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THE RADIATION CHEMISTRY OF THE SYMMETRICAL DICHLOROETHYLENES

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ABSTRACT

Purified, degassed liquid samples of cis- and trans-1,2-dichloroethylene have been irradiated with 40 to 43-Mev helium ions impinging on the liquids. For doses to 10^{21} ev/ml, no effects of total dose were observed. The volatile products found, with yields given from the trans isomer, are C_2H_2 , 1.59; HCl, 1.21; C_2HCl , 0.83; CH_2CCl_2 , 0.25; H_2 , .040; and C_2Cl_2 , 0.004. Yields from the cis- isomer were about 25% higher. With a combination of gas chromatography and mass spectrometry, several products boiling to about $300^\circ C$ were tentatively identified. These include 1,1,2,2 tetrachloroethane, two isomers of 1,3,4,4-tetrachlorobutene-1, and two isomers of 1,2,3,4,4-pentachlorobutene-1. Higher polymers not volatile at 300° were formed in yields of 2.2 (MW = ~303) and 5 (MW = ~375) respectively for the cis- and trans- isomers. The $G(-C_2H_2Cl_2)$ yields of cis- and trans- isomers were 15.1 and 26.1 respectively compared to $G(-C_2H_4Cl_2)$ of 6.2 for 1,2-dichloroethane. A radical mechanism is proposed to explain the formation of the observed products.

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INTRODUCTION

As part of a program of investigating the radiation chemistry of organic compounds containing various functional groups, a number of alcohols³ and ethers⁴ 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 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 a pronounced effect on rates of ionic reactions, this feature is perhaps pertinent to the current issue of the importance of ionic processes in the radiation chemistry of condensed phases.⁷

This paper presents the results of an investigation of the radiolysis products from irradiation of the isomers with helium ions, electrons, and Co^{60} gamma rays. An attempt was made to examine all the products (both low and high molecular weight) in order to derive a reasonable mechanism for the radiation-induced reactions in the pure liquids. Certain kinetic parameters - total dose, density of initial excitation and ionization, and temperature - were varied in exploratory experiments attempting to evaluate various mechanisms.

EXPERIMENTAL

Purification of Compounds

Eastman White Label chemicals were purified by distillation through an 85-plate adiabatic column packed with Podbielniak Helipak No. 3013 stainless steel helices. Gas chromatography and mass spectrometric analyses were used to monitor the distillation, and the purified product was distilled with a boiling range of less than 0.01° and with a cryoscopic purity of $99.98 \pm 0.02\%$. The properties of the purified isomers are listed in Table I.

Table I

Property	Cis- isomer		Trans- isomer	
	Measured	Literature ^(a)	Measured	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°

^aJ. A. Reddick and E. E. Toops, Organic Solvents, Vol. VII of Technique of Organic Chemistry, A. Weissberger, Ed., Second Edition (Interscience, New York, 1955), p. 204-205.

Preparation of Targets

Pyrex glass cells of the type described by Garrison, Haymond, and Weeks⁸ were used for the helium-ion irradiations and for some of the electron irradiations. In some electron irradiations the cell design was modified to consist of a spherical body rather than an Erlenmeyer shape (so that all the electrons would be stopped within the vessel), and a platinum lead was sealed into the glass wall for beam monitoring. Gamma-irradiation cells were cylindrical glass ampoules 1 inch in diameter and 3 inches tall, fitted with break-tip and seal-off tubes.

The purified dichloroethylene isomers were degassed by refluxing under vacuum,⁹ and were vacuum distilled into the appropriate target vessels and sealed 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 microampere. They were conducted at room temperature (approximately 25°), and the temperature was roughly controlled by an air blast against the target, which 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 the manner described previously.¹⁰

Electron irradiations were conducted with the microwave linear electron accelerator which has been described by Lemmon and Mosier.¹¹ In some experiments the total beam from the accelerator was used; in others the beam was magnetically analyzed to select the energy component at 4.6 ± 0.1 Mev. Two experiments employed the 2-Mev Van de Graaff accelerator at the California Research Corporation. Lowest practicable rates of irradiation were used, with air-blast cooling, to keep the targets at or near room temperature.

