V^{+++}, its hydrolysis products $V(OH)^{++}$ and VO^{+}.

2. Data are presented on the ionic states and polarographic characteristics of +2 and +3 vanadium in solutions of dilute acids and alkalies, acetate buffers, and of the various halide ions.

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Free Radical-initiated Reaction of Ethylene with Carbon Tetrachloride

BY R. M. JOYCE, W. E. HANFORD[1] AND J. HARMON

This paper describes the free radical-initiated polymerization of ethylene in the presence of the chain transfer agent, carbon tetrachloride. Because of the simplicity of the products formed from ethylene as a polymerizing monomer, and because carbon tetrachloride is a very efficient chain transfer agent for ethylene, it has been possible to isolate and establish the structures of the products of this chain transfer polymerization reaction. In addition, a qualitative study of the variation of chain length of the products with reaction conditions has been made.

The presence of chlorine in polystyrene prepared in carbon tetrachloride has been observed by several investigators,[2] and Price[3] has advanced the hypothesis that these polymers contained Cl and CCl_3 end-groups. Kharasch[4] has reported the addition of carbon tetrachloride to octene-1 to produce 1,1,1,3-tetrachlorononane, initiated by free radicals from diacyl peroxides. More recently, Kharasch[5] has described the addition of carbon tetrachloride to ethylene at low pressures to obtain a compound believed to be 1,1,1,3-tetrachloropropane. Evidence presented in this paper establishes that this structure is correct.

We have investigated the benzoyl peroxide-initiated reaction of ethylene with carbon tetrachloride over the pressure range 50–15000 lb./sq. in., and have shown that the reaction gives a series of compounds of the formula $Cl(CH_2CH_2)_nCCl_3$. When this reaction is carried out at an ethylene pressure of 1500 lb./sq. in., the major portion of the product comprises the first four members of this series. These compounds have been separated by fractional distillation, and their properties are given in Table I.

TABLE I

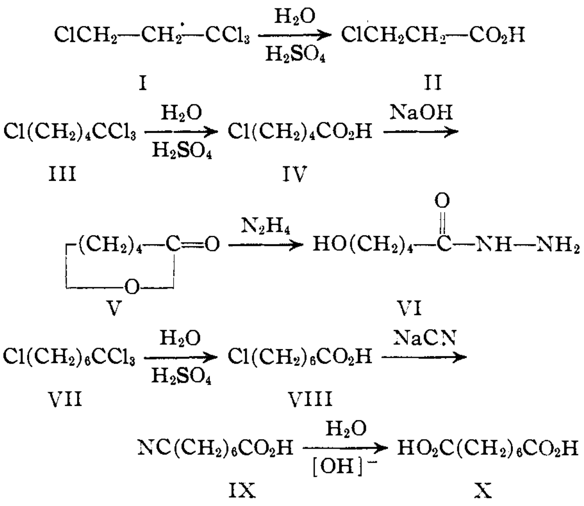
PROPERTIES OF $Cl(CH_2CH_2)_nCCl_3$

n	B. p., °C.	Mm.	$n^{25}D$	d^{25}_4
1	159	760[a]	1.4794[a]	1.4463
	59	24		
2	112	24	1.4859	1.3416
3	143	24	1.4824	1.2535
4	168	20	1.4804	1.1943

[a] Kharasch[5] reported b. p. 155°, $n^{20}D$ 1.4825.

The structures of the first three compounds were established by the reactions shown in Chart I, beginning with the hydrolysis of the CCl_3 group to a carboxylic acid with sulfuric acid and water.[6]

CHART I



$$ClCH_2—CH_2—CCl_3 \xrightarrow[H_2SO_4]{H_2O} ClCH_2CH_2—CO_2H$$

I II

$$Cl(CH_2)_4CCl_3 \xrightarrow[H_2SO_4]{H_2O} Cl(CH_2)_4CO_2H \xrightarrow{NaOH}$$

III IV

$$(CH_2)_4—C{=}O \text{ (ring closed through O)} \xrightarrow{N_2H_4} HO(CH_2)_4—\overset{O}{\overset{\|}{C}}—NH—NH_2$$

