ter fit for the data from the forty-six reactions under consideration.

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COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Indirect Fluorination of Cyanuric Chloride[1]

BY ABE F. MAXWELL,[2] JOHN S. FRY[3] AND LUCIUS A. BIGELOW

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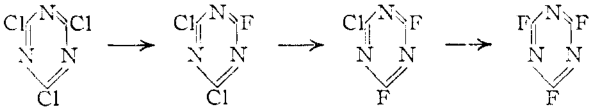
Commercial cyanuric chloride has been subjected to indirect fluorination using various mixed antimony halides under different conditions. Pure $(CNF)_3$, $C_3N_3F_2Cl$ and $C_3N_3FCl_2$ have been prepared in 71, 24 and 20% yield, respectively, and fully characterized.

In connection with work being carried out in this Laboratory dealing with perfluorinated organic compounds containing nitrogen, it became desirable to prepare in considerable amounts the interesting compound cyanuric fluoride, $(CNF)_3$, which is 2,4,6-trifluoro-1,3,5-triazine. This compound could possibly prove a source not only of the unknown $NF_2CF_2NF_2$ but also of $CF_2{=}NF$ and FCN, the last of which is in controversy in the literature. The triazine $(CNF)_3$ already has been reported by Hückel[4] to boil at 150°, but this relatively high boiling point is unlikely, and the experimental data involved are no longer available as a result of the late war. Also it was to be expected that $(CNF)_3$ as well as the corresponding intermediates might be prepared readily from the presently commercially available cyanuric chloride $(CNCl)_3$, by the well known indirect fluorination procedures making use of the various antimony halides, according to the general scheme



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It has been observed that when operating at atmospheric pressure neither SbF_3 alone nor SbF_5 can be used as reagents for this reaction, since the former sublimes and the latter is too reactive. However, SbF_3Cl_2, SbF_3 diluted with $SbCl_5$, and SbF_3 diluted with $SbCl_3$ readily form refluxing mixtures which decrease progressively in reactivity in that order. When cyanuric chloride I was refluxed under anhydrous conditions with SbF_3Cl_2 in such a manner that the lowest boiling portion was progressively distilled off, the fluorination went smoothly to completion; and when the crude product was carefully rectified analytically pure cyanuric fluoride IV, b.p. 74°, f.p. −38°, came over in 71% yield. This proves that the boiling point of 150° given in the literature is incorrect.

However, when I reacted with the milder reagent $SbF_3 + SbCl_5$, and the product distilled off and rectified, both IV and the analytically pure difluoride III, b.p. 113–114°, f.p. 22–23° were formed in 22 and 24% yields, respectively. Finally when I in large excess was treated with the still milder reagent $SbF_3 + SbCl_3$ and all of the product boiling below 190° rapidly distilled off, a mixture of liquid and solid was obtained, which upon rectification finally yielded the analytically pure monofluoride II, b.p. 155°, f.p. 2°, in approximately 20% yield. All of these were clear pungent liquids, extremely sensitive to hydrolysis, but otherwise very stable.

Experimental

The descriptions given below represent the best operating conditions so far developed for preparing the respective compounds. Some 5 to 10 exploratory runs were made in each case in order to determine these optimum conditions.

The research grade cyanuric chloride was kindly donated by the American Cyanamid Company and melted at 146°, corresponding to the literature value. The SbF_3 and $SbCl_5$ were Fisher technical and research grades, respectively, while the $SbCl_3$ was General Chemical reagent grade, which was dried *in vacuo* over $CaCl_2$ before use.

Preparation of Cyanuric Fluoride (IV).—In this case SbF_3 (100 g.) treated with Cl_2 until no more was absorbed at 100° in order to produce SbF_3Cl_2, and $(CNCl)_3$ (50 g.) were placed in a round-bottom flask equipped with a 12″ Vigreux column and a total reflux, partial take-off head. The material was refluxed using a Glass-col mantle and progressively distilled under completely anhydrous conditions until as nearly as possible all of the liquid product had passed over into the receiver. The distillate was then carefully rectified in a 12″ Podbielniak column and there was obtained 26.1 g. of $(CNF)_3$, b.p. 74°, corresponding to a yield of 71.4% based on the $(CNCl)_3$ used. There was no forerun and the still residue was insignificant. Pure $(CNF)_3$ boiled at 74°, froze at −38°, gave a positive test for fluorine, no test for chlorine and was very sensitive to hydrolysis.