Gamma radiolyses were conducted in a 2000-curie Co⁶⁰ source¹² and were monitored by means of a cyclohexane dosimeter, assuming $G(H_2) = 5.6$.¹³

Volatile Products

Gaseous and low-boiling products were determined by draining the target liquid into an evacuated system and refluxing under vacuum while pumping with an automatic Toepler pump.⁹ Fractions volatile at -196°, -125°, -80° were collected and were analyzed with a Consolidated Engineering Corporation model 21-103 mass spectrometer, as described previously.³ Because analyses for HCl are extremely 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 the decrease in gas volume and by gravimetric determination of chloride in the KOH scrubbing pellets. The two methods agreed quite satisfactorily.

Polymer Products

After separation of the low boiling product, the system was opened to air, and the residual liquid drained into an appropriate container. One-hundred-milliliter samples of residual liquid were distilled through a small Vigreux column in order to concentrate the "polymer" product, and it was possible to reduce the volume to 2 to 3 milliliters without distilling or pyrolysis of significant amounts of higher boiling products.

This concentrate was further fractionated by molecular distillation, and the fractions examined by means of gas chromatography, using a 5-mm glass column 2 meters in length with a stationary phase of General Electric silicone fluid 96-40 adsorbed on 40 to 60 mesh Sil-O-Cel firebrick. A sample was 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 times. The separated compounds were then characterized from their mass spectrometer fragmentation patterns. Samples of a number of commercially available chlorinated hydrocarbons, both saturated and unsaturated, were run on the mass spectrometer in order to obtain the necessary correlations between molecular structure and fragmentation patterns. In addition, they were injected into the gas chromatography column to determine sensitivity (detector response per microliter of liquid injected) and emergence-time parameters. Typical polymer chromatograms and additional details concerning assignment of tentative structures to these products are available elsewhere.¹⁴

EXPERIMENTAL RESULTS

Volatile Products

The yields of volatile products for helium-ion irradiations are presented in Fig. 1 as G values, or yield of product per hundred electron volts of energy dissipated in the system. Because the hydrogen yield was least subject to error in analysis and was independent of dose, the yields for each experiment were normalized to the mean hydrogen yield to correct for small errors in monitoring the cyclotron irradiations. The correction in every case is small, of the order

of a few percent. The hydrogen yields presented are the measured values, indicating for each point the relative magnitude of the correction factor applied.

One of the volatile radiolysis products, dichloroacetylene, is not plotted with the other results, although the mean yield is given in subsequent tabulations. The data for this product - by virtue of its low yield, high reactivity, and high solubility in monomer - were quite erratic, and the mean value is probably no better than $\pm 50\%$. Yields of all other volatile products have an estimated accuracy of $\pm 5\%$ on a relative basis and of $\pm 10\%$ on an absolute scale.

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 Table II. The similarity of the results for the volatile products from the helium-ion and gamma radiolyses corroborates the assumption that the yields are independent of irradiation intensity.

Table II

Comparison of 100-ev yields from helium-ion, electron, ^(f) and gamma radiolyses						
Product	Cis-C ₂ H ₂ Cl ₂			Trans-C ₂ H ₂ Cl ₂		
	He ⁺⁺ (a)	e ⁻ (b)	γ (c)	He ⁺⁺ (d)	e ⁻ (e)	γ (c)
H ₂	0.027	<u>0.027</u>	0.02	0.040	<u>0.040</u>	0.03
CH ₂ CHCl	0.34	0.33	0.3	0.25	0.26	0.4
ClC≡CH	1.02	0.90	1.0	0.83	0.82	0.9
ClC≡CCl	0.006	0.003	0.01	0.004	0.002	0.003
HC≡CH	1.83	2.08	1.8	1.59	1.50	1.8
HCl	1.35	1.5		1.21	1.8	0.9
CHCl ₂ CHCl ₂	0.4		0.6	0.4		0.2
C ₄ H ₄ Cl ₄	1.0		13.6	1.0		3.8
C ₄ H ₃ Cl ₅	1.4		0.5	1.1		0.4

