Potentiometric Titration of Dibasic Acids in Dioxane–Water Mixtures

BY RICHARD H. GALE AND CECIL C. LYNCH

In a paper published in 1938 Lynch and LaMer[1] showed that the theory of acid–base titration in dioxane–water mixtures for weak monobasic acids leads to substantially the same relations obtained by Auerbach and Smolczyk[2] and by Söderbäck[3] for titration in aqueous solutions. In this article we have extended the theory to include the titration of weak dibasic acids in dioxane–water mixtures. Titration data on oxalic, malonic, succinic, and glutaric acids are presented in support of the theory.

Theory of Acid–Base Titrations (Dibasic Acids).—From Auerbach and Smolczyk[2] we have the relation between the K_1 and K_2 for a weak dibasic acid

$$K_1K_2 + K_1 m_{H^+}\left(\frac{\dfrac{mx}{w^0} - m^0}{\dfrac{mx}{w^0} - 2m^0}\right) + m^2_{H^+}\left(\frac{\dfrac{mx}{w^0}}{\dfrac{mx}{w^0} - 2m^0}\right) = 0 \tag{1}$$

This is essentially the same as the relation obtained for dibasic acids by Söderbäck[3]

$$K_1^0 K_2^0 + K_1^0 m_{H^+}\left(\frac{B-1}{B-2}\right)f_2 + m^2_{H^+}\left(\frac{B}{B-2}\right)f_1^2 f_2 = 0 \tag{2}$$

where $B = (mx/vc_0) + (m_{H^+}/c)\,[1 + (x/v^0)]$ if the dilution is such that the activity coefficients may be taken as unity; where

x = volume of base used
c = initial concentration
v^0 = initial volume of acid solution
f_1 = activity coefficient of the univalent ions
f_2 = activity coefficient of the divalent ions
m = molarity of base
w^0 = initial weight of solvent
m^0 = initial molality of acid

In a medium where the ionic environment is kept sensibly constant, Eq. (2) reduces to Eq. (1) where $K_1 = K_1^0/f_1^2$ and $K_2 = K_2^0/f_2$. This condition can be achieved by maintaining a relatively high concentration of inert neutral salt which furnishes both univalent and divalent ions to the solution.

Fuoss and Kraus[4] have shown from conductivity studies that ion association in the Bjerrum sense occurs in dioxane–water mixtures; for

(1) Lynch and LaMer, THIS JOURNAL, 60, 1252 (1938).
(2) Auerbach and Smolczyk, Z. physik. Chem., 110, 65 (1924).
(3) Söderbäck, Arkiv. Kemi. Min. och. Geol., 11A, 1 (1934).
(4) Fuoss and Kraus, THIS JOURNAL, 55, 2387 (1933).

univalent ions, association to neutral pairs occurs for dielectric strengths above 10; for univalent and divalent ions together in such media association to neutral pairs and neutral triplets only may be assumed. We shall consider the influence that such ion association has on acid–base titration calculations for dibasic acids.

Consider a solution containing dioxane, water, lithium sulfate of relatively high concentration, a weak dibasic acid, being titrated with a strong base MOH, as sodium hydroxide. We are concerned with the following

(a) $H_2A \rightleftarrows H^+ + (HA)^-$; $K_1 = \left(\dfrac{m_{H^+} \times m_{HA^-}}{m_{H_2A}}\right)$

(b) $(HA)^- \rightleftarrows H^+ + A^-$; $K_2 = \left(\dfrac{m_{H^+} \times m_{A^-}}{m_{HA^-}}\right)$

(c) $Li_2A \rightleftarrows 2Li^+ + A^-$; $K_3 = \left(\dfrac{m^2_{Li^+} \times m_{A^-}}{m_{Li_2A}}\right)$

(d) $M_2A \rightleftarrows 2M^+ + A^-$; $K_4 = \left(\dfrac{m^2_{M^+} \times m_{A^-}}{m_{M_2A}}\right)$

