on the basis of two distinct types of adsorbed hydrogen.

3. Comparison of the accommodation coefficients obtained by numerous investigators on different surfaces leads to the conclusion that the exchange of energy between hydrogen gas molecules and an adsorbed layer of hydrogen was measured in each case.

4. An attempt to remove this adsorbed layer lowered the accommodation coefficient from 0.31 to 0.18 at 350°K.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Some Fluorinated Chlorobenzenes[1]

BY HAROLD SIMMONS BOOTH, HOWARD M. ELSEY[2] AND PAUL E. BURCHFIELD[3]

A survey of the literature revealed descriptions of the preparation of only ortho[4] and para-chlorofluorobenzene.[5] In order to complete the series of monochlorofluorobenzenes the preparation of meta-chlorofluorobenzene from meta-chloroaniline was undertaken.

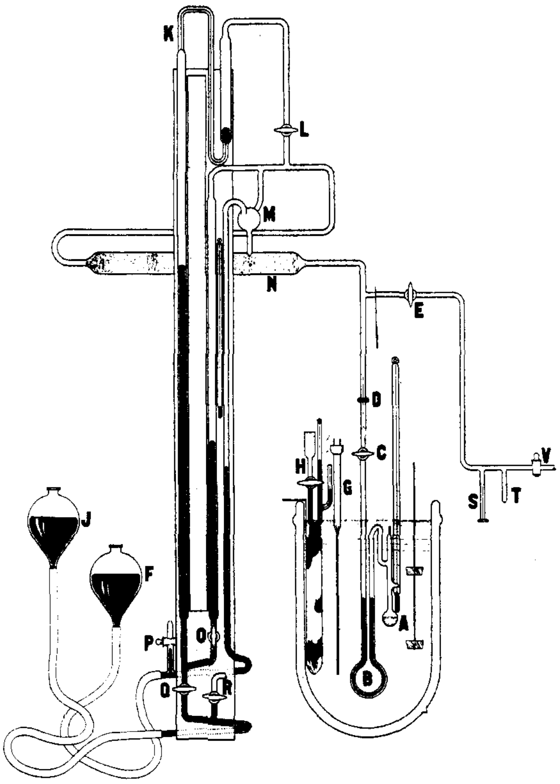

Fig. 1.

De Crauw[6] reported the preparation of 2,4,5-trichlorofluorobenzene from meta-fluoroaniline by several steps. De Crauw stated that a fluorine atom cannot be introduced into the benzene ring ortho to chlorine. The preparation of 2,4,6-trichlorofluorobenzene was attempted in order to extend the knowledge of this class of compounds and to discover whether or not the Balz and Schiemann reaction would effect the introduction of fluorine ortho to chlorine. In addition 2,4,6-trichlorofluorobenzene was successfully prepared from 2,4,6-trichloroaniline.

Experimental

Method of Determining Vapor Pressures

The apparatus for the determination of vapor pressure used in this research consisted of a modified "static isoteniscope,"[7] a suitable thermostat equipped with automatic and manual heat controls, and a modified Germann barometer,[8] shown in Fig. 1.

For the measurement of vapor pressure, a carefully purified sample was introduced into the bulb (A) the volume of which was approximately 2 cc. One arm of the bulb was connected to one side of the short U-manometer (B), the other arm was sealed to a tube (T) connected to a Hyvac pump. The second side of the U-manometer was provided with a stopcock (C) and a flat joint (D) and could also be connected by means of the flat joints (D) and (S) to the Hyvac pump. Both sides of the U-manometer were simultaneously evacuated for some time, and the mercury was carefully heated to its boiling point under the reduced pressure so that residual gases entrapped by the mercury were driven out.

When the mercury cooled, a small part of the sample was condensed on it in (B) and redistilled off in order to completely wash out any residual permanent gases in the sample chamber. The tube (T) connecting the sample bulb to the vacuum system was sealed off while the liquid in A was cooled in liquid air, and the other side of the small manometer was closed by means of stopcock (C).

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(1) From a portion of a thesis submitted by Paul B. Burchfield to the Graduate School, Western Reserve University, June, 1934, in partial fulfilment of the degree of Doctor of Philosophy.

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(3) Holder of the Westinghouse Fellowship in Chemistry, 1932-1934.

(4) Rinkes, *Chem. Weekblad*, **11**, 360, 952 (1914).

(5) Wallach and Heusler, *Ann.*, **243**, 219 (1888); Swarts, *Rec. trav. chim.*, **35**, 131 (1915).

(6) De Crauw, *ibid.*, **48**, 1061 (1929).

(7) A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

(8) A. F. O. Germann, *ibid.*, **36**, 2456 (1914).

The system was introduced into a clear mineral oil bath, contained in a 4-liter Dewar vessel, to such a depth that the space containing the sample was completely immersed. By means of the flat joint (D), the short manometer was connected to the manometer on which the vapor pressures were read.

The temperature was measured on a thermometer graduated to 0.1°. The thermometer, calibrated by the Reichsanstalt, was checked in this Laboratory against a precision platinum resistance thermometer and was found to be correct. The ice point was checked before each period of use. The necessary stem corrections were calculated and were added to the observed reading.

