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Preparation and Properties of Tetrachloroethylene Oxide

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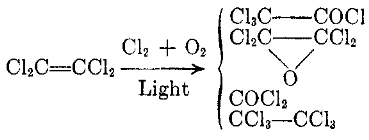
The photochemical oxidation of tetrachloroethylene has been studied by several previous investigators.[1–8] The primary object of these workers was the preparation of trichloroacetyl chloride, with only one making reference to tetrachloroethylene oxide as a byproduct.[5,6]

In the present study, tetrachloroethylene, kept saturated with oxygen and with an excess of chlorine added, was exposed to sunlight at 36–40°. Under these conditions the following products were obtained: trichloroacetyl chloride, tetrachloroethylene oxide, phosgene, and hexachloroethane.

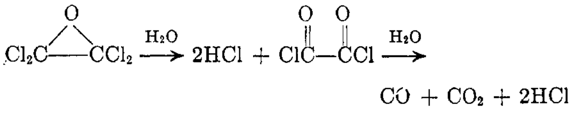


After most of the phosgene was removed, under vacuum, at room temperature, analysis of the liquor was 40 mole per cent trichloroacetyl chloride, 9 mole per cent tetrachloroethylene oxide, 8 mole per cent hexachloroethane, and 43 mole per cent tetrachloroethylene.

Vacuum distillation through a helices-packed, five-foot, distillation column gave a solution whose analysis showed it to contain 40 mole per cent trichloroacetyl chloride, 54 mole per cent tetrachloroethylene oxide, and 6 mole per cent tetrachloroethylene. Trichloroacetyl chloride was removed from this solution by washing with dilute alkali. The tetrachloroethylene was converted, by addition of chlorine, to hexachloroethane, then the solution vacuum distilled through a short, center rod column. A trace of trichloroacetyl chloride was removed with a dilute alkali wash, then the purified tetrachloroethylene oxide dried with calcium chloride. The infrared spectrum (Fig. 1) shows that the material is free from trichloroacetyl chloride, tetrachloroethylene, and hexachloroethane. The photochemical oxidation was repeated at −3–0°, 60–75°, and at 80°. The highest yield of tetrachloroethylene oxide was obtained at 60–75°.

Tetrachloroethylene oxide rearranges to trichloroacetyl chloride upon heating. The specific reaction rates for this conversion at 65°, 80°, and 100° are 6×10^{-7}, 8.9×10^{-6}, and 1.2×10^{-4} $sec.^{-1}$, respectively. The energy of activation is approximately 31.4 kcal./mole.

Tetrachloroethylene oxide reacts readily with methanol in the presence of mercuric chloride, evolving hydrogen chloride and forming methyl trichloroacetate. It reacts rapidly with *N* potassium hydroxide in methanol to give potassium oxalate as the major product. When stirred with either dilute basic or acidic aqueous solutions, the epoxide very slowly partially rearranges to its isomer and partially decomposes to give carbon monoxide, carbon dioxide, and hydrogen chloride. The latter reaction probably forms oxalyl chloride as an intermediate, which then hydrolyses to carbon monoxide, carbon dioxide, and hydrogen chloride.[9] In concentrated



sulfuric acid, however, tetrachloroethylene oxide undergoes rapid and exothermic rearrangement to trichloroacetyl chloride.

EXPERIMENTAL[10]

Photochemical oxidation of tetrachloroethylene. The reactor was made from two sections of borosilicate glass pipe, 2 ft. long by 3 in. diameter, joined together at both ends by 3 in. pipe. The lower section contained a cold finger, while a plane-parabolic mirror of 8 sq. ft. was focused on the upper section. The reactor was charged with 3 gal. of commercial grade (Stauffer) tetrachloroethylene, excess oxygen and chlorine were added, and the solution was agitated and exposed to sunlight for 12 hr. The temperature was controlled at 36–40°. Phosgene was removed by aspiration. Infrared analysis of the solution showed: 40% CCl_3COCl, 9% $(CCl_2)_2O$, 43% C_2Cl_4, 8% C_2Cl_6 (mole %).

Separation of tetrachloroethylene oxide. The solution was distilled through a 5-ft., vacuum-jacketed distilling column of 1-in. diameter, packed with 1/8 inch borosilicate glass helices. Using a reflux/take-off ratio of 30/1, 310 ml., boiling 32–36.3° (45 mm.–38 mm.), was collected in 23 hr. Infrared analysis of the distillate showed: 40% CCl_3COCl, 54% $(CCl_2)_2O$, 6% C_2Cl_4 (mole %).

Trichloroacetyl chloride was removed by washing with dilute aqueous alkali. Tetrachloroethylene was chlorinated

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(10) Infrared analyses were made on a Perkin-Elmer Model 21 Spectrophotometer.

