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ABSTRACT

The synthesis of the cis- and trans- isomers of 1,2 dichloroethylene oxides by the action of oxygen on cis- or trans-1,2 dichloroethylene is described. The cis-1,2 dichloroethylene oxide boils at 111 to 112°, and has a dipole moment of about 1.8, while the trans- isomer boils at 80 to 81° and has a dipole moment of 1.25. From the oxidation of trans-1,2 dichloroethylene, the dichloroethylene oxides are formed immediately if a radical source is present but an induction period occurs without added catalyst. Cis-1,2 dichloroethylene has been observed to react with oxygen to form dichloroethylene oxides only in the presence of a radical source. Evidence from the mass spectra and infrared spectra of the compounds are presented for proof of structure.

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INTRODUCTION

In a previous communication[1] the synthesis of cis- and trans- isomers of 1,2-dichloroethylene oxide (DCEO) by oxidation of cis- or trans-1,2-dichloroethylene (DCE) which had been previously irradiated with 40-Mev helium ions was described and some properties of these compounds were tabulated. It has now been found that radiation or other radical source is not essential to this reaction in the case of trans-DCE, but that reaction with oxygen at elevated temperature is sufficient.

A search of the usual sources revealed no previous report of the existence of 1,2-dichloroethylene oxides. The similar epoxides of tri- and tetrachloroethylenes have been suggested as reaction intermediates,[2,3] but have not been isolated. Müller and Ehrmann reported the photochemical oxidation of dichloroethylenes to yield HCl and resinous products.[4]

EXPERIMENTAL

Reagents

Eastman white label cis-1,2-dichloroethylene (cis-DCE) and yellow label trans- 1,2-dichloroethylene (trans-DCE) were distilled through an 85-plate adiabatic column. The pure products were collected within a 0.01° distillation range. The purified compounds were stored under nitrogen in a refrigerator at 0° until used. A polymer is slowly formed in purified trans-DCE in the presence

* Work done under the auspices of the U. S. Atomic Energy Commission

of oxygen and light, therefore it is important that the compound be stored in an inert atmosphere.[5]

Preparation of 1,2-Dichloroethylene Oxides at Room Temperature

Four 20-ml samples of purified trans-DCE were taken in 125-ml brown bottles fitted with polyethylene-lined screw caps. To these were added 0.0, 0.25, 1.0, and 5.0 g respectively of benzoyl peroxide. The 5.0-g sample exceeded saturation. The gas volume was replaced with oxygen by gentle flushing and the samples were allowed to stand at room temperature ($23\pm2^{\circ}$). Periodically, 1-ml samples were removed for gas chromatographic analysis and the oxygen was replenished. Trans-DCEO was produced at rates shown in Fig. 1. HCl and polymer were formed as products but were not measured.

In a second series of experiments, 50-ml samples of cis-DCE and trans-DCE were taken in 250-ml brown bottles and 1 g benzoyl peroxide added to each. One of the trans-DCE samples was blanketed with nitrogen and no DCEO was produced in 2 weeks' standing at room temperature, albeit copious amounts of both soluble and insoluble polymers were produced. The cis-DCE sample was blanketed with oxygen and produced DCEO at a rate about one-fifth as fast as the comparable sample of oxygen-blanketed trans-DCE.

Preparation of 1,2-Dichloroethylene Oxides at Elevated Temperatures

Some preliminary experiments at $50^{\circ}C$ with trans-DCE blanketed with oxygen and both with and without added benzoyl peroxide showed the rate of formation of DCEO to be 5 to 6 times the rate at room temperature. The induction period without added benzoyl peroxide was reduced from about 5 days at room temperature to about 20 hours at 50°. Figure 2 shows the growth of several products from 100 ml of pure trans-DCE blanketed with oxygen in a 1-liter bottle. Periodically the bottle was cooled, the liquid was sampled, and the oxygen was replenished by gentle flushing. These samples were analyzed by gas chromatography. The compound labeled butene peroxide in Fig. 2 could not be further identified by mass spectrometry other than that it contained two oxygen atoms on a tetrachlorobutene skeleton.

