[Contribution from Mellon Institute and the Department of Chemistry of the University of Pittsburgh]

Infrared Absorption of Hydroxy Compounds in Autoxidizing Linseed Oil[1]

By F. J. Honn, I. I. Bezman and B. F. Daubert

Infrared absorption measurements have been rather widely employed for routine analysis, industrial process control, and the elucidation of molecular structure and reaction mechanisms. Although the deterioration of rubber and other high polymers has been studied with the aid of infrared techniques,[2] there has been little information published demonstrating the application of these techniques to the problem of drying oil oxidation.[3]

Preliminary examination of the infrared spectrum of raw linseed oil before and after vigorous oxidation reveals a marked increase in the intensity of two absorption bands (Fig. 1). The first, a rather broad band at 10.2 μ, is known to be characteristic of the general configuration R—CH$=$CH—R.[4] Its appearance during the oxidation process may result from the production of geometric isomers of the naturally occurring unsaturated fatty acids.[5] The second, a far more distinct band at 2.9 μ, is said to be characteristic of the bonded hydroxyl group. In this instance, as in the many others, the wave length of the infrared absorption band is indicative of the nature of the absorbing group or configuration, while the intensity of absorption is dependent upon the concentration of that group.[6]

Because of its role in the autoxidation process, the hydroxyl band at 2.9 μ has been selected for further study. The degree of absorption at 2.9 μ and therefore the hydroxyl content of a drying oil do not vary uniformly with oxidation time. In Fig. 2, the 2.0–3.0 μ region has been scanned at several stages throughout the oxidation process. During the induction period (zero to four hours), when oxygen uptake and peroxide formation are sluggish, the increase in intensity of absorption at 2.9 μ is correspondingly slow. At the end of the induction period, however, the 2.9 μ band quickly increases in intensity as the various oxidation reactions proceed at a rapidly accelerating pace.

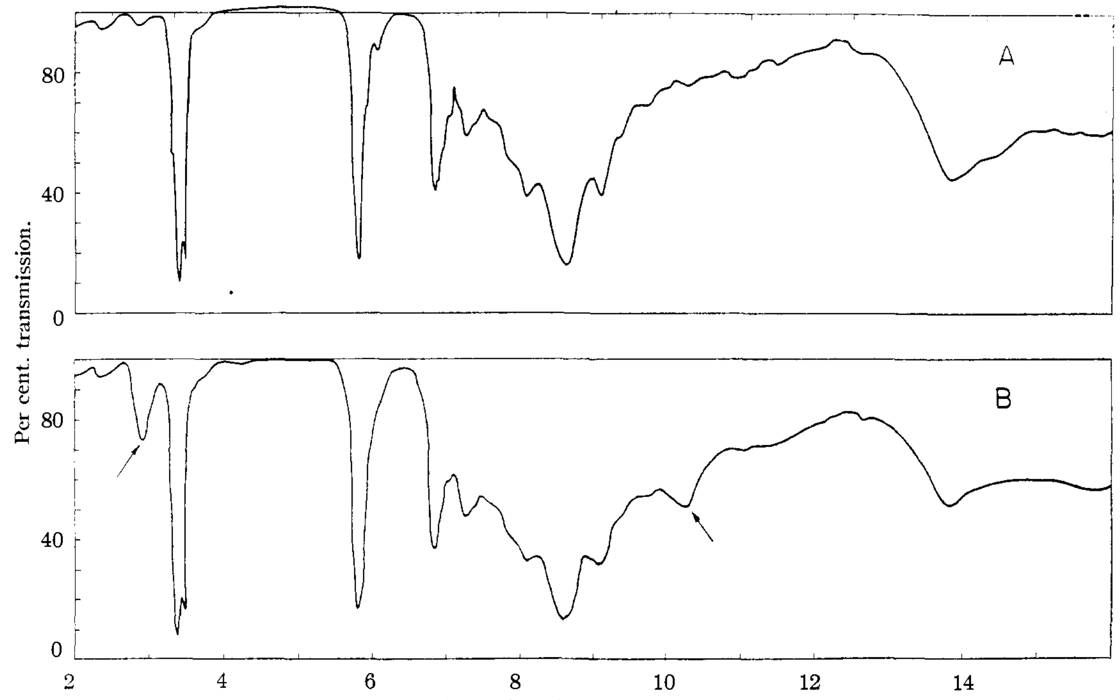

Fig. 1.—Infrared spectra of raw linseed oil: A, before oxidation; B, after oxidation.

