the reaction is believed to be one of oxidation inasmuch as the liquid does not appear to react with water. The fumes have an odor similar to that of ozone. As with the other compounds, little or no reaction with mercury or steel was observed (see Table I).

As expected, the substitution of fluorine for chlorine increases the stability of the compounds in this series. In the determination of the vapor pressures it was observed that the dichloride decomposes around 90°, and the chlorofluoride around 100° whereas the difluoride was observed to be stable up to its normal boiling point, 78.4°.

Although the equations for the vapor pressure of the dichloride and chlorofluoride are reliable only up to around 100°, calculation of the boiling points of these compounds under 760 mm. pressure gives values of 157 and 120°, respectively. Once again the Swarts rule for regular lowering of the boiling point of a compound by substitution of a fluorine atom is valid. One fluorine atom lowers the boiling point from 157 to 120° (Δ = 37°) and the second fluorine substitution cause the boiling point to drop to 78.4° (Δ = 42°).

Summary

Thiophosphorylethoxydichloride was prepared from thiophosphoryltrichloride and ethanol, purified and certain of its physical and chemical properties observed. Upon fluorination, by means of the Swarts reaction with antimony pentachloride as catalyst, thiophosphorylethoxychlorofluoride and thiophosphorylethoxydifluoride were obtained. These new compounds were purified and some of their physical and chemical properties studied.

The properties determined for the above compounds include freezing point, vapor pressure, boiling point, heat of vaporization, Trouton constant, liquid density, solubilities, corrosion tests, and hydrolysis.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Characteristics of +2 and +3 Vanadium. I. Polarography in Non-complexing Solutions[1]

BY JAMES J. LINGANE AND LOUIS MEITES[2]

Previous papers[3,4] from this Laboratory have discussed the polarography of the +2 and +3 states of vanadium in solutions of dilute acids and of oxalates. In these media the V(II)–V(III) couple is thermodynamically reversible at the dropping electrode. The investigation described in this and a following paper was undertaken to extend the information concerning solutions of these ions and of their complexes. The polarographic characteristics of +2 and +3 vanadium have been studied in a wide variety of media, including dilute acids and alkalies, phosphate, acetate, pyridine, and carbonate buffers, and solutions of the halides, thiocyanate, cyanide, thiosulfate, pyrophosphate, borate, benzoate, phthalate, salicylate, tartrate and citrate. This paper discusses only the cases in which no complex ions are formed. The experimental technique was essentially the same as that used in previous studies.[3,4]

Data and Discussion

We have found the half-wave potential for the reduction of vanadic to vanadous ion in 1 N sul-

furic, hydrochloric, or perchloric acid to be -0.508 ± 0.002 v. $vs.$ the saturated calomel electrode, which agrees very well with the standard potential of the couple reported by Jones and Colvin.[5] Zeltzer's determination of this constant[6] actually corresponds to the half-wave potential of +4 vanadium[3]; his solutions appear to have been quantitatively air-oxidized.

As the concentration of free acid is decreased, the wave becomes somewhat irreversible and shifts to more negative potentials. In 0.002 N acid the half-wave potential is -0.59 v. A second small wave at about -0.95 v. develops as the acid concentration is decreased. This wave is due to reduction of the hydrolysis product $V(OH)^{++}$, whose polarographic characteristics are discussed below.

We previously found the anodic half-wave potential of vanadous ion in 1 N sulfuric acid to be -0.50 v.,[3] and the corresponding (anodic) diffusion current constant to be -1.74 ± 0.01.[4] Since this constant is much larger than that found for vanadic ion, 1.41 ± 0.01, it follows that aquovanadous ion must be much smaller than aquovanadic ion. The half-wave potential of this anodic wave is not measurably affected by replacing the sulfuric acid with hydrochloric or perchloric acid.

(1) This paper is based on a thesis submitted by Louis Meites to the Graduate Faculty of Harvard University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in February, 1947.

(2) Present address: Department of Chemistry, Princeton University, Princeton, N. J.

