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A Practical Synthesis of Tetrachloroethylene Oxide

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ABSTRACT

Tetrachloroethylene oxide has been synthesized by direct oxidation of tetrachloroethylene with oxygen in the presence of ultraviolet light. This preparation resulted in a mixture of tetrachloroethylene oxide and trichloroacetyl chloride in approximately equal amounts under the most favorable conditions. Tetrachloroethylene oxide rearranges readily to trichloroacetyl chloride above 60°C with an activation energy E_a of 3.0×10^4 cal/mole and a pre-exponential factor A of 1.9×10^{13} . All attempts to polymerize tetrachloroethylene oxide under a variety of conditions failed.

INTRODUCTION

The literature on the preparation and polymerization of epoxides is extensive [1, 2]. It includes studies of ethylene oxide [3], propylene oxide [4], 2-butene epoxide [5-7], epichlorohydrin [8],

1,4-dichlorobutene-2 epoxide [9], as well as other halogenated epoxides which are basically derivatives of ethylene oxide [8, 11]. The polymerizations of these epoxides are carried out with electrophiles, Lewis and Brønsted acids, and to a smaller extent with nucleophilic initiators. In recent years coordinative anionic initiators derived from aluminum alkyls and zinc alkyls by reaction with water and alcohols, have been used extensively for the polymerization of epoxides.

The preparation and polymerization of completely halogenated epoxides, mostly perfluorinated epoxides [12-20], is published primarily in the patent literature. Tetrafluoroethylene (TFE) was oxidized to tetrafluoroethylene oxide (TFEO) directly with oxygen in the presence of γ -irradiation or ultraviolet light [18] or with H_2O_2 or $KMnO_4$ [20]. TFEO rearranged readily to trifluoroacetyl fluoride and could be pyrolyzed to carbonyl fluoride and difluorocarbene [21]; it hydrolyzed slowly to oxalic acid and HF. With fluoride ions TFEO was polymerized to oligomers [14]. At $-195^\circ C$, TFEO was polymerized to high molecular weight crystalline poly(TFEO) which has a melting point of $42^\circ C$ [15]. Hexafluoropropylene oxide (HFPO) has been synthesized from hexafluoropropylene (HFP) by a number of chemical oxidation methods as well as by direct photochemical oxidation with oxygen [22]. HFPO did not react with radicals or ultraviolet light. However, it could be pyrolyzed to difluorocarbene and trifluoroacetyl fluoride [23]. With ionic catalysts it rearranged to hexafluoroacetone or pentafluoropropionyl fluoride, depending upon the exact reaction conditions [24]. With anionic initiators, preferably with fluoride ions, rubbery polymers of a molecular weight up to 10,000 with unusually good thermal stability have been obtained; cesium fluoride in tetraglyme at relatively low temperatures was the preferred initiator system [16, 17]. The molecular weight of these polymers is limited because of the ease of chain transfer by the fluoride ion which caused chain termination by the formation of acid fluoride end groups and initiation of a new chain.

The direct oxidation of tetrachloroethylene (TCE) was known to result in the formation of trichloroacetyl chloride and phosgene [25]. Kirkbride [26] was able to identify, in addition to trichloroacetyl chloride (TCAC), tetrachloroethylene oxide (TCEO); he oxidized TCE with oxygen in the presence of a mercury arc and chlorine gas at $50-60^\circ C$. After partial oxidation the mixture was treated with water which hydrolyzed TCAC to trichloroacetic acid and left a solution of TCEO in TCE. TCEO was not actually isolated but was converted with aluminum chloride to TCAC. This preparation was later repeated, and TCEO was isolated in a yield of 0.9% [27]. In addition to a considerable amount of TCAC, hexachloroethane was found in

this residue. It was found that TCEO rearranged to TCAC with an activation energy of 31.4 kcal/mole. TCEO boiled at 110°C/760 Torr and melted at -59°C. TCEO was hydrolyzed with sulfuric acid or 1 N potassium hydroxide/methanol solution to oxalic acid. The isolation of TCEO from the reaction mixture was difficult and could not be effected readily because the boiling points of TCEO, TCAC, and TCE are 110, 118, and 121°C, respectively at 760 Torr. The range of boiling points is even less at 40 Torr, at which pressure it was necessary to distill the mixture in order to avoid rearrangement of TCEO to TCAC during the distillation.

The infrared spectrum of TCEO was studied in detail by Derkosch and co-workers [28].

Dobrov and Poluektov [29, 30] studied the oxidation of TCE to TCEO in the presence of Co-60 γ -radiation and obtained TCEO in 20% yield. They also developed and used for the first time a gas chromatographic analysis for the characterization of the reaction mixtures. They did not, however, make an effort to optimize the yield of the oxidation nor did they isolate preparatively TCEO. They postulated a mechanism for the formation of TCEO in an attempt to explain all the observed products and rate equations. In addition to TCAC and TCEO they identified phosgene and hexachloroethane as by-products of the oxidation of TCE. Other workers had also found that the photochemical decomposition of TCAC can lead to the formation of phosgene and hexachloroethane [31].

