VEGETABLE OIL EXTRACTION

Autoxidation Products
of Trichloroethylene

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Trichloroethylene-extracted soybean oil meal has been associated with a refractory, hemorrhagic, aplastic anemia when fed to cattle. Quantitative data on the autoxidation of trichloroethylene were needed to determine whether the oxidation products contributed to the toxicity. The autoxidation with oxygen at 45° to 70° C. yielded about 95% of a liquid mixture and about 5% of gaseous products. The liquid was composed of about equal parts of dichloroacetyl chloride and a very reactive isomer believed to be trichloroethylene epoxide. The gases consisted of phosgene, carbon monoxide, and hydrogen chloride in equimolar quantities. The highly reactive "epoxide" was found to yield chloral, dichloroacetyl chloride, glyoxylic and formic acids, and carbon monoxide in the presence of iron and moisture, which would be found in a soybean oil extraction plant. With this knowledge of the autoxidation products of trichloroethylene, it is possible to make them react under controlled conditions, with soybeans and with soybean oil flakes for toxicity studies.

TRICHLOROETHYLENE has been tried during three different periods in the past 45 years, on a commercial basis as a solvent for extracting oil from soybeans. Each time its use has been abandoned because of the toxicity of the resultant defatted meal to cattle. These commercial ventures have included 17 different plants. Many specimens of trichloroethylene-extracted soybean oil meal have been shown to produce a fatal aplastic anemia when fed to cattle (31, 33, 38, 47). On the other hand no toxicity has ever been observed with properly prepared hexane-extracted soybean oil meal even after the consumption of 6000 pounds per animal over a period of 600 days (30).

Stockman (43) reported on the poisoning of cattle in southern Scotland in 1912. He described the clinical symptoms and postmortem findings of the disease, conducted rather extensive feeding experiments with cattle, and was able to demonstrate conclusively that the cattle deaths were associated with the consumption of trichloroethylene-extracted soybean oil meal. He suggested that the toxicity of the meal might be caused by the reaction of trichloroethylene with the meal during processing. He was unable to produce the characteristic symptoms by feeding the meal to sheep, swine, guinea pigs, or rabbits. He also demonstrated that the feeding of

trichloroethylene itself to cattle did not produce the typical syndrome. In 1923–1925, widespread and severe outbreaks of the same cattle poisoning occurred in Germany and Holland (15). On the basis of Stockman's work, the disease was correctly diagnosed in 1924 (4, 9, 34). The toxic meal was traced to a trichloroethylene–soybean oil extraction plant in Düsseldorf, which subsequently converted to benzene extraction in 1925 (21). Following this outbreak, Stang (41) and Samin (37) established the characteristic blood picture as a leucopenia accompanied by a relative lymphocytosis and suggested damage to the bone marrow as the cause. They also found that the extraction of oil with carbon tetrachloride gave a nontoxic meal, and confirmed Stockman's findings that the disease could not be produced by the feeding of trichloroethylene. Other investigators speculated on the probability of various avitaminoses (5, 20, 21) and phosphatide deficiency (19) caused by the stronger solvent action of trichloroethylene; urease poisoning (49), a toxialbumin (39), and lead poisoning (48) were also claimed as the cause of the toxicity disease.

Feeding experiments initiated by L. A. Maynard of Cornell University in 1938 (45) were subsequently interpreted as demonstrating that trichloroethylene-

extracted soybean oil meal was nontoxic to cattle when processed at higher temperatures (120° C. for 30 minutes). Concurrently an efficient process for extracting oil from soybeans was developed at Iowa State College (44, 45).

During the period of 1947 to 1952, widespread outbreaks of a refractory, hemorrhagic, aplastic anemia occurred in cattle fed trichloroethylene-extracted soybean oil meal produced in plants located in the United States (31, 33, 38, 47), Italy (25), and Japan (23). The toxicity disease observed in these latest outbreaks was in all respects identical with the disease as described earlier by the German and Dutch workers and by Stockman. Extensive clinical studies by several laboratories during these latest outbreaks have extended the previous knowledge of the disease. Trichloroethylene-extracted soybean oil meal has also been reported to be toxic to sheep (17), although in sheep it did not produce the aplastic anemia syndrome observed in cattle.

The authors' examination of new extraction-grade trichloroethylene obtained both from soybean oil extraction plants and from the manufacturer revealed the presence of 0.02% by weight of triethylamine, which is known to be an efficient autoxidation stabilizer (8). As much as 20% of this triethylamine was present as the hydrochloride, depending

upon the age of the solvent. In some cases needlelike crystals of triethylamine hydrochloride were found in the solvent.

Trichloroethylene samples obtained from the work tanks in soybean oil extraction plants were always slightly acidic and never revealed the presence of triethylamine. When a barrel of make-up solvent (0.1 of the plant capacity) was added, the solvent throughout the system showed an absence of base 4 hours later. This meant that the plants were operating with an uninhibited solvent which is known to be susceptible to autoxidation (7, 10, 22, 26, 32).