(continued)

Table II (continued)

-
- ^aAverages of 10 experiments. Not all components determined in every experiment.
- ^bAverage of 4 experiments using total beam from microwave linear electron accelerator, beam collimated at 4.6 ± 0.1 Mev, and 2 Mev electrons from Van de Graaff accelerator.
- ^cCobalt-60 gamma-ray source.
- ^dAverages of 11 experiments. Not all components determined in every experiment.
- ^eMonoenergetic 2-Mev electrons from Van de Graaff. Similar values from microwave accelerator.
- ^fElectron yields normalized to same hydrogen yield as He⁺⁺ irradiations.
-
-

Polymer Products

The approximate polymer G values reported in Table III were calculated from the measured gas chromatograph peak area, the average sensitivity for polychlorinated compounds, an assumed average density of 1.5, and the appropriate molecular weight. The accuracy may be presumed to be at least $\pm 50\%$ for the larger constituents.

The letter designations in Table III imply the degree of confidence in our structural assignment. For compounds marked (a) there is no question, as authentic samples have been compared to the radiolysis product. The (b) designation indicates the identification is based on the same correlations as in the (a) compounds, but that an authentic sample is not available. The (c) designation indicates considerable skepticism because of low abundance and inconsistencies in the mass spectrum. The boiling points listed were derived from an emergence-time correlation,¹⁴ and are given for possible future comparison should authentic samples become available.

Reported as "high polymer" in Table II is the residuum with too low a vapor pressure to render any useful information by these techniques. These compounds were therefore characterized only by average molecular weight, yield, and composition. The trans- isomer "high" polymer contained oxygen from a secondary post- radiolysis reaction; similarly the low molecular weight polymer fraction contained an apparent peroxide component. Although considerable effort was expended in this regard, no useful clues to the identity of these oxygenated products were obtained.

Table III

Product	Estimated normal boiling point (°C)	Approximate G values	
		cis- isomer	trans-(d) isomer
Tetrachlorobutene ^(c) isomer	134	0.02	0.07
1,1,2,2-tetrachloroethane ^(a)	146	0.43	0.4
Peak E, peroxide ^(c) 1,2,3,4-tetrachlorobutene peroxide	159		variable
Tetrachlorobutene-1 1,3,4,4-isomer-I	195	0.77	0.9
Tetrachlorobutene-1 ^(b) 1,3,4,4-isomer-II	223	0.17	
Pentachlorobutene-1 ^(b) 1,2,3,4,4-isomer-I	241	0.73	0.5
Pentachlorobutene-1 ^(b) 1,2,3,4,4-isomer-II	256	0.73	0.5
"High" polymer	>300		
G Value		2.21	5.0
Mol. Wt.		303	376
Composition		(CHCl) _{6.4}	(CHClO) _{0.09} 7.5

^aStructure well established.

^bProbable structure.

^cStructure uncertain, post irradiation oxidation product.

^dAverages of two experiments.