Jeffrey [32] also investigated more recently the oxidation of TCE and found that it can be accomplished with either oxygen or air in the presence of free radical initiators such as azo compounds and peroxides. He also found that this oxidation could be carried out at 60-100°C and at pressures of 200-300 psi in the absence of commonly used inhibitors in TCE. Jeffrey found that at 80°C and approximately 20% TCE conversion, a reaction mixture was obtained which contained 50% TCAC, 40% TCEO, and 10% phosgene. It was not convenient for him to carry out the reaction to more than 20-25% TCE conversion. Above a reaction temperature of 100°C, the yield of TCEO dropped rapidly. The yield of TCEO was not very dependent on the AIBN concentration or the reactor pressure. Most yields of TCEO were about 20% according to their analysis.

It was the purpose of this work to investigate the preparation of TCEO from TCE and optimize the reaction conditions, to study the thermal decomposition of TCEO, and to carry out typical reactions of TCEO with particular emphasis on attempts to use TCEO as a monomer for homo- and copolymerization.

EXPERIMENTAL

Materials

TCE (Eastman Kodak Company) was washed several times with dilute hydrochloric acid, water, and sodium carbonate solution and dried over calcium chloride and finally distilled through a packed column.

Epichlorohydrin, propylene oxide, tetrahydrofuran, and dioxane were dried and distilled prior to use.

Trioxane (Celanese Corp.) and maleic anhydride were purified by recrystallization and dried.

Initiators

SbCl_5 (Alfa Inorganics) was distilled under reduced nitrogen pressure. Triphenyl phosphine (Ph_3P) (Aldrich) was recrystallized from benzene. Lithium tertiary butoxide (LTB) was purified by sublimation at 0.1 Torr and 150°C prior to its use. Triethylaluminum (Texas Alkyls), *n*-butyllithium, (Alfa) and sulfuric acid were used as supplied.

Solvents

Benzene, toluene, and methylcyclohexane were dried and distilled prior to use.

Preparation of TCEO and Attempted PolymerizationOxidation of TCE

TCE (700 g) was placed in a 500-ml photochemical reaction vessel which surrounded a quartz immersion well containing a Hanovia 450-W medium-pressure ultraviolet light source filtered by a sleeve of Pyrex or Vycor. The vessel was equipped with a thermometer, condenser, and sparge to introduce oxygen at the center of the bottom of the TCE cavity which also provided agitation. Water was circulated from a constant temperature bath through the jacket surrounding the TCE cavity and also around the immersion well. The water heated the TCE and cooled the lamp (Fig. 1). In a typical experiment the reaction was carried out at 80°C and oxygen was bubbled through the

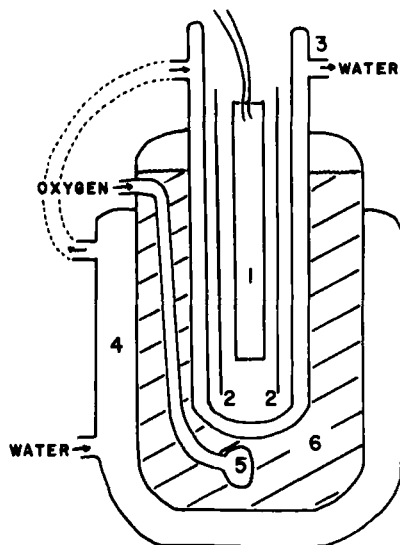


FIG. 1. Photooxidation apparatus: (1) ultraviolet lamp; (2) source filter sleeve; (3) quartz immersion well; (4) constant temperature jacket; (5) oxygen inlet sparge; (6) TCE and oxidation products.

reaction mixture at the rate of 300 ml/min. After the mixture was sparged sufficiently with oxygen (10 min), the lamp was turned on, and samples were taken at intervals and analyzed by gas chromatography (GC). For the preparative synthesis of TCEO, the photooxidation was stopped when it was determined, by GC, that all TCE had been oxidized; this took approximately 10 hr at 80°C. After the reaction was completed, oxygen was bubbled through the solution for a few additional minutes in order to remove phosgene. The solution was then poured onto ice, and the TCAC was allowed to hydrolyze at 0°C. It is essential that the temperature not rise substantially because TCEO might rearrange to TCAC or hydrolyze to oxalic acid at higher temperatures. As the acid chloride was hydrolyzed, 10% sodium hydroxide solution was added to maintain a pH of 7. After the hydrolysis was complete, the product was washed three times each with ammonium carbonate, ammonium hydroxide solution, and finally with water. TCEO was dried over magnesium sulfate and distilled at 46°C/68 Torr; yield, 120 g. A distillation residue remained which

was identified as hexachloroethane by infrared spectra and a melting point of 185-186° C (lit. [33] mp 183-184° C).