When the vapor pressure of the compound was to be measured, stopcock (C) was opened, and the mercury in the U-manometer (B) was brought to the same level by varying the pressure in the space connecting the large and small manometers by means of an air inlet (V) and a leveling bulb (F). The tube (N) was filled with barium oxide so that only dry air would come in contact with the mercury in the large manometer. When the mercury in (B) reached the same level the pressure was read on the large manometer at successive time intervals at constant temperature by a reading telescope until no change was observed in several observations. The observed pressure was corrected for the vapor pressure of mercury, and the necessary correction was applied to convert the observed pressure reading to the equivalent pressure at 0°, on the basis of a glass scale.

The boiling points of the compounds described below were read from the temperature–vapor pressure curves plotted on a large scale.

***m*-Chlorofluorobenzene.**—*m*-Chlorofluorobenzene was prepared from *m*-chloroaniline by the method of Balz and Schiemann.[9] The yield of *m*-chlorofluorobenzene was 60% calculated from the weight of chloroaniline used: b. p. 127.6° at 760 mm. (corr.); m. p. below −78°; d_{25} 1.221; $n^{27.0}_{D}$ 1.4911.

Analysis.—Chlorine was determined by the method of Chablay[10] as modified by Vaughn and Nieuwland.[11]

Anal. Calcd. for C_6H_4FCl: Cl, 27.17. Found: Cl, 27.15, 27.20.

Qualitative tests revealed the presence of fluorine.

Vapor pressure of *m*-chlorofluorobenzene and temperature are related by the equation $\log P$ (mm.) = $(-2342.4/T) - 2.4165 \log T + 15.017$. The average deviation of the calculated values from the observed values is ±1 mm.

2,4,6-Trichlorofluorobenzene was prepared from 2,4,6-trichloroaniline by the method of Balz and Schiemann.[9]

Twenty-four grams of trichloroaniline was added to 40 cc. of concd. hydrochloric acid. A concentrated solution of 8.4 g. of sodium nitrite was slowly added to the cold mixture. The diazonium solution was rapidly filtered to remove unreacted trichloroaniline, after which the diazonium fluoborate was precipitated by the addition of an excess of 45% fluoboric acid. After washing with alcohol and ether the salt was thoroughly dried at 70–80°. Efficient drying of the salt is necessary; otherwise the subsequent decomposition takes place with uncontrollable rapidity. The diazonium fluoborate was obtained in 75% yield.

The diazonium fluoborate was decomposed by heating in an evacuated system. Decomposition began at 187°, but it was necessary to heat to a considerably higher temperature to complete the decomposition. An appreciable quantity of tar was formed with each decomposition. From 13 g. of diazonium fluoborate 7 g. of crude trichlorofluorobenzene was obtained. The crude compound was washed successively with saturated sodium carbonate and 17% sodium hydroxide solutions, dried with barium oxide and repeatedly distilled under reduced pressure (10 mm.). Sixty grams of purified trichlorofluorobenzene was prepared in all: b. p. 208.4° at 760 mm. (corr.); m. p. 11.2°; d_{25} 1.530; $n^{27.2}_{D}$ 1.5429.

Anal. Calcd. for $C_6H_2Cl_3F$: Cl, 53.35. Found: Cl, 53.39, 53.22.

Qualitative tests revealed the presence of fluorine.

Vapor pressure of 2,4,6-trichlorofluorobenzene and temperature are related by the equation $\log P$ (mm.) = $-2452/T - 0.7316 \log T + 9.9389$.

The average deviation of the calculated values from the observed values is ±2.6 mm.

Instability of 2,4,6-Trichlorofluorobenzene.—The sample of 2,4,6-trichlorofluorobenzene on which the vapor pressures were run acquired a deep brown color after it was heated to 215.5°, which denoted thermal instability.

TABLE I

VAPOR PRESSURES OF m-C_6H_4ClF		VAPOR PRESSURES OF 2,4,6-$C_6H_2Cl_3F$	
T, °C.	Press., mm.	T, °C.	Press., mm.
0.0	4.0	25.1	2.0
16.2	10.0	71.8	11.0
24.2	15.0	92.0	21.8
41.3	34.0	120.1	63.3
54.3	61.0	132.7	92.3
69.1	112.0	143.5	132.3
83.0	187.0	154.5	185.9
90.6	246.0	165.1	256.8
102.5	366.5	183.0	411.2
116.1	549.5	192.5	534.1
120.2	618.0	201.8	656.0
124.1	690.5	206.4	729.5
128.7	786.0	211.5	815.6
129.6	805.5	215.5	899.0

Summary

1. The preparation and properties of *m*-chlorofluorobenzene have been described.
2. 2,4,6-Trichlorofluorobenzene has been synthesized and the physical properties have been measured.
3. It has been demonstrated that a fluorine atom may be introduced ortho to chlorine in the benzene ring by means of the Balz and Schiemann procedure.
4. An improved precision technique for the determination of the vapor pressures of liquids has been devised.

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[9] Balz and Schiemann, *Ber.*, **60B**, 1186 (1927).

[10] Chablay, *Ann. chim.*, [9] **1**, 469 (1914).

[11] Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).