V VI

$$Cl(CH_2)_6CCl_3 \xrightarrow[H_2SO_4]{H_2O} Cl(CH_2)_6CO_2H \xrightarrow{NaCN}$$

VII VIII

$$NC(CH_2)_6CO_2H \xrightarrow[[OH]^-]{H_2O} HO_2C(CH_2)_6CO_2H$$

IX X

Under these conditions the tetrachloropropane (I) gave β-chloropropionic acid (II) melting at 40–42°. The tetrachloropentane (III) gave 5-chlorovaleric acid (IV). This was readily converted to δ-valerolactone (V), b. p. 124° (30 mm.), by treatment with aqueous or alcoholic alkali. Reaction of the lactone with hydrazine gave the known hydrazide of 5-hydroxyvaleric acid (VI) melting at 105–107°. The tetrachloroheptane (VII) gave 7-chloroheptanoic acid (VIII). The structure of this acid was proved by reaction with sodium cyanide followed by hydrolysis to suberic acid (X). Similar hydrolysis of the tetrachlorononane gave a chlorononanoic acid which is believed to be the 9-chloro compound. The properties of these chloro acids are shown in Table II.

The reaction of ethylene with carbon tetrachloride has been run at pressures ranging from 50 to 15000 lb./sq. in. The reaction rate increases

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[1] Present address: M. W. Kellogg Company, 225 Broadway, New York 7, New York.

[2] (a) Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937); **A181**, 81 (1937); (b) Breitenbach, Springer and Abrahamczik, *Oesterr. Chem. Ztg.*, **41**, 182 (1938); (c) Springer, *Kautschuk*, **14**, 212 (1938); (d) Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

[3] Price, *Ann. N. Y. Acad. Sci.*, **44**, 351 (*cf.* p. 366) (1943).

[4] Kharasch, Jensen and Urry, *Science*, **102**, 128 (1945).

[5] Kharasch, Jensen and Urry, THIS JOURNAL, **69**, 1100 (1947).

[6] Joyce, U. S. Patent 2,298,430.

TABLE II

PROPERTIES OF $Cl(CH_2)_mCO_2H$

m	B. p. °C.	Mm.	$n^{25}D$	d^{25}_4
4	122–124	8	1.4525	1.1667
6	136–137	5	1.4550	1.0916
8	164–166	7.5	1.4588 (27.5°)	....

markedly with pressure and, unless careful control is maintained, particularly with respect to dissipation of the heat of reaction, violently explosive reactions may occur.[7]

In this connection it is important to provide efficient agitation. The use of a diluent is desirable if the reaction is to be carried out on a scale greater than 500–1000 ml. reactor volume, except at pressures below about 150 lb./sq. in. A diluent is definitely advisable on any scale when the reaction is run above about 1000 lb./sq. in. The most effective diluent for moderating the reaction is water, presumably because of its inertness under reaction conditions and its high specific heat. We have carried out the reaction with a charge comprising 100 g. each of water and carbon tetrachloride and 0.23 g. of benzoyl peroxide in a 400-ml. reactor at 12000 lb./sq. in. It should not be inferred, however, that these conditions are necessarily safe, particularly if the agitation is inefficient. An explosion is a definite possibility should this reaction be attempted on a larger scale, or with a higher ratio of benzoyl peroxide to carbon tetrachloride.

When benzoyl peroxide is employed as initiator, the reaction proceeds smoothly in the temperature range 90–120°. A small amount of benzoyl peroxide suffices to initiate the reaction and it has been our practice not to employ more than 0.003 molecular equivalent of this peroxide based on carbon tetrachloride. As little as 0.0007 molecular equivalent has been used successfully. Within these ranges of benzoyl peroxide concentration, and employing a charge comprising 210 g. of carbon tetrachloride and 35 g. of water at 1400 lb./sq. in. ethylene pressure, we have obtained yields of 300–370 g. of reaction product per gram of benzoyl peroxide. The yields are somewhat lower at lower pressures. The exclusion of oxygen from the reaction mixture is desirable.