TCEO should be stored below 0° C in sealed ampules in order to avoid rearrangement of the compound. TCEO showed a single peak in the ¹³C spectrum at 129.4 MHz (5.72 ppm) upfield from the carbon tetrachloride resonance. The infrared spectrum was identical with that described in the literature [27].

Thermal Rearrangements of TCEO

Approximately 0.05 g of TCEO was sealed into each of several ampules, 4 mm × 30 mm, which had been dried and flushed with nitrogen prior to their use. Before the sealed ampules were used they were stored at -20° C (no rearrangement was detected by GC). An equal number of ampules were also prepared which contained TCEO and 5 mole % LTB (1.25 M in methylcyclohexane). A few tubes contained TCEO and 30 vol % methylcyclohexane as diluent to study concentration effects.

For the study of the rate of rearrangements, each of the three groups of ampules were placed in a thermostated oil bath at 80, 95, and 110 ± 0.2 C. The ampules were withdrawn at intervals and analyzed by GC.

Attempted Polymerizations of TCEO

Ampules were prepared from 8 mm ID Pyrex tubing and had a capacity of 2-3 ml. One end was sealed and a constriction was made between the ends to give a 1-2 mm ID neck for easier sealing. Typically, the initiator was placed in the dried, nitrogen flushed ampule by injecting it through a septum in the case of liquids or solutions, or by adding a solid quickly under nitrogen. The tube was then transferred to a vacuum line and the ampules were evacuated using liquid nitrogen as the coolant. Degassed TCEO was transferred under vacuum of 0.025 Torr into the ampule. The individual ampules were sealed, weighed and placed in the baths of appropriate reaction temperatures: -78, -25, or 25° C.

After the specified time, the tubes were opened, volatile liquids were transferred under vacuum to another ampule and the presence of nonvolatile materials was noted. The volatile products were then analyzed by gas chromatography.

Copolymerizations were attempted in the same manner. Both monomers were distilled into the ampule at 0.025 Torr and the relative volumes estimated from the liquid heights in the ampule.

Measurements

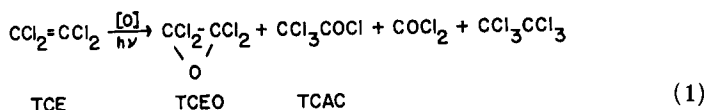
The gas chromatographic analysis involving the oxidation products of TCE was carried out on a Varian 920 GC apparatus with typical conditions: column, $8 \times 1/4$ in.; liquid phase, Apiezon N (15%); solid support, Chromosorb W, acid-washed (dimethyldichlorosilane treated); helium flow rates, carrier gas 45 ml/min, reference gas, 10 ml/min; injector temperature, $105-110^\circ\text{C}$; column temperature, 75°C ; detector temperature, 250°C . An injection of about $0.5 \mu\text{l}$ gave good resolution of the three main fractions. Typical retention times were 12 min for TCEO, 14 min for TCAC, and 17 min for TCE. Minor products observed at 30 sec and 6 min retention times were identified as phosgene and carbon tetrachloride, respectively.

Infrared spectra were taken on a Perkin-Elmer 727 spectrometer.

The ^{13}C spectra were measured on a Bruker HFX-90 spectrophotometer.

RESULTS AND DISCUSSION

TCEO was synthesized directly by photooxidation of TCE in good yield and the optimum conditions were determined [Eq. (1)].



Earlier work [26-32] on the synthesis of TCEO consisted of oxidation of TCE in the presence of ultraviolet light with or without additional sensitizer such as chlorine or oxidation with radical initiators. It was found that the use of chlorine produced a substantial amount of hexachloroethane as a by-product and the yield of TCEO was lowered.

Photooxidation to TCEO does not occur at a reasonable rate below 60°C , and above 80°C the rearrangement to TCAC becomes significant. Figure 2 shows the relative concentrations of TCE, TCEO, and TCAC for a typical photooxidation at 80°C . It can be seen initially that the TCEO concentration exceeded that of TCAC. As a consequence, it appeared that TCAC was produced primarily by the rearrangement of TCEO to TCAC.

