

884. *Radiation Chemistry of Organic Halogen Compounds. Part I.*
The Action of γ -Radiation on Chlorinated Ethylenes.

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Both stereoisomers of 1,2-dichloroethylene polymerise under the influence of γ -radiation but only the *trans*-isomer gives a solid polymer. Trichloroethylene produces lower yields of oligomers, chloroacetylenes, and a solid decachlorohexane. Tetrachloroethylene gives the lowest yield of oligomer and also hexachloroethane, hexachlorobuta-1,3-diene, and hexachloro-4-dichloromethylenecyclopentene.

NUMEROUS attempts to polymerise 1,2-dichloro- (reviewed by Weale¹) and trichloroethylenes,² by heat, pressure, peroxides, or ultraviolet light, have met with only limited success and, when the present work started, there was little information concerning the action of ionising radiations on these compounds. Futrell and Newton³ recently reported an intensive study of the action of α -particles, electrons, and γ -rays on *cis*- and *trans*-1,2-dichloroethylene and Newton⁴ has studied the α -radiolysis of trichloroethylene. We⁵ too have examined the behaviour of these compounds, and of tetrachloroethylene, when exposed to ⁶⁰Co γ -radiation.

Irradiation of *cis*-1,2-dichloroethylene yielded mainly a mixture of liquid oligomers, separable by fractional distillation, and smaller quantities of involatile waxes. The *trans*-isomer, under similar conditions, gave these products in smaller yield and also a considerable amount of a solid polymer. Hydrogen chloride was produced from both compounds, and isomerisation, in both instances, was negligible.

The physical constants of the dimer were in good agreement with those given by Frank and Blackham^{2c} for 1,3,4,4-tetrachlorobut-1-ene obtained by peroxide-initiated polymerisation of 1,2-dichloroethylene. The geometrical isomers of this product were separated by gas-liquid chromatography and the configurations were established by examination of the infrared spectra. The less volatile compound showed a strong absorption at 936 cm.⁻¹ which was absent from the spectrum of the other isomer. Haszeldine⁶

¹ Weale, *J.*, 1952, 2223.

² (a) F.P. 814,423/1937; (b) F.P. 841,728/1939; (c) Frank and Blackham, *J. Amer. Chem. Soc.*, 1950, **72**, 3283.

³ Futrell and Newton, *J. Amer. Chem. Soc.*, 1960, **82**, 2676.

⁴ Newton, U.S.A.E.A. Report UCRL-3240.

⁵ Cooper and Stafford, Proc. Second United Nations Internat. Conf. on Peaceful Uses of Atomic Energy, United Nations, New York, 1959, Vol. XXIX, p. 118.

⁶ Haszeldine, *Nature*, 1951, **168**, 1028.

and Kitson⁷ have reported, and we confirm, that the characteristic absorption at 960—970 cm^{-1} (CH out of plane deformation) normally observed for *trans*-olefins is shifted to about 935 cm^{-1} for *trans*-CH:CHCl and CH:CHBr groups; we therefore assign the *trans*-configuration to the less volatile isomer. The *cis*-isomer had a strong absorption at 1239 cm^{-1} which was absent or very weak for the *trans*-isomer. A third, very minor component, which was detected and concentrated in less volatile fractions of the dimer, had an infrared absorption at 855 cm^{-1} (possibly C:CH₂), suggesting that it might be 2,3,4,4-tetrachlorobut-1-ene. Futrell and Newton³ also found two main components of the tetrachlorobutene fraction and detected three minor ones.

Production of a solid polymer in high yield from 1,2-dichloroethylene has not previously been observed although various authors¹ have obtained small quantities by other methods of polymerisation and have noted that this polymer is produced only, or in greater amount, from the *trans*-isomer. Our preliminary experiments,^{5,8} carried out with monomer which had not been rigorously purified and at a comparatively low dose rate ($\sim 10^{16}$ ev ml^{-1} min^{-1}), indicated that about 75% of the total polymer produced was solid, but in subsequent experiments, under a wide variety of conditions, sometimes approximating to those of the preliminary work, we were unable to achieve such a high yield of the solid. The percentage of solid polymer was normally in the range 9—25% of the total and increased slowly with increasing dose, although the total yield of polymer decreased under the same conditions (see Table). This result suggests that a proportion of the liquid polymers formed initially is incorporated into the solid as polymerisation proceeds.