The proportions of the individual tetrachloroalkanes in the reaction product depend on the concentration of ethylene relative to that of carbon tetrachloride. This concentration can be changed by varying the ethylene pressure. Moreover, at a given pressure, dilution of the carbon tetrachloride with a solvent for ethylene which is relatively inert as a chain transfer agent, such as an aliphatic hydrocarbon, also serves to increase the concentration of ethylene relative to carbon tetrachloride. The variations in chain length of the products formed under various reaction conditions are shown in Table III.

TABLE III

VARIATION IN CHAIN LENGTH OF $Cl(CH_2CH_2)_nCCl_3$ WITH REACTION CONDITIONS

Ethylene pressure, lb./sq. in.	$Cl(CH_2CH_2)_nCCl_3$ Wt. per cent. of total product $n = 1$	$n = 2$	$n = 3$	$n = 4$	$n > 5$
50	77	23	..	..	..
80– 150	62.6	32.0	5.4	..	..
1200–1400	9.5	59.4	22.6	6.5	2.0
1500–1700	3.7	46.7	28.1	13.1	8.4
4000	1.0	24.1	24.5	21.8	28.6
1200–1400[a]	5.7	46.4	28.1	15.3	4.5
1200–1400[b]	1.8	24.0	25.9	21.7	26.6

[a] Organic phase comprised 96 g. of carbon tetrachloride and 59.5 g. of 2,2,4-trimethylpentane. [b] Organic phase comprised 54 g. of carbon tetrachloride and 87.5 g. of 2,2,4-trimethylpentane.

The concept of chain transfer in a free radical polymerization was first proposed by Flory.[8] The following mechanism, by which the tetrachloroalkanes are believed to be formed from ethylene and carbon tetrachloride, has been proposed by others[3,5] for this type of reaction. The establishment of the structures of these tetrachloroalkanes and our failure to isolate compounds of other structures from this reaction support this mechanism.

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3 \qquad (1)$$

$$\cdot CCl_3 + C_2H_4 \longrightarrow Cl_3CCH_2CH_2\cdot \qquad (2)$$

$$Cl_3CCH_2CH_2\cdot + nC_2H_4 \longrightarrow Cl_3C(CH_2CH_2)\cdot_{n+1} \qquad (3)$$

$$Cl_3C(CH_2CH_2)\cdot_{n+1} + CCl_4 \longrightarrow Cl_3C(CH_2CH_2)_{n+1}Cl + \cdot CCl_3 \qquad (4)$$

$$2\cdot CCl_3 \longrightarrow Cl_3CCCl_3 \qquad (5)$$

The initiating radical R· is derived from benzoyl peroxide. It would be expected to be the phenyl radical, since the decomposition of benzoyl peroxide in carbon tetrachloride has been shown to produce chlorobenzene in considerable quantity.[9] However, chlorobenzene has not been isolated as a by-product in this reaction, benzoic acid being the only aromatic compound obtained.

Definite evidence that the $\cdot CCl_3$ radical propagates the chain cycle is provided by the isolation of hexachloroethane from the reaction mixture. During the fractional distillation of the product from a run involving 5.5 kg. of carbon tetrachloride, several grams of hexachloroethane distilled between the C_3 and C_5 cuts.

The above mechanism appears to be the only one operating in this reaction. Careful fractional distillation of the products has failed to reveal the presence of any other types of compounds, such as $Cl(CH_2CH_2)_nCl$ or $Cl_3C(CH_2CH_2)_nCCl_3$. The formation of the former type would require a mechanism in which an initiating free radical reacted with carbon tetrachloride as follows

$$R\cdot + CCl_4 \longrightarrow RCCl_3 + \cdot Cl \qquad (6)$$

This type of free radical reaction is much less probable than reaction 1.[10] Compounds of the type

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[7] (a) Bolt, *Chem. Eng. News*, **25**, 1866 (1947); (b) Joyce, *ibid.*, **25**, 1866 (1947).

[8] Flory, THIS JOURNAL, **59**, 241 (1937).

[9] Böeseken and Gelissen, *Rec. trav. chim.*, **43**, 869 (1924).

[10] Waters, "Chemistry of Free Radicals," Clarendon Press, Oxford, 1946, p. 130.

