

acid-base titration for weak dibasic acids has been extended to include the influence of ion-association of salts in low dielectric media. An equation indicating the effect of ion-association on the acid dissociation was obtained.

2. Potentiometric titrations of the dibasic acids: oxalic, malonic, succinic, and glutaric, have been performed in dioxane-water mixtures containing 50 and 65% dioxane, with a quinhy-

drone-mercurous sulfate electrode chain. Relatively high concentration of lithium sulfate was employed for keeping the ionic environment sensibly constant during the progress of titration, for necessary conductivity, and for the practical elimination of junction potentials. These data were used in support of the extended theory of acid-base titration presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Preparation and Directed Chlorination of 1,1,1-Trifluoropropane

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Trifluoromethyl groups have been synthesized before by halogen exchange between an inorganic fluoride and an organic trihalide RCX_3 (where R was H or CH_3),^{1,2} or by the interaction of antimony trifluoride and an allylic trihalide.³ Attempts to prepare $CH_3CH_2CF_3$ by an extension of these methods indicated the need for modifications.

Preparation of $CH_3CH_2CCl_3$.—Ten moles of commercial propylene dichloride was chlorinated at the boiling point, in the dark, and with iron filings as catalyst⁴ to give six moles of $CH_3CHClCHCl_2$, b. p. 130–133°. Ten moles of this was heated to reflux and vigorously stirred with fifteen moles of 20% aqueous sodium hydroxide,⁵ then distilled (instead of decanted) to give nine moles of $CH_3CH=CCl_2$, b. p. 75–77°. Anhydrous hydrogen chloride was led into ten moles of this olefinic dichloride in the presence of 2 to 3% of aluminum chloride⁶ to yield 4.5 moles of $CH_3CH_2CCl_3$, b. p. 106.5–108.5°.

First Attempted Synthesis of $CH_3CH_2CF_3$.— $CH_3CH_2CCl_3$ was subjected to the customary halogen exchange with antimony trifluoride² in the presence of catalyst. The treatment gave only about 5–10% of $CH_3CH_2CF_3$, and 10% of a mixture of $CH_3CH_2CF_2Cl$ and $CH_3CH_2CFCl_2$. When the halogen exchange was performed without catalyst, practically no fluoride was obtained. Much decomposition was observed, hydrogen chloride was freed, and the only recovered product was $CH_3CH=CCl_2$, which accounted for 50% of the original $CH_3CH_2CCl_3$.

Second Attempt.—The allylic trichloride $CH_2=CHCCl_3$ was prepared by dehydration with phosphorus pentoxide of $CH_3CHOHCCl_3$, obtained by condensing chloral with a methylmagnesium halide.^{7,8} It failed to exchange halogens with antimony fluoride.³

The experimental procedure was then modified and successfully yielded the desired trifluoride, $CH_3CH_2CF_3$. The physical properties, together with those of the intermediate mono- and difluorides ($CH_3CH_2CCl_2F$ and $CH_3CH_2CClF_2$) are listed in the general table.

Preparation of $CH_3CH_2CF_3$.—Ten moles of $CH_3CH=CCl_2$ (prepared as indicated above) and twenty-five moles of hydrogen fluoride were heated in a steel bomb at 75° for five hours, and then at 95° until a pressure of 20 atmospheres was obtained. This treatment generated hydrogen chloride, which was tapped off intermittently through a condenser held at –78°, until the pressure no longer rose to 20 atmospheres by further heating at 95°. The bomb was then cooled to –78°, and its contents poured into another bomb containing 1300 g. of antimony trifluoride combined with 250 g. of chlorine. This bomb was then heated with a free flame and the product tapped off at a pressure of 13 atmospheres. The tapped gases were washed through dilute sodium hydroxide, dried over calcium chloride and condensed with solid carbon dioxide. The condensate amounted to 800 g., from which 3.6 moles of $CH_3CH_2CF_3$, b. p. –13°, and 3.6 moles of $CH_3CH_2CClF_2$ were separated by low temperature distillation.

More trifluoride was obtained from this intermediate difluoride as follows. Ten moles of $CH_3CH_2CClF_2$ were placed in a bomb containing 1300 g. of antimony trifluoride combined with 400 g. of chlorine. Ten moles of hydrogen fluoride was condensed into the bomb which was then heated at 95° on a water-bath. The reaction products were tapped off at 12 atmospheres through a water reflux condenser, and gave on redistillation 8.5 moles of trifluoride and 0.3 mole of recovered material.