(e) $LiHA \rightleftarrows Li^+ + (HA)^-$; $K_5 = \left(\dfrac{m_{Li^+} \times m_{HA^-}}{m_{LiHA}}\right)$

(f) $MHA \rightleftarrows M^+ + (HA)^-$; $K_6 = \left(\dfrac{m_{M^+} \times m_{HA^-}}{m_{MHA}}\right)$

Electroneutrality demands

(g) $m_{M^+} + m_{H^+} + m_{Li^+} = m_{HA^-} + 2m_{A^-} + m_{HSO_4^-} + 2m_{SO_4^-}$

If m^0 is the initial acid molality, then

(h) $m_{H_2A} + m_{MHA} + m_{LiHA} + m_{M_2A} + m_{Li_2A} + m_{HA^-} + m_{A^-} = m^0$

Since (mx/w^0) is the stoichiometric molality the base would have at any time if no reaction occurred in the solution, we obtain a relation

(i) $m_{M^+} + m_{MHA} + 2m_{M_2A} + m_{MHSO_4} + 2m_{M_2SO_4} = (mx/w^0)$

where the m's refer to the molalities of the substances in subscripts (m is the concentration of the base in moles/1000 g. of solution; x is grams of base solution added at any time; w^0 is the initial weight of solvent taken). M is the metal ion of the base MOH.

We shall make the following assumptions to simplify the problem: (j) Bjerrum associations occur in the solvent to the extent of neutral pair and neutral triplet formation only. (k) Sufficient lithium sulfate has been added to maintain a constant ionic environment for both mono- and di-valent ions. (l) The weight of base solution

added to the end-point does not appreciably change the total solution weight. (m) For $MHSO_4$ and LiHA the same extent of association; for M_2SO_4 and Li_2A the same extent of association. Such assumptions would appear reasonable for salts of same ionic type in the same ionic environment.

$$also\ m_{LiHA} + 2m_{Li_2A} = m_{MHSO_4} + 2m_{M_2SO_4}\ \ (m')$$
$$also\ m_{Li^+} = m_{HSO_4^-} + 2m_{SO_4^-}\ \ \ \ \ \ \ \ (m'')$$

Combining (g), (i), (m'), and (m'')

$$m_{HA^-} + 2m_{A^-} - m_{H^+} + m_{MHA} + 2m_{M_2A} + m_{LiHA} + 2m_{Li_2A} = (mx/w^0)$$

Substituting for m_{MHA} from (f); for m_{M_2A} from (d); for m_{LiHA} from (e); for m_{Li_2A} from (c); for m_{M^+} from (g); and for m_{HA^-} from (b)

$$\left(\frac{m_{H^+} \times m_{A^-}}{K_2}\right) + 2m_{A^-} - m_{H^+} + \left[\left(\frac{m_{H^+} \times m_{A^-}}{K_2}\right) - 2m_{A^-} - m_{H^+}\right]\left(\frac{m_{H^+} \times m_{A^-}}{K_2 K_6}\right) + 2\left(\frac{m_{H^+}}{K_2} + 2\right)^2\left(\frac{m^3_{A^-}}{K_4}\right) + \left[\left(\frac{m_{Li^+} \times m_{H^+}}{K_2 K_5}\right) + \left(\frac{2m^2_{Li^+}}{K_3}\right)\right]m_{A^-} = \left(\frac{mx}{w^0}\right)$$

Now, m_{H^+} is negligible compared with $2m_{A^-}$ and also as compared with (mx/w^0); hence

$$\left[\left(\frac{m_{H^+}}{K_2}\right) + 2 + \left(\frac{m_{Li^+} \times m_{H^+}}{K_2 K_5}\right) + \left(\frac{2m^2_{Li^+}}{K_3}\right)\right]m_{A^-} + \left(\frac{2}{K_4}\right)\left[\left(\frac{m_{H^+}}{K_2}\right) + 2\right]^3 m^3_{A^-} + \left[\left(\frac{m_{H^+}}{K_2} + 2\right)\left(\frac{m_{H^+}}{K_2 K_6}\right)\right]m^2_{A^-} = \left(\frac{mx}{w^0}\right)$$