Yields of hydrogen chloride and polymer produced by γ -irradiation of chlorinated ethylenes.

Dose rate (10^{17} ev ml^{-1} min^{-1})	Total dose (10^{20} ev ml^{-1})	G(HCl) (molecules per 100 ev)	G(total polymer) ^a	Solid in total polymer (%)
(i) <i>trans</i> -1,2-Dichloroethylene				
4.36 ^a	0.95	1.2	239	9.7
"	1.91	1.0	236	11.2
"	3.82	1.0	229	21.1
0.78 ^b	2.32	—	225	18.8
"	3.58	—	221	19.9
"	6.00	—	210	22.1
"	8.35	—	207	23.4
"	11.03	—	204	24.8
(ii) <i>cis</i> -1,2-Dichloroethylene ^a				
4.36	3.25	1.5	134	0
"	4.87	1.2	142	0
"	6.50	1.5	138	0
(iii) Trichloroethylene ^a				
4.88	5.48	4.4	31	—
"	10.96	4.5	34	—
"	21.92	3.7	34	—
(iv) Tetrachloroethylene ^{b, c}				
0.9	4800		9	

Irradiated in sealed evacuated ampoules. ^b Irradiated in annular vessels without complete exclusion of air. ^c Approximate values. ^a Estimated as number of monomer molecules removed per 100 ev absorbed.

Futrell and Newton³ also observed the production of solid polymer from *trans*-1,2-dichloroethylene but did not report the yield. Our polymer was a colourless powder, partly soluble in *NN*-dimethylformamide and in 1,1,2,2-tetrachloroethane but insoluble in most of the usual organic solvents. It softened above 240° and decomposed with charring above 290°. Weak infrared absorption at 1629 and 936 cm^{-1} showed the presence of

⁷ Kitson, *Analyt. Chem.*, 1953, **25**, 1470.

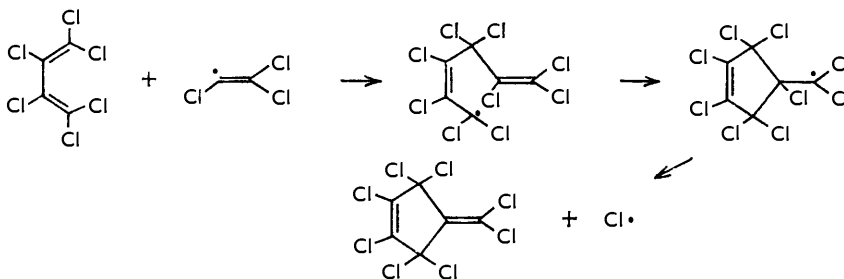
⁸ B.P. Specification C. 12,659/57, July 1958.

unsaturation (probably terminal $\text{CH}:\text{CHCl}$ groups) and an X-ray powder photograph showed the absence of crystallinity.

The main product of γ -irradiation of trichloroethylene was a mixture of liquid and waxy oligomers with smaller quantities of hydrogen chloride, a crystalline solid, and explosive volatile material believed to be a mixture of mono- and di-chloroacetylenes. Newton⁴ reported the production of these chloroacetylenes by α -radiolysis of trichloroethylene. Fractions corresponding closely to dimer and trimer were separated by distillation, and the physical constants of the dimer were in good agreement with those reported^{2c} for the supposed 1,1,3,3,4,4-hexachlorobut-1-ene obtained by peroxide-initiated polymerisation of trichloroethylene. Analysis of the solid indicated a molecular formula $\text{C}_6\text{H}_4\text{Cl}_{10}$ (decachlorohexane) and its infrared spectrum confirmed the absence of unsaturation. In the larger-scale experiments the stabiliser (a nitrogen compound), present in the trichloroethylene, was not removed before irradiation; this had little effect on the yield of polymer, but the yield of hydrogen chloride decreased and chloroacetylenes were absent from the irradiated solution; during the early stages of irradiation, a crystalline, water-soluble solid, containing nitrogen and ionic chlorine, separated but this disappeared as the dose increased and it was not examined further.