Anal. Calcd. for $(CNF)_3$: F, 42.2; mol. wt., 135. Found: F, 42.4; mol. wt. (Victor Meyer), 135, 138.

Preparation of Cyanuric Difluorochloride (III).—Commercial $(CNCl)_3$ (170 g.), SbF_3 (340 g.) and $SbCl_5$ (85 g.) were placed in a round-bottom flask and electrically heated until the contents melted and refluxed. After 1 hr. the liquid product amounting to 60 cc. was distilled off, kept under an atmosphere of nitrogen and finally fractionated through the 12″ Podbielniak column. There were obtained $(CNF)_3$, b.p. 73° (20 cc.), transition (10 cc.), and the difluorochloride $C_3N_3F_2Cl$ (III), b.p. 113.5 (20 cc.). The

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[1] This material was presented at the September, 1956, Meeting of the American Chemical Society in Atlantic City, and has been constructed from the Master's Theses presented by Abe F. Maxwell and John S. Fry to Duke University in June, 1956, and June, 1955, respectively.

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[3] O. N. R. Research Assistant 1954–1955.

[4] W. Hückel, *Nachr. Akad. Wiss. Göttingen, Math. Phys. Klasse*, **1**, 55 (1946).

yields were 22 and 24%, respectively, based on $(CNCl)_3$. Pure $C_3N_3F_2Cl$ boiled at 113–114°, froze at 22–23°, gave positive tests for both fluorine and chlorine, and was very sensitive to hydrolysis.

Anal. Calcd. for $C_3N_3F_2Cl$: Cl, 23.4; mol. wt., 152. Found: Cl, 23.3; mol. wt. (Victor Meyer), 149, 149.

Preparation of Cyanuric Fluorochloride (II).—Commercial $(CNCl)_3$ (60 g.), SbF_3 (20 g.) and $SbCl_5$ (10 g.) were placed in a round-bottom flask equipped with a total reflux, partial take-off head with a thermometer inserted in a well at the top. The flask was then heated with a Glass-col mantle and all of the liquid product distilled over as rapidly as possible under anhydrous conditions keeping the reflux temperature below 190°. Approximately 15 cc. of a mixture of solid and liquid was obtained. This product was combined with 25 cc. of similar material obtained earlier and the mixture rectified through an 18″ heated column packed with glass helices. There was obtained: forerun, b.p. 114–152° (5 cc.); a colorless liquid central cut, b.p. 152° (25 cc.); and residue, b.p. 153–190° (10 cc.). The central cut was rectified carefully through a 12″ Podbielniak column, and finally there was obtained: forerun, b.p. 114–115° (3 cc.); $C_3N_3FCl_2$(II), b.p. 155° (16 cc.); and high boiling residue (6 cc.). The yield of II was about 20% based on $(CNCl)_3$ used. Pure $C_3N_3FCl_2$ boiled at 155°, froze at 2°, gave positive tests for both fluorine and chlorine and was sensitive to hydrolysis.

Anal. Calcd. for $C_3N_3FCl_2$: F, 11.3; mol. wt., 168. Found: F, 11.2; mol. wt. (Victor Meyer), 166, 171.5.