In 1911, Erdman (10) showed that trichloroethylene undergoes autoxidation in the presence of air or oxygen, with or without light, to produce phosgene, dichloroacetyl chloride, carbon monoxide, and hydrogen chloride. In 1932, Carlisle and Levine (7) reported on the acidity developed when trichloroethylene was exposed to air and oxygen in the presence of light. In 1934, Mugdan and Wimmer (27) reported that the liquid oxidation products of trichloroethylene consisted primarily of about equal parts of dichloroacetyl chloride and a second product assumed to be trichloroethylene epoxide. Treatment of the liquid oxidation mixture with 0.1% of a tertiary amine or heating under pressure at 200° C. yielded dichloroacetylchloride as the sole product. Treatment with anhydrous metal chlorides gave a mixture of dichloroacetyl chloride and chloral. In 1937, Müller and Schumacher (26) reported on the "chlorine-sensitized," photochemical oxidation of trichloroethylene, in which dichloroacetyl chloride was obtained in yields of 85 to 95%. In 1942, Kirkbride (22) patented a process for the photochemical oxidation of trichloroethylene in which 70% is converted to dichloroacetyl chloride. He also showed that after the oxidation was initiated by ultraviolet light, the light could be dispensed with because the reaction became autocatalytic. The liquid oxidation mixture contained a product which appeared to be trichloroethylene epoxide which, on treatment with catalytic amounts of an amine, rearranged to dichloroacetyl chloride. Catalytic amounts of aluminum chloride gave chloral.

This paper reports findings on the autoxidation products of trichloroethylene, in work undertaken to obtain information required for reaction of these products, under controlled conditions, with soybeans and with soybean oil flakes for toxicity studies.

Analytical Methods

Total Acidity The oxidation of trichloroethylene was followed by pipetting 0.10 ml. of the reaction mixture into 50 ml. of water (25° to 30° C.) and titrating to a phenolphthalein end point.

Chloride The neutralized mixture obtained from determining total acidity was used for titrating chloride by the Mohr method. The results are reported as moles of chloride liberated per 147.4 grams ($C_2HCl_3 + \frac{1}{2}O_2 \rightarrow C_2HOCl_3 = 1$ mole of oxidation mixture).

Iodine Value A method developed for the determination of phosgene (28) was used. The oxidation mixture (0.1 ml.) was added to 25 ml. of dry acetone containing 2.5% sodium iodide and allowed to stand for 30 minutes in the dark. Ice water (50 ml.) was added and the liberated iodine titrated immediately with sodium thiosulfate. The results are reported in Table II as atoms of iodine liberated by 147.4 grams (1 mole) of the oxidation mixture.

Total Chlorine With hydrolyzates of oxidation mixtures, sodium carbonate was added, followed by ignition. Total chlorine was then determined by the Mohr method.

With unhydrolyzed liquid oxidation products, total chlorine was determined by the method of Rauscher (35) using precautions on neutralizing the acid chloride with ethanolamine. This step was accomplished by first diluting the sample with dioxane, cooling, and adding the ethanolamine dropwise through the top of the condenser.

Carbon Monoxide The gas liberated on hydrolyzing the liquid oxidation mixtures was collected over mercury and absorbed in a saturated solution of acidified cuprous chloride. Carbon monoxide was further confirmed by its catalytic reduction of phosphomolybdates in the presence of acidified palladium chloride (12).

An alternative method involved oxidation over copper oxide and absorption of the carbon dioxide in a sodium hydroxide trap. Oxygen was introduced through the reaction mixture during hydrolysis, and the combined gases were passed through a trap cooled with solid carbon dioxide–acetone and an alkali trap before going into the copper oxide ignition tube.

Dichloroacetic Acid Identity was established by its boiling point of 189–90° C., neutral equivalent of 129, and the melting point of its p-bromophenacyl ester, 90° to 99° C. Quantitative estimation is based on isolation by three successive extractions from aqueous solutions with equal volumes of ether and distillation. In each case the quantity isolated agreed closely with that found by titrating the acid in an aliquot of the ether extract (small amount of formic acid present) and with that calculated from the organic chlorine content of the hydrolyzate—i.e., total chlorine less Mohr chloride.

Formic Acid **Dimedon Method.** Aqueous hydrolyzates of oxidized trichloroethylene were heated to boiling while acidic to drive off carbon dioxide. The hydrolysis mixture was placed in a round-bottomed flask and cooled on cracked ice. Magnesium ribbon was added along with concentrated hydrochloric acid (added in three increments at 30, 45, and 60 minutes). With occasional shaking the reduction of formic acid to formaldehyde was complete in 2 hours and a clear solution was obtained.

The formaldehyde was then determined by the dimedon method of Yoe and Reid (50). The melting point of the dimedon derivative was 189–190° C. Formic acid was then estimated by reference to a standard curve made by reducing known amounts of formic acid.

The addition of glyoxylic, glycolic, oxalic, and dichloroacetic acids to formic acid did not alter the results.

Azeotropic Distillation. Continuous ether extraction after water hydrolysis of oxidized trichloroethylene quantitatively removed the formic and dichloroacetic acids and about one third of the glyoxylic acid. Formic acid was then azeotropically distilled from the ether residue with pentane. Pentane was distilled from the azeotropic mixture. Formic acid was determined by oxidation with mercuric chloride and by measuring the liberated carbon dioxide (36), then checked by weighing the mercurous chloride (3).

Chromotropic Acid Method. When glyoxylic and glycolic acids were absent, as in the triethylamine-rearranged product, formic acid was determined by reduction with magnesium and hydrochloric acid and the formaldehyde was measured colorimetrically with chromotropic acid as described by Grant (14).