Irradiation of tetrachloroethylene gave hexachloroethane, hexachlorobuta-1,3-diene, octachlorobut-1-ene (dimer), hexachloro-4-dichloromethylenecyclopentene,* and an oil of low volatility, probably consisting of higher oligomers.

Like Futrell and Newton,³ we⁵ consider the fission of a carbon-chlorine bond to be the principal radiolytic reaction in all the examples studied, and indeed this appears to be a feature of radiolysis in most halogen compounds.⁹ The polymers, which are in all instances the main products, are then produced by a free-radical chain mechanism initiated by attack of a chlorine atom on a monomer molecule. The yields of polymer decrease, as expected, with increasing chlorine substitution, and *trans*-1,2-dichloroethylene gives a greater yield (including the solid) than the *cis*-compound. Futrell and Newton³ also obtained greater total polymer yields from the *trans*-isomer but their *G* values are lower than in the present work because of the higher dose rate employed. In the case of tetrachloroethylene, where polymerisation is relatively least important, hexachlorobutadiene, the product of dimerisation of the initially formed trichlorovinyl radicals, can be readily isolated. Hexachloro-4-dichloromethylenecyclopentene may be a secondary product arising by attack of a trichlorovinyl radical on hexachlorobutadiene:



Futrell and Newton³ consider that chloroacetylene and most of the hydrogen chloride, arising from the dichloroethylenes, are the products of "molecular" elimination of hydrogen chloride from an excited substrate molecule; this may also be true for the dichloroacetylene and hydrogen chloride produced from trichloroethylene. If this is the case, the action of traces of stabiliser (chemical nature unknown) in suppressing the yields of these compounds could be due to energy transfer from excited molecules of the olefin to the stabiliser.

* This compound was at first incorrectly identified⁵ as octachlorocyclohexa-1,3-diene.

⁹ Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, London, 1960, p. 94.

EXPERIMENTAL

The radiation unit contained a ^{60}Co source (~ 100 c) and was similar in design and operation to that described by Gibson and Pierce.¹⁰ Irradiations at the higher dose rates were carried out, by courtesy of Dr. W. Wild, inside a hollow cylindrical ^{60}Co source at the Atomic Energy Research Establishment, Harwell. Liquids were irradiated either (a) after degassing, in sealed evacuated glass ampoules (~ 40 ml. capacity) or (b) in cylindrical glass vessels of annular cross section enclosing the source. In the latter case, the vessels were fitted with ground-glass stoppers, but no other precautions were taken to exclude air. Dose rates quoted were determined by using the aqueous ferrous sulphate-sulphuric acid system¹¹ and are corrected for the greater electron density of the absorbing liquids. The G value for formation of ferric ion was taken as 15.5. Gas-liquid chromatography was carried out with apparatus of conventional design involving columns of kieselguhr (Johns-Manville Celite 545) impregnated with Silicone oil MS 550 (Hopkin and Williams).

Purification of Materials.—Commercial 1,2-dichloroethylene (May and Baker) was the source of both isomers, which were separated by fractional distillation and redistilled immediately before use. The purity of the two isomers was checked by gas-liquid chromatography; in the quantitative experiments the *trans*-isomer contained less than 0.5% of *cis*-compound, and the *cis*-isomer contained less than 0.1% of *trans*-compound; in the large-scale experiments each isomer contained less than 10% of the other. Trichloroethylene (Merck) was washed with 2*N*-hydrochloric acid, water, 2*N*-sodium carbonate, and water; after drying (CaCl_2) it was fractionated and redistilled immediately before use; for the large-scale experiments, no purification was carried out. Tetrachloroethylene (Merck or Hopkin and Williams) was washed with 2*N*-hydrochloric acid until no further yellow colour was produced in the aqueous layer, then with water, dried (P_2O_5), and distilled through a short column immediately before use.