The strongly directing effect of fluorine clusters upon chlorination^{9,10} was verified once more when $CH_3CH_2CF_3$ was subjected to the action of chlorine in sunlight, in a glass container and in the presence of water. The distillation of the reac-

(1) Henne, *THIS JOURNAL*, **59**, 1200 (1937).

(2) Henne and Renoll, *ibid.*, **58**, 889 (1936).

(3) Henne, Whaley and Stevenson, *ibid.*, **63**, 3478 (1941).

(4) Levine and Cass, U. S. Patent 2,119,484, May 31, 1938.

(5) Cass, U. S. Patent 2,134,102, Oct. 25, 1938.

(6) Levine and Cass, U. S. Patent 2,179,218, Nov. 7, 1939.

(7) Vitoria, *Rec. trav. chim.*, **24**, 265 (1905).

(8) Kharasch, *et al.*, *THIS JOURNAL*, **63**, 2558 (1941).

(9) Henne and Renoll, *ibid.*, **59**, 2434 (1937).

(10) Henne and Haeckl, *ibid.*, **63**, 2692 (1941).

GENERAL TABLE									
No.	Name	F. p., °C. ^a	B. p., °C.	d_{20}^4	n_D^{20}	MR	ARF ^b	Chlorine, % Calcd. Found	Fluorine, % Calcd. Found
1	CH ₃ CH ₂ CCl ₂ F		66.6	1.2090	1.3910	25.74	1.05		
2	CH ₃ CH ₂ CClF ₂		25.8	1.1311	1.3330 at 8°	20.84	1.06	31.0 31.20	
3	CH ₃ CH=CClF		24.8	at 8°	1.3780 at 8°				
4	CH ₃ CH ₂ CF ₃	-148.8	-13						
5	CH ₂ ClCH ₂ CF ₃	-106.2	45.1	1.3253	1.3350	20.67	1.02	26.8	
6	CHCl ₂ CH ₂ CF ₃	- 93.2	72.4	1.4408	1.3631	25.77	1.09	42.5 42.2	34.1 33.0
7	CCl ₃ CH ₂ CF ₃	- 41.7	95.1	1.5511	1.3900	30.78	1.14	52.8 52.5	
8	CCl ₃ CCl ₂ CF ₃	+109.0	153.1					65.7 65.6	
9	CCl ₂ =CClCF ₃	-114.7	88.3	1.6188	1.4095	30.48	1.20	53.3 53.3	28.6 28.3
10	CHCl=CClCF ₃	-109.2	53.7	1.4653	1.3670	25.27	1.08	43.0 42.6	
11	CCl ₂ =CHCF ₃	- 87.2	55.1	1.4605	1.3690	25.48	1.15	43.0 43.7	
12	CH ₃ CHClCF ₃		30.0		1.3150			26.8 27.3	
13	CH ₃ CCl ₂ CF ₃	+ 13.8	48.8	1.3842	1.3478	25.81	1.11	42.5 42.9	
14	CH ₂ ClCHClCF ₃		76.7		1.3671			42.5 41.8	
15 ^c	CCl ₂ FCCl ₂ CF ₃	+ 41.74	112.4					55.9 56.2	29.9 29.6
16 ^c	CClF ₂ CCl ₂ CF ₃	- 4.30	72.0	1.6681	1.3519	30.77	1.12	44.8 44.4	40.0 40.0

^a Complete freezing curves were taken with a resistance thermometer accurate to 0.01°. The slope of the plateaus was used as criterion of purity. ^b ARF is the atomic refraction for fluorine calculated by subtracting from MR (molecular refraction calculated by the Lorentz-Lorenz formula) the accepted increments for C (2.418), H (1.1), Cl (5.967), and double bond (1.733). It usually amounts to 1.10 ± 0.10. The method of calculation is responsible for the relatively large lack of precision. ^c J. K. Stevenson, Dissertation. The Ohio State University, 1942.

tion products yielded successively CH₂ClCH₂CF₃, CHCl₂CH₂CF₃, CCl₃CH₂CF₃ and CCl₃CCl₂CF₃. It was noted that the chlorination had a strong tendency to stop at the trichloride stage, then proceeded directly to the pentachloride. No evidence for the presence of the tetrachloride was found. The physical properties of the chlorinated compounds are listed in the general table.