(3) J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

(4) J. J. Lingane and L. Meites, *ibid.*, **69**, 1021 (1947).

(5) G. Jones and J. H. Colvin, *ibid.*, **66**, 1563 (1944).

(6) S. Zeltzer, *Coll. Czechoslov. Chem. Commun.*, **4**, 319 (1932).

Vanadic ion in 1 N acid solutions shows no anodic wave, nor is vanadous ion oxidized beyond the +3 state in these solutions.

Polarograms of +3 vanadium in unbuffered potassium chloride solutions consist of several very irreversible waves, whose total height decreases as hydrous vanadic oxide precipitates. Since several species are clearly involved, the overall half-wave potentials are meaningless.

Polarograms of +3 vanadium in acetic acid–sodium acetate buffers (1 M total acetate) are presented in Fig. 1. These polarograms consist of two cathodic waves whose relative heights are a function of pH. Thus, at pH 4.1 the over-all diffusion current constant is 2.21 times that of the first wave alone, at pH 5.4 the ratio is 2.44, and at pH 6.3 it is 2.72. The individual diffusion current constants have been determined only in the buffer of pH 5.4, where they are, respectively, 0.57 ± 0.01 and 1.39 ± 0.01. The total diffusion current constant is so close to that found for a one-electron reduction of +3 vanadium in 1 N sulfuric acid that the reduction in these acetate media must proceed only to the +2 state and the doublet waves must be attributed to two different molecular species of +3 vanadium in sluggish equilibrium.
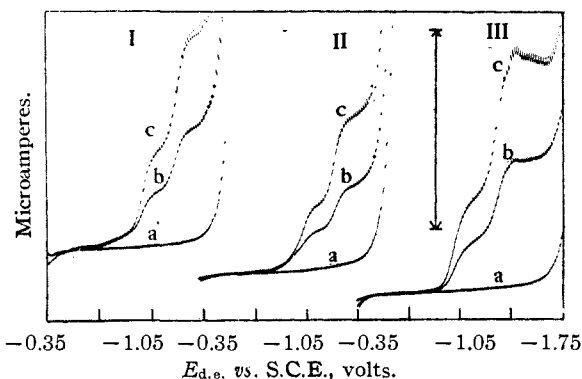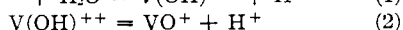

Fig. 1.—Polarograms of (a) 0, (b) 1.83, and (c) 3.44 millimolar +3 vanadium in acetic acid–sodium acetate buffers (1 M total acetate) of pH (I) 4.10, (II) 5.40, and (III) 6.30. The height of the arrow corresponds to six microamperes.

These species are most probably $V(OH)^{++}$ and VO^+ formed by hydrolytic dissociation of the aquovanadic ion

$$V^{+++} + H_2O = V(OH)^{++} + H^+ \quad (1)$$
$$V(OH)^{++} = VO^+ + H^+ \quad (2)$$

Since the relative height of the first wave decreases with increasing pH, this wave corresponds to reduction of $V(OH)^+$ and the second wave results from reduction of the more hydrolyzed species VO^+. It is not possible to compute the exact relative concentrations of the two species in the body of the solution from the relative wave heights. At potentials on the first wave the equilibrium in reaction 2 tends to shift to the left as $V(OH)^{++}$ is

removed by the electrode reaction, and consequently the relative height of the first wave tends to be larger than corresponds to the true relative concentration of $V(OH)^{++}$ in the body of the solution. In an acetate buffer of pH 5.4 the ratio of the second to first wave heights is 1.44, from which we conclude that the $(VO^+)/V(OH)^+$ ratio in the body of the solution is equal to or greater than 1.44. This is consistent with the data for the hydrolysis of vanadic ion given by Jones and Ray.[7]