A comparable sample of cis-DCE blanketed with oxygen but without added catalyst showed no production of DCEO in one month at 50°.

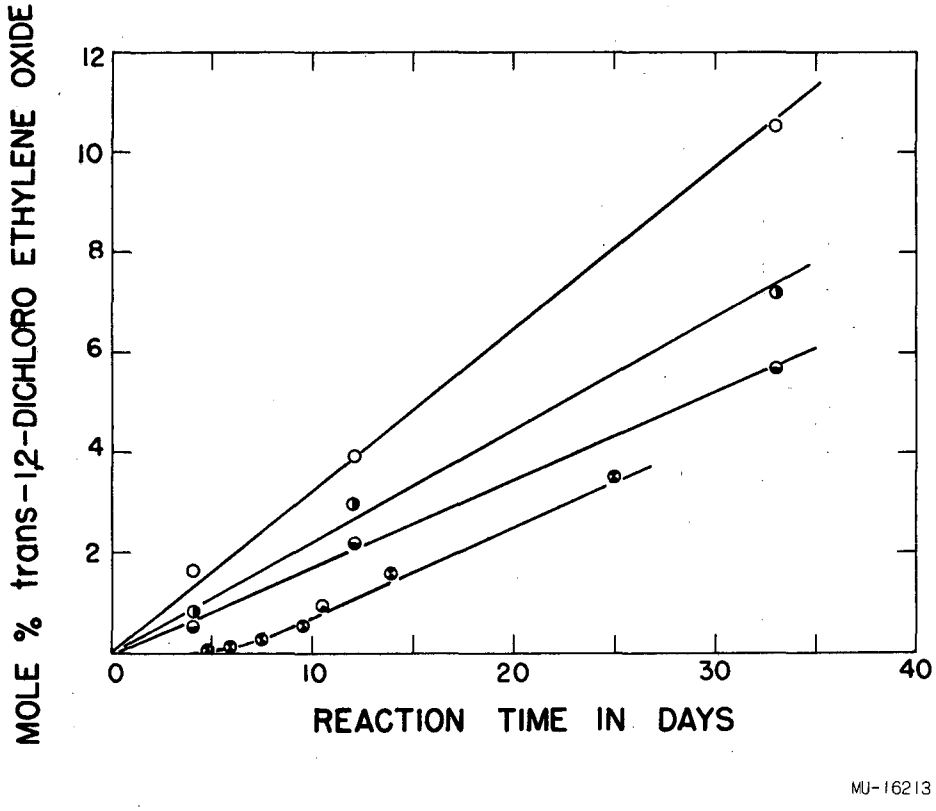

Fig.1 Buildup of trans-1,2-dichloroethylene oxide in trans-1,2-dichloroethylene at room temperature at various concentrations of benzoyl peroxide.

○ 5 g benzoyl peroxide in 20 ml trans-DCE.

◐ 1 g benzoyl peroxide in 20 ml trans-DCE.

⊖ 0.25 g benzoyl peroxide in 20 ml trans-DCE.

⊗ pure trans-DCE.

