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CIS- AND TRANS-ISOMERS OF 1,2-DICHLOROETHYLENE OXIDE

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THE RADIOLYTIC SYNTHESIS OF THE
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June 1958

Among the suggested means of utilization of radioactive wastes from atomic energy plants is the synthesis of new compounds which cannot be made efficiently by ordinary chemical methods. An example of such a synthesis is the radiolytic preparation of heptadecene-8 described by Burton and Breger.¹ In the course of some investigations on the radiation chemistry of the symmetrical dichloroethylenes, the cis and trans forms of 1,2-dichloroethylene oxide have been produced. These compounds have not been previously reported, and in view of the current interest in radiation utilization, we are presenting preliminary data on the radiolytic synthesis and physical properties of these compounds.

The cis and trans forms of 1,2-dichloroethylene were irradiated in glass cells² in vacuo with 40-Mev helium ions impinging on the liquid. After irradiation, the low-boiling and gaseous products were separated by vacuum techniques.³ The residual high-boiling products plus the bulk of the 1,2-dichloroethylene were stored in glass-stoppered bottles in the presence of air after preliminary analysis for high-boiling products. In samples that had stood several months, two peaks were found in GLP chromatograms (nonyl phthalate column) that were not present in samples chromatographed immediately after irradiation. These peaks were concentrated in the pot liquid by distillation through a small Vigreux column and were further concentrated and purified by running repeated GLP chromatograms of the pot liquid, collecting the respective peaks each time. By this means samples of 1 gm and 0.2 gm of the two respective peak materials were isolated in relatively pure form. These were further purified by use of a Silicone oil (G.E. 96-40) column with collection of the respective components. These are referred to as dichloroethylene

oxide I and dichloroethylene oxide II according to their respective GLP chromatographic emergence times.

The relative yields of oxide I to oxide II from trans 1,2-dichloroethylene was about 4.6 : 1. The ratio from irradiated cis 1,2-dichloroethylene was smaller but has not been well determined because of the much lower yield from this isomer.

The compounds isolated have been characterized as the cis and trans isomers of 1,2-dichloroethylene oxide by mass-spectrometer spectral patterns and by comparison of the infrared spectra with the spectra of the cis and trans forms of 2,3-epoxybutane. All the compounds have the CH band in the region 2950 to 3050 wave numbers which Henbest, Meakins, Nicholls, and Taylor have suggested as being characteristic of the substituted oxirane ring,⁴ and all exhibit bands in the three regions where Patterson⁵ and others have assigned the $\text{C} \begin{array}{l} \diagup \text{O} \diagdown \\ \text{---} \end{array} \text{C}$ skeletal motions.⁵ The mass spectra, with parent masses at 112 to 117 mass units, give the empirical formula $\text{C}_2\text{H}_2\text{Cl}_2\text{O}$ from isotope ratio arguments. Chemical analysis for C, H, and Cl yielded 21.2%, 1.97%, and 63.5% for oxide I; and 21.2%, 1.92%, and 63.6% for oxide II. The calculated values for $\text{C}_2\text{H}_2\text{Cl}_2\text{O}$ are 21.27%, 1.78%, and 62.78%.

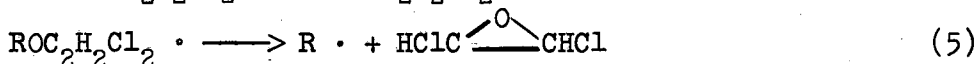
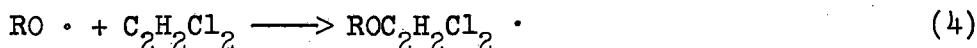
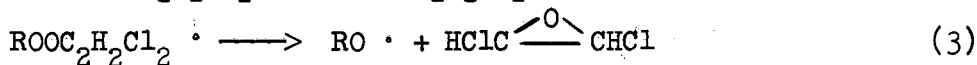
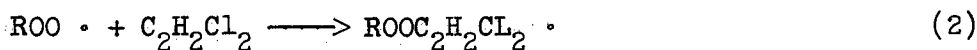
Known compounds of this composition, dichloroacetaldehyde and chloroacetylchloride, were shown to differ from oxide I and oxide II in both mass spectrometer ionization patterns and GLP chromatographic retention times.

Some physical properties of these two compounds are listed in Table I. It has not been possible to decide unequivocally which compound is the cis form and which is the trans form. An argument can be made from the comparison of the infrared spectra of oxides I and II with the spectra of the 2,3-epoxybutanes that oxide I is the cis form and oxide II the trans form.

Table I

Physical properties of 1,2-dichloroethylene oxides		
	Compound I	Compound II
boiling point	80-81°	111-112°
melting point	-43°	-63°
$D_{25/4}$	1.405	1.470
n_D^{25}	1.438	1.452
M.W. (cryoscopic)	115.6	
M.W. (M.S. inlet pressure)	113.2	115.2

At present one can only speculate as to the origin of these compounds. Yields of oxide I as high as $G = 9$ were found in old samples of irradiated trans 1,2-dichloroethylene. As this is as large as the total yield of "polymer" determined immediately after irradiation, a chain reaction for the formation of the oxides is indicated. An attractive possibility is an auto-oxidation reaction⁶ using a long-lived free radical present in very low concentration as the intermediate.



Preliminary tests with other sources of radicals (benzoyl peroxide) in the presence of oxygen showed that small yields of both the dichloroethylene oxides are formed from both cis- and trans-1,2-dichloroethylenes.

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