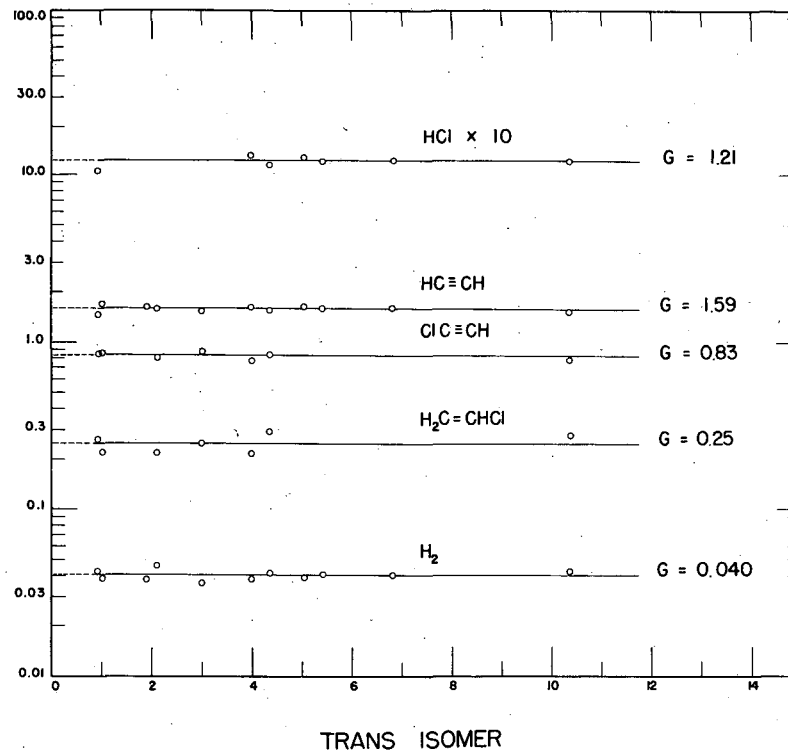
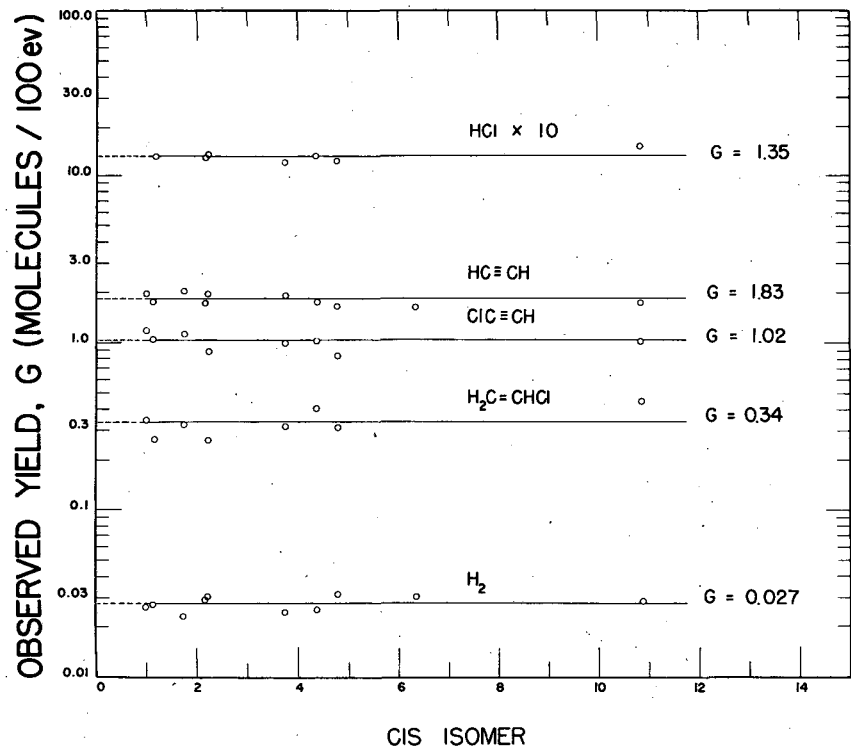
Effect of Experimental Parameters

The yields of volatile products from the two isomers are plotted as functions of total dose in Fig. 1. The data are fitted best by a straight line of zero slope over the range of measurement, 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 behavior 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 Table II, 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 used. The electrons delivered by this accelerator were pulses of 2-microsecond 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-ray radiolyses in Table II shows no significant change in the G values, implying the absence of track effects in events leading to the formation of these products. Among the high boiling products the yield of dimer is somewhat higher for the gamma-ray radiolyses. The high-polymer G values quoted are doubtless incorrect because of inaccuracies in measuring the small yields produced with the gamma source available. Nevertheless, the ratio of dimer to s-tetrachloroethane, measured on the same gas chromatographic run, is significantly higher in gamma-ray than in helium-ion irradiations. This is consistent with the mechanism proposed for their production.