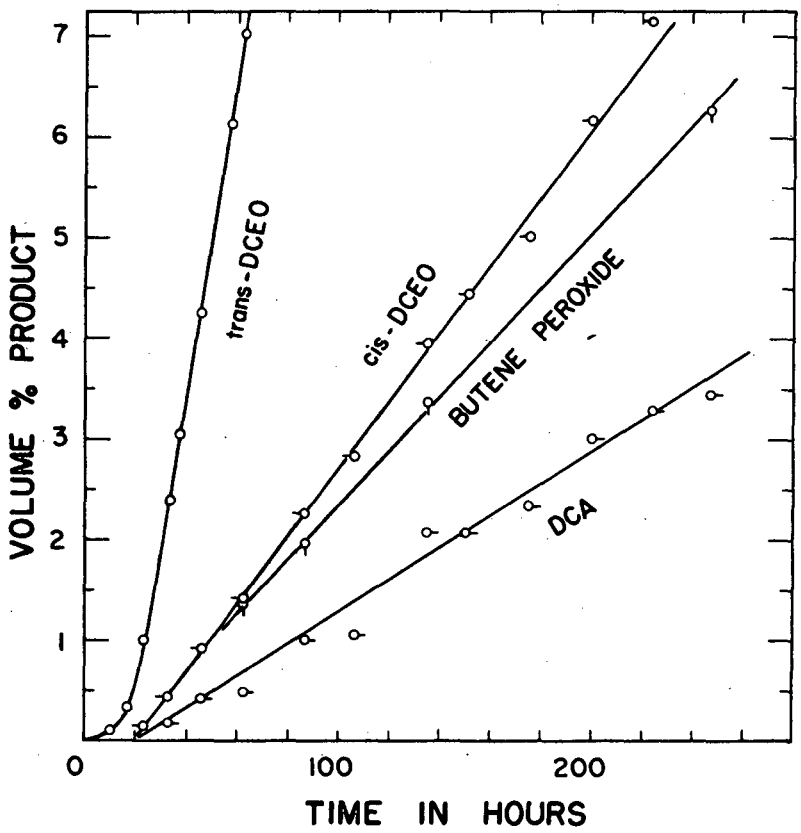

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Fig. 2 Growth of products formed in oxidation of trans-1,2-dichloroethylene at 50°C and 1 atmos O_2 pressure.

- ○ trans-1,2-dichloroethylene oxide (trans-DCEO).
- -○ cis-1,2-dichloroethylene oxide (cis-DCEO).
- ○- dichloroacetaldehyde (DCA).
- ○ Probably a butene peroxide, identification uncertain.

Oxygen Bubbling Experiments

An attempt at production of larger quantities of DCEO by bubbling oxygen through samples of boiling cis- and trans-DCE containing 5 g benzoyl peroxide per 100 ml was only partially successful. The reagents were contained in a 1-liter three-necked flask, the necks containing respectively a thermometer, an oxygen inlet tube, and a Dewar type condenser. The condenser was cooled with dry ice in the cis-DCE setup, while in the trans-DCE setup the condenser was kept near -50° by a controlled heat leak to a liquid nitrogen reservoir. This higher condenser temperature was necessary to prevent plugging, as the freezing point of trans-DCE is only -49.8°.[6]

The trans-DCE was allowed to react 3 days, during which time there was a continuous buildup of DCEO and polymer and the pot temperature rose from 48° to 55°. After shutdown, the volatile liquids were separated from the polymer by vacuum evaporation in a 2-liter rotating evaporator. From 400 ml (500 g) of trans-DCE, the yield of polymer, a waxy semisolid material, was 165 g, the volatile material recovery was 175 g which analyzed (by gas chromatography) 17.4% trans-DCEO, 4.2% cis-DCEO, 0.35% dichloroacetaldehyde, 10.3% cis-DCE, 46.8% trans-DCE, and 21% mixed higher-boiling materials. There was a net loss of some 160 g of material, presumably by evolution of HCl gas, and evaporation of solvent with the excess oxygen through the condenser.

The cis-DCE was allowed to react for 6 days, during which time the pot temperature rose from 60° to 70°. From 200 ml of cis-DCE the yields of products were 8.1 ml trans-DCEO, the 3.6 ml cis-DCEO, 0.5 ml dichloroacetaldehyde, and 142 ml high-boiling liquid products which were mainly isomers of tetrachlorobutene.