In the autoxidation process there are formed several functionally distinct groups containing the (O–H) linkage, which can contribute to 2.9 μ absorption. They are (1) the hydroperoxide group (O–O–H), (2) the carboxy group (–CO–

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[1] Contribution from the Multiple Fellowship on Cork sustained at Mellon Institute by the Armstrong Cork Co., Lancaster, Pa.

[2] J. O. Cole and J. E. Field, *Ind. Eng. Chem.*, **39**, 174 (1947).

[3] F. J. Kolb and E. A. Hauser, *Paint, Oil, Chem. Rev.*, **110**, No. 23, 104 (1947).

[4] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 403 (1948).

[5] P. C. Rao and B. F. Daubert, This Journal, **70**, 1102 (1948).

[6] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120–140 (1947).

OH), (3) the simple alcoholic group (-C-OH), and (4) possibly other groups, such as that found in free liquid water (H-O-H). Classes (3) and (4) may be grouped conveniently as the "R-OH fraction."

Each of these hydroxy compounds can be accounted for by mechanisms usually advanced to explain drying oil autoxidation.[7–11] Farmer and co-workers[7–8] have demonstrated the formation of hydroperoxides by the attack of molecular oxygen upon the carbon alpha to a double bond. They have indicated, moreover, that such hydroperoxides may undergo further reaction with a carbon–carbon double bond to form epoxy and hydroxy derivatives.[9] More vigorous oxidation of the C=C linkage, of course, may result in its complete rupture, with the formation of carboxylic acids. Later in the oxidation process, particularly at elevated temperatures, water is released by the condensation of hydroxy derivatives to form polymers.[10] Other hydroxy substances, such as phospholipids and mucilages, are to be found in unrefined drying oils.[11]

Where associated in a mixture as complex as a raw drying oil, the various hydroxy components appear only as the single, broad 2.9 μ absorption band. Their individual peaks, occurring at closely neighboring wave lengths, are not resolved even by a high dispersion calcium fluoride prism.

Because the spectroscopic approach alone has failed to delineate the relative concentrations of the various hydroxy compounds, we have devised a combined chemical–spectroscopic method. Of the three types of hydroxy compounds mentioned, two can be estimated with considerable accuracy by chemical means. Hydroperoxides can be determined iodometrically and carboxylic acids by acid–base titration. In contrast, alcoholic hydroxyl analyses, such as the acetyl or Zerewitinoff procedures, do not yield reliable, unequivocal data in the presence of hydroperoxides. Furthermore, drying oils in the process of oxidation contain unstable substances, so that milder analytical techniques are desirable.

By means of the chemical–spectroscopic method, the so-called ROH fraction can be calculated by subtracting the sum of the hydroperoxide and carboxylic acid contributions, measured chemically, from the total hydroxyl content, measured optically. To perform this subtraction, the specific absorption coefficients of the (-OOH) and (-COOH) groups must be known, to permit conversion of their chemical concentrations to "optical concentrations."

From measurements of the optical densities of representative hydroxy compounds at several concentrations, it has been demonstrated that these compounds, in the range of concentrations encountered in an autoxidizing drying oil, obey Beer's law: $-\log T$ = optical density = kcl, where k is specific absorption coefficient, a proportionality constant; c is concentration of absorbing group, in g./l.; and l is thickness of absorbing medium, in cm. From the data plotted in Fig. 3, these absorption coefficients have been calculated and expressed in appropriate units.