The half-wave potential of the first wave in acetate buffers is −0.970 v. at pH 4.1, −0.978 v. at pH 5.4, and −1.008 v. at pH 6.3. Corresponding values for the second wave are, seriatim, −1.232, −1.245 and −1.300 v. Since both waves are somewhat irreversible, little thermodynamic significance can be attached to the magnitude of either rate of shift. However, the fact that a given pH change causes approximately twice as great a shift of the half-wave potential of the second wave as the first is in agreement with the expected relative effect of hydrogen ion if the electrode reactions are, respectively

$$V(OH)^{++} + H^+ + e = V^{++} + H_2O \text{ and}$$
$$VO^+ + 2H^+ + e = V^{++} + H_2O$$
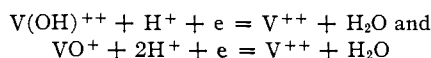
In an acetic acid–sodium acetate buffer of pH 5.4, +2 vanadium yields a double anodic wave as shown in Fig. 2. The first wave has a half-wave potential of −0.886 v. and a diffusion current constant of −1.090 ± 0.007. The half-wave potential of the second wave is −0.106 v. and its diffusion current constant is −3.36 ± 0.06. The
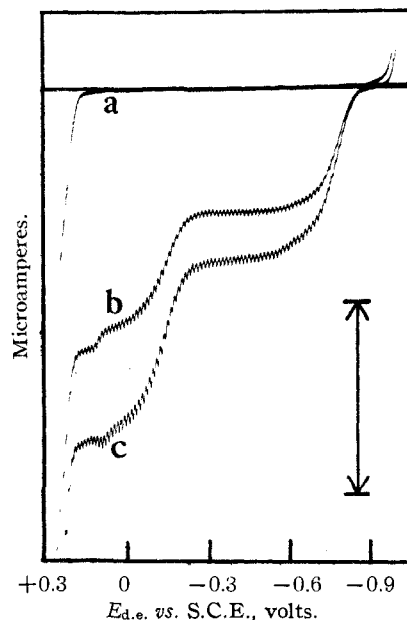

Fig. 2.—Polarograms of (a) 0, (b) 2.83, and (c) 3.96 millimolar +2 vanadium in an acetic acid–sodium acetate buffer (1 M total acetate) of pH 5.40. The height of the arrow corresponds to ten microamperes.

(7) G. Jones and W. A. Ray, THIS JOURNAL, **66**, 1571 (1944).

ratio of the diffusion current constants, 3.08, indicates that the waves are due to successive 1- and 3-electron oxidations of the +2 vanadium to the +3 and + 5 states. Plots of $-E_{d.e.}$ against log $(i/i_d - i)$ have slopes of -73 and -54 mv. (according to the common sign convention, this slope is negative for an anodic wave) instead of the -59.1 and -29.6 expected[4] for reversible -1 and -2 electron oxidations. Therefore neither stage of the oxidation proceeds strictly reversibly, and the $V^{+3} \rightarrow V^{+5}$ stage is less reversible than the $V^{+2} \rightarrow V^{+3}$ step.

Hydrous vanadic oxide is quantitatively precipitated on addition of solutions of +3 vanadium to a supporting electrolyte containing 1 M sodium hydroxide and 0.08 M sodium sulfite, and polarograms made immediately after the solutions are composited show no anodic or cathodic wave. However, even though the solutions are protected against air-oxidation by both hydrogen and sulfite, a double anodic wave at about -0.46 and -0.38 v. soon develops and rapidly increases in height as the solution ages. We have succeeded in keeping solutions of very powerful reducing agents (e. g., vanadous oxalate[4]) for hours without measurable air-oxidation, and hence it appears that alkaline suspensions of vanadic hydroxide are actually thermodynamically metastable. Since +5 vanadium gives no anodic wave whatever, and +4 vanadium in this medium gives only a single anodic wave at -0.432 v.,[3,8] the reaction which takes place probably produces two hypovanadite ions at approximately equal concentrations and in slow equilibrium with each other.