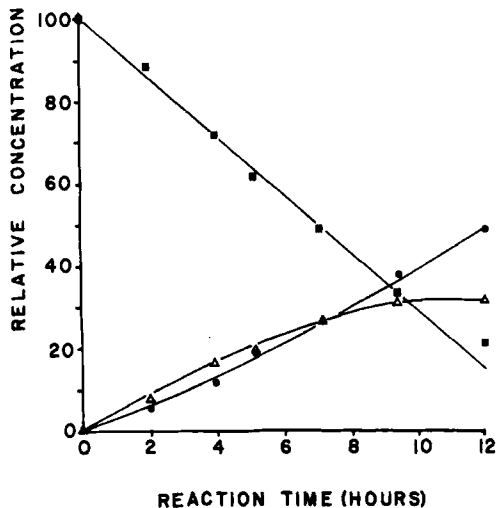


FIG. 2. Products of photooxidation of TCE at 80°C with a Pyrex filter; (■) TCE; (△) TCEO; (●) TCAC.

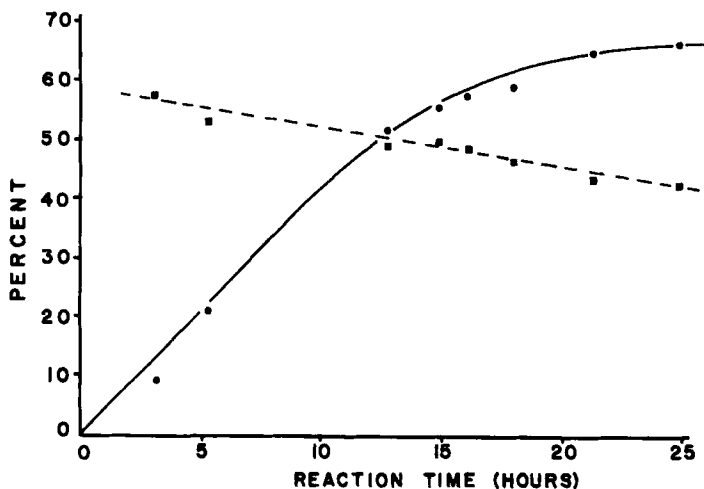


FIG. 3. Conversion of TCE to TCEO at 60°C with a Pyrex filter: (●) conversion of TCE; (■) yield of TCEO.

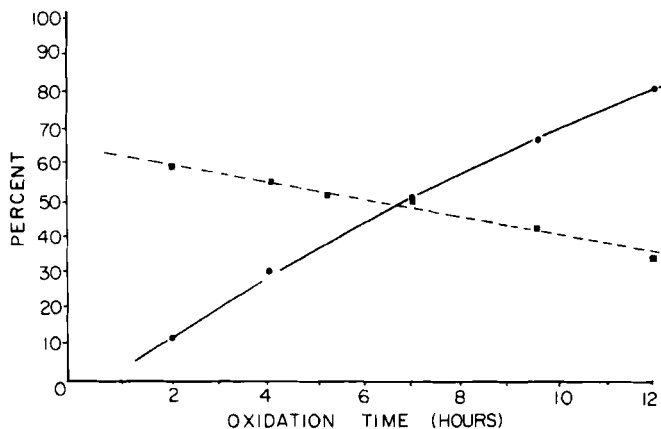


FIG. 4. Conversion of TCE to TCEO at 80° C with a Pyrex filter: (●) conversion of TCE; (■) yield of TCEO.

A better comparison for the relative formation of TCEO and TCAC can be obtained when the yield of TCEO and the conversion of TCE are plotted as functions of oxidation time. In Fig. 3, on using a Pyrex filter at 60° C, it is shown that the initial yield of TCEO was nearly 60% at low conversion of TCE. After 24 hr the yield of TCEO had dropped below 45% at a conversion of 70% of TCE. At 80° C, with the use of a Pyrex filter, the initial yield of TCEO was near 60% at a conversion of 10% of TCE and decreased after 12 hr to approximately 40% to 80% conversion of TCE (Fig. 4). Figure 5 shows a slightly higher rate, but similar tendency, when using a Vycor filter.

As earlier investigators have pointed out, much of the problem of isolation of TCEO was the separation of three compounds with very close boiling points where one of the compounds is thermally unstable and cannot be held at the boiling point for an extended period of time. Some investigators [27] first hydrolyzed TCAC, isolated the solution of TCEO in TCE, chlorinated TCE, and then isolated TCEO which is much lower boiling than the hexachloroethane.

We have chosen to isolate TCEO preparatively by oxidizing TCE completely to a mixture of TCAC and TCEO. TCAC could now be removed by hydrolyzing the mixture in ice water to HCl and trichloroacetic acid, TCEO could be isolated and distilled directly. The initially high yield of TCEO at low TCE conversion was ultimately reduced at high TCE conversions. Nevertheless, a 20% distilled yield of TCEO could be realized at 100% conversion after a relatively simple workup procedure.