Irradiation of 1,2-Dichloroethylenes.—*trans*-1,2-Dichloroethylene was degassed and sealed, under a vacuum, in glass ampoules which were irradiated for different times at a dose rate of 4.36×10^{17} ev ml.⁻¹ min.⁻¹. Hydrogen chloride was then estimated by treatment of an aliquot part with standard sodium hydroxide and back-titration. Solid polymer was removed by filtration, washed with ether, dried, and weighed. Monomer was then removed from the filtrate by distillation until the residue had constant weight. Irradiations were also performed, without degassing but after previous distillation of the samples under nitrogen, in an annular vessel (435 ml.) for different times at a dose rate of 0.78×10^{17} ev ml.⁻¹ min.⁻¹. In working-up of the larger irradiated samples, the final residue of oily polymers yielded a further small quantity of solid on addition of ether.

cis-1,2-Dichloroethylene was irradiated in sealed ampoules at a dose rate of 4.36×10^{17} ev ml.⁻¹ min.⁻¹ and the products were estimated as described for the *trans*-isomer; no solid polymer was produced.

Fractionation and Characterisation of the Oligomers from 1,2-Dichloroethylenes.—A sample of liquid polymer (53 g.) produced by irradiation of 90% *trans*-1,2-dichloroethylene was distilled under reduced pressure and yielded fractions: (a) dimer (7 g.), b. p. 82–84°/15 mm., n_D^{20} 1.5146, d_4^{20} 1.473 (lit.,^{2c} b. p. 88°/20 mm., n_D^{20} 1.5150, d_4^{20} 1.473); (b) trimer (10.5 g.), b. p. 105–120°/2 mm., n_D^{20} 1.5392, d_4^{20} 1.559; (c) tetramer (6 g.), n_D^{20} 1.5493; (d) viscous oils and waxes (6 g.); and (e) charred residue (24 g.). The dimer, trimer, and tetramer were treated with bromine in carbon tetrachloride, and the solid products were recrystallised from acetic acid to yield, respectively: (a) 1,2-dibromo-1,3,4,4-tetrachlorobutane, m. p. 102–103° (Found: C, 14.0; H, 1.0; Hal, 84.9. $\text{C}_4\text{H}_4\text{Br}_2\text{Cl}_4$ requires C, 13.6; H, 1.1; Hal, 85.3%); liquid dibromide(s) were also produced; (b) 1,2-dibromo-1,3,4,5,6,6-hexachlorohexane, m. p. 121–124° (Found: C, 16.3; H, 1.4; Hal, 82.5. $\text{C}_6\text{H}_6\text{Br}_2\text{Cl}_6$ requires C, 16.0; H, 1.4; Hal, 82.6%); (c) 1,2-dibromo-1,3,4,5,6,7,8,8-octachlorooctane, m. p. 246–249° (Found: C, 18.0; H, 1.7; Hal, 80.5. $\text{C}_8\text{H}_8\text{Br}_2\text{Cl}_8$ requires C, 17.5; H, 1.5; Hal, 81.0%).

The polymer (164 g.) produced by irradiation of 90% *cis*-1,2-dichloroethylene yielded similar fractions in different proportions, as follows: (a) dimer (70 g.), b. p. 83–84°/15 mm., n_D^{20} 1.5155, d_4^{20} 1.474; (b) trimer (40 g.), b. p. 105–120°/2 mm., n_D^{20} 1.5388, d_4^{20} 1.558; (c)

¹⁰ Gibson and Pierce, *Chem. and Ind.*, 1957, 613.

¹¹ Amplett, *Discuss. Faraday Soc.*, 1952, 12, 145.

tetramer (5 g.), n_D^{20} 1.5486; (*d*) viscous oils and waxes (10 g.); and (*e*) charred residue (39 g.). These oligomers yielded the same dibromides as were obtained from the *trans*-isomer.