The 80° irradiation of cis-1,2-dichloroethylene resulted in an increase of approximately 25% in the yields of all volatile products, probably because of the decreased viscosity of medium. This may be interpreted as the result of diffusion of radical fragments out of the cage of solvent molecules, reducing the extent of primary recombination. Since 55° produced only a relatively small effect, precise temperature control was not critical; and the measures employed were quite adequate.



ENERGY ABSORBED BY SYSTEM, $\text{ev/ml} \times 10^{-20}$

Fig. 1. Yields of some volatile products formed in the helium ion irradiation of cis- and trans- 1,2-dichloroethylenes at various energy input levels.

MUB-214

Other Products

A specific search was made for some compounds which it seemed likely would be formed in the radiolyses. In testing for free chlorine, two of the helium-ion targets were modified so that they could be swept with dry nitrogen after irradiation, and the effluent gases were passed through a KI absorption train. Addition of starch solution gave no iodine color after 30 minutes' sweeping, showing $G(\text{Cl}_2) < 0.0005$ for both isomers. Similarly an examination of the infrared spectra of polymer fractions for absorptions attributable to 1,2,3,4,5,6-hexachlorocyclohexane isomers¹⁵ yielded negative results. No δ or ϵ isomers were detectable, but the complexity of the polymer spectra made it impossible to rule out the presence of trace quantities of the α , β , and γ isomers. It was concluded that cyclization of the polymer at the trimer stage is not an important feature of the radiolysis mechanism.

Stoichiometry

For comparison purposes a sample of 1,2-dichloroethane was irradiated, establishing $G(-\text{C}_2\text{H}_4\text{Cl}_2) = 6.2$ for the saturated analog of the dichloroethylenes. A similar stoichiometric analysis gave $G(-\text{C}_2\text{H}_2\text{Cl}_2) = 15.1$ and 26.1 for cis- and trans-1,2-dichloroethylene, respectively, indicating that rather short chain reactions occur in these systems. Details of the material balance are presented in Tables IV and V, giving some additional indication of the completeness of the analytical detection and measurement of the products formed.

Table IV

Stoichiometry of helium-ion radiolysis of cis-1,2-dichloroethylene				
Product	Mean G value	Atom balance		
		C	H	Cl
Hydrogen	0.027		0.054	
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	1.35		1.35	1.35
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
		30.9	30.2	29.4
G (-C ₂ H ₂ Cl ₂)	15.1			

Table V

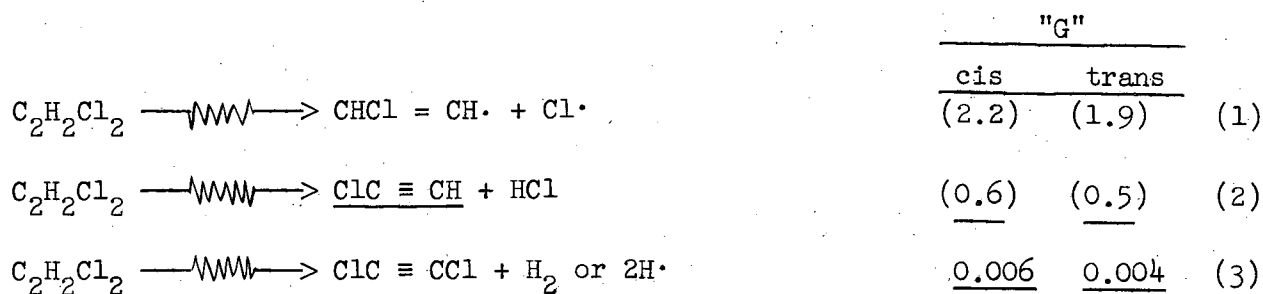
Stoichiometry of helium-ion radiolysis of trans-1,2-dichloroethylene				
Product	Mean G value	Atom balance		
		C	H	Cl
Hydrogen	0.040		0.08	
Vinyl chloride	0.25	0.50	0.75	0.25
Chloroacetylene	0.83	1.66	0.83	0.83
Dichloroacetylene	0.004	0.008		0.008
Acetylene	1.59	3.18	3.18	
Hydrogen chloride	1.21		1.21	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
		52.8	52.6	51.6
G (-C ₂ H ₂ Cl ₂)	26.1			

