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# A New Route to Chlorinated Vinyl Ethers

High temperature chlorinolysis and cracking led to high recovery weights

M CBEE and Devaney (7) have investigated the chlorinolysis of polychlorinated hydrocarbons from propane through hexane, but no information is available on chlorinolysis of polychlorinated ethers. The objects of the investigation were to determine what products would be obtained by the chlorinolysis of bis-(2-chloroethyl) ether, and to investigate the thermal cracking of polychlorinated ethers in an attempt to prepare unsaturated chloro ethers and the possibility of preparing commercially useful materials from by-product bis(2-chloroethyl) ether.

## Experimental

**Chlorination.** All chlorinations were conducted in a borosilicate glass tube, 60 cm. long and 60 mm. in diameter, with a sintered-glass bubbler sealed into the bottom and a 45/50 standardtaper joint at the top. This allowed for insertion, from the top, of a glass cooling coil (20 cm. long) and a glass thermometer well. A Friedrichs condenser prevented escape of volatile products. The ultraviolet light activation came from a General Electric Type

<sup>1</sup> Present address, Cleveland Industrial Research, Cleveland, Ohio R-S bulb almost touching the reactor tube.

Most of the chlorinated products were made at 100° C.; a few, up to 174° C. The products were fractionally distilled to obtain the polychlorinated ethers.

Chlorinolysis and Thermal Cracking. The liquid chloroethers were gravityfed at predetermined rates, with metered amounts of chlorine or nitrogen, into a glass helix immersed in a molten salt bath (Aeroheat 300). The reaction tubes were made in 12-mm. borosilicate glass with a tiny thermowell at the exit for temperature measurement of the gaseous reaction product. Reaction gases were quenched quickly at the exit; most of them condensed at that point. The gas stream was then passed through three dry ice traps to catch as much of the low-boiling products as possible. Temperatures investigated were from 300° to 500° C. with residence times of 0.1 to 5.0 seconds.

Chlorinolysis left clean reactor walls; during cracking reactions the tubes became thinly coated with black deposits. The crude reaction products were yellow to light brown for chlorinolysis and light brown to dark brown for cracking; they were fractionally distilled in each experiment.

### **Results and Discussion**

Chlorination. 1,2-Dichloroethyl 2chloroethyl ether was prepared in approximately 68% yield by stopping the chlorination of bis(2-chloroethyl) ether at a weight gain of 0.7 gram atom of chlorine per mole (8). Bis(1,2-dichloroethyl) ether (boiling point at 27 mm. 108–14° C.,  $d_4^{20}$  1.451,  $n_D^{20}$  1.4886, total chlorine found 67.0%, hydrolyzable chlorine found 35.7%) was obtained in 54% yield. No published physical constants are available for this isomer. (Hydrolyzable chlorine refers to the  $\alpha$ -chlorine atoms which can be titrated in water-ethyl alcohol medium, 2 to 1 by volume, with standard sodium hydroxide to phenolphthalein end point.)

A rather crude pentachlorodiethyl ether boiling from 127° to 135° C. at 25 mm. of mercury pressure  $(n_{20}^{20} 1.5016)$ was obtained and a liquid octachlorodiethyl ether (pure symmetrical isomer is crystalline) was distilled from 95° to 105° C. at 0.5 mm. of mercury pressure  $(n_{20}^{20} 1.516)$ .

Above  $100^{\circ}$  C. 10 to 18% of the starting material was ruptured at the ether linkage. The two fragments were mono-, di-, or trichloroacetyl chlorides and a polychloroethane (five isomers