Glyoxylic Acid **2,4-Dinitrophenylhydrazone.** This derivative was quantitatively isolated from the aqueous hydrolyzates of the liquid oxidation mixtures. Precautions were necessary to prevent hydrolysis and loss of the hydrazone during the recrystallization and isolation steps, and the method of Iddles (18) was found to be most applicable. The hydrazone was characterized by its melting point of 189–90° C., decomposed (6), its neutral equivalent of 254, and its elementary analysis. Calculated: N, 22.05; C, 37.80; H, 2.38. Found: N, 22.2; C, 37.8; H, 2.2.

Permanganate Method. Titration with potassium permanganate in 3N sulfuric acid (16) was used with water hydrolyzates where no other reducing products were found. With aqueous alkali hydrolyzates, corrections were used for oxalate and glycolate to check the dinitrophenylhydrazone method.

Hydroxylamine Method. Hydroxyl-

amine titration (40) for total aldehydes checked the dinitrophenylhydrazone method, and titration with acid permanganate on water hydrolyzates established the absence of other aldehydes.

Cannizzaro Reaction. A modified Winkler titration was used as a check for glyoxylic acid content. The acid hydrolyzate was first heated to boiling to remove carbon dioxide and then neutralized to a phenolphthalein end point. Standard alkali was then added (5 ml. of 1N sodium hydroxide for each millimole of glyoxylate), and the solution was heated to 80° to 90° C., which quantitatively converted glyoxylate to oxalate and glycolate (11). Barium chloride was then added to precipitate oxalate, which was then determined by backtitration to a phenolphthalein end point. Each millimole of sodium hydroxide used up is equivalent to 2 millimoles of glyoxylate.

Oxalate The hydrolyzates of the liquid oxidation mixtures were neutralized to pH 7.0 with ammonia, calcium acetate was added, and the precipitated oxalate was titrated with acid permanganate as described by Andrews and Viser (2).

Glycolic Acid The absence of this compound in water hydrolyzates was established when determination of glyoxylic acid by the quantitative isolation of the dinitrophenylhydrazone and titration with acid permanganate were found to be in agreement. Its presence in alkaline hydrolyzates was established by precipitating glyoxylate and oxalate with barium at pH 10, acidifying and extracting dichloroacetic acid with ether, and evaporating the water layer to obtain needlelike crystals of glycolic acid. Melting point, 76° to 80° C. Neutral equivalent: calculated, 76; found, 78.

Titration with acid permanganate and correcting for glyoxylic and oxalic acids (16) indicated the presence of glycolic acid in the same molar quantity as oxalic acid.

Chloral After rearrangement of oxidized trichloroethylene with triethylamine, or with ferric or aluminum chloride, an aliquot was added to water and allowed to hydrolyze. Excess of standard sodium hydroxide was then added and the liberated formic acid determined by back-titration with sulfuric acid in the prescribed manner (29).

Chloral was further confirmed by separating the organic layer from the aqueous alkaline reaction mixture and recovering the chloroform in 85% of the calculated yield: boiling point 61° C.; $[\eta]^{18°}$ 1.4469.

Carbon Dioxide The gas was liberated by boiling acidified hydrolyzates and collected in two alkali traps connected in series. Carbon dioxide was then titrated by the Winkler method (46).

Experimental and Discussion of Results

Preliminary Work The extent of oxidation of trichloroethylene can be followed by the total acidity produced on addition of a sample to water and titrating to a phenolphthalein or thymol blue end point. The results of such a titration are empirical, in that the temperature affects the values obtained. For example, 0.1 ml. of a preparation (No. 2, Table II) that required 24.8 ml. of 0.1N sodium hydroxide at room temperature used up 30.1 ml. when titrated in ice water. A fading end point which is attributed to glyoxylic acid may be observed.

Trichloroethylene is stabilized against autoxidation by alkaline earth oxides and carbonates; amines; essential oils, such as camphor, turpentine, and pine oil; alkaloids, caffeine, and quinine (8); alcohols; and phenols (24). These stabilizers are very effective in the liquid state, and those which have boiling points close to that of trichloroethylene are said to be effective in the vapor state (8). Butanol was used as a stabilizer by the German extraction plant in 1923–1925 (13). Another plant operating in England from 1939 to 1950 used 0.2% triethylamine (13). The extraction-grade trichloroethylene examined contained 0.02% by weight of triethylamine, which was apparently effective in stabilizing the solvent prior to plant use. However, it was readily lost when the solvent was put into a soybean oil extraction plant. The phosphatides in the soybean oil and the extracted soybean flakes might be expected to offer protection against oxidation in the liquid state. However, protection in the vapor state during desolventization of the extracted flakes and during stripping of solvent from the oil is doubtful.

Trichloroethylene obtained from work tanks of soybean oil extraction plants was found to be stable in the absence of air when stored in the dark up to one year. However, autoxidation readily occurred in the liquid state in the presence of air or oxygen with or without light.

When the triethylamine was removed from new extraction-grade trichloroethylene, oxidation with air or oxygen occurred only in the presence of light. Trichloroethylene vapors continuously circulated through a 20-foot coil of $\frac{1}{8}$-inch iron pipe held at 180° C. for 240 hours failed to produce appreciable acid either wet or dry. When air was introduced into the vapors, the total acidity at the end of 240 hours was 0.06N. These results indicate that neither hydrolysis nor pyrolysis is probable in a soybean oil extraction plant.