The DCEO fractions were isolated from the vacuum-evaporated fractions of these runs by careful distillation through a small Vigreaux column, collecting fractions in the boiling ranges 79 to 81° and 110 to 112°. Ten ml of ethylbenzene was added as a chaser to prevent decomposition of the pot residues in collecting the 110-to-112° fractions. The products collected in this manner were about 95% trans-DCEO and 85% cis-DCEO respectively. These fractions were further purified by running 0.1-ml batches on a nonyl phthalate-firebrick gas chromatographic column and collecting the respective DCEO peaks in cold traps. The trans-DCEO prepared in this manner is contaminated with small amounts

(< 1%) of benzene probably arising from a side reaction of the benzoyl peroxide. Benzene is not separated by these techniques. The gas chromatrographic separation must be made at the lowest practicable temperature, as there is some isomerization of the epoxides to dichloroacetaldehyde and chloroacetylchloride in the column. This is most serious with the cis-DCEO, in which case both these products move ahead of the cis-DCEO, forming a plateau extending from the emergence time of the isomer to that of the cis-DCEO. The tails of these plateaus are always collected with the product, resulting in some contamination.

Higher-Pressure Synthesis

To study the effect of pressure on the rate of the reaction, a series of experiments was run at 50° in glass bulbs sealed with 4-mm pressure stopcocks lubricated with graphited Silicone grease. Most of these bulbs leaked, but the lower-pressure runs which showed no evidence of leakage indicated the initial rate of formation of DCEO from trans-DCE to be proportional to the square root of the oxygen pressure.

An experiment in which trans-DCE was placed under oxygen at 50 psig in a stainless steel tank heated to 50°C and agitated by rocking resulted in the production of only dichloroacetaldehyde. There was considerable attack of the stainless steel, as evidenced by the resulting green solution. The metal or metal ions present completely isomerized any DCEO formed.

An all-glass-and-Teflon apparatus was made from a 30-inch length of 4-inch industrial glass pipe, sealed at one end and fitted with a 1-inch industrial glass pipe flange at the other. This was sealed with a Teflon gasket and valve system as shown in Fig.3. The system was evacuated and filled with oxygen, then the Teflon plug was removed and 250 ml (313 g) of puified trans-DCE added through a narrow-necked funnel. The plug was replaced but not tightened and 35 psig oxygen (0.87 mole total) was added through the needle valve, a, and the plug then tightened. The bomb was heated at 60° in a rocking heater for 43 hours. The system was cooled to room temperature, then the bottom quarter of the bomb was cooled in dry ice for one-half hour, and the gases - excess oxygen and HCl - were vented through the needle valve. The liquid products were removed, separated by distillation, and analyzed by gas chromatrography as previously described. Yields: waxy polymer, 43 g; total volatile liquid, 236 g (170 ml); trans-DCEO, 24.6 ml; cis-DCEO, 5.5 ml; dichloroacetaldehyde, 2.5 ml;