Chlorination.—Chlorine and CH₃CH₂CF₃ were first allowed to interact in sunlight, in vapor phase, in the manner previously reported, and the chlorinated product was subjected to further chlorination in liquid phase.^{9,11} A sample of the reaction product was analyzed by distillation, and gave approximately 100 g. from 43.4 to 46.4°; 20 g. from 48 to 71°; 200 g. from 71 to 73°; 20 g. from 73 to 93°; 125 g. between 93 and 96°; and 20 g. above 96°. From these fractions were isolated, by redistillation, a monochloride boiling at 45.1°, a dichloride boiling at 72.4° and a trichloride boiling at 95.1°. Their physical properties are listed in the general table. There may have been a small amount of another monochloride at 30–35°, where 5 g. of distillate was collected; intermediate fractions did not yield any definite compound, but remained sufficiently large to indicate the possible presence of very small quantities of isomers.

Rechlorination of 116 g. of the dichloride fraction gave 132 g. of the trichloride, boiling from 93 to 95°. The chlorination tended to stop there, but when exposed to bright summer light, it proceeded further to the pentachloride, without any indication of ever stopping at the tetrachloride stage.

As a contrast, CH₃CH₂CCl₃ was treated with chlorine under the same experimental conditions

which had been used for CH₃CH₂CF₃. All possible isomers were formed and there seemed to be a preponderance of chlorination on the center carbon. This indicated that any directing effect that the CCl₃ group may have is not of the same order of magnitude as that of the CF₃ group and is moreover acting in the reverse direction. The first chlorination gave: 5% of recovered CH₃-CH₂CCl₃, 15 to 20% of CH₃CHClCCl₃, 5 to 10% of CH₂ClCH₂CCl₃, 30% of CH₃CCl₂CCl₃, 10 to 15% of CH₂ClCHClCCl₃, 5% of CHCl₂CH₂CCl₃ and 5 to 10% of more highly chlorinated products.

In order to establish the formulas listed in the general table, the compounds were first analyzed for chlorine and fluorine. The reasons for not making fluorine analyses in every case but only at important stages, have been given before.^{3,10} The results are in the table.

The next step consisted of proving that three fluorine atoms are placed together on a terminal carbon atom. This results from the facts that compound no. 8 is identical with CCl₃CCl₂CF₃ prepared before in a different way³; that it is different from the other isomeric trifluoropentachlorides^{9–13}; and that it has been transformed into trifluoroacetic acid.¹⁴ It follows that compounds 1 and 2 have all three of their halogen atoms on the same terminal carbon atom.

The place of the chlorine atoms was considered

(11) McBee, Henne, Hass and Elmore, *THIS JOURNAL*, **62**, 3340 (1940).

(12) Henne and Ladd, *ibid.*, **60**, 2491 (1938).

(13) Henne and Renoll, *ibid.*, **61**, 2489 (1939).

(14) Henne and Alderson, unpublished.

next. The monochloride (no. 5) obtained from $\text{CH}_3\text{CH}_2\text{CF}_3$ can only be $\text{CH}_2\text{ClCH}_2\text{CF}_3$ (the proposed formula) or $\text{CH}_3\text{CHClCF}_3$. By comparison with previously reported halogenated derivatives of propane, it can be predicted that $\text{CH}_2\text{ClCH}_2\text{CF}_3$ should boil about 45° (the observed boiling point) while $\text{CH}_3\text{CHClCF}_3$ should boil about 30° . The synthesis of the latter was performed to clinch the matter; it boiled at 30° .

Synthesis of $\text{CH}_3\text{CHClCF}_3$.—A treatment of $\text{CH}_3\text{CHClCF}_3$ with mercuric oxide in an excess of hydrogen fluoride¹⁵ at 100° yielded 80% of a compound, b. p. 30° , which analyzed correctly for $\text{C}_3\text{H}_4\text{ClF}_3$ and must be $\text{CH}_3\text{CHClCF}_3$, because its complete chlorination yields the known $\text{CCl}_3\text{CCl}_2\text{CF}_3$, not the known $\text{CCl}_3\text{CClFCCl}_2$, a fact which eliminates the isomeric formula $\text{CH}_3\text{CHF}_2\text{CF}_2\text{Cl}$.