Analyses for the iron content of commercial soybean oil meals gave an average of 145 p.p.m. (three samples) where hexane was used as an extraction solvent and 230 p.p.m. (five samples) where

trichloroethylene was used. These results are indicative of greater corrosion with trichloroethylene and decomposition of the solvent.

When benzoyl peroxide or partially oxidized trichloroethylene was added to unstabilized trichloroethylene as a catalyst, the oxidation proceeded in the dark when painted borosilicate glass or an iron bomb was used, into which air or oxygen was introduced under pressure. The rate of oxidation appeared to be unaffected when glycine was added to trichloroethylene catalyzed with benzoyl peroxide.

These preliminary experiments demonstrated that trichloroethylene obtained from the work tanks of soybean oil extraction plants contained no oxidation stabilizer and readily underwent a free-radical type of autoxidation under mild conditions. The solvent appeared to be stable to pyrolysis and hydrolysis at the maximum temperature found in extraction plants.

Preparation of Trichloroethylene for Oxidative Studies Triethylamine was removed from extraction-grade trichloroethylene by shaking with dilute hydrochloric acid. Excess hydrochloric acid was removed by washing with water until free of chloride ions. Subsequent treatment followed three different methods: (A) drying over calcium chloride, which was removed and followed by drying over magnesium oxide for 24 hours; (B) drying over Drierite for 24 hours; and (C) drying over Drierite followed by distilling at atmospheric pressure. In addition (D), trichloroethylene obtained from the work tank of a soybean oil extraction plant was distilled and used, and (E), trichloroethylene containing 0.02% by weight of triethylamine was treated with dry hydrogen chloride and oxidized. In general, erratic results were obtained when the drying agents were removed by filtration without subsequent distillation (Methods A and B), and long induction periods were sometimes experienced. When dried, inhibitor-free trichloroethylene was distilled (Method C), uniform results with little or no induction periods were attained.

Autoxidation Products of Trichloroethylene Table I lists the products obtained by passing oxygen through trichloroethylene at 65° to 70° C., when catalyzed with benzoyl peroxide. No substantial difference was caused by varying the amount of catalyst a hundredfold, stopping the reaction at various stages, or adding a layer of water (experiment 4) to the trichloroethylene. The water appeared to slow down the oxidation rate slightly. The liquid product was analyzed by rearranging with triethylamine, hydrolyzing with water, and separating the organic (trichloroethyl-

Table I. Autoxidation Products of Trichloroethylene

Expt. No.	Conditions Time, hours	Temp., °C	Oxidation,[a] %	Gases COCl₂	CO	HCl	CO₂ from Bz₂O₂	Liquid[c] ClCH₂COOH	HCl
1[d]	50	70	29.3	0.039	0.038	0.40	0.0008	0.906	0.97
2[d]	68	66	80.0	0.037	0.038	0.038	0.0006	0.935	0.92
3[e]	41	65	72.6	0.062	0.062	0.062	0.046	0.910	0.96
4[f]	79	65	27.7	0.061	0.061	0.061	0.005	0.924	0.923

(Header span: "Mole per Mole Trichloroethylene Oxidized[b]" — "Gases" over COCl₂, CO, HCl, CO₂ from Bz₂O₂; "Liquid[c]" over ClCH₂COOH, HCl)

[a] Determined by amount of trichloroethylene recovered at time reaction was stopped.
[b] Moles recovered for each mole of trichloroethylene actually oxidized.
[c] Products found after rearranging with triethylamine followed by hydrolysis.
[d] Catalyst 0.001 mole Bz₂O₂ per mole trichloroethylene.
[e] Catalyst 0.10 mole Bz₂O₂ per mole trichloroethylene.
[f] One mole H₂O and 0.01 mole Bz₂O₂ per mole trichloroethylene.

Table II. Liquid Oxidation Product of Trichloroethylene

Prepn. No.	TCE[a] Used Grams	Moles	Prepn.[c]	Catalyst, Moles/mole TCE	Oxidation Temp., °C	Time, hours	Yield[b] Wt. %	Moles	Total Acidity, Ml. 1.0N NaOH/Ml.	Sp. Gr. 20°/20°	Moles/147.4 G. Oxidation Mixture H+	Cl−	I.V.[d]
Cl₂CHCOCl	...	...	..	...	..	...	...	..	20.7	1.534	2.00	1.00	0.08
1	2592	19.79	A	0.001 Bz₂O₂	70	111	91	81	20.0	1.534	2.00	1.00	...
2	497	3.78	A	0.001 Bz₂O₂	70	78[e]	92	82	24.8	...	2.38	1.40	...
3	1183	9.00	A	0.001 Bz₂O₂	70	264[e]	89	79	20.6	...	2.05	1.10	...
4[f]	785	5.97	B	10 ml. No. 7	45	233	92	82	26.6	1.539	2.54	1.60	1.49
5	1500	11.40	B	0.001 Bz₂O₂	45	424	b	..	24.5	1.546	2.34	1.36	1.08
6	394.2	3.00	C	0.001 Bz₂O₂	70	46[e]	60	53	26.9	1.542	2.58	1.62	1.24
7	394.2	3.00	C	g	70	178	91	81	27.2	1.540	2.58	1.65	1.45
8	394.2	3.00	C	1 ml. No. 7	50	156	b	..	26.3	1.543	2.45	1.50	1.30
9	412.4	3.15	C	1 ml. No. 4	50	145	b	..	27.7	1.543	2.63	1.67	1.30
10	585.8	4.48	C	10 ml. No. 9	55	71	90	80	26.9	1.541	2.60	1.63	1.50
11	610.0	4.64	D	0.001 Bz₂O₂	70	193	95	85	25.0[h]	1.548	2.50	1.55	1.37
12	230.0	1.75	E	0.001 Bz₂O₂	70	140	52	46	19.8	...	1.90	0.95	0.08

