[Contribution from Department of Chemistry, Kansas State University]

The Rearrangement of Certain Trichloromethylcarbinols to α-Chloro Acid Chlorides[1a]

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A study of the reaction of sulfuric acid upon a number of selected trichloromethylcarbinols is reported. *t*-Trichloromethylcarbinols having two methyls or one methyl together with one chloromethyl attached to the carbinol carbon gave good yields of the corresponding α-chloro acid chlorides by a pinacol type of rearrangement. The presence of water in the reaction mixture caused hydrolysis of part of each α-chloro acid chloride to the corresponding α-chloro acid. With 100% sulfuric acid and essentially anhydrous trichloro-*t*-butyl alcohol, α-chloroisobutyryl chloride was isolated in yields of 58–64% by this new method. Rearrangement of 1,1,1,3-tetrachloro-2-methyl-2-propanol gave α,β-dichloroisobutyryl chloride. The action of sulfuric acid on *t*-trichloromethylcarbinols having secondary hydrogen alpha to the tertiary carbinol carbon gave predominantly mixtures of crude trichloro olefins and tar along with small amounts of the α-chloro acid. *t*-Carbinols that offer no internal structural and electronic assistance for forming the transitory carbonium ion necessary for the pinacol type of rearrangement failed to give the reaction. Thus, 1,1,1-trichloro-3-nitro-2-propanol and 2,2,2-trichloroethanol gave no appreciable reaction with sulfuric acid. 1,1,1-Trichloro-2-phenyl-2-ethanol reacted but was converted to a polymeric gum.

The accepted mechanism of the pinacol–pinacolone rearrangement[2] involves protonation of the hydroxyl function followed by concerted formation of a carbonium ion and movement of a methyl group with its pair of electrons. It seemed of interest to subject chloretone (trichloro-*t*-butyl alcohol) to the conditions of this rearrangement to determine if it could be converted to α-chloroisobutyryl chloride. This paper reports the results of a study of the action of sulfuric acid on this alcohol and a number of other trichloromethylcarbinols.

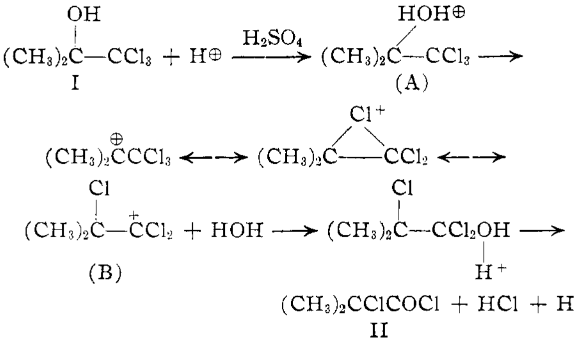
Table I

HOH[a] in the butanol, %	Total time of reacn., min.	Yield of acid chloride, %	Yield of acid, %
0.16[b]	34	64[b]	17
.2[b]	29	58[b]	25
.5	34	54	27
.6	30	48[c]	28
1.3	53	43[c]	36
1.7	48	39[c]	36
2.9	60	17	..
4.4	150	None	72

[a] Analyses with Karl Fisher reagent according to the method of Mitchell and Smith (J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N.Y., 1948, pp. 65–71). [b] Benzol Products Co. anhydrous trichlorobutanol was used here and repeatedly gave yields of 60% or higher. [c] Average of three reactions.

Concentrated sulfuric acid reacts with trichloro-*t*-butyl alcohol hemihydrate at 50° and below to give 84% of α-chloroisobutyric acid. Use of 98.5% sulfuric acid on the hemihydrate between 20 and 25° raised the yield of α-chloroisobutyric acid to 94%. With 100% sulfuric acid and essentially anhydrous trichloro-*t*-butyl alcohol, α-chloroisobutyryl chloride was obtained in yields of 58–64%. It is essential that the internal reaction temperature does not rise above 50°; otherwise extensive decarbonylation of the acid chloride occurs.