Curves I in Fig. 3 are polarograms of +3 vanadium in weakly acid (pH about 3) 1 M potassium fluoride. No wave due to reduction of the vanadium is observed; the wave which appears in the residual current curve is probably due to an impurity in the potassium fluoride used. A color-
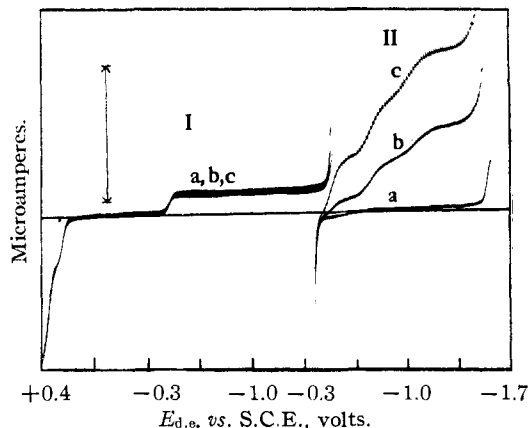
less precipitate, possibly of $K_2VF_5 \cdot H_2O$,[9] is formed in these mixtures. This is the most insoluble salt of + 3 vanadium encountered in the whole of the present work.

Solutions of +2 vanadium in the same medium (Curves I, Fig. 4) give three approximately equal anodic waves, with half-wave potentials of -0.701, -0.1_5, and $+0.2_1$ v. The first wave, which has a diffusion current constant of -1.96 ± 0.01, corresponds to oxidation to the +3 state. The other waves, which are too ill-defined for accurate measurement, must therefore represent oxidation to the +4 and +5 states. The vanadous–vanadic fluoride couple in this medium is very irreversible: the slope of the plot of $-E_{d.e.}$ against log $(i/i_d - i)$ is -166 mv., instead of the -59.1 mv. expected[4] for a reversible one-electron oxidation.
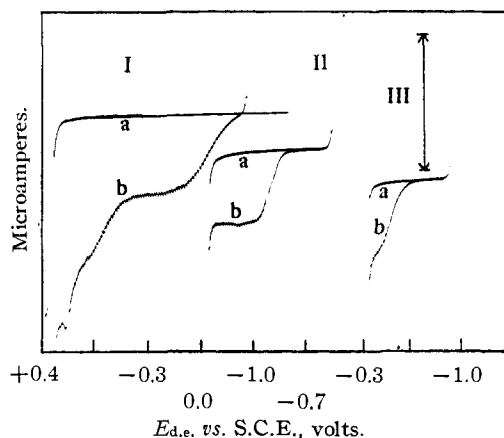

Fig. 4.—Polarograms of (I) (a) 0 and (b) 2.03 millimolar +2 vanadium in 1 M potassium fluoride, (II) (a) 0 and (b) 1.55 millimolar +2 vanadium in 1 M potassium bromide, and (III) (a) 0 and (b) 1.47 millimolar +2 vanadium in 1 M potassium iodide. The height of the arrow corresponds to ten microamperes.

In a 1 M potassium bromide solution (Curves II, Fig. 4), +2 vanadium gives a single well-defined anodic wave whose half-wave potential is -0.495 v. The magnitude of the corresponding diffusion current constant, -2.03 ± 0.03, indicates that the oxidation proceeds only to the +3 state. Plots of $-E_{d.e.}$ against log $(i/i_d - i)$ have slopes of -74 mv., and this small irreversibility appears to be the cause of the deviation from the reversible half-wave potential of the vanadous–vanadic couple.

Solutions of +3 vanadium in 1 M potassium bromide give a double cathodic wave (Fig. 5) with half-wave potentials at -0.43 and -0.87 v. Both waves are well-defined, but the ratio of their diffusion current constants varies with the pH: at pH 6 the diffusion current constant for the total second wave is 3.3 times that of the first wave alone, at pH 4.7 the ratio is 1.75, and at pH 4 it is 1.46. Below pH 4 the over-all diffusion current

Fig. 3.—Polarograms of (a) 0, (b) 1.83, and (c) 3.44 millimolar +3 vanadium in (I) 1 M potassium fluoride and (II) 1 M potassium iodide. The height of the arrow corresponds to ten microamperes.

