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Free Radical-Initiated Reaction of Ethylene with Halomethanes

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In recent publications from this Laboratory[2,3] the free radical-initiated reaction of ethylene with polyhalogenated methanes has been described and with carbon tetrachloride the product was shown to consist of a series of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes. This paper reports the identification of the products of the reaction of ethylene with other halogenated methanes, including chloroform, chloroiodomethane, methylene chloride, methylene iodide, methylene bromide and methyl iodide. These structures are shown in Table I.

TABLE I

REACTION OF ETHYLENE WITH HALOGENATED METHANES

Halogenated methane	Type of product
$CHCl_3$	$H(CH_2CH_2)_nCCl_3$
CH_2ClI	$I(CH_2CH_2)_nCH_2Cl$
CH_2Cl_2	$Cl(CH_2CH_2)_nCH_2Cl$
CH_2I_2	$I(CH_2CH_2)_nCH_2I$
CH_2Br_2	$Br(CH_2CH_2)_nCH_2Br$
CH_3I	$I(CH_2CH_2)_nCH_3$

The results show that the reaction is quite general and afford additional support for the mechanism of chain transfer reactions in free radical polymerizations discussed in our preceding paper[2] and by Kharasch.[4] The structure of the products of the reaction of ethylene with chloroform indicates that a free radical attacks chloroform to remove a hydrogen atom and to form a $\cdot CCl_3$ radical, in accord with the experience of Kharasch[4] and of Böeseken and Gelissen.[5] All other polyhalogenated methanes investigated in this work were attacked by free radicals with removal of a halogen atom.

The reactions were carried out by heating and agitating a mixture of the halomethane, water (which served as a heat transfer fluid), and a small amount of benzoyl peroxide under ethylene pressure in a pressure reactor. Pressures ranged from 100 to 900 atm., the higher pressures being employed with the more reactive halomethanes in order to increase the average chain length of the product. In each case the mixture of reaction products was separated into its components by fractional distillation through a 24″ still (16 mm. bore) packed with $^3/_{16}''$ glass helices. The major individual components were identified as described in the Experimental Section.

The average chain length of the products of these reactions varies inversely with the reactivity of the halomethane. As noted by Kharasch,[4] this reactivity diminishes as the number of halogen atoms in the methane decreases. The relative reactivity of the halogens is $I > Br > Cl$. With a given halomethane, the average chain length of the reaction product increases with increasing concentration (*i. e.*, pressure) of ethylene relative to halomethane in the reaction system.

In carrying out free radical reactions of this type under superatmospheric pressure, the possibility of an explosive reaction should be kept in mind. These reactions tend to become more and more rapid as the reaction pressure is increased and, particularly with the more reactive halomethanes, explosions become increasingly probable.[6] The use of water is important in moderating the vigor of the reaction. The equipment should be properly barricaded and protected by an adequate rupture assembly.

Experimental

Reaction of Ethylene with Chloroform.—A silver-lined tubular steel pressure reactor of 400-ml. capacity equipped with an external heater, thermocouples, a gas inlet valve and mounted on an agitating machine was used for carrying out this reaction. The reactor was charged in an atmosphere of nitrogen with 150 g. of chloroform, 100 g. of water and 1.5 g. of benzoyl peroxide; then ethylene was admitted under 25 atm. pressure. The internal temperature was raised gradually to 100° and the pressure was maintained at 90 to 100 atm. for ten hours by the intermittent addition of ethylene from a high pressure storage vessel. The total pressure drop caused by the absorption of ethylene was 115 atm. and practically all of this occurred during the first three hours. The organic phase of the reaction mixture was separated from the aqueous phase. The products from two experiments were combined and fractionally distilled under reduced pressure. The cuts shown in Table II were obtained.