This rearrangement of the chloroalcohol can be represented as a modification of the pinacol–pinacolone type that proceeds according to the scheme



$$\underset{\text{I}}{(CH_3)_2\overset{\overset{\large OH}{|}}{C}—CCl_3} + H^{\oplus} \xrightarrow{H_2SO_4} \underset{(A)}{(CH_3)_2\overset{HOH^{\oplus}}{C}—CCl_3} \longrightarrow$$

$$(CH_3)_2\overset{\oplus}{C}CCl_3 \longleftrightarrow (CH_3)_2C\overset{Cl^+}{——}CCl_2 \longleftrightarrow$$

$$\underset{(B)}{(CH_3)_2\overset{\overset{\large Cl}{|}}{C}—\overset{+}{C}Cl_2} + HOH \longrightarrow (CH_3)_2\overset{\overset{\large Cl}{|}}{C}—CCl_2\underset{\underset{\large H^+}{|}}{O}H \longrightarrow$$

$$\underset{\text{II}}{(CH_3)_2CClCOCl} + HCl + H^{\oplus}$$

The effect of different percentages of water of hydration in the trichloro-*t*-butyl alcohol is summarized in Table I.

The same basic scheme was used to explain the reactions of hydrated trichloro-*t*-butyl alcohol with chlorobenzene and bromobenzene in presence of aluminum chloride, which yielded α-chloroisobutyric acid in yields as high as 37%.[3]

In contrast to the facile rearrangement of trichloro-*t*-butyl alcohol, 1,1,1,3-tetrachloro-2-methyl-2-propanol, prepared by a peroxide-catalyzed reaction of sulfuryl chloride with chloretone, reacted very slowly with 100% sulfuric acid at 25°. However, at 40–50° the rearrangement was complete in about 5 hours. The yields of α,β-dichloroisobutyryl chloride ranged up to 47%; α,β-dichloroisobutyric acid (13%) was also obtained.

This rearrangement probably proceeds by the same scheme shown above. The strong opposing inductive effect of the $-CH_2 \rightarrow Cl$ group in 1,1,1,3-tetrachloro-2-methyl-2-propanol hinders the loss of water from the carbinol carbon in the transformation of (A) to (B) above. This explanation is consistent with the fact that each of three rearrangements of 1,1,1,3-tetrachloro-2-methyl-2-propanol required about 65 times as long for comple-

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[1a] Abstracted from a portion of the Ph.D. thesis of E. A. Ikenberry and from a portion of the Ph.D. thesis of E. B. W. Ovist submitted to the Graduate School, Kansas State University, in partial fulfillment of their respective Ph.D. degrees.

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[2] (a) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, Chapter 3, pp. 45–49. (b) *Ann. Repts. Chem. Soc. (London)*, **27**, 114 (1930); **30**, 181 (1933); **36**, 195 (1939).

[3] D. G. Kundiger and Huey Pledger, Jr., This Journal, **78**, 6099 (1956).

tion of reaction as did six typical rearrangements of 1,1,1-trichloro-2-methyl-2-propanol.

t-Trichloromethylcarbinols that offer no internal structural and electronic assistance for forming the transitory carbonium ion did not give rearrangement. Thus, 1,1,1-trichloro-3-nitro-2-propanol and 2,2,2-trichloroethanol gave no appreciable reaction with either concentrated or 100% sulfuric acid. 1,1,1-Trichloro-2-phenyl-2-ethanol gave essentially none of the pinacol type rearrangement as no acid chloride or no acid product was detectable. In the latter case, although hydrogen chloride was evolved from reaction with sulfuric acid, the only isolable product was reddish polymeric gum.