[a] Trichloroethylene.
[b] Undetermined amount of TCE carried out by excess oxygen. Moles based on Cl₂C=CHCl + ¹/₂ O₂, M. W. 147.4.
[c] See Experimental for meaning of A, B, C, etc.
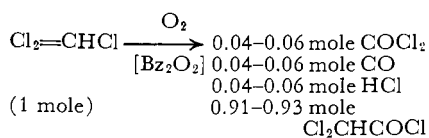[d] Atoms of iodine liberated from NaI-acetone.
[e] Reacted additional 24 hours without change.
[f] Calcd. for C₂HOCl₃: C, 16.28; H, 0.69; Cl, 72.17. Found: C, 16.6; H, 0.72; Cl. 72.1.
[g] Catalyzed by 10 ml. of TCE obtained from work tank of soybean oil extraction plant.
[h] Degassed under vacuum 30 minutes; lost 1.7% by weight of HCl.

ene) phase. The results are as follows:

$$\text{Cl}_2\text{=CHCl} \xrightarrow[\text{[Bz}_2\text{O}_2]]{\text{O}_2}$$

0.04–0.06 mole COCl₂
0.04–0.06 mole CO
0.04–0.06 mole HCl
0.91–0.93 mole Cl₂CHCOCl
(1 mole)

A small amount of extra carbon dioxide was obtained and was attributed to the benzoyl peroxide because it varied with the amount of catalyst used. As equimolar quantities of carbon monoxide and hydrogen chloride were found, it is assumed that they stem from formyl chloride. The recovery of dichloroacetic acid was not quantitative—i.e., by distillation—and the quantities reported here may be slightly low. Nevertheless, a small percentage of other products could be expected.

It therefore appeared that the major share of the autoxidation products could be expected in the liquid oxidation mixture. The small amount of phosgene produced did not appear to be a likely source of the toxicity in soybean oil meal. Furthermore, Stang and his students (37) extracted soybeans with carbon tetrachloride, which would be expected

to give phosgene, without producing a toxic meal.
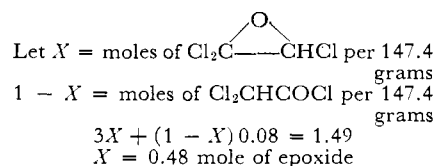
Preparation of Liquid Oxidation Mixtures

In order to make a more detailed study of the liquid products, a number of batches of trichloroethylene were oxidized to completion. Variations were made in the size of the batches, method of preparation, temperature, and catalysts. The results of 12 of these experiments are listed in Table II. The yields obtained in these experiments were always low because considerable trichloroethylene was carried off by the excess oxygen. The oxidation was stopped after the total acidity became constant for 8 to 24 hours. When 10 ml. of the liquid oxidation mixtures were decomposed in water, no insoluble phase was present, indicating less than 1% of unoxidized trichloroethylene. Where the trichloroethylene was dried and distilled before oxidation (Methods C and D), the total acidity obtained was rather constant, and a substantial quantity of the previously reported "epoxide" (22, 27) appeared to be present. In Nos. 1 and 3, the oxidation product appeared to consist primarily of dichloroacetyl chloride which may have

been caused by small amounts of magnesium or of calcium salts from the drying agents used in their preparation, which acted as rearranging catalysts. In experiment 7, the catalyst consisted of a small amount of trichloroethylene from the work tank of a soybean oil extraction plant. The work-tank sample was collected in a bottle, and the catalyst could have developed as a result of exposure to light. Several other batches (Nos. 4, 8, 9, and 10) were also oxidized using oxidized trichloroethylene to which benzoyl peroxide was not added. The nature of this catalyst was not determined, but it could be a small amount of free chlorine or a peroxide.

The specific gravity of preparations containing trichloroethylene epoxide was consistently higher than that for dichloroacetyl chloride. The moles of hydrogen and chloride ions found on hydrolyzing 0.1 ml. in 50 ml. of water are calculated to 147.4 grams of the oxidation mixture, and the values obtained increased as the epoxide content increased. The iodine value reported indicates the atoms of iodine liberated by 147.4 grams of the oxidation mixture when added to sodium iodine in dry acetone. This reaction is character-

istic of such compounds as phosgene (28) and α,α-dichloroethers. After correction for the iodine liberated by dichloroacetyl chloride, the iodine values obtained indicate that each epoxide molecule liberates 3 atoms of iodine. Thus the approximate epoxide content may be calculated from the iodine value.