When $m^3_{A^-}$ and $m^2_{A^-}$ are small compared with m_{A^-}, a condition true for weak acids at low concentrations, only the first term on the left of the equation is significant; hence

$$m_{A^-} = \left[\frac{K_2(mx/w^0)}{2K_2 + m_{H^+} + K_2\left(\frac{2m^2_{Li^+}}{K_3} + \frac{m_{Li^+} \times m_{H^+}}{K_2 K_6}\right)}\right]$$
(A)

Combining (a), (b), (h), (m'), and (m''), where

$$K_1 K_2 = \left(\frac{m^2_{H^+} \times m_{A^-}}{m_{H_2A}}\right)$$

we obtain the relation

$$m_{A^-} + \left(\frac{m^2_{H^+} \times m_{A^-}}{K_1 K_2}\right) + \left(\frac{m_{H^+} \times m_{A^-}}{K_2}\right) + m_{MHA} + m_{M_2A} + m_{LiHA} + m_{Li_2A} = m^0$$

Similar substitution as used above leads to the expression

$$m_{A^-} = \left[\frac{m^0}{1 + \left(\frac{m^2_{H^+}}{K_1 K_2}\right) + \left(\frac{m_{H^+}}{K_2}\right) + \left(\frac{m^2_{Li^+}}{K_3}\right) + \left(\frac{m_{Li^+} \times m_{H^+}}{K_2 K_6}\right)}\right]$$
(B)

Equating through m_{A^-} in (A) and (B), and collecting all terms of $(K_1 K_2)$ and (K_1)

$$K_1 K_2 + K_1 m_{H^+}\left[\frac{\left(\frac{mx}{w^0} - m^0\right)(1 + K)}{\left(\frac{mx}{w^0} - 2m^0\right)(1 + K')}\right] + m^2_{H^+}\left[\frac{\left(\frac{mx}{w^0}\right)}{\left(\frac{mx}{w^0} - 2m^0\right)(1 + K')}\right] = 0$$

where $K = (m_{Li^+}/K_5)$ and $K' = (m^2_{Li^+}/K_3)$.

In case of a great extent of ionization of salts, the values of K and K' approach zero, and the Eq. (1) is obtained.

Multiplying both sides of the above equation by $(1 + K')$, we obtain

$$K_1 K_2(1 + K') + K_1(1 + K)\left[\frac{\frac{mx}{w^0} - m^0}{\frac{mx}{w^0} - 2m^0}\right]m_{H^+} + \left[\frac{\frac{mx}{w^0}}{\frac{mx}{w^0} - 2m^0}\right]m^2_{H^+} = 0$$

or

$$K_1^* K_2^* + K_1^*\left[\frac{\frac{mx}{w^0} - m^0}{\frac{mx}{w^0} - 2m^0}\right]m_{H^+} + \left[\frac{\frac{mx}{w^0}}{\frac{mx}{w^0} - 2m^0}\right]m^2_{H^+} = 0$$
(3)

where $K_1^* = K_1(1 + K)$ and $K_2^* = K_2[(1 + K')/(1 + K)]$. Thus, we obtain an equation identical in form with Eq. (1) in which, however, the constants, K_1^* and K_2^*, differ from the classical constants, defined in Eq. (A) and (B), by a constant factor.

The solution of the problem of determining K_1^* and K_2^* is through plotting of ξ as abscissa and η as ordinate, where

$$\xi = m_{H^+}\left(\frac{mx/w^0 - m^0}{mx/w^0 - 2m^0}\right) \quad \eta = m^2_{H^+}\left(\frac{mx/w^0}{mx/w^0 - 2m^0}\right)$$

for the equation $K_1^* K_2^* + K_1^* \xi + \eta = 0$, is that of a straight line; $\eta = -K_1^* \xi - K_1^* K_2^*$, where $(-K_1^*) = m$ (slope); $(-K_1^* K_2^*) = b$ (intercept on η); and $(-K_2^*) = a$ (intercept on ξ). The plots obtained from titration of dibasic acids in dioxane–water mixtures should give support for this modified theory of titration. Figure 3 shows results obtained for the acids investigated.