Identification of Ethylene–Chloroform Reaction Products.—The structures of the products described in Table II were established as 1,1,1-trichloroalkanes by hydrolysis with strong sulfuric acid as described previously,[2] followed by identification of the resulting acids. Five grams of the fraction to be identified was stirred vigorously with 25 ml. of concentrated sulfuric acid and 0.25 ml. of water on a steam-bath for one and one-half hours. The mixture was cooled, poured on ice and steam distilled. The organic component was extracted from the steam distillate with ether. The ether solution was dried over magnesium sulfate and the ether was distilled through a fractionating column. The residues usually weighed about 3 g. and possessed the odors characteristic of aliphatic monocarboxylic acids. The first two members of this series, and the corresponding authentic samples of propionic acid and valeric acid, were converted to the *p*-bromophenacyl esters by a standard procedure appearing in the literature.[7] However, for the higher members of the series (heptanoic acid and above) better results were obtained by the modified procedure described below.

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[2] Joyce, Hanford and Harmon, THIS JOURNAL, **70**, 2529 (1948).

[3] Hanford and Joyce, U. S. Patent 2,440,800.

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

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

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

[7] Shriner and Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 157, 222.

Table II

Properties and Identification of $H(CH_2CH_2)_nCCl_3$ from the Reaction of Ethylene with Chloroform

Cut	n	Wt., g.	B. p., °C.	B. p., Mm.	$n^{25}D$	d^{25}_4	Cl analysis, % Calcd.	Cl analysis, % Found	p-Bromophenacyl ester Hydrolyzed product, m. p., °C.	p-Bromophenacyl ester Known $H(CH_2CH_2)_n$-COOH, m. p., °C.	Mixed m. p., °C.	Lit.[7] m. p., °C.
1	1	17	35–36	60	1.4462	1.2836	72.2	70.26	63–65	63–65	63–65	63
			105	760								
2		9	35–80	60								
3	2	54.5	80–82	60^a	1.4521	1.1843	60.6	59.94	76–77	75–76	75.5–76.5	75
4		8.5	59–86	15								
5	3	33	86–87	15	1.4555	1.1212	52.33	51.65	71–72	71–72	71–72	72
									$78–79^b$	$77–78^b$	$77.5–78.5^b$	
6		9	34–61	0.4								
7^c	4	21.5	58–60	0.25^d	1.4582	1.0786	46.01	45.93	66–67	66–67	66–67	68
8		11	61–88	0.35								
9	5	6	88–91	0.35	1.4620	1.0604	41.05	41.67	70–71	70–71	70–71	68
10		36.5	(Liquid still residue)									

[a] Kinney and Spliethoff, This Journal, 71, 746 (1949), prepared this compound from carbon tetrachloride and n-butylmagnesium chloride and report b. p. 56–57° (20 mm.), $n^{20}D$ 1.4540. [b] p-Toluidide. [c] This fraction contained a small amount of material which crystallized upon cooling. This was identified by m. p. and mixed m. p. as benzoic acid. Analytical data were obtained on the fraction after the benzoic acid had been removed by scrubbing with 5% aqueous sodium hydroxide. [d] Kharasch, ref. 4, prepared this compound from octene-1 and chloroform, and report b. p. 65–70° (0.5 mm.), $n^{20}D$ 1.4620.

One gram of the acid and 0.3 g. of solid potassium hydroxide were dissolved in 25 ml. of ethanol, then 1 g. of p-bromophenacyl bromide was added and the resulting solution was refluxed for one and one-half hours. The mixture was filtered while hot (to remove potassium bromide) and the filtrate was cooled in an ice-bath. The p-bromophenacyl ester separated as a white crystalline solid (platelets). It was filtered, washed first with cold ethanol and then with water and finally recrystallized from 10 ml. of ethanol. The recrystallized products obtained from the various fractions by this procedure were white, they melted sharply and the yields were 0.7–0.8 g. The melting points were not depressed when the individual esters were mixed with the p-bromophenacyl esters prepared by the same procedure from authentic samples of the corresponding acids (see Table II).