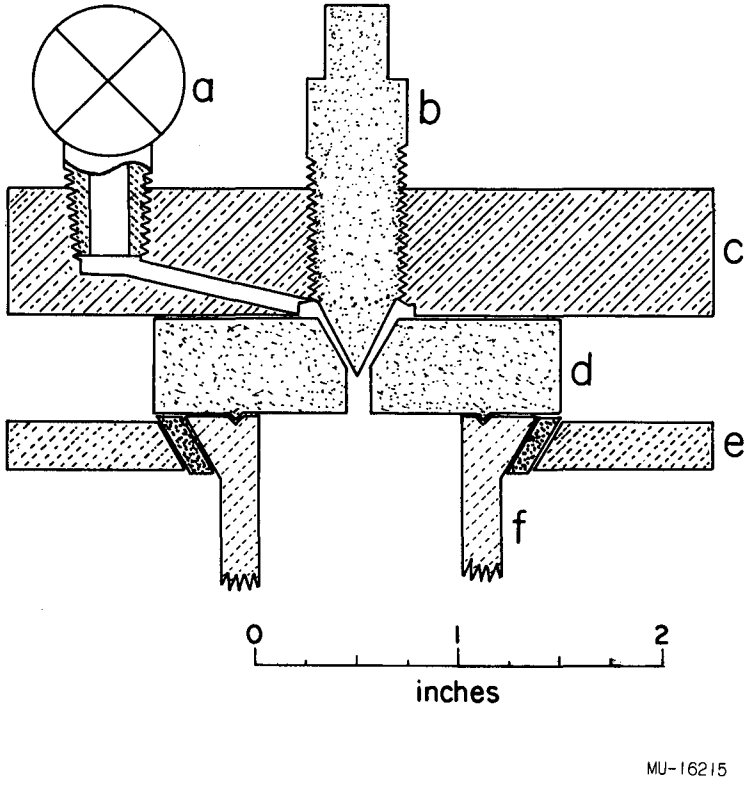

Fig.3 Valve and closure for all-glass-and-Teflon bomb for production of dichloroethylene oxides.

(a) Brass or stainless steel needle valve.

(b) Teflon needle, 1/2-inch Teflon rod, 1/2-20 threads, squared top, 55° point.

(c) 5/8-inch brass plate.

(d) 1/2-inch Teflon sheet, 60° taper valve seat.

(e) Metal flange and spacer for 1-inch glass pipe. Clamping bolts to Plate are not shown.

(f) Flanged 1-inch glass pipe opening on 30-inch bomb of 4-inch industrial glass pipe.

cis-DCE, 3.4 ml; and trans-DCE, 134 ml. The combined yield of DCEO isomers was 43 g (0.38 mole) or 44% based on added oxygen, assuming 1 mole of DCEO to be formed per mole of added oxygen.

A repeat run of this experiment using 50 psig oxygen pressure resulted in destruction of the apparatus after 3 days' operation at 60°. The cause of the mild explosion was not determined.

Gas-Phase Oxidation of Trans-DCE

A slow stream of oxygen gas was bubbled through trans-DCE at 0°C. It was then passed through a 1-inch-diameter tube about 24 inches long heated in a tube furnace. The section of tube inside the furnace was packed with glass beads. Condensable materials were collected in a dry ice trap at the exit end of the tube. At temperatures up to 200°, no reaction was observed. At 300°, the trans-DCE was isomerized to a mixture of 60% cis-DCE and 40% trans-DCE, the thermal equilibrium composition at this temperature as reported by Olson and Maroney.[7] At the same time 0.3% DCEO and 0.2% dichloroacetaldehyde were formed. At 400°, the trans-DCE was again isomerized, and other products formed in small amounts were dichloroacetaldehyde, chloroacetylchloride, and acetaldehyde. No DCEO was observed at 400°.

Irradiation of Cis-DCE in Oxygen Atmosphere

As cis-DCE did not react in the absence of a catalyst, 100 ml of cis-DCE to which was added two millimoles of oxygen gas was irradiated with 42.5-Mev helium ions. A small yield of DCEO was present at the end of the irradiation, and these were augmented by further growth in an atmosphere of air. Three months after irradiation 1 millimole of trans-DCEO and 1.4 millimoles of cis-DCEO were present.

Determination of Dielectric Constants and Dipole Moments

Approximate values of the dielectric constants for the two isomers of DCEO were determined by measuring the increase in capacitance of a small cell when filled with the respective compounds. The cell was constructed of 10-mil gold foils clamped tightly to a 1.5-mm Teflon sheet separator in which a 14-mm-

diameter hole was cut. A 1-mm-wide outlet at the top of the cell was provided for filling with a syringe. The volume of the cell was about 0.15 ml. The change in capacitance of the cell on filling with liquid was measured with a Tektronix Type 130 LC meter.[8] An empirical plot of capacitance vs. ϵ for several liquids of known dielectric constant gave a linear plot extrapolating to $\epsilon = 1$ at zero capacitance (empty cell). Measurements of the low- and high-boiling forms of DCEO gave values of $\epsilon = 3.95$ for the isomer boiling at 80° and $\epsilon = 8.7$ for the isomer boiling at 111°. As the sample of high-boiling isomer used in this measurement contained about 10% ethyl benzene, the value found represents a minimum value for this isomer.