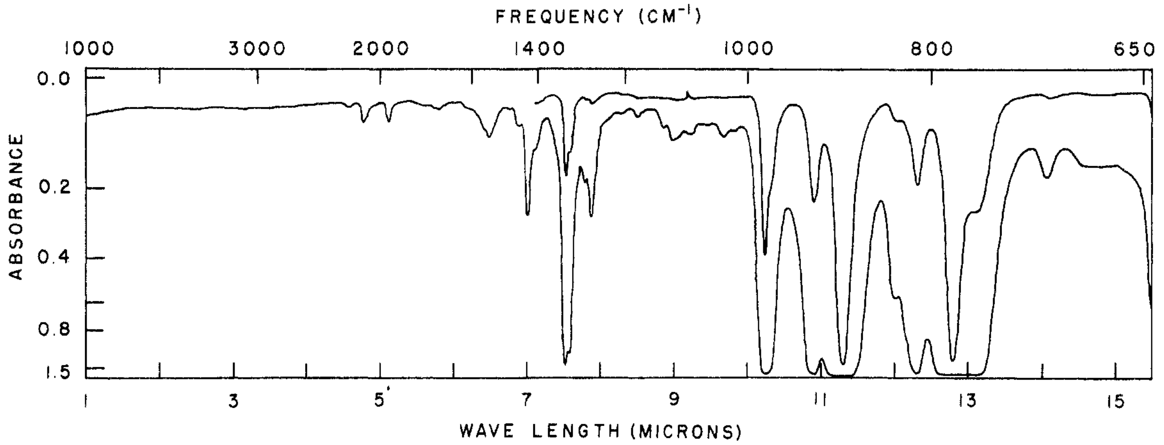

FIG. 1. INFRARED SPECTRA OF TETRACHLOROETHYLENE OXIDE; Determined on the pure liquid in a 0.0273 mm. cell; and a 2.5% carbon disulfide solution in a 0.109 mm. cell (10–14 microns).

to hexachloroethane by addition of chlorine and exposure to sunlight. This solution was distilled through an 18-in., modified center-rod column at 40° (65 mm.). A trace of trichloroacetyl chloride was removed with a caustic-water wash and the material was dried with calcium chloride. One hundred ml. of purified tetrachloroethylene oxide was recovered, n_D^{25} 1.4588, d_4^{25} 1.63, b.p. *ca.* 110° (1 atm.), f.p. −58° to −59° (corr.). Molecular weight, by freezing point depression of benzene, was 189 (theoretical 182). Boiling point data are in Table I.

Anal. Calcd. for C_2Cl_4O: Cl, 78.0%. Found 77.5%.

TABLE I

BOILING POINT DATA OF TETRACHLOROETHYLENE OXIDE

Pressure, Mm.	Temperature, ° C.
50	35.2
100	50.8
150	60.3
200	68.5
250	74.5
760 (Extrapolated)	109

Oxidation of tetrachloroethylene at various temperatures. Chlorine and oxygen were continuously passed through 35–40 ml. tetrachloroethylene in a 50–60 ml. glass bulb with the solution exposed to sunlight. Temperature was controlled externally. The results are given in Table II.

TABLE II

OXIDATION OF TETRACHLOROETHYLENE AT VARIOUS TEMPERATURES

Temperature, ° C.	Reaction Time (Min.)	$(CCl_2)_2O$, Vol. %	CCl_3COCl, Vol. %
−3–0	30	Trace	7
60–75	30	5	16
80	25	6^a	20^a

(a) Results are analyses of filtrate after the solution was cooled and filtered to remove excess hexachloroethane. Filtrate contained 21% C_2Cl_6.

Thermal rearrangement. Tubes containing the epoxide were immersed in boiling baths of methanol (65°), benzene (80°), and water (100°). The solutions were analyzed by infrared at 1-hr. intervals.

Reactions. A. Tetrachloroethylene oxide (9×10^{-4} mole) was stirred with 1*N* sodium hydroxide solution. A gas slowly evolved (5×10^{-4} mole) which was identified by infrared analysis to be carbon monoxide. The solution was extracted with carbon disulfide and tests for chloride and trichloroacetate on the extract were positive.[11]

B. Tetrachloroethylene oxide (9×10^{-3} mole) was stirred with 12*N* sulfuric acid, evolving a gas (3.5×10^{-3} mole) whose infrared analysis showed it to contain carbon monoxide and carbon dioxide. The acid solution contained 1.45×10^{-2} equivalent of chloride.

C. Tetrachloroethylene oxide, stirred with 96% H_2SO_4, reacted rapidly (exothermic) without evolution of gas. Infrared analysis of the acid-insoluble layer showed it to be trichloroacetyl chloride.

D. Tetrachloroethylene oxide (2.2×10^{-3} mole) was dissolved in 1*N* potassium hydroxide-methanol solution. The solution was acidified with hydrochloric acid, then boiled to remove the methanol and excess hydrogen chloride. Saturated barium chloride solution was added and a precipitate (0.37 g.) was collected. This product was undoubtedly barium oxalate, and corresponded to 1.65×10^{-3} mole of the latter.

E. With methanol containing a small amount of mercuric chloride, tetrachloroethylene oxide undergoes a rapid exothermic reaction after an induction period of a few minutes. The infrared spectrum of the reaction product is almost identical to that of methyl trichloroacetate.

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(11) $AgNO_3$ was used for chloride test; cuprous chloride and ammonia for trichloroacetate test.

A Crystalline Monoprocaine Salt of Pyridoxal Phosphate

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Pyridoxal phosphate is a coenzyme involved in transamination processes, in amino acid decar-