Hydrolysis of the products formed by the reaction of ethylene with chloroform to the corresponding carboxylic acids followed by identification of the acids as described above and in Table II has served to identify the original products as normal 1,1,1-trichloroalkanes formed by the chain transfer polymerization of up to 6 moles of ethylene with 1 mole of chloroform. Products containing a higher proportion of ethylene were formed but they were not isolated or identified.

Reaction of Ethylene with Chloroiodomethane.—The apparatus and procedure for this reaction were the same as described in the preceding experiment. The reactor was charged with 50 ml. of water, 50 g. of chloroiodomethane, 0.5 g. of benzoyl peroxide, and air was removed from the system by evacuating it to 100 mm. of mercury pressure. Ethylene pressure was applied to the system and the temperature and pressure were maintained at 95° and 500–600 atm., respectively, for eleven hours, during which time a total pressure drop of 300 atm. was observed. The reaction product was taken up in ether, dried with anhydrous magnesium sulfate, and the ether was distilled leaving the product a light yellow liquid which weighed 64 g. The products of two runs were combined (total weight 129 g.) and fractionally distilled under reduced pressure to give a series of four constant-boiling fractions as shown in Table III.

Table III

Properties of $I(CH_2CH_2)_nCH_2Cl$ from the Reaction of Ethylene with Chloroiodomethane

n	Yield, g.	B. p., °C.	B. p., Mm.	$n^{20}D$	Analyses, % Calcd. Cl	Analyses, % Calcd. I	Analyses, % Found Cl	Analyses, % Found I
1	16	57	10	1.5472	17.34	62.11	18.51	61.49
								61.45
2	20	93–95	10	1.5285	15.25	54.63	16.74	53.27
		69.5	2				16.49	53.41
3	19.5	95	2	1.5153	13.61	48.76	14.75	46.95
							14.61	46.86
4	10.5	122	2	1.5088	12.29	44.03	12.81	43.62
							12.86	43.62
>4	34	Still residue		....	...	...	...	...

The first two members of this series were identified as 1-chloro-3-iodopropane and 1-chloro-5-iodopentane by the preparation of the N,N′-diphthalimide derivatives and comparison with authentic derivatives. In the preparation of these derivatives a mixture of 2.5 g. of the halogen compound and 4 g. of potassium phthalimide was heated in a test-tube in an oil-bath at 200° for two hours with occasional stirring. The mixture was cooled and extracted with hot benzene. The residue left after evaporation of the benzene was washed with dilute sodium hydroxide and recrystallized from glacial acetic acid. The N,N′-polymethylenediphthalimide derivatives were obtained as nearly white crystals. The melting point of the phthalimide derivative obtained from the first fraction (where n is 1 in Table III) was 196–197° (uncor.).

Anal. Calcd. for $C_{19}H_{14}N_2O_4$: N, 8.38. Found: N, 8.51, 8.45.

The melting point of an authentic sample of N,N′-trimethylenediphthalimide was 196–196.5° (uncor.) and the mixed melting point with the diphthalimide from the first fraction was 196–197° (uncor.). Thus the first fraction was identified as 1-chloro-3-iodopropane. The melting point given in the literature for N,N′-pentamethylene diphthalimide is 186°[8] and the melting point of the phthalimide derivative of the second fraction was 184–185° (uncor.). This serves to identify the second fraction of Table III as 1-chloro-5-iodopentane. On the basis of chlorine and iodine analyses, and by inference from the structures of the first two products just described, the third and fourth fractions listed in Table III are believed to be 1-chloro-7-iodoheptane and 1-chloro-9-iodononane, respectively.

Reaction of Ethylene with Methylene Chloride.—The pressure reaction vessel previously described was charged with 100 ml. of water, 100 g. of methylene chloride and 0.5 g. of benzoyl peroxide. The mixture was agitated and maintained at 75–100 atm. ethylene pressure and 200° for

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(8) Baldwin, *J. Chem. Soc.*, 2963 (1929).