The Onsager equation may be used to calculate an approximate dipole moment[9] by using the above determined values of the dielectric constant and previously measure values of the density and refractive index. This gave values of 1.25 and 1.8 for the low- and high-boiling isomers of DCEO respectively. The physical properties of cis- and trans-DCEO are tabulated in Table I.

Table I

Physical properties of dichloroethylene oxides

	trans- form	cis- form
b.p.	$80 - 81^{\circ}$	$111 - 112^{\circ}$
m.p.	-43°	-63°
$D^{25/4}$	1.405	1.470
n_D^{25}	1.438	1.452
ϵ	3.95	8.7
μ (Debye units)	1.25	1.8

DISCUSSION

The chemical identities of these compounds have been determined from the mass spectrometer ionization patterns as measured with a Consolidated Electrodynamics Corporation Model 21-103 mass spectrometer and from the infrared absorption spectra as measured with a Perkin-Elmer Model 21 spectrophotometer. The principal peaks in the mass spectra of the two compounds are listed in Table II. The relative abundances of the peaks in the mass groups 112, 114, and 116 are characteristic of a compound containing two chlorine atoms. The lack of a peak at mass 111 shows that hydrogen fragmentation from the ion at mass 112 does not occur. Therefore mass 113 must be the carbon isotope peak of mass 112. The ratio of peaks at masses 112 and 113 shows the presence of two carbon atoms in the molecule, hence the empirical formula must be $C_2H_2Cl_2O$. Comparison of the observed peak heights for the two compounds at masses 112 to 117 with the calculated peak heights using normal isotope abundances for C, H, Cl, and O shows the composition to be fixed beyond question. In addition, the molecular weight of the low-boiling isomer from the freezing-point depression in benzene was 115.6, while the values found by expansion of known volumes of liquid into the mass spectrometer inlet volume and measurement of the pressure produced (micromanometer) were 113.1 and 115.2 for the low- and high-boiling isomers respectively. (Theory for $C_2H_2Cl_2O$ = 112.95). Therefore the peaks at masses 112 to 116 are the parent mass group. Microanalyses of the purified compounds confirm this composition.[1]

Table II

Principal peaks in the mass spectra of the cis- and trans- 1,2-dichloroethylene oxides[a,b]

m/q	Ion group[c]	Pattern	
		Cis-DCEO	Trans-DCEO
12	C^+	5.58	7.50
13	CH^+	12.71	15.62
14	CH_2^+	9.70	9.12
16	O^+	1.31	1.44
24	C_2^+	1.32	1.74
25	C_2H^+	4.18	5.57
26	$C_2H_2^+$	5.84	7.59
28	CO^+	3.42	4.57
29	CHO^+	58.22	67.12
35	Cl^+	16.24	15.17
36	HCl^+	3.77	5.72
37		5.32	5.12
38		1.25	1.92
40	C_2O^+	0.50	0.65
41	C_2HO^+	1.91	2.71
42	$C_2H_2O^+$	1.17	3.33
47	CCl^+	12.14	16.02
48	$CHCl^+$	100.00	100.00
49	CH_2Cl^+	60.03	97.12
50		32.68	32.95
51		18.15	29.68
59	C_2Cl^+	0.32	0.56
60	C_2HCl^+	1.41	2.19
61	$C_2H_2Cl^+$	1.48	1.52
62		0.53	0.71
63	$COCl^+$	2.89	2.83
65		0.92	0.89

Table II (cont'd)

m/q	Ion group[c]	Pattern	
		Cis-DCEO	Trans-DCEO
70	Cl_2^+	0.65	0.05
72		0.42	0.03
74		0.07	0.01
76	C_2HOCl^+	2.01	2.61
77	$C_2H_2OCl^+$	1.40	2.94
78		0.69	0.92
79		0.45	0.96
82	CCl_2^+	0.12	0.08
83	$CHCl_2^+$	7.09	6.58
84	$CH_2Cl_2^+$	5.46	6.75
85		4.60	4.26
86		3.42	4.35
87		0.77	0.72
88		0.55	0.69
112	$C_2H_2Cl_2O^+$	7.04	8.38
113		0.16	0.19
114		4.52	5.38
115		0.10	0.12
116		0.74	0.87
117		0.02	0.01
Sensitivity (div/u) at m/q = 48		30.1	24.6

a. n-butane, m/q 43 = 100.0, 58 = 12.6, 39 = 18.3, 29 = 42.5, 27 = 44.1, 15 = 10.8; sens, 43 = 69.9 div/u

b. Peaks of carbon and oxygen isotopes not generally shown.

