$$

$$R_4 \longrightarrow CHCl_2CHClCH=CHCl + Cl \cdot \quad (14)$$

$$R_4 + C_2H_2Cl_2 \longrightarrow CHCl_2(CHCl)_4CHCl \cdot \quad (15)$$
$$(R_5)$$

$$R_5 \longrightarrow CHCl_2(CHCl)_2CH=CHCl + Cl \cdot \quad (16)$$

$$R_5 + C_2H_2Cl_2 \longrightarrow \text{higher polymer} \quad (17)$$

This represents the main sequence of reactions. Reactions 10, 13 and 14 are those suggested by Bauer[24] for the free-radical-induced dimerization of dichloroethylene. A number of such reaction sequences involving polyhalo radicals of relatively low reactivity have been suggested.[25]

The tetrachlorobutene isomers formed in largest yield in radiolysis are the same compounds as those formed in the benzoyl peroxide induced polymerization of dichloroethylenes. In the radiolysis, small yields of other tetrachlorobutene isomers are found and these may arise from other reactions involving the radicals R_1 and R_3. There was no

difference observed in the isomeric composition of the hexachlorohexanes formed (reaction 16) by helium ions, γ-rays or benzoyl peroxide initiation.

The pentachlorobutenes observed in radiolysis can arise from at least two sources. The reaction R_2 with R_3 yields a pentachlorobutene directly as shown in reaction 18. The amount of R_2

$$CHCl=CCl \cdot + CHCl_2-CHCl \cdot \longrightarrow$$
$$(R_2) \qquad\qquad R_3$$
$$CHCl-CHCl-CCl=CHCl \quad (18)$$
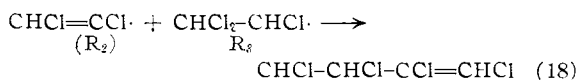
radical postulated formed in reactions 4, 6, 7 and 8 is equivalent to about two-thirds of the pentachlorobutene yield observed in helium ion irradiations. Unless there is another reaction sequence producing radicals R_2, the excess pentachlorobutene yield must be formed by another mechanism. There appears to be some excess hydrogen in the higher polymer and a mechanism involving hydrogen abstraction from radical R_4 may also contribute to the pentachlorobutene yield.

The yields of the main sequence polymers as well as isomerization (reaction 11) increase in changing the radiation source from helium ions to γ-rays, and such compounds as tetrachloroethane and pentachlorobutenes decrease in yield. These results are consistent with the differences in radical density, in these two types of irradiation. With benzoyl peroxide, where the radical density is very low, no tetrachloroethane or pentachlorobutene was found, while the yields of tetrachlorobutenes and higher polymer were increased. Recombination of radicals R_1 and $Cl \cdot$ in the expanding helium ion tracks reduces the total polymer yields significantly in helium ion relative to that observed in γ-ray irradiations. The lower relative yields of polymers larger than the dimers from the benzoyl peroxide polymerizations is ascribed to the increased rate of decomposition of radical R_4 at the higher temperature over addition of another molecule of dichloroethylene. It has been found previously (and we also qualitatively observed) that at lower temperatures the ratio of higher polymers to dimer is increased in the benzoyl peroxide induced polymerization of these compounds.[26]

Recently Cooper and Stafford[27] reported results on the polymer products formed in irradiating cis- and trans-1,2-dichloroethylenes. Their results and interpretation are consistent with the results reported here.

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The Imine Radical and the Thermal Decomposition of Hydrazoic Acid[1]

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In the present work, we have performed experiments in which we have thermally decomposed measured amounts of hydrazoic acid in a flowing system and passed the products over a liquid nitrogen cooled finger. All the products were collected and analyzed so that a complete mass balance was obtained. We think that the imine radical is formed in the primary step $HN_3 \rightarrow NH + N_2$, but we do not know either the mechanism of formation of ammonium azide or the nature of the blue material; possibly a small fraction of the NH may reach the cold finger and form a colored polymer, $(NH)_x$.

Introduction

Although the blue material formed by cooling suddenly the thermal decomposition products of hydrazoic acid was discovered about ten years ago[3] and has been extensively investigated in several laboratories,[4] neither its composition nor the nature of the substance causing the blue color are known. The following facts have been established: the material has an intense blue color and is stable indefinitely at liquid nitrogen temperatures; on warming to about $-125°$ it changes irreversibly to a white material without any appreciable evolution of gas. The blue material is paramagnetic and has a broad absorption band in the visible with its center at about 6400 Å. One of the difficulties in studying the blue material is that all work must be done below its transition point $-125°$. It does not dissolve in any of the rather limited number of substances that are liquid below $-125°$ and we have not succeeded in making it react with anything on the cold finger; even atomic hydrogen had no effect.[4a] The present work is the first step in a larger program to determine the nature of the blue material and the mechanism of the reaction.

Experimental

Hydrazoic acid was generated in small quantities, as required, by slow mixing of concd. sulfuric acid with dry sodium azide. Hydrazoic acid can be kept safely and indefinitely as a gas at about 100 mm. pressure. It was purified by freezing the gas to $-125°$ and pumping on it to remove any

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nitrogen or carbon dioxide. The mass spectrometer pattern compared favorably with one obtained at the Bureau of Standards.[5]

Hydrazoic acid from a small storage reservoir was led through a quartz tube about 12 mm. i.d., surrounded by a sliding furnace and fitted with a thermocouple well. The length of the furnace and its position on the quartz tube could be varied. The gases leaving the quartz tube passed over a liquid nitrogen cooled finger and then through a series of traps so that the various products could be collected and analyzed. The gas entering the furnace was at a pressure of about 0.5 mm. and the pressure at the cold finger was less than 0.1 mm.

The most volatile products of the decomposition are nitrogen and hydrogen and their collection and estimation proved a difficult problem. It was solved finally by arranging the apparatus so that the pumping system could be bypassed and replaced by a bulb immersed in a storage tank of liquid helium. At the end of the run, the bulb was removed from the liquid helium and the contents analyzed on the mass spectrometer after the pressure, temperature and volume had been measured. We have found this method to be vastly superior to all others that we tried and recommend its use for the collection and measurement of permanent gases under conditions similar to ours whenever liquid helium is available. In all our runs, the permanent gases consisted of nitrogen containing 5 to 10% of hydrogen.

At the end of a run, the cold finger was allowed to warm slowly to about $-40°$. During this part of the experiment, the blue material changed to white at about $-125°$ and at a little higher temperature either undecomposed hydrazoic acid or ammonia came off. The gas was collected in a bulb at liquid nitrogen temperatures and when all the gas was cooled, it was allowed to warm to room temperature; after the pressure, temperature and volume were measured, it was analyzed on the mass spectrometer. The white residue, which is solid at room temperature, has a small vapor pressure and was sublimed into a small weighing bottle and weighed directly. The substance was tested frequently for hydrazine which was found to be absent and a mass spectrometer analysis gave a pattern characteristic of a one to one mixture of ammonia and hydrazoic acid.[6]

On the average, about 2 mmoles (about 0.1 g.) of HN_3 was used in each of our experiments. Work with larger quantities is exceedingly hazardous and even with these small quantities occasional explosions occurred. Needless to say, all work should be done behind a shatterproof glass screen.

Experimental Results

We have made preliminary runs in which we obtained complete mass balances and studied the effect of changing the length of the furnace, changing the temperature and changing the distance of the end of the furnace from the cold finger.

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(6) Additional confirmation of the identity of the white residue was provided by H. S. Pieser and coworkers, National Bureau of Standards, who showed that the solid gave an X-ray diffraction pattern identical with NH_4N_3.