DISCUSSION

An examination of Tables I, II, IV, and V reveals that the yields for the various products from the two isomers do not differ significantly. Yields of all products except "high" polymer and hydrogen are slightly lower for the trans- isomer than for cis-1,2-dichloroethylene. This is in agreement with the suggestion that the decomposition of the cis- form of ethylenic compounds is more extensive than of the trans- form,^{16,17} and with the observation that the trans-1,2-dichloroethylene is more readily polymerized than the cis- isomer.¹⁸ The difference in hydrogen yield may be explained in a consideration of the detailed mechanism. Thus it may be concluded either that ionic reactions are not predominantly responsible for the products observed, or that the effect of differences in dielectric constants is too subtle to be detected in the gross analysis. A much more detailed study would be necessary to eliminate all possibilities of ionic processes, but the present data can best be interpreted as reactions of uncharged species.

The absence of pronounced differences in radiolytic behavior of the two isomers further suggests that the same reaction mechanism is operative, and the simplest mechanism adequate to explain the data is a free-radical sequence similar to that proposed by Willard and Hanrahan for alkyl iodides.¹⁹ In the equations which follow, quantities loosely called "G" values are used to indicate the stoichiometry of the reaction sequence. The magnitudes of these numbers serve to indicate the relative importance of a given reaction in the radiolysis process. Parentheses, (), indicate that the value is derived from the requirement for a material balance in the mechanism, where underlining denotes that the G value is based on a measurement of the ultimate product underlined in that equation. A combination of underlining and parentheses indicates that the value is in part derived from the mechanism and in part taken from a measured yield.

Primary Processes

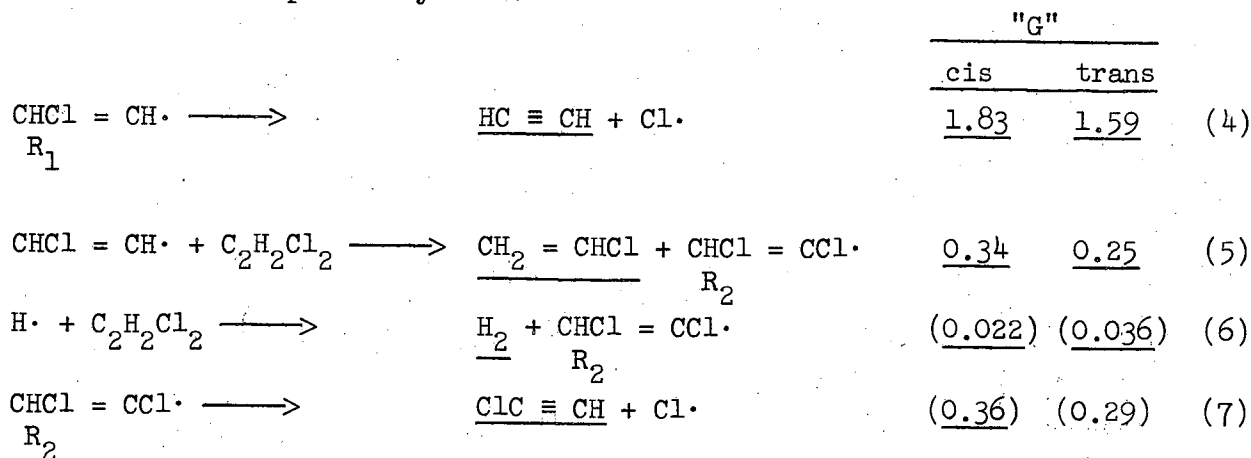


The principal primary act in the radiolysis system is postulated as the scission of a C-Cl bond as in Reaction (1). This is consistent with the mass spectrometer fragmentation patterns of the dichloroethylenes,²⁰ in which the base peak of the spectra represents such a scission of the molecule ion. Furthermore, 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.²¹

Part of the chloroacetylene produced in the radiolysis can best be explained by the unimolecular primary elimination of HCl in Reaction (2). The alternative process, involving splitting off H and Cl atoms, would be acceptable but for the absence of sufficient hydrogen-excess products. The only hydrogen "sink" available is the high polymer, and it seems unlikely that hydrogen radical reactions would produce no compounds boiling below 300°.