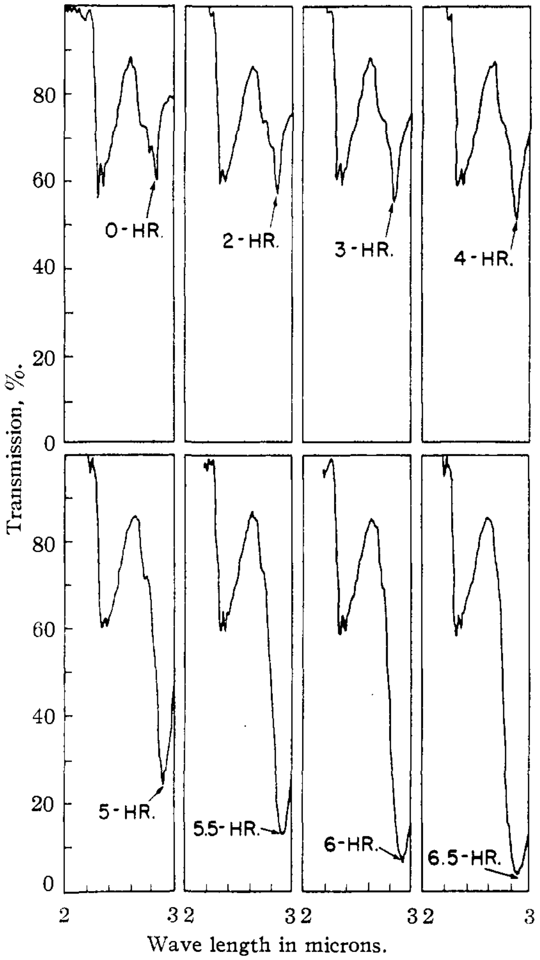

Fig. 2.—Changes in 2.9μ hydroxyl band during linseed oil autoxidation.

Experimental

Apparatus.—All spectroscopic measurements for which data are presented were made on a Baird infrared recording spectrophotometer, equipped with a rock salt prism. Experiments involving the use of a calcium fluoride prism, however, were conducted with a Perkin-Elmer spectrometer. A quartz cell, of fixed 0.187 mm. thickness, proved convenient for autoxidized oils as well as solutions of representative hydroxy compounds. Because only the hydroxyl band at 2.9 μ was of immediate concern, the quartz cut-off near 4.0 μ did not interfere.

Hydroxy Compounds.—Ethyl myristate (Eastman Kodak Co., m.p. 10–12°) was employed as a stable, inert ester solvent for the various hydroxy compounds. Methyl

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(7) E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 119–122 (1943).

(8) D. A. Sutton, *ibid.*, 242–243 (1944).

(9) E. H. Farmer, G. F. Bloomfield, A. Sundralingam and D. A. Sutton, *Trans. Faraday Soc.*, **38**, 348–356 (1942).

(10) K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., 1947, p. 324.

(11) A. E. Bailey, "Industrial Oil and Fat Products," Interscience Publishers, Inc., New York, N. Y., 1945, p. 22 ff.

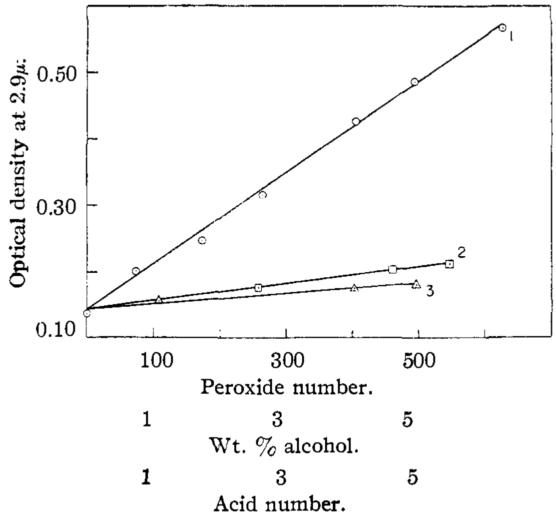

Fig. 3.—Optical densities of solutions of hydroxy compounds in ethyl myristate as a function of their concentrations: 1, methyl hydroperoxide oleate; 2, *n*-octadecanol; 3, palmitic acid.