Both 1,1,1-trichloro-2-methyl-2-propanol and 1,1,1,3-tetrachloro-2-methyl-2-propanol rearranged to α-chloro acid chlorides and α-chloro acids with relatively little accompanying dehydration. In contrast the action of sulfuric acid on trichloromethylcarbinols having secondary hydrogen alpha to the *t*-carbinol carbon caused extensive dehydration. For example, 1,1,1-trichloro-2-methyl-2-octanol gave a mixture of crude isomeric trichlorononenes (44%) as indicated by carbon, hydrogen, chlorine analyses and infrared spectrum, along with 15% of 2-chloro-2-methyloctanoic acid and about 30% tar. The opposite mode of addition, the gradual introduction of the 1,1,1-trichloro-2-methyl-2-octanol into 100% sulfuric acid rather than *vice versa*, gave 26% of fairly pure 2-chloro-2-methyloctanoic acids, but the yield of the mixture of trichlorononenes decreased markedly to 9% and the tar increased to about 50%.

The pinacol rearrangement of 1-trichloromethyl-1-cyclohexanol (two secondary α-hydrogens) gave a small yield (less than 10%) of a mixture of acids indicated by infrared spectra and analyses as a mixture of 1-chlorocyclohexanecarboxylic acid and 1-cyclohexenecarboxylic acid. The remainder was converted to polymeric gums and a tan polymeric material of indefinite composition.

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Experimental[4,5]

α-Chloroisobutyric Acid by Rearrangement of Trichloro-*t*-butyl alcohol (Chloretone) (I) with Sulfuric Acid.—Chloretone *hemihydrate* was added slowly, with stirring, to a variety of concentrations of sulfuric acid, to test the effect of concentration. This addition was made to the same relative volume of the sulfuric acid solution, 200 ml. of the acid per mole of the alcohol hemihydrate. A cooling bath was required to maintain the temperature at 20–25° or at 50°. After subsidence of the evolution of HCl, the reaction mixture was poured over cracked ice. The organic material was extracted with benzene, dried, the benzene distilled, and the α-chloroisobutyric acid isolated by distillation, b.p. 91° (17 mm.). The yields of this acid isolated from the various concentrations of sulfuric acid (%) and the reaction temperatures were: 94% from (98.5%) at 20–25°; 84% from (96%) at 50°; 62% from (90%) at 70°; 34% from (80%) at 120°; and no reaction from (50%) at reflux temperature. The higher reaction temperatures (70 and 120°) were found necessary in order to obtain appreciable speed of reaction (evolution of HCl) with the lower concentrations of sulfuric acid. Extensive evolution of carbon monoxide was detected with 96% sulfuric acid at temperatures above 50°.

α-Chlorisobutyryl Chloride (II) by Rearrangement of Trichloro-*t*-butyl Alcohol (I) with 100% Sulfuric Acid.—Because of the violence of this reaction, it was best controlled with the following specially designed apparatus. The reaction vessel consisted of a cylindrical water jacketed Pyrex tube (6 × 60 cm.) equipped with a stopcock at the bottom. The top was closed with a rubber stopper fitted with a mechanical stirrer, an inlet tube for sulfuric acid which extended to the bottom of the reactor, a spray orifice at the top through which small amounts of a defoaming agent (such as petroleum ether, b.p. 35°) could be added from time to time by forcing it in gently with air pressure, and an outlet to a water scrubber for the HCl formed in the reaction. With this special apparatus, the following procedure was used. Trichloro-*t*-butyl alcohol (3 moles) was placed in the reactor and 270 ml. of 100% sulfuric acid was pumped into the reactor at the rate of 8 to 16 ml./min. depending on the vigor of the initial and continuing reaction. Stirring was begun as soon as sufficient butanol was dissolved to free the stirrer paddle. Foaming caused by the vigorous reaction with the nearly anhydrous butanol was controlled by introducing very small amounts of petroleum ether (b.p. 35°) from time to time through the spray orifice directed at the stirrer shaft at the upper surface of liquid. The build-up of the foaming action is such that it carried the reactants from the reactor in complete absence of a defoaming agent. Most of the small amount of petroleum ether added is carried off in the exit HCl gas while the reaction is allowed to proceed at about 25° (external cooling).