c. Ion identification at mass containing Cl^{35} isotope. Some overlapping occurs with ion containing Cl^{37} isotope.

Known compounds of empirical formula $C_2H_2Cl_2O$ are dichloroacetaldehyde and chloroacetylchloride. Mass spectrometer fragmentation patterns and gas chromotography retention times for authentic samples of these compounds differ significantly from those of the substances produced in this work. Therefore, the structures of cis- and trans-1,2-dichloroethylene oxide have been assigned the two compounds produced here. The structure 1,1-dichloroethylene oxide was not eliminated unambiguously from consideration of infrared and mass spectra, but this compound is almost certainly unstable with respect to isomerization to dichloroacetaldehyde, and the chemical structure of the starting DCE makes the formation of this latter compound unlikely.

The mass peaks at m/q 82 to 88 are not consistent with the 1,2-dichloroethylene oxide structure unless both hydrogen and chlorine rearrangements occur. These peaks arise from the CCl_2^+, $CHCl_2^+$, and $CH_2Cl_2^+$ ions with their respective chlorine and carbon isotope peaks. In the mass spectrum of chloroacetylchloride, where the chlorine atoms are on neighboring carbon atoms, the ion $CH_2Cl_2^+$ at mass 84 occurs to the extent of 1.6% of the base peak, showing that combined hydrogen and chlorine rearrangements occur. In dichloroacetaldehyde, the peak at mass 84 is 46% of the base peak, showing a large hydrogen rearrangement. In the acetyl chloride mass spectrum, $CHCl^+$ and CH_2Cl^+ are 1.7 and 1.5% respectively of the base peak. In these cases, as with the $CH_2Cl_2^+$ peak from DCEO, the rearrangement occurs (with further fragmentation in acetylchloride) to leave a neutral carbon monoxide molecule. Rearrangements promoted by the stability of the residual carbon monoxide have been observed before. King and Long have discussed such hydrogen rearrangements in the formate esters.[10] Therefore, such a rearrangement in DCEO is not inconsistent with the postulated structure. The agreement between the two DECO spectra in the mass group 82 to 88 further suggests that they are closely related compounds rather than compounds differing radically in structure.

The infrared spectra of the two compounds are in agreement with the conclusion that they are isomeric forms of 1,2-dichloroethylene oxide. Spectra of the two compounds were compared to spectra of the cis- and trans-isomers of 2,3 epoxybutane. All four compounds show the band at 2950 to 3050 cm^{-1} which Henbest and co-workers have suggested is characteristic of the CH band of the substituted oxirane ring.[11] Further they all have bands in the three regions where Patterson and others have assigned the $C\overset{O}{\diagup\diagdown}C$ skeletal motions.[12] For the

epoxybutanes these are 770, 882, and 1276 cm^{-1}; and 810, 885, and 1258 cm^{-1} for the cis- and trans- isomers respectively. The low-boiling isomer of DCEO has analoguous bands at 775, 917, and 1265 cm^{-1} and the high-boiling isomer at 775, 920, and 1251 cm^{-1}. The low-boiling isomer has no band in the region 1400 to 1500 cm^{-1} where CH_2 absorption would appear. The high-boiling isomer showed a very weak band in this region which may, at least in part, be ascribed to impurities. Small amounts of dichloroacetaldehyde and chloroacetylchloride were present in the infrared sample.