Reaction (3) is included to account for the observed yield of dichloroacetylene. The magnitude and uncertainty in the "G" value make it insignificant in the present discussion, and other mechanisms can account for it equally well.

Subsequent reactions of these intermediates are postulated to account for the volatile-product yields:



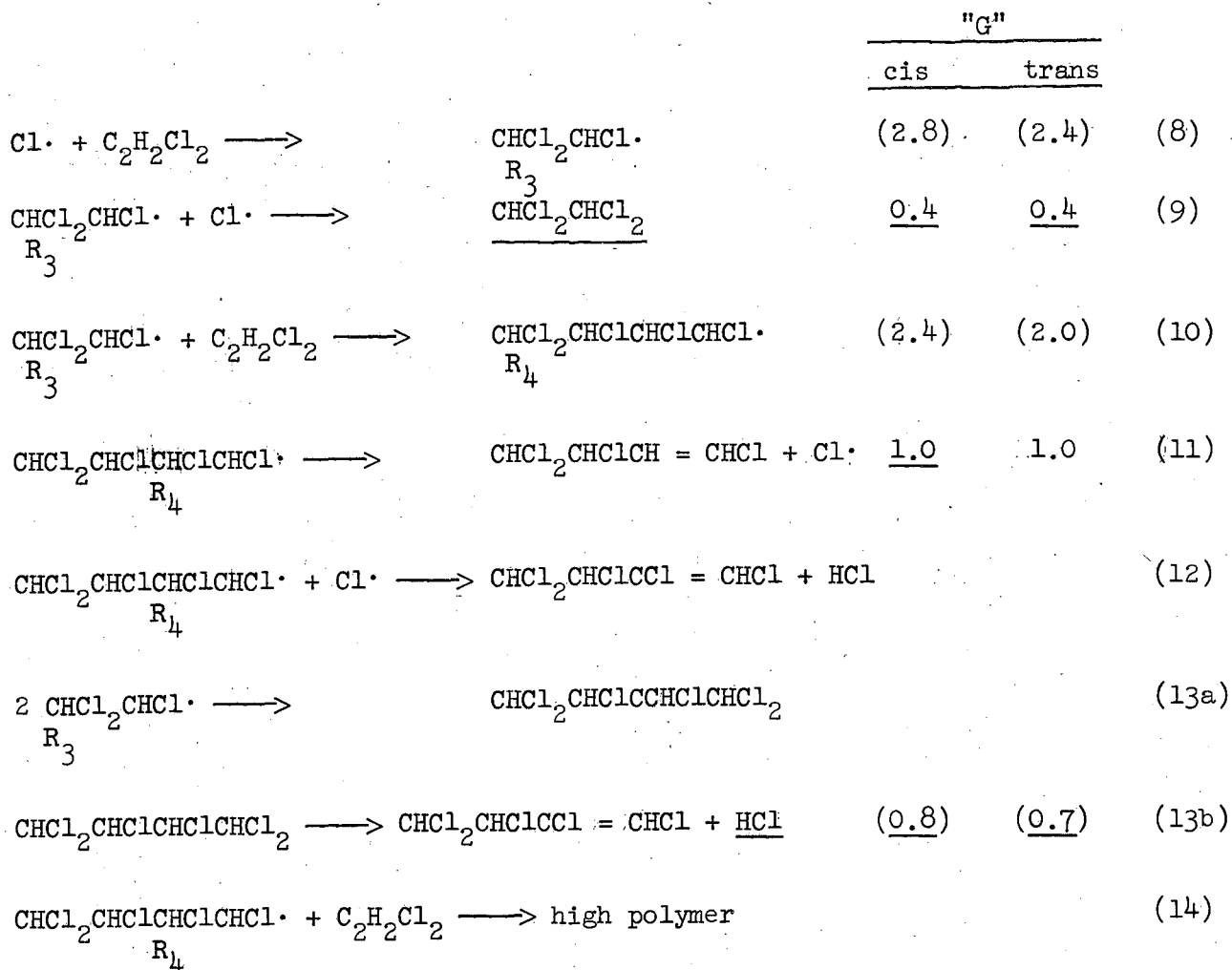
A large share of the R_1 radical species must have sufficient energy to split off an additional chlorine atoms as in Reaction (4) to explain the high yields of acetylene observed. An alternative decomposition sequence involving direct molecular elimination of Cl_2 would be acceptable, but no Cl_2 was observed as a product. Hence subsequent reactions to remove molecular chlorine with a very high efficiency would be required in the alternative mechanism, and the simpler sequence seems preferable.