Within a few minutes after the sulfuric acid addition was completed, the solution became cloudy and shortly thereafter a particularly violent stage of reaction occurred. This was accompanied by rapid evolution of HCl and lasted about 5 min. As the reaction subsided the reaction mixture separated into two layers and stirring was stopped. The system was allowed to stand 5 min. and the bottom layer (sulfuric acid with its dissolved acid chloride) was drained. The upper layer consisted of α-chloroisobutyryl chloride, a small amount of dissolved hydrogen chloride and a small amount of petroleum ether. This acid chloride was distilled at once to give pure α-chloroisobutyryl chloride, b.p. 58–59° (80 mm.) or b.p. 62–65° (112 mm.). The sulfuric acid layer was poured over crushed ice, extracted with benzene, washed, dried, the benzene distilled, and the residue distilled to give α-chloroisobutyric acid, b.p. 91–92° (17 mm.). Effects of different concentrations of water in the trichlorobutanol are shown in Table I.

α,β-Dichloroisobutyryl Chloride and α,β-Dichloroisobutyric Acid by Rearrangement of 1,1,1,3-Tetrachloro-2-methyl-2-propanol.—In the same apparatus described above for the synthesis of α-chloroisobutyryl chloride, and using the same general procedure, 255 g. (1.2 moles) of the pure anhydrous tetrachloro alcohol named was treated with 110 ml. of 100% sulfuric acid at 40–50° and gave 98.1 g. (47%) of α,β-dichloroisobutyryl chloride after 5.5 hours of reaction time. This new acid chloride had b.p. 89–90° (85 mm.), n^{20}D 1.4688 d^{20}_4 1.388.

Anal. Calcd. for $C_4H_5Cl_3O$: C, 27.35; H, 2.8; Cl, 60.68. Found: C, 27.40; H, 2.7; Cl, 60.50.

The sulfuric acid layer was hydrolyzed to yield 24.3 g. (13%) of α,β-dichloroisobutyric acid, b.p. 113–114° (15 mm.), n^{20}D 1.4825, d^{20}_4 1.450. This product contained 44.98% Cl; calcd. 45.22%.

The yield of the acid chloride varied significantly with the size of the run, but the total yield of both acid chloride and the corresponding acid varied very little. Thus, in two other runs conducted in the same way except for moles of carbinol used, the results were: from 2.48 *M* of the carbinol, obtained 92.5 g. (21%) of the acid chloride and 114.6 g. (29%) of the acid; from 3.0 *M* of the carbinol, obtained 154.5 g. (29%) of the acid chloride and 101 g. (20%) of the acid.

The α,β-dichloroisobutyryl chloride was converted to *p*-chlorophenyl and 2,4-dimethylphenyl α,β-dichloroisobutyrate by heating with the appropriate phenol in presence of aluminum chloride. The *p-chlorophenyl α,β-dichloroisobutyrate* boiled at 112–114° (1.0 mm.), n^{20}D 1.5281, d^{20}_4 1.358.

Anal. Calcd. for $C_{10}H_9Cl_3O_2$: C, 44.86; H, 3.36; Cl, 39.81. Found: C, 45.01; H, 3.29; Cl, 39.68.

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(4) All m.p.'s and b.p.'s are uncorrected.

(5) Elemental analyses by Weiler and Strauss, Oxford, England.

The 2,4-*dimethyl* α,β-*dichloroisobutyrate* boiled at 94–99° (0.4 mm.) and melted at 68.0–68.5° upon two crystallizations from ethanol–water. The first m.p. obtained before recrystallization was 67.5–68°.

Anal. Calcd. for $C_{12}H_{14}Cl_2O_2$: C, 55.20; H, 5.36; Cl, 27.15. Found: C, 55.23; H, 5.14; Cl, 26.98.