# Table I. Chlorinolysis and Cracking Ethers

	Reaction Number					Reaction Number									
	1	2	3	4	5	1	2	3	4	5	6	7	8	9	10
	Bis(2-chloroethyl) ether				Tetrachlorodiethyl ether										
Temp., ° C. [reactor-exit gas]	480 00	450- 395	450- 388	450 10	450- 05	300- 290	400- 332	400- 365	400 367	400- 367	450- 377	450- 366	450- 395	450 347	500- 457
Moles gas/mole ether							002	000					0.0	010	
Chlorine	6	0.5			• • •	0.5	2.1	0.6	0.4		None	0.6	0.6	• • •	0.5
Nitrogen			5.3	4.5	4.5			• • •	1.8	3.8	None		2.3	5.8	
Residence time, sec.	0.03	0.1	0.1	1.0	5.0	1.0	1.0	1.0	1.0	1.0	1.0	0.1	0.1	0.1	0.1
Recovered product, wt. %	111	98	96	96	80	103	85	90	86	77	68	100	84	87	64
Vinyl chloride		5		1	11		7	2	3	2	1	1	2	3	10
Mixed chlorohydrocarbons <sup>a</sup>	54	4	1		• • •	1	39	11	6	2	3	4	8	2	23
Acetyl chlorides + chloroacetal- dehyde	11	17	б	8	7	2	27	12	8	8	11	9	16	1	16
Vinyl 2-chloroethyl ether		4		1	7			13	17	19	19	17	16	19	
2-Chlorovinyl 1,2-dichloro <sup>b</sup>															
Unreacted ethyl ether	11	34	93	81	23	54	14	40	55	59	62	53	52	58	32
More highly chlorinated ethers						39	7	8	8	6	2	2	3	13	10
Distillation residue	22	36	• • •	9	52	4	6	14	3	4	2	4	3	4	9

<sup>a</sup> Typical distribution (wt. %): Vinylidene chloride, 6; methylene chloride, 5; *cis*-dichloroethylene, 5; chloroform, 53; trichloroethylene + trichloroethane, 32. <sup>b</sup> B.p., 3 mm., 49-54°,  $n_D^{20}$  1.4873. Total chlorine, found 59.7%, theory 60.5%.

from trichloroethane to hexachloroethane were found).

Chlorinolysis and Cracking. Dr-CHLORODIETHYL ETHER. The bis(2chloroethyl) ether reacted more completely under more severe conditions, but more high-boiling residues and products from the rupture of C-O and C-C bonds resulted (Table I). For thermal cracking with a 50-fold increase in reaction time, conversion increased 7 to 77%.

The highest recovered weight was 7%, of vinyl 2-chloroethyl ether and 11% of vinyl chloride. The distillation residue from run 5 was far more viscous than any with more highly chlorinated starting materials. This suggests polymerization of some products before they were cooled.

TRICHLORODIETHYL ETHER. Conversion of 1,2-dichloroethyl-2-chloroethyl ether to 2-chlorovinyl 2-chloroethyl ether (boiling point at 58° to 62°,  $n_{\rm D}^{20}$  1.4680, total chlorine found 52.7% at 450° C. with a 0.1-second residence time amounted to 11%.

Thermal cracking at  $450^{\circ}$  C. for 0.1 second resulted in 37% reaction, compared to 7% for the dichloroether. Furthermore, 57% of that reaction was dehydrochlorination to the 2-chlorovinyl 2-chloroethyl ether with lesser amounts of cleavage products and residues. Thus, cracking gives twice as much vinyl ether per pass as chlorinolysis and better chances for recycle of the 63% of unreacted starting material.

Tetrachlorodiethyl Ether. Chlorinolysis of bis(1,2-dichloroethyl) ether gave products of the best purity obtained in this study. Up to 19% of 2-chlorovinyl 1,2-dichloroethyl ether can be obtained per pass (Table I).

TEMPERATURE VARIABLE. When the reactor wall temperature was increased from 300° to 500° C., rupture products increased from 3 to 49%. The highest yield of vinyl chloride came from reaction at 500° C., but little unsaturated ether was formed.

Liquid phase dehydrochlorination was attempted by distillation of the tetrachlorodiethyl ether at atmospheric pressure. The temperature in the flask ranged from 210° to 230° C. with very little hydrogen chloride evolution noted. The ether linkage in this compound is stable for at least 0.5 hour at 200° C., at least 1 second at 300° C., and 0.1 second at close to 400° C. (No. 9). TIME VARIABLE. A tenfold increase

in residence time increased the amount of reaction, residues formed and rupture products.