TABLE IV

PROPERTIES OF $Br(CH_2CH_2)_nCH_2Br$

n	Yield, g.	Properties found	Properties given	M. p., °C.[i]
1	10	B. p. 76–77° (40 mm.)	B. p. 160–163° (719 mm.)[a]	T 61–62
		d^{25}_4 1.890	d^{25}_4 1.987[b]	A 62–63
		n^{25}_{D} 1.5150	n^{25}_{D} 1.5249[b]	M 62–63
2	9.5	B. p. 70–72° (2 mm.)	B. p. 95.5° (10 mm.)[c]	T 48–49
		d^{25}_4 1.657	d^{20}_4 1.6995[c]	A 48–49
		n^{25}_{D} 1.5075	n^{20}_{D} 1.5136[c]	M 48–49
		n^{20}_{D} 1.5102		
3	9.5	B. p. 96–97° (2 mm.)	B. p. 132° (11 mm.)[d]	
		d^{25}_4 1.517	d^{15}_4 1.5254[d]	T 54–55
		n^{25}_{D} 1.5026	n^{15}_{D} 1.5033[d]	A 54.5[f]
		n^{15}_{D} 1.5081		
4	6.5	B. p. 121–125° (1.5 mm.)	B. p. 121° (2 mm.)[e]	T 110–111[a,g]
		d^{25}_4 1.428	d^{15}_4 1.415[e]	A 110–111[b,h]
		n^{25}_{D} 1.4981		M 110–111

[a] Geromont, *Ann.*, **158**, 730 (1871). [b] Lange's Handbook, 4th Ed., p. 825 (Beil. I, 110). [c] Johnson, *J. Chem. Soc.*, 1531 (1933). [d] Heilbron, "Dictionary of Organic Compounds," Vol. I, p. 695 (1943 edition). [e] *Ibid.*, Vol. I, p. 711; Chuit, *Helv. Chim. Acta*, **9**, 265 (1926). [f] Muller and Rolz, *Monatsh.*, **48**, 733 (1927). [g] Brassylic acid, prepared by malonic ester synthesis from this fraction. [h] Brassylic acid, prepared by hydrolysis of known dimethyl brassylate. [i] M. p. of polymethylene diphenoxide from polymethylene dihalide: T, this work; A, authentic dihalide; M, mixture melting point.

three hours, during which time the pressure drop due to ethylene absorption was 31 atm. The volatile portion of the reaction mixture was separated from the non-volatile portion (7.8 g.) by steam distillation. The unreacted methylene chloride was removed from the steam-volatile portion by fractional distillation; this left 6.3 g. of liquid boiling above 100°. This portion of the product was combined with similar products obtained in other experiments (total weight 15 g.) and fractionally distilled.

The first fraction weighed 1.8 g. and distilled at 65° (120 mm.) or 118–119°. Trimethylene chloride is reported in the literature to boil at 119° (740 mm.).[9]

Anal. Calcd. for $C_3H_6Cl_2$: Cl, 62.7. Found: Cl, 60.8.

The phthalimide derivative of this product was prepared as described in the chloroiodomethane experiment and found to melt at 196.5–197.5° (uncor.). The mixed melting point with an authentic sample of N,N′-trimethylenediphthalimide was 196–197.5° (uncor.). These data establish the identity of the first fraction as trimethylene chloride.

Other flats on the distillation curve were obtained at 59–61° (10 mm.) (0.6 g.), corresponding to the b. p. of 1,5-dichloropentane, and at 58–61° (0.6 mm.) (0.5 g.). Approximately 9 g. of the original steam-volatile portion was left as a high-boiling still residue.