The dichloride (no. 6) can only be $\text{CHCl}_2\text{CH}_2\text{CF}_3$ (the proposed formula) or $\text{CH}_2\text{ClCHClCF}_3$, because it is derived from the monochloride $\text{CH}_2\text{ClCH}_2\text{CF}_3$ discussed in the preceding paragraph. The first formula is correct, because the compound differed from the two dichlorides obtained in the chlorination of $\text{CH}_3\text{CHClCF}_3$.

Chlorination of $\text{CH}_3\text{CHClCF}_3$.—Chlorination of 93 g. of $\text{CH}_3\text{CHClCF}_3$ in sunlight, under water, in a glass flask, equipped with a dry-ice reflux condenser, gave 111 g. of product, 80% of which was composed of dichlorides. Of this, two-thirds was $\text{CH}_3\text{CCl}_2\text{CF}_3$ and one-third $\text{CH}_2\text{ClCHClCF}_3$.

The trichloride (no. 7) b. p. 95.1° , can only be $\text{CCl}_3\text{CH}_2\text{CF}_3$ (the proposed formula) or $\text{CHCl}_2\text{CHClCF}_3$. The proposed formula is correct, because the alternate compound was synthesized and proved to be different.

Synthesis of $\text{CHCl}_2\text{CHClCF}_3$.— $\text{CHCl}_2\text{CH}_2\text{CF}_3$ treated with alcoholic alkali gave $\text{CHCl}=\text{CHCF}_3$; the latter treated with chlorine gave $\text{CHCl}_2\text{CHClCF}_3$, b. p. 106.8° , which was different from the trichloride obtained from $\text{CH}_3\text{CH}_2\text{CF}_3$.

Several reactions were tried to obtain a picture of the reactivity of the chlorine atoms located in beta position to the CF_3 group.

$\text{CH}_2\text{ClCH}_2\text{CF}_3$ failed to react with magnesium or with ethylmagnesium bromide. By a treatment with potassium hydroxide, it readily lost the elements of hydrogen chloride, but no hydrogen fluoride.

$\text{CHCl}_2\text{CH}_2\text{CF}_3$ reacted readily with alcoholic alkali quantitatively to yield $\text{CHCl}=\text{CHCF}_3$.

$\text{CCl}_3\text{CH}_2\text{CF}_3$ lost hydrogen chloride easily when treated with an alkali. The chlorine atoms appeared easily replaceable with mercury fluoride, and preliminary experiments pointed to the ready formation of $\text{CF}_3\text{CH}_2\text{CF}_3$.

$\text{CCl}_3\text{CCl}_2\text{CF}_3$, subjected to the customary treatment with antimony trifluorodichloride yielded quantitatively $\text{CCl}_2\text{FCCl}_2\text{CF}_3$ and $\text{CClF}_2\text{CCl}_2\text{CF}_3$,¹⁶ whose physical properties are listed in the general table.

Summary

Loss of hydrogen chloride makes impractical the synthesis of $\text{CH}_3\text{CH}_2\text{CF}_3$ from $\text{CH}_3\text{CH}_2\text{CCl}_3$ by halogen exchange with antimony fluoride. However, $\text{CH}_3\text{CH}_2\text{CCl}_2\text{F}$ is easily synthesized by addition of hydrogen fluoride to $\text{CH}_3\text{CH}=\text{CCl}_2$, and it is readily transformed into $\text{CH}_3\text{CH}_2\text{CF}_3$ by halogen exchange. The chlorination of the trifluoride in sunlight is strongly directed to yield successively $\text{CH}_2\text{ClCH}_2\text{CF}_3 \rightarrow \text{CHCl}_2\text{CH}_2\text{CF}_3 \rightarrow \text{CCl}_3\text{CH}_2\text{CF}_3 \rightarrow \text{CCl}_3\text{CCl}_2\text{CF}_3$. The chlorination tends to stop with the formation of the trichloride, then proceeds directly to the pentachloride. A list of new fluorochloro derivatives of propane is tabulated.

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(15) Henne, *THIS JOURNAL*, **60**, 1569 (1938).

(16) J. K. Stevenson, Dissertation, The Ohio State University, 1942.