1,1,1,3-Tetrachloro-2-methyl-2-propanol by Peroxide-catalyzed Reaction of Sulfuryl Chloride with Trichloro-*t*-butyl Alcohol.—Trichlorobutanol (178 g., 1 mole) was dissolved in 500 ml. of dried carbon tetrachloride and the solution maintained at reflux throughout the following reaction period. Benzoyl peroxide (5 g.) was added and then purified sulfuryl chloride (148 g., 1.1 moles) was added dropwise. Later a second 5 g. of the peroxide was added and the refluxing continued; total reaction time 5–6 hours. From each of two such runs a 73% and a 70% yield of the tetrachloro compound and also a 9% yield of a dechlorinated product were isolated by the following procedure. The solvent and unreacted sulfuryl chloride were distilled and the residue fractionated under reduced pressure to give 43 g. of forerun that was mostly returned trichloro-*t*-butyl alcohol, followed by 154 g. of approximately pure 1,1,1,3-tetrachloro-2-methyl-2-propanol, b.p. 97–105° (15 mm.), and 21 g. at b.p. 105–116° (15 mm.), mostly dichlorinated starting material. These two latter fractions were blended and refractionated to give 98.4 g. (46%) of highly purified 1,1,1,3-tetrachloro-2-methyl-2-propanol, b.p. 98–100° (14 mm.), $n^{20}D$ 1.5138–1.5145, d^{20}_4 1.591. This product was analyzed: C, 22.68; H, 2.71; Cl, 66.63; Calcd.: C, 22.64; H, 2.83; Cl, 66.91. (The reported[6] b.p. of this compound, made by an entirely different method, is b.p. 92° (12 mm.).)

From this fractionation, the dichlorinated trichloro-*t*-butyl alcohol was also obtained. The analytical sample boiled at 112–113° (14 mm.), $n^{20}D$ 1.5252, d^{20}_4 1.614.

Anal. Calcd. for $C_4H_6Cl_5O$: C, 19.48; H, 2.03; Cl, 72.00. Found: C, 19.96; H, 2.20; Cl, 72.03.

Instead of benzoyl peroxide as the catalyst for this preparation, α,α′-azodiisobutyronitrile (3 g.) was used and gave about the same yield of 1,1,1,3-tetrachloro-2-methyl-2-propanol. The use of di-*t*-butyl peroxide gave a 30% yield of the tetrachloro product.

Synthesis of 1,1,1-Trichloro-2-methyl-2-octanol.—This compound was synthesized by a modification of the procedure of Weizmann, Bergmann and Sulzbacher.[7]

The preferred procedure is not to employ a solvent such as methylal or ethylal but rather to use simply an excess of the 2-octanone being allowed to react with chloroform. Twenty reactions were run in preparing 1,1,1-trichloro-2-methyl-2-octanol. Different amounts of potassium hydroxide used (0.2 to 1.2 equivalents per mole of chloroform) did not significantly affect the yields of the trichloromethylcarbinol obtained. 2-Octanone (2.0 moles) and chloroform (1.0 mole) were treated at a temperature of 0–5° with powdered potassium hydroxide (1.0 mole; analytical grade, 85% with 15% water) in small portions with stirring. After one hour, the reaction mixture was poured over crushed ice, stirred, the organic layer separated, and the aqueous layer extracted with ether. The ethereal extracts and the organic layer were combined and the ether and excess reactants removed by fractionation. Continued fractionation gave 31.5 g. (13%) of **1,1,1-trichloro-2-methyl-2-octanol**, b.p. 137–140° (19 mm.), $n^{20}D$ 1.4770, d^{20}_4 1.160.

This compound slowly decomposes from heat during distillation, giving off hydrogen chloride as was detected and proved. Different samples were tried in different distillations, and even at b.p. 87° (0.6 mm.) the same partial evolution of hydrogen chloride occurred and no better analyses could be obtained than those reported here. Calcd. for $C_9H_{17}Cl_3O$: C, 43.71; H, 6.88; Cl, 43.23. Found: C, 45.57; H, 7.18; Cl, 39.78. Redistillations gave less effective percentage values for the elements due to further loss of HCl. However, the obtained samples of 1,1,1-trichloro-2-methyl-2-octanol were essentially this compound as infrared analyses showed this to be the case. The partial loss of HCl under distillation explains the analytical values. When the same reaction (same amounts) was run for double the previous reaction time, substantially the same results were obtained.