For preparation 4:

Let X = moles of Cl_2C——$CHCl$ per 147.4 grams

$1 - X$ = moles of $Cl_2CHCOCl$ per 147.4 grams

$$3X + (1 - X)0.08 = 1.49$$
$$X = 0.48 \text{ mole of epoxide}$$

The iodine value was followed during the course of several oxidations and was found to increase parallel with the total acidity. It therefore appeared that the epoxide formed at a constant rate during the oxidation of trichloroethylene.

Aqueous potassium iodide liberated only a small, inconsistent amount of iodine when added to the oxidation mixtures. When the oxidation mixtures were hydrolyzed with water, aqueous potassium iodide failed to liberate iodine. Also, there was no arsenious oxide titer with the aqueous hydrolyzates, indicating the absence of oxidizing compounds.

The liquid oxidation products were stored in the refrigerator for as long as one year without apparent change other than that caused by moisture which was taken up while samples were being removed.

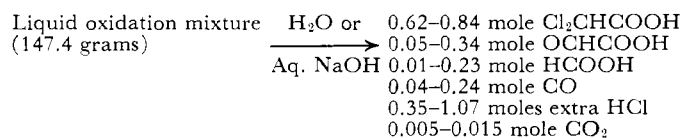**Distillation of Liquid Oxidation Mixture** Fractional distillation at reduced pressure of 152 grams of a liquid oxidation mixture (No. 10, Table II) containing 48 to 49% of trichloroethylene epoxide resulted in a yield of 30% containing approximately 70% of the epoxide. The epoxide appeared to boil about 12° lower (94–95° C.) than dichloroacetyl chloride at atmospheric

pressure. Because of a tendency of the epoxide to rearrange to dichloroacetyl chloride during distillation procedures, no further attempt was made to isolate it in pure form. Instead, its properties were studied in the mixtures which appeared to contain about equal parts of dichloroacetyl chloride and trichloroethylene epoxide.

Hydrolysis Products of Liquid Oxidation Mixtures Hydrolysis of the liquid oxidation mixtures with water or with aqueous alkali was always accompanied by various amounts of rearrangement of the epoxide to the acid chloride. With equivalent amounts of water, substantially complete rearrangement occurred. With large volumes of cold water, there was substantial hydrolysis of the epoxide to glyoxylic acid and small amounts of carbon monoxide and formic acid. With alkali and with hot water, less glyoxylic acid and more carbon monoxide and formic acid were obtained.

The products found in several hydrolysis experiments are listed in Table III. The results may be summarized as follows:

Liquid oxidation mixture (147.4 grams) $\xrightarrow{\text{H}_2\text{O or Aq. NaOH}}$
0.62–0.84 mole $Cl_2CHCOOH$
0.05–0.34 mole $OCHCOOH$
0.01–0.23 mole $HCOOH$
0.04–0.24 mole CO
0.35–1.07 moles extra HCl
0.005–0.015 mole CO_2

The extra hydrochloric acid represents that not attributed to dichloroacetyl chloride and can be correlated with hydrolysis of the epoxide. The carbon dioxide found cannot all be attributed to benzoyl peroxide, and at least part of it must stem from trichloroethylene. It probably stems from phosgene formed during hydrolysis. After carbon dioxide was boiled out of aqueous hydrolyzates, followed by excess alkali, no more carbon dioxide was obtained, indicating the absence of trichloroacetic

acid which might stem from the oxidation of chloral. Although the absence of chloral was not definitely established, its absence was evidenced by substantially complete recovery of chlorine from alkaline hydrolyzates without appearance of chloroform. Alkaline hydrolyzates always contained oxalic and glycolic acids as a result of a Cannizzaro reaction on glyoxylic acid (11).

Liquid ammonia and hot ethyl alcohol appeared to react with the epoxide without a great deal of rearrangement. On the other hand, diphenylamine gave complete rearrangement, and only the amide of dichloroacetic acid was found.

Rearrangement Experiments The liquid oxidation mixtures were rearranged by the known methods (22, 27) in order to determine their composition from hydrolysis products. The results obtained by rearranging preparations described in Table II, with triethylamine and with ferric and aluminum chlorides, are given in Table IV. Dichloroacetyl chloride and chloral were given the same treatment and are included for comparison. The percentage of loss in weight observed during rearrangement is also recorded. A small but fairly constant amount of this loss was carbon dioxide. A variable amount of hydrogen chloride was liberated, and more was obtained with aluminum chloride, probably because the reaction was more vigorous and there was a tendency for the reaction mixture to get hotter. The hydrogen chloride is believed to stem from moisture that had gotten into the liquid oxidation products.

The difference between total equiva-

Table III. Hydrolyses Products of Liquid Oxidation Mixtures

(Calculated to moles per 147.4 g.—i.e., $C_2HCl_3 + 1/2 O_2 \rightarrow C_2HOCl_3$)