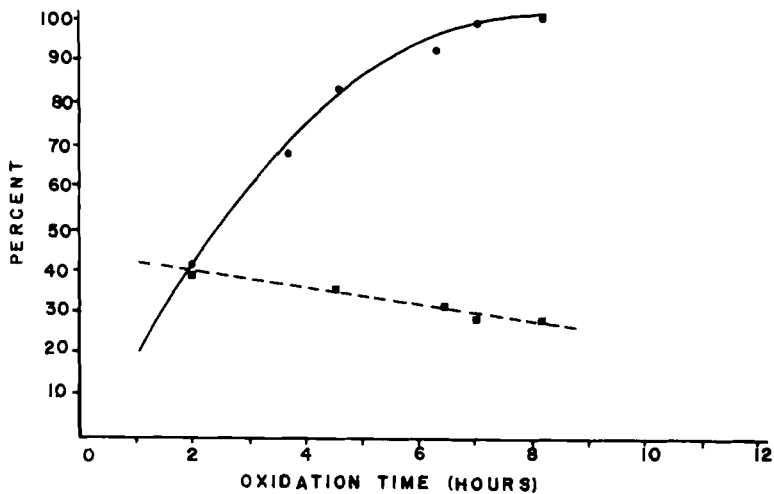


FIG. 5. Conversion of TCE to TCEO at 80°C with a Vycor filter: (●) conversion of TCE; (■) yield of TCEO.

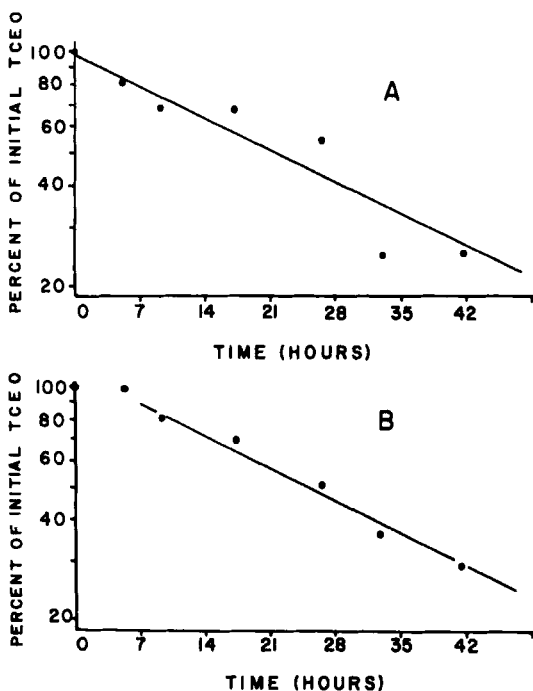


FIG. 6. Thermal rearrangement of TCEO to TCAC at 80°C: (A) pure TCEO; (B) TCEO with 7.4 mole % LTB.

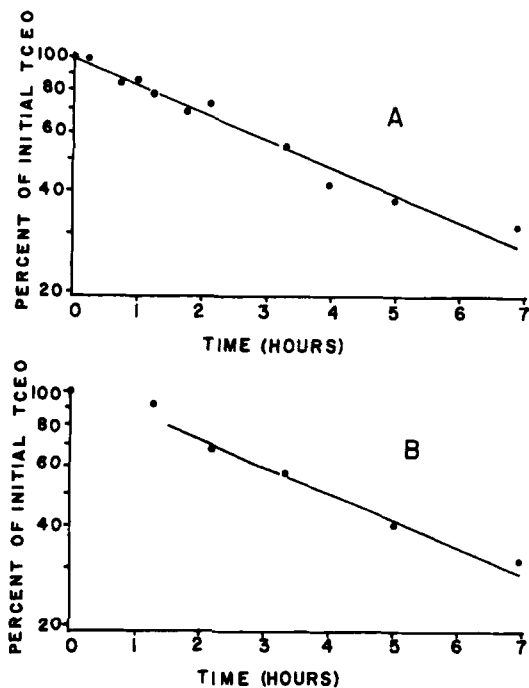


FIG. 7. Thermal rearrangement of TCEO to TCAC at 95°C: (A) pure TCEO; (B) TCEO with 7.4 mole % LTB.

It has been known that TCEO rearranged thermally to TCAC. From the work on HFPO and TFEO it was suspected that this rearrangement is ionic in character and was probably catalyzed by trace amounts of nucleophilic or electrophilic compounds present as impurities. As a consequence, TCEO was purified for the degradation studies to a high degree until the GC chromatogram showed less than 100 ppm of impurities. The thermal rearrangement of TCEO at 80, 95, and 110°C is shown in Figs. 6, 7, and 8. Thermal rearrangement of TCEO at 80°C (Fig. 6B) and at 95°C (Fig. 7B) was also carried out in the presence of LTB in an attempt to neutralize acidic impurities.