hydroperoxide oleate was prepared[12] by ultraviolet irradiation and autoxidation of pure methyl oleate, and isolated by low-temperature crystallization. Its Wheeler peroxide number of 4200 indicated a purity of about 69%. The balance of the material was substantially unreacted methyl oleate. Palmitic acid (m.p., 61–62°) was highly purified by recrystallization from acetone. The alcohol employed was *n*-octadecanol, an Eastman Kodak Co. product of m.p. 56.5–58°.

Procedure of Absorption Coefficient Measurement.—Solutions of each of the hydroxy compounds were made to several known concentrations. The optical density of each solution was then determined at 2.9 μ (Table I); for each compound, optical density was plotted as a function of a concentration. The resulting linear relationships are shown in Fig. 3. Absorption coefficients were calculated from the slopes of these straight lines. By preparing several mixtures, calculating their total hydroxyl contents from the appropriate coefficients and comparing the values so obtained with observed optical densities (Table II), infrared absorption of the three compounds at 2.9 μ was shown to be an additive function of their concentrations. In every case, the deviation lay close to or within the ± 1% transmission error normally expected of the Baird instrument.

Table I

Optical Densities of Methyl Hydroperoxido Oleate, Palmitic Acid and *n*-Octadecanol in Ethyl Myristate Solution

Wt. % COOH	Wt. % OOH	Wt. % OH	Acid no.[a]	Peroxide no.[b]	Optical density at 2.9μ
....Ethyl myristate solvent only....					0.138
0.495	...	..	1.08	...	.155
1.84	...	..	4.03	...	.172
2.26	...	..	4.96	...	.180
...	6.30	..	..	265	.316
...	9.63	..	..	404	.426
...	1.78	..	..	75	.201
...	11.7	..	..	492	.484
...	4.10	..	..	172	.247
...	14.9	..	..	627	.567
...	...	5.44	..	...	.210
...	...	2.57	..	...	.174
...	...	4.60	..	...	.202

[a] Defined as the mg. of potassium hydroxide required to neutralize free acids in a 1-g. sample. [b] Wheeler method; *cf.* K. S. Markley, *op. cit.*, p. 463.

Table II

Additivity of Infrared Absorption of Hydroxy Compounds

Acid no.	Peroxide no.	Wt. % OH	Calcd. optical density equiv. to total OH content	Observed optical density at 2.9μ
...	166	..	0.247	0.244
...	389	..	.389	.385
10.3	168	..	.312	.305
5.57	...	3.72	.214	.210
3.33	100	1.59	.241	.220
3.17	188	4.91	.332	.332

Linseed Oil Oxidation.—Raw linseed oil, in 1500-ml. quantities, was oxidized in a glass and stainless steel apparatus at 85° by passing dry air through the oil at the rate of 4000 ml./min. and vigorously agitating the oil with a beater rotating at 1725 r.p.m.

Results and Discussion

The absorption coefficients determined for three representative hydroxy compounds are: (1) Palmitic acid, k = 0.375/acid no.-cm.; (2) methyl hydroperoxido oleate, k = 0.0364/peroxide no.-cm.; (3) *n*-octadecanol, k = 0.675/wt. per cent.-cm.

In Fig. 4, a typical linseed oil autoxidation has been analyzed by means of the chemical–spectroscopic method. The total hydroxyl content has been divided into its three major components: R–OOH, R–COOH, R–OH. The concentration of each component, expressed in optical density, has been plotted as a function of oxidation time. The data from which the curves are drawn are assembled in Table III.