Expt.	Sample No. (See Table II)	Hydrolysis Conditions	Total Acid Equiv.	Chloride Ions, Moles	$Cl_2CHCOOH$ or Deriv., Mole	$OCHCOOH$ or Deriv., Mole	HCOOH, Mole	CO, Mole	CO_2, Mole	Extra[a] HCl, Moles
A	2	60 vol. H_2O, 4°	2.64	1.69	0.62	0.34	0.01	0.04	. . .	1.07
B	4	15 vol. H_2O, 27°	2.32	1.41	0.74	0.18	0.033	0.087	0.005	0.68
C	10	Equiv. H_2O, 28°	. . .	. . .	0.92	. . .	Present	Present	0.01	. . .
D	4	15 vol. H_2O, 75°	2.16	1.20	0.85	0.057	0.06	0.10	. . .	0.35
E	10	5 vol. H_2O + equiv. NaOH. 10°	2.40	1.41	0.73	0.10[b]	0.12	0.15	Present	0.68
F	4	15 vol. H_2O + excess NaOH, 30°	2.52	1.54	0.66	0.060[c]	0.23	0.24	0.015	0.88
G	2	Liquid NH_3 in EtO_2	. . .	1.92	0.56	0.44[d]	. . .	. . .	. . .	1.36
H	2	Hot ethyl alcohol	. . .	. . .	0.64	. . .	. . .	. . .	. . .	. . .
I	9	ϕ_2NH in Et_2O, 0° → 25°	. . .	0.97	0.94	. . .	. . .	. . .	. . .	0.03

[a] Not attributed to Cl_2CH–$COCl$.
[b] Includes 0.028 mole oxalate and 0.028 mole glycolate.
[c] Includes 0.015 mole oxalate and 0.015 mole glycolate.
[d] Estimated from colored Schiff base compound found.

Table IV. Hydrolysis Products of Rearranged Liquid Oxidation Mixtures

Prepn. No.[a]	Moles per 147.4 Grams of Rearranged Product									Loss in Weight on Rearrangement, Wt.%[b]		
	Rearranged with Et₃N			Rearranged with FeCl₃			Rearranged with AlCl₃					
	H^+	Cl^-	Chloral	H^+	Cl^-	Chloral	H^+	Cl^-	Chloral	Et₃N	FeCl₃	AlCl₃
Cl₂CHCOCl	2.00	1.00	0.00	2.00	1.00	0.00	2.00	1.00	0.00	None	...	None
Chloral	...	...	...	0.00	0.00	1.00	0.00	0.00	1.00	...	None	None
4[c]	1.91	0.93	0.014	0.99	0.49	0.49	1.03	0.51	0.47	1.3	0.64	2.3
5	1.92	0.94	0.030	1.37	0.68	0.30	1.38	0.69	0.30	0.53	0.40	1.6
7	1.92	0.94	0.011	0.98	0.49	0.49	1.06	0.53	0.46	1.33	0.52	1.1
10	1.96	0.95	0.019	1.02	0.52	0.48	1.01	0.52	0.49	1.13[d]	0.88	2.4
11	1.91	0.93	0.015	1.11	0.55	0.44	1.11	0.56	0.45	0.5	1.0[e]	2.0
12	...	...	...	1.92	0.96	0.01	...	...	...	...	...	...

[a] Corresponds to Table II.
[b] Volatiles were HCl and CO₂.
[c] After heating at 80° C. for 48 hours followed by rearranging with FeCl₃: H^+, 1.72; Cl^-, 0.86; chloral 0.15 moles per 147.4 grams.
[d] Degassing rearranged product under vacuum 30 minutes; lost 0.5% by weight of HCl.
[e] Found 0.8 gram HCl and 0.2 gram CO₂.

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lents of acid and Mohr chloride indicated 0.97 to 0.99 equivalent of carboxylic acid and 0.01 to 0.02 mole of chloral per 147.4 grams of oxidation mixture in the triethylamine rearranged mixture. Discounting No. 5, which had apparently become partially rearranged, probably because of moisture, both ferric and aluminum chlorides gave 0.44 to 0.49 mole of chloral and 0.49 to 0.56 equivalent of carboxylic acid. Anomalous results were obtained with No. 12. This preparation was made by oxidizing trichloroethylene containing triethylamine hydrochloride. It appears that amine hydrochlorides are rearranging catalysts. Iron wire was as effective a rearranging catalyst as anhydrous ferric chloride. This finding indicates that it might be possible for the epoxide to rearrange to chloral in a soybean oil extraction plant.
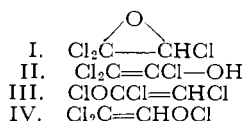
In order to examine further the products in the rearranged mixtures, several large batches were rearranged with triethylamine. The results of one of these experiments are shown in Table V.

Carbon, hydrogen, and chlorine balances based on elementary analyses of the starting material indicate that probably all of the products contained in the mixture were found.

In another experiment 147.4 grams of No. 7, Table II, were rearranged with 0.2 gram of aluminum chloride. The loss in weight was 1.6 grams. The liquid product was hydrolyzed with 50 ml. of water and distilled under reduced pressure to give two fractions. By titration the low-boiling fraction contained 0.041 equivalent of carboxylic acid, which on ether extraction and distillation proved to be dichloroacetic acid and 0.40 mole of chloral hydrate; after addition of excess alkali, the organic layer was separated and distilled to yield 0.34 mole of chloroform: boiling point 61° C.; [η]¹⁸° 1.4469. Mohr chloride determination indicated 0.49 mole of hydrochloric acid. The higher boiling fraction contained 0.466 mole of dichloroacetic acid (by distillation), 0.08 mole of chloral (by titration), and 0.02 mole of hydrogen chloride.