It was expected that if the general rearrangement was influenced by nucleophiles, the rearrangement of TCEO to TCAC should have been accelerated in the presence of LTB. On the other hand, if it were influenced by acidic impurities, the presence of LTB should

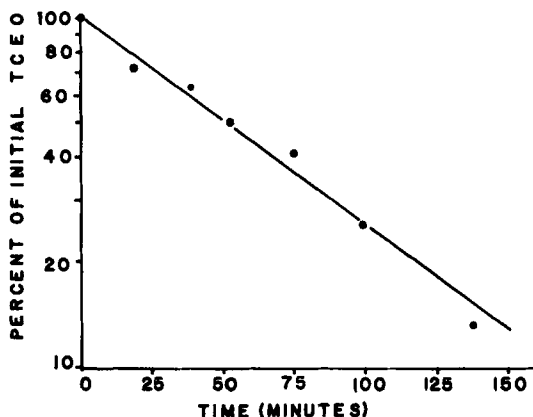


FIG. 8. Thermal rearrangement of TCEO at 110°C (pure TCEO).

have retarded the thermal rearrangement reaction. As it may be seen from Figs. 6B and 7B, the thermal rearrangement of TCEO was not substantially influenced by the presence of LTB although it could be argued that LTB reacted relatively rapidly with the TCEO and was rendered useless after a brief period. The position of the second data point in both Figs. 6B and 7B could be interpreted as indicating that there is an inhibition of the thermal reaction which might indicate that this thermal reaction is actually acid catalyzed. The effect of the diluent, methylcyclohexane, was found negligible.

We believe that TCEO rearranges to TCAC by the following mechanism. Trace chloride ion impurities cause the initial formation of TCAC from TCEO [Eq. (2)], but the "uncatalyzed" rearrangement is actually catalyzed by TCAC [Eq. (3)], which was formed by the reaction of Eq. (2).

The thermal rearrangement of TCEO followed first-order kinetics with a rate constant of $9.2 \times 10^{-6} \text{ sec}^{-1}$ at 80°C, 5.35×10^{-5} at 95°C, and 2.5×10^{-4} at 110°C. The rate constants could be plotted on an Arrhenius plot, and the activation energy E_a and the pre-exponential factor A were determined (Fig. 9) as $E_a = 3.0 \times 10^4 \text{ cal/mole}$ and $A = 1.9 \times 10^{13}$, in very good agreement with Frankel's results [27]. A similar study was made for the thermal rearrangement of TFEO by Lenzi and Meli [21]. They measured the rates of rearrangement between 119 and 141°C and found them to be first order in this

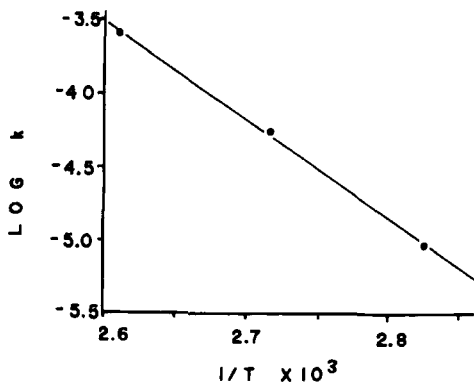
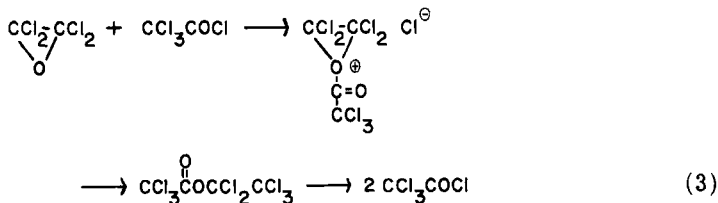
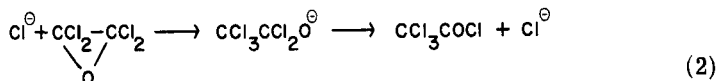


FIG. 9. Arrhenius plot of thermal rearrangement of TCEO to TCAC.

temperature range. They calculated values for E_a of 3.36×10^4 cal/mole and $A = 5 \times 10^{13}$. Gozzo and Camaggi [34] also studied the reactivity of TFEO and found that liquid TFEO did not react with butyllithium but did rearrange to the acid fluoride with BF_3 . This observation seems to be similar to our observation that LTB was also unreactive toward TCEO.

Reactions of TCEO

Frankel [27] reported earlier that TCEO reacted with methanol to give methyl trichloroacetate, a result which we confirmed. In

addition, dimethyl oxalate was also identified by its gas chromatographic retention time as well as by its infrared spectrum after isolation [35]. Ginsberg [36] had also isolated diethyl oxalate from the reaction of TCEO with ethanol.