Reaction of Ethylene with Methylene Iodide.—This experiment was carried out by the procedure described in the first experiment. The reactor was charged with 50 ml. of water, 0.5 g. of benzoyl peroxide and 50 g. of methylene iodide. The operating temperature, pressure and time were 95°, 425–450 atm. and eleven hours, respectively. The observed pressure drop due to the absorption of ethylene was 20 atm. The crude product was a liquid which, upon fractional distillation, yielded 12 g. of a liquid b. p. 115–120° (30 mm.), n^{20}_{D} 1.6385, n^{15}_{D} 1.6412, believed to be trimethylene iodide. The literature physical constants for trimethylene iodide are b. p. 110° (19 mm.), n^{15}_{D} 1.6363.[10] There was only 3.5 g. of higher-boiling product formed in this experiment and this was left as a still residue.

Reaction of Ethylene with Methylene Bromide.—The pressure reactor described in the first experiment was charged with 100 ml. of water, 100 g. of methylene bromide and 1 g. of benzoyl peroxide. The mixture was heated with agitation at 99–101° under 310–350 atm. ethylene pressure for eight and one-half hours, during which time the total pressure drop was 115 atm. The product, which was a heavy oil, was separated into two fractions by steam distillation. The steam-volatile portion was separated into two fractions by distillation. The lower-boiling fraction consisted of 30 g. of unchanged methylene bromide while 18 g. of a clear yellow liquid reaction product was left as a high-boiling residue. Liquid products of this type amounting to 72 g. and obtained from several experiments were combined and fractionally distilled under reduced pressure. The characterization and identification of the products are summarized in Table IV.

The portion of the original product which was non-volatile with steam was a grease-like solid and weighed 11 g. It was extracted with ether and the soluble portion (10 g.) was found to contain 34.40% bromine. This is believed to be a mixture of high molecular weight polymethylene bromides of average composition $Br(CH_2CH_2)_{10.9}CH_2Br$.

Reaction of Ethylene with Methyl Iodide.—The pressure reactor previously described was charged with 50 g. of methyl iodide, 100 ml. of water and 0.5 g. of benzoyl peroxide. The mixture was agitated and maintained at 92–96° under 775–900 atm. ethylene pressure for ten hours, during which time the pressure drop due to ethylene absorption was 275 atm. The crude reaction product was a liquid which was exhaustively steam distilled. The steam-volatile portion was extracted from the aqueous layer with ether, the ether solution was washed with sodium bisulfite solution, dried, and the ether was separated by fractional distillation, leaving 9 g. of a liquid residue. This residue was fractionally distilled under reduced pressure. Practically the entire product distilled below 115° (2 mm.), but only one constant-boiling fraction was obtained. This fraction distilled at 50° (2 mm.) and weighed 2 g.

Anal. Calcd. for $C_7H_{15}I$: I, 56.10. Found: I, 55.98, 56.38; n^{15}_{D} 1.4925. $n^{15}_{\mathrm{He\ yellow}}$ 1.4929 is given for *n*-heptyl iodide.[11]

That portion of the original product which was not volatile with steam weighed 15.5 g. and was a tan wax-like solid.

Anal. Found: I, 27.15, 27.17; mol. wt. (cryoscopic), 420, 430.

The iodine analysis corresponds to a mixture of alkyl iodides having an average formula of $CH_3(CH_2CH_2)_{11.6}I$ (average mol. wt. 467.5).

Acknowledgments.—The authors wish to express their gratitude to various other members

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[9] Reboul, *Ann. chim. phys.*, [5] **14**, 460 (1878).

[10] Dionneau, *Ann. chim.*, [9] **3**, 257 (1915).

[11] Deffet, *Bull. soc. chim. Belg.*, **40**, 385 (1931).

of this Laboratory, especially to Dr. J. R. Roland and Dr. S. L. Scott who assisted with the experimental work, to Mr. H. S. Young and his group who operated the pressure equipment, and to Dr. J. W. Stillman and his group who made the analytical determinations.

Summary

The free radical-initiated reaction of ethylene with several halomethanes under superatmospheric pressure has been studied. Series of products of the general formula $X(CH_2CH_2)_nY$ are obtained, in which X is hydrogen or halogen, and Y is the remainder of the halomethane molecule. The average chain length, *n*, varies inversely with the reactivity of the halomethane.