Curve 1 represents the change in total hydroxyl content, measured by infrared absorption at 2.9 μ. Curve 4 depicts the change in hydroperoxide concentration, determined chemically by the Wheeler method and converted to optical units by means of the absorption coefficient. Carboxylic acid optical concentrations, obtained similarly and then added to the hydroperoxide concentrations, yield curve 3. If curve 3 is subtracted point by point from curve 1, the resultant curve 2 indicates the change in the R–OH component.

Initially the R–OH fraction in a raw drying oil is a complex mixture of alcoholic hydroxy compounds, phospholipids, mucilages and water. As autoxidation proceeds, however, the increase in the R–OH component depicted in Fig. 4 can be ascribed only to an increase in the concentration of alcoholic hydroxy compounds. Although water is liberated in the process, its contribution to the 2.9 μ absorption band seems to be negligible. During the first stages of oxidation, linseed oil is

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[12] C. E. Swift, F. G. Dollear and R. T. O'Connor, *Oil and Soap*, **23**, 355–359 (1946).

TABLE III

CONCENTRATIONS OF HYDROXY COMPOUNDS IN AN AUTOXIDIZING DRYING OIL

Oxidation time, hr.	Total OH content	Peroxide no.	Peroxide O. D.[a]	Acid no.	Acid O. D.	Net ROH[b]
0	0.26	5	0.02	3.0	0.02	0.22
1	.26	13	.03	2.9	.02	.21
2	.27	20	.03	2.9	.02	.22
3	.27	27	.04	3.0	.02	.21
4	.29	38	.045	2.9	.02	.225
4.5	..	44	.05	3.0	.02	...
5	.31	50	.055	3.0	.02	.235
5.5	.31	59	.06	3.2	.02	.23
6	.32	72	.07	3.0	.02	.23
6.5	.36	98	.09	3.1	.02	.25
7	.43	161	.13	3.2	.02	.28
7.5	.55	260	.20	3.6	.025	.325
8	.72	368	.27	4.2	.03	.42
8.5	.79	402	.295	4.8	.035	.46
9.5	.92	382	.28	5.8	.04	.60

[a] Values for peroxide optical density include the constant cell absorption of 0.02. [b] Net ROH = (total OH) − (peroxide O.D. + acid O.D.)

not sufficiently hydrophilic to dissolve an appreciable quantity of water. In one instance saturation of an unoxidized linseed oil with water raised the water content from 0.14 to 0.33% and the optical density at 2.9 μ from 0.276 to 0.284—a difference within the limits of error of the spectrophotometer. Saturation of an oxidized linseed oil, on the other hand, lifted the water content form 0.37 to 0.95%. But in this case the optical density at 2.9 μ was already so great that no increment could be detected.

During the induction period in a typical linseed oil autoxidation (zero to six hours in Fig. 4), no carboxylic acids are formed. Curves 3 and 4, therefore, are parallel. Since these curves rise at the same rate as the total hydroxyl content, the R–OH component remains substantially constant. It appears, on the basis of this evidence, that those peroxides formed during the induction period are essentially all hydroperoxides.

Later in the oxidation process, however, there is not as much assurance that all peroxides formed are of R–OOH type, because the Wheeler iodometric procedure, from which the R–OOH is derived, measures the sum total of all oxidizing compounds in the oil. The hydroperoxide values should then be regarded as maximum values.

During the "transition" period (six to eight hours in Fig. 4), the R–COOH contribution begins to increase, while the R–OOH component rises rapidly to a maximum. At the same time the total hydroxyl content rises even more rapidly, causing a sharp increase in the R–OH fraction. The transition period, then, is a time of rapid peroxide formation and decomposition.

As the drying oil begins to polymerize (over eight hours in Fig. 4), the rate of peroxide decomposition exceeds that of formation, while carboxylic acids continue to form. Curves 3 and 4, therefore, diverge, while the R–OH component rises even more sharply.