Dipole Moments

The relative values of the dipole moments, approximately 1.25 Debye units for the low-boiling compound and 1.8 for the high-boiling compound, are consistent with the assignment of the trans- configuration to the low-boiling compound and cis- configuration to the high-boiling compound. Without specific structural information on the two compounds it appears superfluous to attempt a closer justification of the specific values of the moments found. The structural assignments of the identity of the trans- compound with the lower-boiling isomer and the cis- with the higher-boiling isomer is supported by chemical evidence. The ratio of low-boiling to high-boiling compounds produced from trans-DCE is 4.6, but this ratio is only 2.2 from cis-DCE with added benzoyl peroxide and is less than 1 from cis-DCE irradiated under oxygen. Further evidence corroborating this assignment is given from the mass spectra of these compounds. Cl_2^+ ion in the mass spectrum of the cis- isomer is 0.28% of the total peaks in the spectrum while it is only 0.02% in the mass spectrum of the trans- isomer. A comparison of the cis- and trans-DCE mass spectra shows the cis-DCE to have a Cl_2^+ ion contribution of 0.35% of the total peak height, while trans-DCE shows a Cl_2^+ ion contribution of only 0.01% of the total peaks. A similar correlation is found in the ratio of Cl^+ to HCl^+ ions in the two types of compounds. Both trans-DCE and trans-DCEO yield relatively more HCl^+ than do the corresponding cis- isomers of these compounds.[13]

Mechanisms

Examples of auto-oxidations in chlorinated hydrocarbon systems are well known. Walling has discussed these and postulated a mechanism for the formation of polychloroacetylchlorides from the auto-oxidation of trichloroethylene and tetrachloroethylene.[14] This mechanism may be modified slightly to include

epoxide formation as an intermediate step. A similar set of reactions can be postulated for the oxidation of the 1,2-dichloroethylenes, but the unusual result is the formation of epoxides rather than the more stable compounds chloroacetylchloride or dichloroacetaldehyde. An alternate mechanism for the formation of epoxy compounds from ethylenic compounds is the decompostion of radicals of the type

$$ROOCHClCHCl \longrightarrow RO\cdot + HClC\overset{O}{\triangle}CHCl;$$

as discussed by Walling[15] for the analogous formation of styrene peroxide. This mechanism leaves the fate of the RO· radical unexplained. Additional information on the kinetics of the reactions is necessary for a more definite formulation of the mechanism.

The kinetics are complicated by the production of polymer as a competing process to epoxide formation. Preliminary evidence from the experiments described here shows polymer formation to proceed in the absence of oxygen if radicals are present, and with greater availability of oxygen there is correspondingly less polymer formed. HCl is also a by-product of both epoxide formation and polymer formation and its sources have not been investigated.

The role of oxygen has also not been completely defined. Its action in the oxidation of trans-DCE depends on the presence of radicals, as was shown by immediate formation of epoxide when a radical source was added and the existence of an induction period when no radicals were initially present. An experiment to study the dependence of rate of oxygen pressure indicated the initial rate to be proportional to $(O_2)^{1/2}$, but this dependence is not firmly established because of experimental difficulties. The dependence found may represent the pressure dependence of the induction period and not the rate of the reaction proper.

In conclusion, the known factors in the synthesis of dichloroethylene oxides may be summarized as follows. Both cis- and trans-DCE are oxidized with oxygen to DCEO in the presence of radicals either from an added radical source or from previous irradiation with ionizing radiations. Pure trans-DCE in the presence of oxygen produces DCEO after an induction period. Both the rate of formation of DCEO from trans-DCE and the induction period are temperature-dependent, and a temperature increase of 25° decreases the induction period and increases the rate of formation by a factor of about 5. In the absence of

added radicals, cis-DCE does not react with oxygen to form DCEO. Both cis- and trans-DCEO are produced from either isomer of DCE, but the ratio of cis- to trans-DCEO is higher from cis-DCE than from trans-DCE. The conversion of DCEO to the more stable dichloroacetaldehyde and chloroacetylchloride is promoted by heat and catalyzed by metals or metal ions from stainless steel.

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