$Cl_3C(CH_2CH_2)_nCCl_3$ could be formed by a chain termination reaction involving the combination of two growing radicals such as those produced in equations (2) and (3). However, the termination reaction (4) evidently predominates so that these compounds are not formed to any significant extent.

Experimental

Small-Scale Reaction of Ethylene with Carbon Tetrachloride.—A stainless steel-lined tubular pressure reactor having an internal volume of about 350 ml. and equipped with a thermocouple well and gas inlet was charged with 210 g. (1.36 moles) of freshly distilled carbon tetrachloride, 35 g. of water, and 0.47 g. (0.00194 mole) of benzoyl peroxide ("Lucidol"). The reactor was evacuated, pressured to 500 lb./sq. in. with ethylene, and placed horizontally in a shaking box equipped with a heater. When the temperature of the reaction mixture had been raised to 70°, the pressure was increased to 1400 lb./sq. in. by injection of ethylene, and the heating was continued. The reaction mixture was maintained at 95°, and the pressure in the range 1200–1400 lb./sq. in. by injection of additional ethylene as required, for five hours. The reaction product was then removed from the cooled reactor, separated from the water, and dried over anhydrous magnesium sulfate. After removal of the unreacted carbon tetrachloride by distillation, a preliminary fractional distillation gave the following results

Cut	B. p., °C.	Mm.	Weight, g.	Weight per cent.
C_3	<90	12	11.7	7.2
C_5	90–115	11	97.0	59.7
C_7	115–145	11	36.0	22.2
C_9	145–175	11	12.5	7.7
$>C_9$	Residue		5.0	3.2

The pure compounds can be obtained from these cuts by redistillation (*cf.* Table I).

Large-Scale Reaction of Ethylene with Carbon Tetrachloride.—A horizontal stainless steel autoclave having a capacity of 12.5 l., equipped with a horizontal agitator, a thermocouple well, gas inlet, and rupture disc assembly, was charged with 4420 g. of carbon tetrachloride (28.7 moles), 4420 g. of water, and 10 g. (0.0414 mole) of benzoyl peroxide. The reactor was purged twice by pressuring with ethylene to 300 lb./sq. in. and venting. The reactor was then pressured to 510 lb./sq. in. with ethylene and heated with stirring. When the temperature reached 85° the pressure was increased to 1500 lb./sq. in. by injection of additional ethylene from a storage vessel. A rapid reaction set in when the temperature reached 95° and the temperature rose to 139° in about five minutes, the pressure remaining constant at 1600 lb./sq. in. during this period. The reactor was cooled slowly to 100°, maintaining the pressure in the range 1500–1700 lb./sq. in. by injection of additional ethylene as required. The lack of further pressure drop when the temperature was maintained at 100° indicated that the reaction had ceased and the mixture was cooled and discharged.

The water was separated from the organic phase and the latter was washed with 10% sodium carbonate solution and twice with water. It was then dried over anhydrous magnesium sulfate. The carbon tetrachloride was removed from the product in a stripping still and careful fractional distillation of the residue gave the following results:

Cut	Weight, g.[a]	Weight % of total	Molecular equivalents of carbon tetrachloride
C_3	126	3.7	0.69
C_5	1580	46.6	7.53
C_7	951	28.1	4.00
C_9	444	13.1	1.67
$>C_9$	285	8.5	0.95[b]
Total	3386	100.0	14.84

[a] These figures do not include small amounts of intermediate cuts and a few grams of hexachloroethane distilling between the C_3 and C_5 cuts. [b] Analysis of the residue indicated the composition $Cl(CH_2)_{10.5}CCl_3$.

Of the carbon tetrachloride charged, 1565 g. was recovered, leaving 2855 g., 18.54 moles, to account for. The yield of isolated compounds based on carbon tetrachloride was (14.84/18.54) × 100 = 80.0 per cent.

Structure of 1,1,1,3-Tetrachloropropane.—A mixture of 25 g. of 1,1,1,3-tetrachloropropane, 100 g. of 96% sulfuric acid, and 1 g. of water was stirred vigorously while heating on a steam-bath for one and one-half hours. At the end of this time, the evolution of hydrogen chloride had ceased and a dark, homogeneous solution resulted. The solution was cooled, poured onto 300 g. of ice, and extracted continuously with ether overnight. The ether solution was dried over magnesium sulfate, filtered, and distilled to obtain 9 g. (55% of the theoretical) of *beta*-chloropropionic acid boiling at 110° (20 mm.) and melting at 40–42°.