When TCEO was allowed to react with equimolar amounts of ethanol, ethyl trichloroacetate was obtained as the primary reaction product, and ethyl oxalate as a by-product. After 12 hr reaction time at room temperature, TCEO reacted with isopropanol to give the two expected esters, but in the case of tertiary butyl alcohol and TCEO after 24 hr only the tertiary butyl trichloroacetate, but no oxalate, was isolated.

TCEO reacted with a number of primary, secondary, and tertiary amines to form water-soluble salts which were not characterized further.

Dimethyl sulfoxide reacted readily with TCEO to form a gel. On addition of water, a white solid deposited which was identified by its infrared spectrum as paraformaldehyde. The 2,4-dinitrophenylhydrazone was also prepared and was identical with formaldehyde 2,4-dinitrophenylhydrazone (mp 164-165°C, pure or mixed).

Attempted Polymerization and Copolymerizations of TCEO

Attempts were made to carry out the homopolymerization of TCEO. Compounds which are known to act as either cationic or anionic initiators were added to TCEO and were allowed to react at various temperatures for up to 4 weeks. Up to 2 mole % of the potential initiators were used at temperatures of -78, -25, and 25°C. In no case has any polymer of TCEO been observed although some compounds caused the rearrangement of TCEO to TCAC even at -78°C. SbCl_5 , FeCl_3 , Ph_3P , and Pruitt's catalyst (FeCl_3 /epichlorohydrin) gave a 100% yield of TCAC at 25°C. TCEO was also quantitatively converted to TCAC with SbCl_5 at -25 and at -78°C. In the presence of CsF (with pentaglyme or 1 vol % 15-crown-5 crown ether) at 25 and at -78°C, an 80% TCEO to TCAC transformation was obtained. $\text{CF}_3\text{SO}_3\text{H}$ gave only 5% rearranged TCAC at -25 and -78°C. TCEO remained unchanged with LTB at 25°C, with butyllithium and LTB at -25°C, and with Ph_3P , butyllithium, and LTB at -78°C. With Al Et_3 and $\text{Al Et}_3:\text{H}_2\text{O}$ (1:1) at -78°C no rearrangement was observed, but at 25°C a reaction of TCEO with the aluminum alkyls was noticed which caused the formation of TCAC. The same mixture of 60% TCEO and 40% TCAC was also obtained when an ethereal solution of EtMgBr was added to TCEO. The results of these attempted polymerizations are shown in Table 1.

TABLE 1. Attempted Homopolymerizations of TCEO (Reaction Time: 2 Weeks)

Potential initiator	Composition of product		
	25° C	-25° C	-78° C
SbCl ₅	100% TCAC	100% TCAC	100% TCAC
FeCl ₃	100% TCAC	—	—
Pruitt's Catalyst	100% TCAC	—	100% TCAC
CF ₃ SO ₃ H	—	95% TCEO + 5% TCAC	95% TCEO + 5% TCAC
CsF (Pentaglyme or 15-crown-5-ether)	20% TCEO + 80% TCAC	—	30% TCEO + 70% TCAC
Ph ₃ P	100% TCAC	—	100% TCEO
BuLi	—	100% TCEO	100% TCEO
LTB	100% TCEO	100% TCEO	100% TCEO
AlEt ₃ or AlEt ₃ :H ₂ O (1:1)	60% TCEO + 40% TCAC, dark brown solution	—	No reaction until warmed to 25° C; then same product mixture as at 25° C
EtMgBr (ether)	60% TCEO + 40% TCAC	—	—

Attempts were also made to polymerize TCEO with ultraviolet and γ -irradiation. TCEO samples (0.5 ml) were sealed into a quartz tube under vacuum. The sealed tubes were cooled to -80°C and placed 8 cm from the ultraviolet lamp. No filter sleeve was used, and the TCEO received the full spectrum of light. After 40 min the solution had turned pale yellow, and after 1.5 hr, a reddish brown. No further changes occurred until the reaction was stopped after 16 hr. GC analysis of the liquid showed that about 80% of TCEO had rearranged to TCAC.

TFEO had been successfully polymerized to high molecular weight, crystalline poly(TFEO) by γ -irradiation from a Co-60 source. It was reported that the highest rate of polymerization was achieved a few degrees below the melting point of TFEO and no polymer was formed in the liquid state [15].

A number of samples of TCEO were vacuum sealed and placed in a Dewar flask containing Dry Ice and chloroform to maintain the temperature below the melting point of TCEO. The Dewar was then placed in a radiation field with an intensity of 72,000 rad/hr as measured by ferrous sulfate dosimetry. Two samples were removed at each of three intervals after receiving the indicated amount of radiation. In 6.25, 23.5 and 28.5 hr the samples were exposed to 0.45, 1.70, and 2.05 Mrad, respectively. No polymers were formed in either case, and the volatile material was shown by GC to be identical to the original TCEO in all cases.