The Reference E. m. f.—In order to apply the general theory to a titration, it is necessary to know the relation between e. m. f. of the cell measured and the activity of the hydrogen ion, or for constant ionic environment, the molality

of the hydrogen ion. If we impose the latter conditions during titration, the relation can be simply established in a manner similar to that described by Lynch and LaMer.[1]

Thus, for the cell described in the experimental part for obtaining E^0 values

$$E_{298} = E^0 - 0.05915 \log m_{H+} \qquad (4)$$

and

$$(E_{298} + 0.05915 \log m_{H_2SO_4}) = E^0 - 0.05915 \log \left(\frac{m_{H+}}{m_{H_2SO_4}}\right)$$

at $m_{H_2SO_4} = 0$, we set $\log (m_{H+}/m_{H_2SO_4}) = 0$ and $E^0 = (E_{298} + 0.05915 \log m_{H_2SO_4})$.

This limiting value may be obtained by extrapolation, and the Eq. (4) employed for calculation of the hydrogen ion molality from e. m. f. measurements.
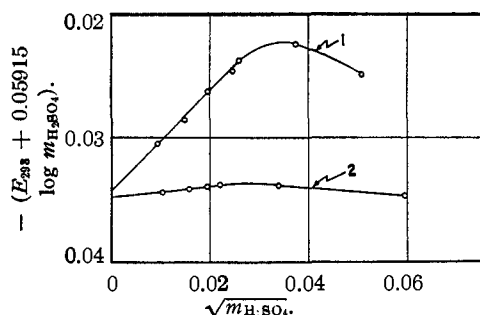

Fig. 1.—Extrapolation plots for E^0 values of the cell: 1, dioxane/water ratio 1.002, $m_{Li_2SO_4} = 0.3002$, $E^0 = -0.0344$ v.; 2, dioxane/water ratio 1.856, $m_{Li_2SO_4} = 0.05263$, $E^0 = -0.0347$ v.

Experimental

Potentiometric titrations were made at 25° in two dioxane–water mixtures in which the ratios were 1.002 and 1.856, respectively, using oxalic, malonic, succinic, and glutaric acids as examples of the series of weak dibasic organic acids. As in the case of lithium chloride, large additions of lithium sulfate produce immiscibility in the dioxane–water system, which sets an upper limit to the permissible concentration of lithium sulfate.

A previous study by Lynch and LaMer[1] of the system sodium hydroxide–dioxane–water at 25° showed that small amounts of sodium hydroxide produced immiscibility. Thus it was necessary to add approximately 1.6 molal caustic in aqueous solution in the form of the titrating base from a weighing pipet to keep the dilution factor under one per cent.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Company was purified by the method described by Eigenberger[5] with slight modifications. The product was kept over metallic sodium, from which it was distilled from an all glass apparatus, as needed.

Acids.—Reagent grade acids from the Eastman Kodak Company were recrystallized and analyzed for purity using

carbonate-free sodium hydroxide solution in aqueous solution. All were chemically pure within 0.1%.

Lithium Sulfate.—Merck C. P. Lithium Sulfate was used without further purification. Aqueous solutions of this salt had a pH of 6.0.

Solutions.—All solutions were prepared by direct weighing, and all titrations were made by weight. Thus, the concentrations are expressed in weight per cent. or by molality.