CONCENTRATION OF CHLORINE. An increase from 0.6 to 2.1 moles of chlorine per mole of chloroether increased rupture threefold. Little vinyl ether was formed at the higher mole ratio, although over-all reaction increased somewhat.

CHLORINOLYSIS OR CRACKING. Cleavage at the ether linkage is twice as great in chlorinolysis as in cracking.

HIGHER CHLOROETHERS. Chlorinolysis and cracking were carried out on pentachlorodiethyl and octachlorodiethyl ethers at 450° C. and a 0.1second residence time. The infrared spectra (1) of the distilled products showed absorption peaks characteristic of unsaturated ethers, but the yields were much lower than for the other starting materials.

CRUDE HEPTACHLORODIETHYL ETHER. Conditions leading to as high as 98%rupture at the ether linkage are summarized in Table II. Contrary to other findings (2, 9), unsaturated chlorohydrocarbons were obtained, with acetyl chlorides.

Increasing residence times two- to threefold or temperatures from 425° to 475° C. had no marked effect on the products. Increasing the mole ratio of chlorine to chloroether from 0.5 to 3 increased the amount of tetrachloro-

ethylene relative to trichloroethylene; the amount of trichloroacetyl chloride also increased. A further increase in the mole ratio to 5 increased hexachloroethane formation. Cracking led to less reaction per pass than chlorinolysis. Recycle of the high-boiling residues resulted in more of the same products obtained by cleavage of the ether.

## Conclusions

High temperature chlorinolysis and cracking of chlorinated diethyl ethers is a new route to chlorinated vinyl ethers (3, 6); recovered weights of up to 21% are obtained.

Whereas former workers obtained mainly saturated haloethanes as fragments from C-O bond rupture, all six chloroethylenes were obtained in this work. Other rupture products included all three chloroacetyl chlorides and chloroacetaldehyde. C--C bond cleavage led to methylene chloride, chloroform, and carbon tetrachloride, but not phosgene.

#### **Literature Cited**

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#### Literature

chloroethers

Lit. Ref.

(10)

(4)

(2, 9)

(5)

(7)

(8)

via

Table II. Chlorinolysis and Cracking of Crude Heptachlorodiethyl Ether

	Reaction Number										
	1	2	3	4	5	6	7	8	9ª		
Temp., ° C. [reactor-exit gas]	475-	475-	475-	475-	475-	435-	425-	475-	475		
	20	30	23	23	35	390	389	06	30		
Moles gas/mole ether											
Chlorine	0.5	0.5	3.0	5.0	3.0	0.4	0.6		0.5		
Nitrogen		• • •						2			
Residence time, sec.	1	2	3.5	3.5	1	1	3.5	5	2		
Recovered product, wt. %	85	85	102	103	97	83	91	78	96		
Mixed chlorohydrocarbons <sup>b</sup>	10	13	6	5	8	7	8	5	15		
Trichloroethylene	19	18	6	1	5	20	16	16	5		
Mono- + dichloroacetyl chlo-											
rides	6	6	1	1	3	10	1	1	1		
Trichloroacetyl chloride	19	22	43	43	42	17	35	26	26		
Tetrachloroethylene	13	14	26	26	27	11	21	17	16		
Hexachloroethylene			16	22	13		5	7			
Distillation residue	330	27°	2	2	2	35°	14	34	38°		

<sup>a</sup> Recycling of residues from previous runs. <sup>b</sup> Includes C<sub>2</sub>Cl<sub>5</sub>, 25-50% of these residues. <sup>c</sup> Typical distribution (wt. %): methylene chloride 1.9; vinylidene chloride 4.1; trans-dichloroethylene 6.7; *cis*-dichloroethylene 5.9; chloroform 18.5; carbon tetrachloride 59.7; 1,2-dichloroethane 3.8.

Unsaturated

Williamson synthesis

sition of ethers

chloropentanes

ported this work.

Vinyl 2-chloroethyl ether from 2,2'dichlorodiethyl ether + NAOH Aldehydes and saturated hydro-

carbons from thermal decompo-

Alkyl halide + alcohol from normal ether cleavage with HX

Cyclization by chlorinolysis of

1,2,2'-Trichlorodiethyl ether from direct chlorination of 2,2'-di-