Chromatography of the Tetrachlorobutene Fraction.—The dimer (1 ml.) was chromatographed at 130° in nitrogen (300 ml. min.⁻¹) on a column (8 ft. × 1 in.) packed with firebrick (40—60 mesh) impregnated with tritoyl phosphate (30% w/w of packing). Passage of the effluent through a U-tube at -78° yielded, after 250 min., *cis*-1,3,4,4-tetrachlorobut-1-ene, b. p. 193—195°/760 mm., n_D^{20} 1.5132 after redistillation (Found: C, 25.8; H, 2.0; Cl, 72.2. C₄H₄Cl₄ requires C, 24.8; H, 2.1; Cl, 73.1%) and, after 310 min., the *trans*-isomer, b. p. 197—198°/760 mm., n_D^{20} 1.5198 after redistillation (Found: C, 25.8; H, 2.2; Cl, 71.8%). When a shorter column was used, separation was less efficient but later fractions contained a substance with infrared absorption at 855 cm.⁻¹.

Irradiation of Trichloroethylene.—Trichloroethylene (3857 g.), with stabiliser present, was irradiated for 358 hr. (total dose approximately 8×10^{23} ev). After 24 hr., needle-shaped crystals filled the vessel but only a trace of solid (A) remained when irradiation ceased. Removal of monomer by distillation afforded a dark-brown viscous oil (64 g.) containing a solid (B). A portion of the oil (43 g.), after removal of solid (4.1 g.) by dilution with ethanol and filtration, yielded on distillation fractions: (*a*) slightly impure dimer (12 g.), b. p. 41°/0.01 mm., n_D^{20} 1.5440, d_4^{20} 1.674 (lit.,^{2c} n_D^{20} 1.5461, d_4^{20} 1.676), giving no reaction with bromine; (*b*) orange oils (14.5 g.) which could not be further purified; and (*c*) charred residue (12.4 g.). Solid (A), needles, m. p. 224—229°, contained nitrogen and ionic chlorine. Solid (B) formed plates, m. p. 216—217°, from chloroform (Found: C, 16.7; H, 1.0; Cl, 82.1%; *M*, 430. Calc. for C₆H₄Cl₁₀: C, 16.7; H, 0.94; Cl, 82.3%; *M*, 431). Trichloroethylene (free from stabiliser) was also irradiated in sealed evacuated ampoules (dose rate, 4.88×10^{17} ev ml.⁻¹ min.⁻¹) as described for the dichloroethylenes. During distillation, a vigorous evolution of gas occurred at 20—40°, culminating in a flash and deposition of carbon in the Vigreux column; this is attributed to the presence of mono- and di-chloroacetylenes. After removal of monomer by distillation, the residual oil was separated from the solid (B) by dilution with ethanol, filtration, and evaporation of the ethanol. The residue, which possibly still contained a little of compound (B) in solution, was weighed. Similar experiments were carried out with stabiliser present.

Irradiation of Tetrachloroethylene.—Tetrachloroethylene (393 ml.) was irradiated for 232 hr. (total dose 48×10^{22} ev). Removal of monomer by distillation then afforded a red, viscous oil (12 g.); hexachloroethane (0.3 g.), m. p. and mixed m. p. 185—186°, solidified in the condenser. Distillation of the oil provided the fractions: (*a*) hexachloroethane (0.1 g.); (*b*) hexachlorobuta-1,3-diene (2 g.), b. p. 60—80° (bath temp.)/0.01 mm., ultraviolet and infrared spectra identical with those of an authentic specimen; (*c*) hexachloro-4-dichloromethylene-cyclopentene (0.4 g.), prisms (from benzene), m. p. and mixed m. p. 182—183°, infrared and ultraviolet spectra identical with those of an authentic specimen;¹² (*d*) octachlorobut-1-ene (3 g.), b. p. 100—120° (bath temp.)/10⁻⁴ mm., n_D^{20} 1.5844, ν_{\max} 1642 cm.⁻¹ (Found: C, 14.3; Cl, 85.3%; *M*, 335. C₄Cl₈ requires C, 14.5; Cl, 85.5%; *M*, 332); and (*e*) a red, very viscous oil (5 g.), b. p. 140—180° (bath temp.)/10⁻⁴ mm.

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¹² McBee, Ungnade, Rakoff, and Dinbergs, *J. Amer. Chem. Soc.*, 1955, **77**, 4379.