Hydrogen abstraction by radical R_1 in Equation (5) is presented to account for the production of vinyl chloride, also producing a radical R_2 . Reaction (6) is postulated as the source for the remaining hydrogen. Because of the relative ease with which a hydrogen atom can escape the Franck-Rabinowitch cage, both molecular and atomic mechanisms for hydrogen production should 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. To account for this difference there must be an additional source for hydrogen atoms, such as Reaction (2) proceeding to a small extent by the alternative process of successive elimination of $H\cdot$ and $Cl\cdot$ atoms. 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 spectrometer fragmentation patterns.¹⁷ The m/q 95 and 94 peaks in the trans- fragmentation patterns, 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.

Reaction (7) is given as a subsequent decomposition of radical R_2 , analogous to Reaction (4). Similar decompositions of chloro-radicals have been observed in other systems, as in the formation of vinyl chloride in the pyrolysis of dichloroethane by the decomposition of the CH_2Cl $CHCl\cdot$ radicals.²²

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.



Reactions (8), (10), and (11) are those considered responsible for the free-radical-induced dimerization of dichloroethylene reported by Bauer.²³ A number of such reaction sequences involving intermediate polyhalo radicals of relatively low reactivity have been characterized.²⁴ The structure of the major dimer product and the mechanism for its production were partially substantiated by comparison with an authentic sample prepared by means of the benzoyl peroxide induced dimerization of dichloroethylene.

Several reaction sequences could be written for the production of pentachlorobutenes, the simplest being abstraction by $\text{Cl}\cdot$ as in reaction (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 are undetectable because of lower vapor pressures; or one might argue that the structural assignment derived from mass spectral considerations of these products is incorrect. Perhaps a better explanation is the production of a hexachlorobutane by Reaction (13a) followed by dehydrohalogenation in (13b). The dehydrohalogenation could, of course, occur by hydrogen abstraction by chlorine atoms, followed by splitting off of a chlorine atom from the polychloro free radical. The structural specificity of the direct dehydrohalogenation stems from the reasonable presumption that HCl elimination removes chlorine 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.²²

It should be noted that the G value in Reaction (13b) is based on the HCl yield and is smaller for both isomers than the measured pentachlorobutene yields. This result may arise from the inaccuracy of determination of the pentachlorobutene yields. Lowering the G of pentachlorobutene by an appropriate amount worsens the chlorine balance of the stoichiometry result; however, the probable error of the chlorine microanalyses of the high polymer 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, as in Reaction (14). The chains presumably are terminated by radical-radical reactions or by splitting off chlorine atoms, as is the case for the lower-molecular-weight condensation products.

In summary, the radiolysis products from the symmetric dichloroethylenes are compatible with a series of free-radical reactions. Primary interaction resulting partly in C-Cl bond cleavage and partly in molecular 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. The radiolytic behavior is somewhat simpler than might have been expected for such compounds.

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