A Modified Preparation of 1-Trichloromethyl-1-cyclohexanol.—This modification represents a simplification compared to the procedure reported previously.[7] The preferred procedure is to use a 4-to-1 mole ratio of cyclohexanone to chloroform and no added solvent. Chloroform (1.0 mole) was mixed with cyclohexanone (4.0 moles) and 0.5 mole of potassium hydroxide was gradually added at 0–5°. Reaction was continued at 0–5° for one hour. The reaction mixture was worked up as in the preceding experiment, and nearly all of the unconverted cyclohexanone (98%) was recovered for use again. Further fractionation gave 81.5 g. (37%) of 1-trichloromethyl-1-cyclohexanol, b.p. 120–124° (14 mm.). This distillate crystallized for the most part from the remaining small portion of liquid and the white crystals were filtered and dried, m.p. 58–59°.

Anal. Calcd. for $C_7H_{11}Cl_3O$: C, 38.65; H, 5.06; Cl, 48.90. Found: C, 38.17; H, 5.15; Cl, 49.03.

Reaction from Adding 1,1,1-Trichloro-2-methyl-2-octanol to 100% Sulfuric Acid.—About 50% of tar resulted from this reaction at 25–45°, cooled by running water. The substituted octanol (169 g., 0.65 mole) was introduced slowly to 125 ml. of 100% sulfuric acid wth power stirring. After reaction ceased (no more HCl evolved), the reaction mixture was allowed to stand. It stayed as one liquid phase, was poured over flaked ice, warmed to 25°, and the organic layer was separated. Extracts of the water layer with chloroform and ether were combined with the organic layer. It was thoroughly emulsified by rapid power stirring with a large excess of sodium bicarbonate solution at 100° for 3 hours. Part of the organic layer went into the alkaline solution with evolution of CO_2. The neutral insoluble organic layer was separated.

Acidification of the separated alkaline layer gave an oily layer of an organic acid. It was removed, washed with water several times and dried. Fractionating twice gave 33.2 g. (26% of 2-chloro-2-methyloctanoic acid), b.p. 121.5–126° (2.4 mm.), in 8 distillate cuts. Of this amount 13.4 g. (11%) was analytically pure 2-chloro-2-methyloctanoic acid, $n^{20}D$ 1.4555–1.4550, b.p. 122–124° (2.4 mm.); neut. equiv. 188, calcd. 192.5.

Anal. Calcd. for $C_9H_{17}ClO_2$: C, 55.00; H, 8.65; Cl, 18.41. Found: C, 55.73; H, 8.60; Cl, 18.25.

The infrared spectrum of this acid supported the assigned structure because of essential identity with the infrared spectrum of an authentic sample of α-chloroisobutyric acid.

Washing of the neutral organic layer with water several times, followed by drying and distillation away from the large amount of tar, gave 58 g., b.p. 86–111° (2 mm.). Of this distillate, 42 g. was stirred with excess concd. sulfuric acid at 10° to dissolve out any admixed by-products soluble in this acid. The sulfuric acid layer was separated and the other insoluble-in-acid layer was washed thoroughly with water, with sodium bicarbonate, again with water, dried, and distilled. Besides the large tar residue, 14.5 g. (9%) of fairly pure trichlorononenes distilled at 94.5–99° (2 mm.), $n^{20}D$ 1.4830–1.4831. Direct comparison of this material with the distillate of trichlorononenes in the following experiment indicated both distillates were mixtures of trichlorononenes inasmuch as both checked in b.p., in refractive index and in infrared spectrum.