(8) J. J. Lingane and L. Meites, *Anal. Chem.*, **19**, 159 (1947).

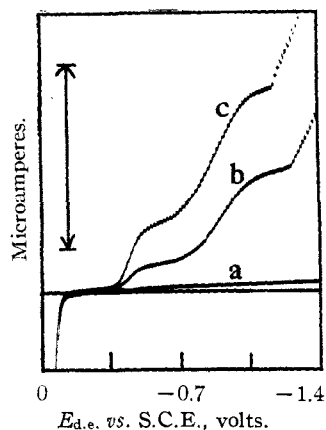(9) E. Petersen, *J. prakt. Chem.*, [2] **40**, 48 (1889).

Fig. 5.—Polarograms of (a) 0, (b) 1.83, and (c) 3.44 millimolar +3 vanadium in 1 M potassium bromide, pH 2.5. The height of the arrow corresponds to ten microamperes.

constant is 1.940 ± 0.009, while that of the first wave alone is 1.419 ± 0.005, and the ratio is 1.37 ± 0.01. Since the over-all constant is close to that which corresponds to a one-electron oxidation of +2 vanadium in the same medium, it follows that the reduction of +3 vanadium must also in-volve only one electron, and consequently that the waves are due to the reduction of two species in sluggish equilibrium. Since both waves are irre-versible (the slopes of plots of $E_{d.e.}$ against log $(i/i_d - i)$ are 74 and 170 mv., respectively), po-larographic identifications of these species are im-possible.

Only one ill-defined anodic wave is observed with solutions of +2 vanadium in 1 M potassium iodide (Curves III, Fig. 4). This wave has a half-wave potential of −0.49 v. and a diffusion current constant of −2.275 ± 0.03; it represents oxida-tion to the +3 state.

Solutions of +3 vanadium in 1 M potassium iodide show a triple cathodic wave (Curves II, Fig. 3) at a pH of about 2.5. The half-wave po-tentials of these waves are −0.46, −0.71 and −0.98 v. At pH values between 2 and 3 the total diffusion current constants of the second and third waves are 0.792 ± 0.003 and 2.75 ± 0.02, and the fact that the latter figure is fairly close to the value found for a one-electron oxidation of +2 vanadium leads to the conclusion that the sum of all three waves represents reduction only to the +2 state.

Table I contains data on the variation of the half-wave potentials of +3 vanadium with pH and potassium iodide concentration. These data were assembled from polarograms of which Fig. 6 is representative.

The half-wave potentials of the two waves given by +3 vanadium in an iodide-free acetate buffer of pH 5.0, calculated by interpolation in the data quoted previously, are −0.98 and −1.24 v. These figures are in good agreement with those observed in the presence of 1 M iodide; the small

Table I

Half-wave Potentials of +3 Vanadium at Varying pH and Potassium Iodide Concentration

The figures represent the half-wave potentials, in volts, referred to the saturated calomel electrode.

KI, molar	pH → 1.8	2.5	4.0[a]	5.0[a]	6.0[a]	13[b]
0.10	....	....	.....	−1.03	.....	N. R.[c]
				−1.28		
0.33	....	....	.....	−1.01	.....	N. R.
				−1.26		
1.00	−0.49	−0.47	−0.978	−1.018	~1.038	N. R.
	−0.97	−0.71	−1.183	−1.256	~1.283	
		−0.98				

[a] Acetic acid–sodium acetate buffer (1 M total acetate). [b] 0.1 M sodium hydroxide. [c] N. R.: not reducible, hydrous vanadic oxide quantitatively precipitated.