In order to prepare the dioxane–water–lithium sulfate solutions, aqueous solutions of lithium sulfate were prepared and analyzed for sulfate. The aqueous lithium sulfate was then mixed with dioxane to the proper ratio. This was also the method of obtaining dioxane–water–sulfuric acid solutions which were added to the dioxane–water–lithium sulfate solutions to give the sulfuric acid solutions used in determining the E^0 values for the cells. The other acid solutions were prepared by adding the acids directly to the dioxane–water–lithium sulfate solutions.
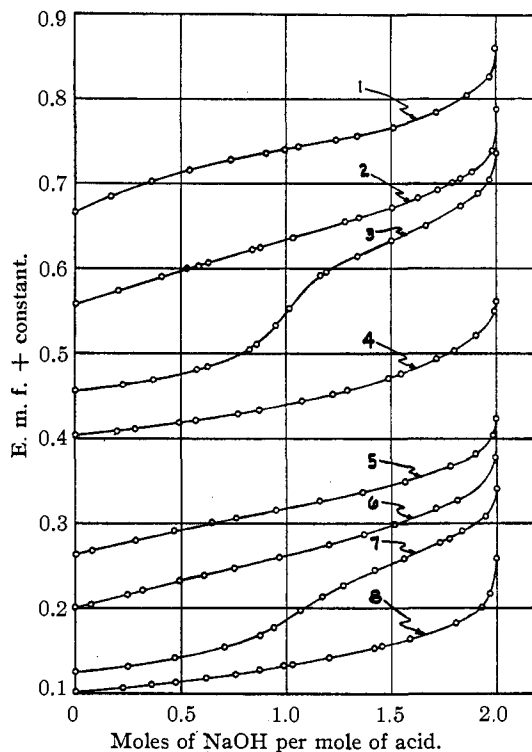

Fig. 2.—Titration curves for the acids:

	Dioxane-water
Curve 1, Glutaric; Curve 2, Succinic	ratio = 1.856
Curve 3, Malonic; Curve 4, Oxalic	Molality of Li₂SO₄ = 0.05263
	Dioxane-water
Curve 5, Glutaric; Curve 6, Succinic	ratio = 1.002
Curve 7, Malonic; Curve 8, Oxalic	Molality of Li₂SO₄ = 0.3002

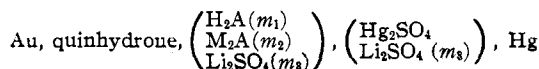**Apparatus.**—The titration cell is represented symbolically as

$$\text{Au, quinhydrone,} \begin{pmatrix} H_2A(m_1) \\ M_2A(m_2) \\ Li_2SO_4(m_3) \end{pmatrix}, \begin{pmatrix} Hg_2SO_4 \\ Li_2SO_4(m_3) \end{pmatrix}, Hg$$

(5) Eigenberger, J. prakt. Chem., 130, 75 (1931).

TABLE I

VALUES OF K_1^* AND K_2^* FOR THE ACIDS AT 25°

Acid	Molality (m_0) acid	Dioxane–water ratio	Dielectric constant	Molality Li_2SO_4	K_1^*	K_2^*	K_1^*/K_2^*
Oxalic	0.01010	1.002	34.3	0.3002	. . . .	. . . .	. . .
Malonic	.007825	1.002	34.3	.3002	1.92×10^{-5}	1.60×10^{-6}	120
Succinic	.01020	1.002	34.3	.3002	2.10×10^{-4}	2.60×10^{-5}	8.1
Glutaric	.007056	1.002	34.3	.3002	8.70×10^{-5}	3.42×10^{-5}	2.5
Oxalic	.007716	1.856	21.8	.05263	2.66×10^{-3}	3.05×10^{-4}	8.7
Malonic	.01026	1.856	21.8	.05263	2.60×10^{-3}	4.20×10^{-6}	620
Succinic	.007358	1.856	21.8	.05263	1.09×10^{-4}	7.54×10^{-6}	14.5
Glutaric	.008334	1.856	21.8	.05263	4.40×10^{-5}	1.13×10^{-5}	3.9