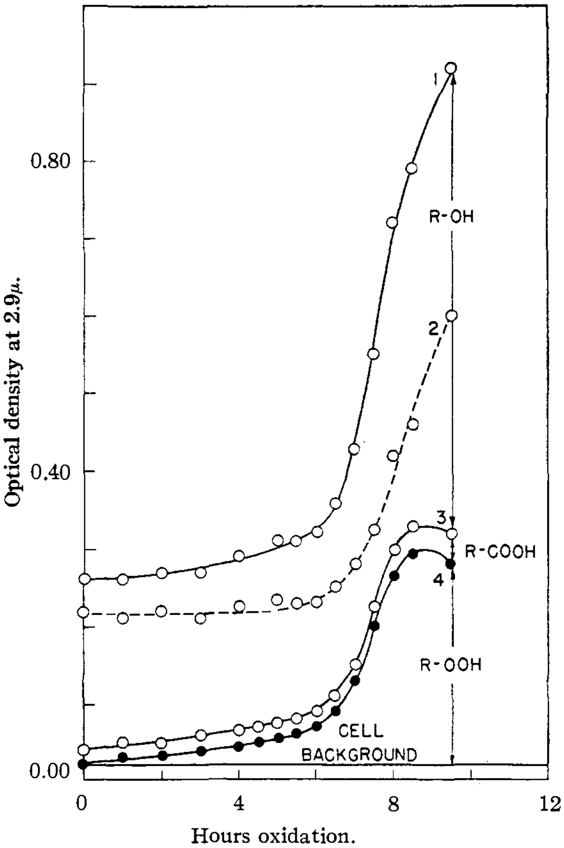

Fig. 4.—Analysis of a typical linseed autoxidation process: 1, total hydroxyl content; 2, net R–OH component; 3, sum of hydroperoxide and acid contributions; and 4, hydroperoxide contribution.

Infrared absorption measurements of autoxidizing drying oils at 2.9 μ serve as a rapid means of determining the end of the induction period, since the total hydroxyl content rises sharply at that point. In conjunction with chemical analyses, infrared techniques offer further confirmation of the role of hydroperoxides in autoxidation. It should now be possible to make use of the absorption coefficient reported for the alcoholic hydroxyl group and so determine the reaction products of peroxide decomposition.

Acknowledgment.—We wish to thank Messrs. J. H. Lieblich and R. B. Hannan of the Department of Research in Chemical Physics of Mellon Institute for their aid in making spectroscopic measurements.

Summary

1. A combined chemical–spectroscopic analytical method has been devised to permit a detailed breakdown of the autoxidation reaction.
2. Infrared absorption coefficients have been

determined for three representative hydroxy compounds.

3. The role of hydroperoxides and their decomposition products in autoxidation has been further investigated.

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[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Pyrolysis and Chlorinolysis of Some Perchlorinated Unsaturated Hydrocarbons[1]

BY J. A. KRYNITSKY AND H. W. CARHART

In earlier work,[2] it was shown that the pyrolysis of octachlorocyclopentene yields hexachlorocyclopentadiene, chlorine and small amounts of hexachlorobenzene. It has been reported[3] that both hexachloroethane and octachloropropane give carbon tetrachloride and tetrachloroethylene on thermal decomposition. Carbon tetrachloride and tetrachloroethylene have been reported[4] as being highly stable.

Prins[6,7] has shown that one mole of chlorine adds rapidly and quantitatively in sunlight to tetrachloroethylene, hexachloropropene and hexachlorocyclopentadiene without causing rupture of the carbon chain. On the other hand, hexachloroethane,[3] hexachloro-1,3-butadiene,[5] octachloro-1,3-pentadiene,[7,8] and octachlorocyclopentene,[2,8,9,10] have been reported either to resist the action of chlorine or, under drastic conditions, to be cleaved by it.

In the present work, tetrachloroethylene, hexachloropropene, hexachloro-1,3-butadiene and octachloro-1,3-pentadiene were subjected both to vapor phase pyrolysis and to the action of chlorine at temperatures up to 500°. In addition, hexachloropropene and octachloro-1,3-pentadiene were exposed to prolonged heating in the liquid state at their reflux temperatures and to chlorination under similar conditions. Small samples of two isomeric C_6Cl_8 compounds having melting points of 43–44° and 182–183° were also decomposed at 500°, and a sample of hexachloro-1,3-butadiene was treated with chlorine in bright sunlight for an extended period of time.