differences are probably not significant. There-fore, according to our earlier interpretation of this same double wave, the wave at −1.0 v. must be due to reduction of $V(OH)^{++}$ and the wave at −1.2 v. to the reduction of VO^+. As would be predicted from this, the relative height of the first wave decreases with increasing pH and increasing hydrolysis, and the effect of pH on the half-wave potential of the second wave is about twice as great as on that of the first wave. Then the second wave at pH 1.8 must also be due to reduc-tion of $V(OH)^{++}$, while the first, since it is at the same potential as the wave given by +3 vanadium in 1 N acid solutions, must be due to reduction of the simple vanadic ion. The wave at −0.71 v., which appears only when the pH is close to 2.5, is difficult to explain. It may be due either to a hydroxy-iodo complex of vanadic ion or to a com-pound such as $HV(SO_4)_2$,[10] but there is no definite evidence to confirm either supposition.
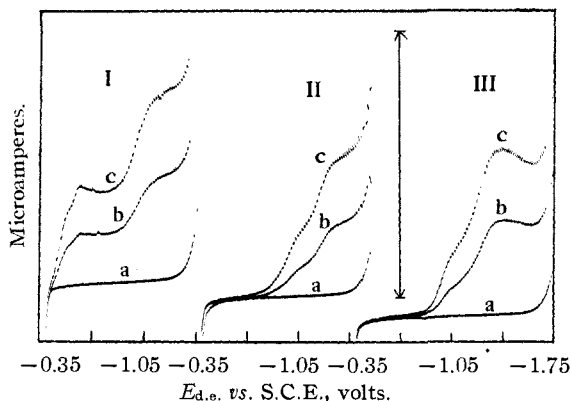

$E_{d.e.}$ vs. S.C.E., volts.

Fig. 6.—Polarograms of (a) 0, (b) 1.83, and (c) 3.44 millimolar +3 vanadium in 1 M potassium iodide, pH (I) 1.8 (0.02 N sulfuric acid), (II) 4.0, and (III) 5.5. The solutions of (II) and (III) contained acetic acid–sodium acetate buffers (1 M total acetate). The height of the arrow corresponds to twenty microamperes.

Summary

1. Acidic solutions of +3 vanadium are shown to contain, in addition to simple vanadic ion,

(10) H. T. S. Britton and G. Welford, J. Chem. Soc., 761 (1940).

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

2. Data are presented on the ionic states and polarographic characteristics of $+2$ and $+3$ vana-

dium in solutions of dilute acids and alkalies, acetate buffers, and of the various halide ions.

CAMBRIDGE, MASS.   RECEIVED JANUARY 23, 1948

Free Radical-initiated Reaction of Ethylene with Carbon Tetrachloride
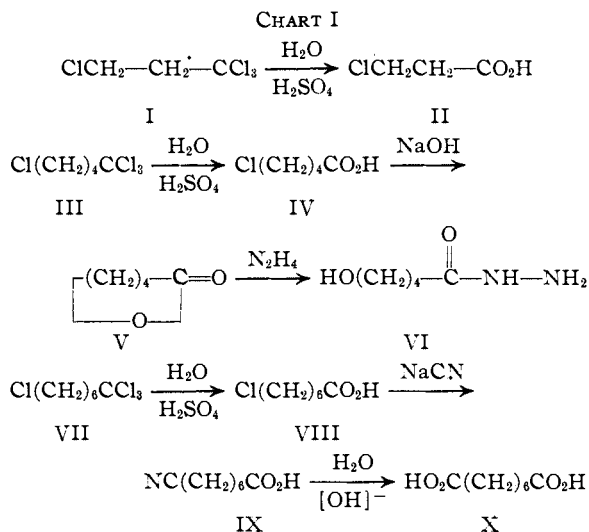
BY R. M. JOYCE, W. E. HANFORD[1] AND J. HARMON

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 $Cl(CH_2CH_2)_n$-CCl_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.

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

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

I   II

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

III   IV

$$\overset{\ulcorner}{\underset{\llcorner\!\_O\_\lrcorner}{(CH_2)_4}}\text{—}C{=}O \xrightarrow{N_2H_4} HO(CH_2)_4\text{—}\overset{O}{\overset{\|}{C}}\text{—}NH\text{—}NH_2$$

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

TABLE I

PROPERTIES OF $Cl(CH_2CH_2)_nCCl_3$

n	°C.	B. p., 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.

(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.