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The Synthesis of Polymeric Ethers

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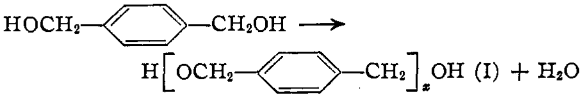
The investigation described in this paper has been concerned with the application of the familiar acid catalyzed etherification reaction of aliphatic alcohols to the preparation of polymeric ethers. While the etherification of ordinary aliphatic alcohols is extremely slow and is complicated by side reactions other than condensation, it has long been known[2] that benzyl alcohol in the presence of small amounts of acidic substances reacts rapidly at elevated temperatures with evolution of water to yield benzyl ether. The self-condensation of compounds in which two methylol groups are attached to an aromatic nucleus should result, therefore, in the formation of polymeric ethers.

We have found that *p*-xylylene glycol condenses readily above 150° in the presence of 0.1% by weight of sulfamic acid to yield the polymeric ether



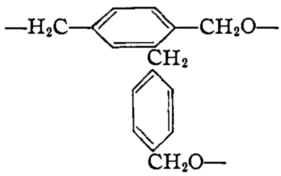
(I) + H_2O

The only previous work done on such condensations is that of Hjelt[3] who reported that *o*-xylylene glycol condenses rapidly at 70° in dilute sulfuric acid to an insoluble, infusible, amorphous substance having the approximate composition C_8H_8O. While the polymer we obtained by the self-condensation of *p*-xylylene glycol contained appreciable quantities of gel, due presumably to a small proportion of condensation at ortho positions on the nucleus, further results have shown that suitably constituted glycols can be condensed to give linear high melting crystalline polyethers with molecular weights exceeding five thousand in some cases. To avoid nuclear condensation, the following substituted dimethylolbenzenes were used as monomers: dimethyloldurene, dimethylolisodurene and dimethylolmesitylene. The former two compounds, as well as the bis-(chloromethyl) intermediates from which they were prepared, have not been reported previously.

Discussion

Although the dimethylolbenzenes are stable compounds when heated under nitrogen at 50–75° above their melting points for periods as long as eight hours, the introduction of as little as 0.05% by weight of an acid or acid forming catalyst causes rapid evolution of water. *p*-Toluenesulfonic acid, sulfamic acid, ferric chloride, stannous chloride, zinc chloride, sodium bisulfate, calcium chloride, cadmium chloride, cobaltous chloride, magnesium chloride and various benzylic chlorides such as bis-(chloromethyl)-isodurene have proved effective in promoting polymerization. Sulfamic acid was chosen for most of the experiments as it induces rapid etherification with virtually no discoloration at the high temperatures of reaction employed.

At 200° with 0.1% by weight of sulfamic acid, *p*-xylylene glycol reacts rapidly, the viscosity of the melt increases, and after twenty minutes gelation occurs. The polymer obtained in this manner was semi-crystalline at room temperature and about 10% of it was soluble in benzene from which it could be crystallized, m. p. 120–122°. The gel was also semi-crystalline with a melting point of about 180°. Carbon–hydrogen analyses (see Table I) of both sol and gel were in close agreement with the values calculated for the linear polyether (I). A small proportion—too small to be detected by carbon–hydrogen analysis—of condensation at the ortho positions with the formation of branched units (II)



(II)

would account for the formation of network structure as indicated by the occurrence of gelation.[4]

When dimethyloldurene (III) similarly reacts at 340°, very rapid evolution of water occurs and the melt solidifies within five minutes. That

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[2] S. Cannizarro, *Ann.*, **92**, 113 (1854).

[3] E. Hjelt, *Ber.*, **19**, 1539 (1886).

[4] P. J. Flory, THIS JOURNAL, **63**, 3083 (1941).