Opposite Mode of Addition, 100% Sulfuric Acid to 1,1,1-Trichloro-2-methyl-2-octanol.—When the opposite mode of addition with about the same ratio of reactants was used at 35–45°, the pattern of results was quite different. A much higher yield of trichlorononenes (44%) was obtained in contrast to the 9% yield before. Tar formation was decreased about 20%; chloroacid formation was about 10% less. From reaction of 165 ml. of 100% sulfuric acid with 218 g. (0.845 mole) of the 1,1,1-trichloro-2-methyl-2-octanol, workup gave 26.4 g. (15%) of 2-chloro-2-methyloctanoic acid, b.p. 100–102° (1 mm.), $n^{20}D$ 1.4545–1.4569. Fractionation of the neutral organic materials gave 87 g. (44%) of a mixture indicated as trichlorononenes, b.p. 62–78° (0.7 mm.), inasmuch as the material contained very little or no oxygen by analyses and typical cuts of the distillate gave approximately correct analyses for a trichlorononene. A typical cut, b.p. 74–75° (0.7 mm.), contained: C, 48.20; H, 7.10; Cl, 44.4. These percentages add up to 99.7% and are reasonably close to the values for the theoretically derived trichlorononene and its allylic rearrangement isomer under the conditions. The heating during distillation at 0.7 mm. caused the trichlorononenes to evolve a

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[6] F. Arndt, S. Amende and W. Ender, *Monatsh.*, **59**, 202 (1932).

[7] C. Weizmann, E. Bergmann and M. Sulzbacher, THIS JOURNAL, **70**, 1189 (1948).

small amount of hydrogen chloride, which was detected in the exhaust gas. This fact explains the elemental analyses for C, H and Cl as compared to the theoretical values for pure 1,1,1-trichloro-2-methyl-2-octene or its allylic isomer, 1,1,3-trichloro-2-methyl-1-octene: C, 47.21; H, 6.54; Cl, 46.37. On a representative number of fractions of the trichlorononenes, infrared spectra indicated the presence of 1,1,3-trichloro-2-methyl-1-octene as there were strong bands at 6.18 and 11.09 μ characteristic of $-C(CH_3)=CCl_2$ since $CH_2ClC(CH_3)=CCl_2$ has strong bands at 6.19 and 11.09 μ.

Reaction of 1-Trichloromethyl-1-cyclohexanol with 95% Sulfuric Acid.—Seventy-five grams of 1-trichloromethyl-1-cyclohexanol, prepared as above, m.p. 58–59°, was added slowly with stirring and external cooling to 32 ml. of concentrated sulfuric acid, keeping the reaction temperature at 20–40°. When hydrogen chloride substantially ceased to be evolved, the black viscous mixture was poured over ice and water, stirred, the organic layer extracted with carbon tetrachloride, washed with water many times, dried, and fractionated. Only 7 g. (less than 10% yield) of organic acids, b.p. 115–120° (0.1 mm.), n^{20}D 1.4751, was distillable and obtained. This small yield of acids, as a single fraction, was indicated by its infrared spectrum to be 52% 1-chlorocyclohexanecarboxylic acid and 48% 1-chlorocyclohexenecarboxylic acid, consistent with the 11.4% chlorine and 58.2% carbon contents found for this mixture. These indications from the infrared were based on a broad diffuse band typical of acids (2.8–4.0 μ), the carbonyl bands for the carboxylic acid group at 5.86, 7.85 and 7.95 μ, and one component present to the extent of about 50% contained C=C because of a very strong band at 6.09 μ. Bands for C–H at 3.4 and 3.5 μ were present and absorption at 13.5 μ is probably due to the carbon–chlorine stretch of the cyclic tertiary chlorine atom in 1-chlorocyclohexanecarboxylic acid. Practically all of the remainder of the products was a gummy polymer which was discarded; 9 g. of tan solid polymers of wide indefinite melting range was also obtained and discarded.

Reaction of Other Trichloromethylcarbinols with Sulfuric Acid.—(A) Ten grams of pure 1,1,1-trichloro-3-nitro-2-propanol was mixed with 10 ml. of 100% sulfuric acid and stirred continuously at 50–70° for 0.5 hour, then at 70–80° for 0.5 hour, then at 80–85° for 0.5 hour. No reaction occurred since no HCl was evolved. The reaction mixture was poured over crushed ice and worked up. No indications of formation of an acid chloride or of an organic acid appeared; the original 1,1,1-trichloro-3-nitro-2-propanol was recovered. (B) Five grams of pure 2,2,2-trichloroethanol was mixed with 5 ml. of 100% sulfuric acid and stirred at temperatures up to 80° for several hours; no HCl evolution occurred. The 2,2,2-trichloroethanol was recovered. (C) Twenty grams of 1,1,1-trichloro-2-phenyl-2-ethanol, b.p. 148–150° (16–17 mm.), n^{20}D 1.5673, was added to stirred 100% sulfuric acid and the temperature gradually increased up to 90° in order to obtain substantial HCl evolution. No organic acid or acid chloride was isolable. Instead, a reddish gum, which was not further investigated, was obtained.