the solvent, one of the dioxane–water mixtures, extends throughout the cell. This cell avoids liquid junctions by making contact in the acid solution through a lithium sulfate–dioxane–water bridge connected by a ground glass joint. The bridge, by means of the glass joints, also avoids mixing and loss by diffusion during the titration. All measurements were made with the cell in a water thermostat at $25.0 \pm 0.1°$.
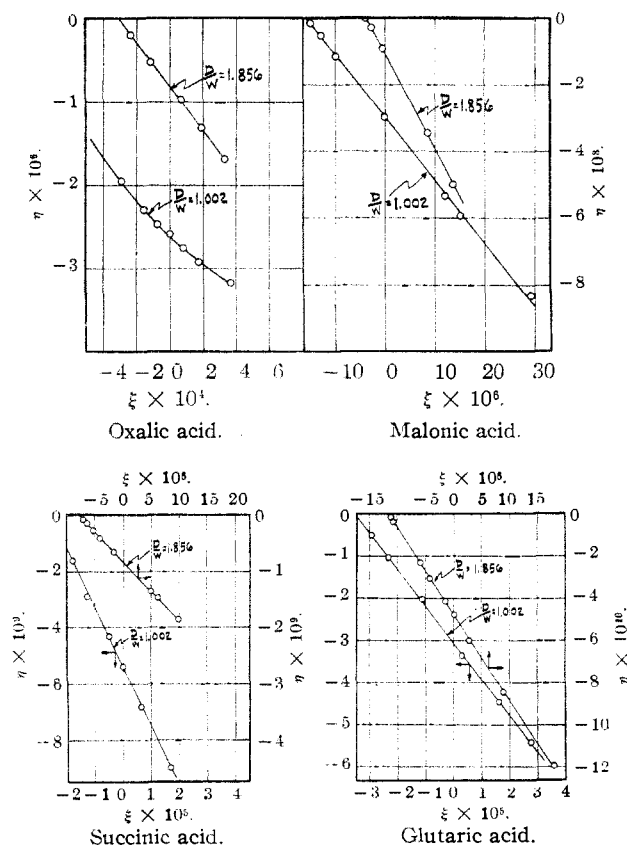

Fig. 3.—Graphical method for determining dissociation constants at 25°.

E. m. f. measurements were made with a Leeds and Northrup Type K potentiometer, and a Type P galvanometer, sensitive to 0.00072 microampere per scale unit. The Weston standard cell was checked frequently against other standard cells. The mercurous sulfate electrodes in the dioxane–water–lithium sulfate solution were found reproducible to ± 0.1 mv. over a period of four days. Measurements were reproducible to within ± 0.3 mv.

Experimental Data and Results

The E^0 values of the cells were determined by measuring a series of cells of the type

$$\text{Au, quinhydrone,} \left(\begin{array}{c} Li_2SO_2(m_2) \\ H_2SO_4(m_1) \end{array}\right), Hg_2SO_4, Hg$$

in which the solvent was dioxane–water. Linear extrapolation of the function $(E_{298} + 0.05915 \log m_{H_2SO_4})$ against the $\sqrt{m_{H_2SO_4}}$ to zero concentration of the acid gave the E^0 value. Figure 1 gives the data and E^0 values for the two dioxane–water ratios chosen.

The titration data for the four acids are as shown in the curves of Fig. 2. It was observed that the cell e. m. f. drifted when the end-point was overreached. Accordingly, only data to the neutralization point are included.

From the titration data, the ξ and η values in the neighborhood of half neutralization were obtained for each acid in each concentration of dioxane. The plots of these functions are given in Fig. 3, and the values of the constants as calculated from the data are collected in Table I. Values in the range 25–75% neutralization were used in the extrapolations. The dielectric constants are from the data of Åkerlöf and Short.[6] It should be noted that the dioxane–water ratios and the molalities are initial values, and that during titration small changes occur in all these values.

The straight lines are evidence that the relation (Eq. 3) is satisfied for titration of dibasic acids in such media. Only the oxalic acid in approximately 50% dioxane showed variance from the straight line plot. This may be explained by the assumption that the oxalic acid first dissociation is that of a relatively strong acid.

Summary

1. The Auerbach and Smolczyk treatment of

(6) Åkerlöf and Short, THIS JOURNAL, 58, 1241 (1936).

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.

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

BY ALBERT L. HENNE AND ATHERTON M. WHALEY

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 catalyst[4] 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 chloride[6] 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 trifluoride[2] 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).