Results and Discussion

Pyrolyses.—Both tetrachloroethylene and hexachloro-1,3-butadiene were found to be quite thermostable as no pyrolysis products were found on heating at 500°.

Hexachloropropene was recovered unchanged after a six-hour reflux (210–213° pot temperature). Vapor phase pyrolysis became appreciable at temperatures over 400° and yielded carbon tetrachloride, tetrachloroethylene and hexachloroethane as the major products. The amounts of these products obtained are summarized in Table I. In addition to these, a minor quantity of hexachlorobenzene was isolated from the 490–500° pyrolysis but not at the lower temperatures. A compound, C_6Cl_8 (m. p. 43–44°), was also obtained from the products of pyrolysis at 450–460° and 490–500°. It is believed that this compound is the same as the C_6Cl_8 (m. p. 45°) prepared by Prins[11] to which he assigns the structure 1-(trichloromethyl)-pentachloro-2,4-cyclopentadiene. In the pyrolysis of hexachloropropene, carbonization was insignificant and very little, if any, chlorine was evolved. In contrast to hexachloropropene, prolonged refluxing decomposed octachloro-1,3-pentadiene completely. The principal products of the reflux and vapor phase pyrolyses were carbon tetrachloride, hexachloro-1,3-butadiene and hexachlorocyclopentadiene. The amounts of these compounds and hexachlorobenzene found are given in Table II. Small amounts of hexachloroethane were obtained from the vapor phase but not from the reflux pyrolyses. Traces of tetrachloroethylene were found in all but the 400–410° pyrolyses. Two other compounds, octachlorocyclopentene and C_6Cl_8 (m. p. 182–183°) were isolated from the products of the reflux pyrolysis. The latter compound was shown to be identical with a C_6Cl_8 compound prepared by Prins[6] to which he assigns the probable structure 1-(dichloromethylene)-hexachloro-2-cyclo-

TABLE I

PRINCIPAL PYROLYSIS PRODUCTS OF HEXACHLOROPROPENE

Temp., °C.	Moles product/mole starting material			
	CCl_4	C_2Cl_4	C_2Cl_6	C_3Cl_6 (recovered)
Reflux[a]	0	0	0	*ca.* 1
400–410	Trace	0.03	0.01	0.94
450–460	0.04	.28	.12	.57
490–500	.11	.67	.21	Trace
490–500	.14	.70	.24	Trace

[a] Refluxed six hours. Pot temperature, 210–213°.

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[1] The opinions contained in this paper are the authors' and are not to be construed as official or reflecting the views of the Department of the Navy.

[2] Krynitsky and Bost, THIS JOURNAL, **69**, 1918 (1947).

[3] McBee, Hass, *et al.*, *Ind. Eng. Chem.*, **33**, 176 (1941).

[4] Hurd, "The Pyrolysis of Carbon Compounds," Reinhold Publishing Corp., New York, N. Y., 1929, p. 132. It is also stated that hexachloro-1,3-butadiene is quite thermostable; however, Fruhwirth[5] has shown that the compound previously thought to have been hexachloro-1,3-butadiene was in all probability octachlorocyclopentene.

[5] O. Fruhwirth, *Ber.*, **74B**, 1700 (1941).

[6] H. J. Prins, *J. prakt. Chem.*, **89**, 414 (1914).

[7] H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

[8] Bost and Krynitsky, THIS JOURNAL, **70**, 1027 (1948).

[9] McBee, Hass and Pierson, *Ind. Eng. Chem.*, **33**, 181 (1941).

[10] McBee, Hass and Bordenca, *ibid.*, **35**, 317 (1943).

[11] H. J. Prins, *Rec. trav. chim.*, **65**, 184 (1946).