Structure of 1,1,1,5-Tetrachloropentane.—A mixture of 1260 g. of 1,1,1,5-tetrachloropentane and 1500 g. of 96% sulfuric acid was stirred vigorously and heated to 90–95° on a steam-bath. A vigorous evolution of hydrogen chloride set in. A solution of 180 g. of water and 330 g. of concentrated sulfuric acid was then added under the surface of the reaction mixture over a period of one hour. After maintaining the heating and stirring for an additional hour, the reaction mixture was cooled and poured onto 2500 g. of cracked ice. The crude separated acid was extracted with three 500-cc. portions of carbon tetrachloride. The combined carbon tetrachloride solutions were washed well with water and the carbon tetrachloride was then removed in a stripping still. The resulting product was purified by distillation through a precision still, and there was obtained 639 g. (78% of theoretical) of 5-chlorovaleric acid boiling at 128–131° (11 mm.).

A solution of sodium hydroxide in methanol (406 ml., 2.0 *N*) was placed in a 1-liter 3-necked flask equipped with a stirrer, thermometer and dropping funnel. The solution was cooled to 10–15° and a solution of 111 g. of 5-chlorovaleric acid in 150 ml. of methanol was added, maintaining the temperature below 15°. The resulting solution was made neutral to phenolphthalein by adding methanolic sodium hydroxide solution, and was refluxed with stirring for two hours. It was then cooled and filtered. The methanol was removed from the filtrate in a stripping still and the residue distilled through a precision column, yielding 63 g. (77.5% of the theoretical) of δ-valerolactone boiling at 92° (8 mm.), n^{26}_{D} 1.4550.

One-half gram of the lactone was heated on a steam-bath with 2 ml. of 85% aqueous hydrazine for one hour and then evaporated under reduced pressure. The resulting hydrazide of 5-hydroxyvaleric acid solidified and was recrystallized from ethanol, melting point 105–107°.

Structure of 1,1,1,7-Tetrachloroheptane.—One gram of 1,1,1,7-tetrachloroheptane was stirred vigorously with 10 ml. of concentrated sulfuric acid on a steam-bath for one and one-half hours. The mixture was cooled, poured on ice, extracted with ether, and the ether solution dried over magnesium sulfate. Half of the solution was evaporated, the residue neutralized with sodium hydroxide and treated with *p*-phenylphenacyl bromide. There was obtained the *p*-phenylphenacyl ester of 7-chloroheptanoic acid, melting at 73–75°.

Anal. Calcd. for $C_{20}H_{23}O_2Cl$: Cl, 10.72. Found: Cl, 10.83.

The second portion of the ether solution was evaporated and the residue neutralized with *N*/3 sodium hydroxide. Two-tenths gram of sodium cyanide was added to the solution and the mixture was refluxed for five hours. One and one-half grams of potassium hydroxide was then added and the solution refluxed for six hours; ammonia was evolved during this operation. The resulting solution was cooled and acidified to congo red with hydrochloric acid. The precipitated suberic acid was collected on a filter and recrystallized from water, m. p. 138–140°; neut. eq., 86.4. There was no depression of the melting point when mixed with an authentic sample of suberic acid.

Hydrolysis of 1,1,1,9-Tetrachlorononane.—A mixture of 500 g. of concentrated sulfuric acid and 15 g. of water was heated to 95° with stirring on a steam-bath, and 133 g. (0.5 mole) of 1,1,1,9-tetrachlorononane was dropped in over a period of one hour. Stirring and heating were continued for three hours. The solution was then cooled, poured on 1200 g. of cracked ice, and extracted with two 100-ml. portions of carbon tetrachloride. The extract was dried over magnesium sulfate and distilled to obtain 55 g. (57% of the theoretical) of a chloro acid, presumably 9-chlorononanoic acid, boiling at 163.5–167° (7.5 mm.); n^{36}_{D} 1.4540; calcd. for $C_9H_{17}O_2Cl$: neut. eq., 192.5; found: neut. eq., 192.8.