Attempts were also made to use TCEO as comonomer with various monomers. Solid polymers were found in some copolymerization attempts as shown in Table 2. When the material was isolated, the infrared spectrum in each case showed it to be homopolymer of the starting monomer without evidence of incorporation of any TCEO. This information was useful and demonstrated that there were no impurities in the sample of TCEO which terminated polymerization. The lack of polymerizability was inherent in TCEO.

TCEO with an equimolar amount of epichlorohydrin with AlEt_3 at 25°C gave an oily liquid, but at -25°C a solid amorphous polymer was formed in good yield. The infrared spectra showed these to be poly-epichlorohydrin with no incorporation of TCEO. Propylene oxide and TCEO at a 3:2 ratio with $\text{AlEt}_3\text{:H}_2\text{O}$ at -25°C gave a low yield of amorphous polymer which was identified as poly(propylene oxide) homopolymer. TCEO with trioxane at a ratio of 1:1, 3:1 and 1:3 with SbCl_5 in TCE at 45°C gave a high yield of polyoxymethylene homopolymer, and gas chromatographic analysis of the mother liquid showed that TCEO had remained unchanged. Butadiene and TCEO at the ratio of 1:1 and 1:5 with butyllithium in hexane at 25°C gave no polymer but a small amount of water-soluble residue which was

TABLE 2. Attempted Copolymerization of TCEO (Reaction Time: 2 Weeks)

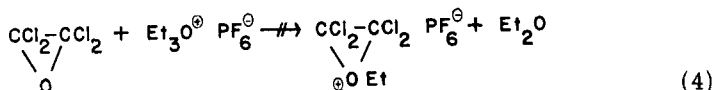
Comonomer (ratio) ^a	Initiator (solvent) ^b	Temperature (°C)	Observations
Epichlorohydrin, 1:1	AlEt ₃ (Hexane)	25	Oily liquid
Propylene oxide	AlEt ₃ :H ₂ O	-25	Solid amorphous polymer formed in good yield; shown by IR to be pure PECH with no TCEO incorporated Low yield of amorphous polymer shown by IR to be PPO homopolymer
Trioxane 1:1 3:1 1:3	SbCl ₅	45	High yield of POM homopolymer; GC shows TCEO unchanged
Maleic anhydride 1:15	SbF ₅ (Neat)	55	No change; GC showed 5% TCEO, 95% TCAC
Phenyl isocyanate 2:1	Ph ₃ P (Hexane)	-78	No change; GC showed only unchanged starting materials
Butadiene 1:1 1:5	BuLi (Hexane)	25	No polymer; small amount of water-soluble residue (LiCl)
Tetrahydrofuran 1:1	AlEt ₃	-25	No change
Dioxane 1:1	AlEt ₃	25	No change

^aTCEO: comonomer ratio^bInitiator concentration 1.0 mole %.

identified as lithium chloride. Homopolymerizations of epichlorohydrin, propylene oxide, trioxane, and butadiene were carried out under the same conditions as the attempted copolymerization in order to see if TCEO had interfered with the polymerization in any way. This did not seem to be the case. In all cases, the homopolymers were obtained in good yield.

Attempts at copolymerization of TCEO were made with phenyl isocyanate at a 2:1 ratio with Ph_3P in hexane at -78°C and at a 1:1 ratio with AlEt_3 at -25°C . No physical change was observed, and the gas chromatographic analysis showed that TCEO had not rearranged.

TCEO was also treated with triethyloxonium hexafluorophosphate, an initiator for cationic polymerization of cyclic ethers. There was no change either in the physical appearance or in the GC analysis of the mixture on standing 3 hr at 25°C . The PMR spectrum of equimolar solutions of TCEO and the triethyloxonium salt in dichloromethane showed no detectable interaction between the triethyloxonium cation and the oxygen of TCEO. Such a reaction would liberate diethyl ether, which would be detectable by PMR in concentrations as low as 3 mole % of the oxonium salts [38] [Eq. (4)]. It was therefore concluded that TCEO is stable to cationic attack by this initiator.



From these experiments it can be concluded that TCEO could readily be prepared in good yield and at high polymerization grade purity. It did not polymerize or copolymerize under a variety of conditions, nor did it undergo an alkylation reaction on the oxygen atom of the tetrachlorooxirane ring. The electron deficiency of the oxygen seems to be responsible for this behavior. The electron deficiency of the carbonyl oxygen of chloral is also responsible for the poor performance of chloral in cationic polymerization [39].

Rearrangement of TCEO to TCAC was readily accomplished with acids or thermally by an apparently ionic mechanism. This would allow TCEO to be used as an acylating agent at the end of a reaction. TCEO could be used as an inert solvent or diluent for an ionic polymerization. The reaction could be carried out without interference of the acylation reagent and the acylating agent could be simply generated by heating after the polymerization was completed.

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