Evidence for Trichloroethylene Epoxide

The epoxide was not isolated and identified. However, the properties of the oxidation mixtures offer considerable evidence for the epoxide structure. The following isomeric structures have been considered:

$$
\begin{array}{l}
\text{I.} \quad Cl_2C\!\!\!\overset{O}{\diagup\diagdown}\!\!\!CHCl \\
\text{II.} \quad Cl_2C\!\!=\!\!CCl\!-\!OH \\
\text{III.} \quad ClOCCl\!=\!CHCl \\
\text{IV.} \quad Cl_2C\!\!=\!\!CHOCl
\end{array}
$$

Structures III and IV should give hypochlorous acid on hydrolysis, and none was found. Structure II, being an alcohol, should react with dichloroacetyl chloride and liberate hydrogen chloride; this was not observed. Structure I, trichloroethylene epoxide, should have the properties of an α,α'-dichloroether as well as those of an epoxide. The ease with which the chlorine atoms were hydrolyzed and the liberation of iodine from an iodide under anhydrous conditions are typical of such an ether. The ease with which it undergoes isomeric rearrangement would be expected of an epoxide. It did not add hydrogen chloride in a typical epoxide manner.

At solid carbon dioxide temperature, the quantity of hydrogen chloride absorbed by an oxidation mixture was equivalent to the epoxide content. However, the gas rapidly boiled off on warming to −30° C. Failure to react with hydrogen chloride is attributed to the ether properties.

Studies with the liquid oxidation mixtures demonstrated that the epoxide hydrolyzed to yield glyoxylic and formic acids and carbon monoxide with greater amounts of 1-carbon compounds in the presence of alkali. These results are analogous to the hydrolysis of oxalyl chloride. to give carbon dioxide, carbon monoxide, and hydrogen chloride for which an epoxide intermediate has been postulated (42).

Summary and Conclusions

Extraction-grade trichloroethylene containing triethylamine as an oxidation stabilizer was found to be resistant to autoxidation. However, this water-soluble inhibitor was soon lost in the operation of a soybean oil extraction plant, and the resultant solvent was capable of developing its own catalyst, which caused autoxidation to proceed in the absence of light. The autoxidation of

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Table V. Products Obtained after Rearranging Oxidized Trichloroethylene[a] with Triethylamine

	Mole	Grams	Carbon, Moles	Hydrogen, Moles	Chlorine, Moles
Elementary analysis Found[c]	...	147.4	2.04	1.1	2.99
Cl₂CHCOCl	0.942	138.8	1.884	0.942	2.826
Cl₂CHCOOH[d]	0.024	3.1	0.048	0.048	0.048
Cl₃CCHO	0.014	2.7	0.028	0.014	0.042
HCl[d]	0.044	1.6	...	0.044	0.044
CO₂[e]	0.01	0.3	0.01	...	...
Polymer[f]	0.008	1.0	0.016	0.008	0.024
Total		147.5	1.986	1.056	2.984
Recovery, %		100.0	97.3	96.0	99.8

[a] Preparation 4, Table II.
[b] Analysis of starting material, %. C, 16.6; H, 0.72; Cl, 72.1.
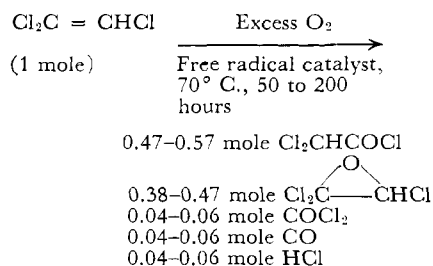[c] Also traces of formic and glyoxylic acids.
[d] Resulted from moisture getting into oxidation mixture subsequent to preparation.
[e] Probably stems from phosgene.
[f] Moles calculated on C₂HCl₃.

trichloroethylene proceeded in the presence of benzoyl peroxide without light, provided the temperature was high enough to decompose the peroxide to free radicals.

On autoxidation, about 95% of the trichloroethylene was converted to a liquid and about 5% was oxidized to gaseous products. This ratio appeared to be maintained throughout the course of the reaction. The liquid mixture was composed of about equal parts of dichloroacetyl chloride and a very reactive isomeric compound which appeared to be trichloroethylene epoxide. The gases consisted of phosgene, carbon monoxide, and hydrogen chloride in equimolar quantities. The products obtained as well as the reaction conditions used are summarized as follows:

$$Cl_2C = CHCl \xrightarrow[\substack{\text{Free radical catalyst,} \\ 70° C., 50 \text{ to } 200 \\ \text{hours}}]{\text{Excess } O_2}$$

(1 mole)

0.47–0.57 mole $Cl_2CHCOCl$

0.38–0.47 mole $Cl_2C\overset{O}{—}CHCl$

0.04–0.06 mole $COCl_2$

0.04–0.06 mole CO

0.04–0.06 mole HCl

The trichloroethylene epoxide had a higher specific gravity and a lower boiling point than dichloroacetyl chloride. It readily rearranged to dichloroacetyl chloride and chloral, depending upon the catalyst present. On addition to water or aqueous alkali, part of it rearranged to dichloroacetyl chloride, which in turn was hydrolyzed, and the remainder was hydrolyzed directly to glyoxylic acid, carbon monoxide, formic acid, and hydrogen chloride.

An understanding of the autoxidation products of trichloroethylene facilitates toxicity studies of their reaction products with soybeans and soybean oil meal. The results of these toxicity studies are the subject of a separate publication.

Nomenclature

"Soybean oil meal" is the term adopted to designate solvent-extracted soybean flakes that have been cooked and ground for feed (7).

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