Summary

The benzoyl peroxide-initiated reaction of ethylene with carbon tetrachloride gives a series of compounds having the general formula $Cl(CH_2CH_2)_nCCl_3$. When the reaction is carried out at 1500 lb./sq. in. the product is comprised principally of these compounds in which n has the values 1–4. The effect of reaction conditions on the proportions of individual members of this series in the reaction product is described.

Wilmington, Del. Received September 25, 1947

[Contribution from the Department of Chemistry, University of Delaware]

I. The Peroxide-Catalyzed Chlorination of Trimethylchlorosilane and *t*-Butyl Chloride[1]

By J. J. McBride, Jr., and H. C. Beachell

Trimethylchlorosilane has been chlorinated directly by Krieble and Elliot, a mixture of chlorination products being obtained.[2] Chlorination by sulfuryl chloride in the presence of benzoyl peroxide has been applied to various aliphatic hydrocarbons[3] and to certain organosilicon compounds.[4,5] This method of chlorination, however, has not been applied to trimethylchlorosilane, nor to its carbon analog, *t*-butyl chloride, previous to this work. The results are of interest in furnishing further information on the deactivation effect of the $-SiCl$ group on an alpha methyl group. (Sommer and Whitmore report that, like methylchloroform, methyltrichlorosilane cannot be chlorinated in this way.[4]) The chlorination of *t*-butyl chloride by the same method affords a means of comparing the relative effect of a silicon atom and a carbon atom in this reaction

Trimethylchlorosilane.—Refluxing an equimolar mixture of trimethylchlorosilane and sulfuryl chloride in the presence of benzoyl peroxide for several hours gave no detectable amount of chlorination product. When the experiment was repeated, however, using chlorobenzene as an inert diluent to increase the reflux temperature, a 38% yield of chloromethyldimethylchlorosilane was obtained after four hours. The yield of product was increased to 52% by adding the sulfuryl chloride dropwise to the refluxing mixture of trimethylchlorosilane and chlorobenzene. Density and refractive index have been determined for chloromethyldimethylchlorosilane. These are new physical constants for this compound.

In the majority of cases of fractionation of the reaction mixture, it was found that when almost all the chloromethyldimethylchlorosilane had been distilled off and there was a high concentration of higher boiling material left, *i. e.*, chlorobenzene and residue, the temperature dropped abruptly from 116° to about 71° where equilibrium was attained. The boiling point of dimethyldichlorosilane is given as 70°.[6] The identity of the material was established by determination of density, which is given in the literature[6] and by analysis for hydrolyzable chlorine. The presence of dimethyldichlorosilane may be due to disproportionation of chloromethyldimethylchlorosilane at a temperature above its boiling point or to the pyrolysis of unidentified polymeric by-products. No evidence for the presence of higher chlorinated products has been found, and other experimental evidence indicates that the reaction is limited to the introduction of a single chlorine under the conditions of the experiments.

The molar refraction for chloromethyldimethylchlorosilane was calculated by the Lorentz and Lorenz formula using the values obtained for density and refractive index. A value of 34.41 was obtained. This is in excellent agreement with the value of 34.70 obtained by addition of the atomic refraction equivalents. (The value used for silicon is that given by Whitmore for silicon in trimethylchlorosilane.[7])

***t*-Butyl Chloride.**—The chlorination of *t*-butyl chloride was carried out under the same conditions as that of trimethylchlorosilane. When an

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(1) Abstracted from a thesis by J. J. McBride, Jr., submitted to the faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science.

(2) Krieble and Elliot, This Journal, **67**, 1810 (1945).

(3) Kharasch and Brown, *ibid.*, **62**, 925 (1940).

(4) Sommer and Whitmore, *ibid.*, **68**, 485–487 (1946).

(5) Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488–489 (1946).

(6) Rochow, "Chemistry of the Silicones," John Wiley and Sons, New York, N. Y., 1946.

(7) Whitmore, *et al.*, This Journal, **68**, 475 (1946).