MANHATTAN, KANSAS

[COMMUNICATION NO. 2043 FROM THE KODAK RESEARCH LABORATORIES]

Mechanism of the Peroxidatic Activity of Iron(III)–EDTA in the Catalyzed Reaction of Hydrogen Peroxide with *p*-Amino-N,N-diethylaniline

BY PAUL M. MADER

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The rate of disappearance of hydrogen peroxide in its reaction with *p*-amino-N,N-diethylaniline, catalyzed by the ferric iron–EDTA complex, has been measured polarographically in the *p*H range 9.67–10.54. The kinetic data are explained by assuming that the catalyst oxidizes the diamine and is rapidly regenerated by reaction of the reduced catalyst with hydrogen peroxide. The kinetic data show that the purple complex formed between hydrogen peroxide and ferric iron–EDTA is not an active catalyst for the diamine–peroxide reaction. The equilibrium constant for the reversible oxidation of the diamine by the catalyst has been determined at several *p*H values.

In a study of reactions occurring in an aerated photographic color developer containing EDTA [(ethylenedinitrilo)-tetraacetic acid], it was found that traces of iron salts cause the hydrogen peroxide, formed in the autoxidation of the developing agent, to react with the developing agent rather than with the sodium sulfite present in the developer.[1] This effect was shown to be due to catalysis of the reaction of hydrogen peroxide with the developing agent, *p*-amino-N,N-diethylaniline. There is little doubt that the active catalyst is the ferric iron–EDTA complex, since catalysis of comparable degree is not observed in the absence of EDTA. In this reaction, then, the complex acts as a peroxidase. The present paper reports the results of a study of the kinetics and mechanism of this catalyzed reaction.

In the kinetic experiments, the concentration of hydrogen peroxide was measured continuously using the polarograph. The reactions were carried out in the presence of 4-chloro-1-naphthol, which reacts rapidly with the oxidation product of *p*-amino-N,N-diethylaniline to give an insoluble indoaniline dye.[2] It was helpful to remove the oxidation product, since it gives a polarographic current which interferes with the analysis for hydrogen peroxide, and since it apparently reacts further with the hydrogen peroxide, thus complicating interpretation of the rate data.

Carbonate buffers containing 5.4×10^{-3} *M* EDTA were used in all the experiments. The temperature was 25°, and the ionic strength was 0.38.

Experimental

Materials.—All inorganic chemicals were reagent-grade (except $NaHSO_3$ and $Na_2S_2O_4$) and were obtained from the General Chemical Division of Allied Chemical and Dye Corp. The (ethylenedinitrilo)-tetraacetic acid tetrasodium salt and the reagent grade disodium salt were obtained from the Geigy Chemical Corp. Photographic grade *p*-amino-N,N-diethylaniline hydrochloride was recrystallized from ethanol. The 4-chloro-1-naphthol,[3] crystallized from ligroin, melted at 124–126°. Double-distilled water was used.

Preparation of the Indoaniline Dye.—A solution of 5 g. of $K_3Fe(CN)_6$ in 100 ml. of water was added rapidly to a solution consisting of 1.0 g. of *p*-amino-N,N-diethylaniline hydrochloride, 0.5 g. of 1-naphthol (1-naphthol gives the same dye as 4-chloro-1-naphthol[2]), 5 g. of $Na_2CO_3 \cdot H_2O$, 12 ml. of

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(2) L. K. J. Tong and M. Carol Glesmann, THIS JOURNAL, **79**, 583 (1957).

(3) H. Kast, *Ber.*, **44**, 1337 (1911).