DURHAM, NORTH CAROLINA

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAINT LOUIS UNIVERSITY, AND THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Etherates of Lithium Borohydride. II. The System Lithium Borohydride–Diethyl Ether

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Pressure–composition isotherms at 25.0, 0.0, −35.3, −45.2, and −63.5° for the system lithium borohydride–diethyl ether indicate that two solid diethyl etherates, $LiBH_4 \cdot (C_2H_5)_2O$ (I) and $(LiBH_4)_2 \cdot (C_2H_5)_2O$ (II), exist. Values for the heats, free energies and entropies of dissociation of these compounds per mole of diethyl ether evolved at 25° are ΔH_d = (I) 13.36 and (II) 11.90 kcal.; ΔF_d = (I) 1.26 and (II) 1.67 kcal.; and ΔS_d = (I) 40.6 and (II) 34.3 e.u. The standard heats and free energies of formation and absolute entropies at 25° are $\Delta H_f{}^0$ = (I) −118.6 and (II) −164.3 kcal./mole; $\Delta F_f{}^0$ = (I) −60.3 and (II) −91.2 kcal./mole; and S^0 = (I) 63.4 and (II) 84.7 e.u. Approximate values for the heats of solution of lithium borohydride (III) and its diethyl etherates in diethyl ether at 25° are (III) −3.8, (I) +2.1 and (II) −2.9 kcal./mole. Solubility data for lithium borohydride in diethyl ether over the temperature range −112 to 25.0° are presented. The state of aggregation of the solute in lithium borohydride–diethyl ether solutions at room temperature is about 2 to 3 times its formula weight, as evidenced by deviations from Raoult's law.

Results and Discussion

Pressure–composition isotherms for the system lithium borohydride–diethyl ether are presented in Fig. 1. These isotherms give clear evidence for the existence of two solid etherates. Abrupt pressure changes occur at lithium borohydride mole fractions (n_2) 0.500 and 0.667, denoting phase transformations between the diethyl etherate of lithium borohydride, $LiBH_4 \cdot (C_2H_5)_2O$, previously described by Schlesinger and his coworkers[3]; and the hitherto unreported hemi-(diethyl etherate), $(LiBH_4)_2 \cdot (C_2H_5)_2O$; and lithium borohydride. Representative data for isotherms at 25.0, 0.0, −35.3, −45.2 and −63.5° are listed in Table I. Also included is a partial isotherm at 15.0° in the region of the saturated solution from which the solubility of lithium borohydride may be calculated.

The absence of a discontinuity of the phase diagrams at $n_2 = 0.33$ shows unambiguously that a bis-(diethyl etherate) of lithium borohydride does not exist even at temperatures as low as −63.5°.[4] This places the lithium borohydride–diethyl ether system in marked contrast to the lithium borohydride–dimethyl ether system, in which a stable bis-(etherate) is readily formed.[5] On the other hand, the two systems are similar in that no etherates lower than an hemi-(etherate) were found.

Heats of dissociation of the two diethyl etherates of lithium borohydride were determined from the dissociation pressures of the respective etherates at various temperatures, Table II. That the data are well represented by a simple linear equation (Table III and II) indicates that the heats of dissociation for the processes

$$2LiBH_4 \cdot (C_2H_5)_2O(s) = (LiBH_4)_2 \cdot (C_2H_5)_2O(s) + (C_2H_5)_2O(g) \quad (1)$$

and

$$(LiBH_4)_2 \cdot (C_2H_5)_2O(s) = 2LiBH_4(s) + (C_2H_5)_2O(g) \quad (2)$$

are constant in the temperature range considered. Extrapolation of the dissociation pressure–temperature data to lower temperatures show an intersection at −40° and 0.17 mm.; below −40° only lithium borohydride diethyl etherate is stable.

Values for the various thermodynamic quantities associated with the dissociation processes described by equations 1 and 2 at 25° are summarized in Table III. The data in Table III may be combined with the thermodynamic properties of lithium borohydride and diethyl ether to allow cal-

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[1] Taken in part from a thesis presented to the Graduate School of Saint Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1957.

[2] Taken in part from a thesis presented to the Graduate School of Saint Louis University in partial fulfillment of the requirements for the degree of Master of Science, February, 1955.

[3] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).

[4] E. Wiberg, H. Nöth and R. Uson, *Z. Naturforsch.*, **11b**, 490 (1956), report failure to isolate lithium borohydride bis-(diethyl etherate) at temperatures down to −80°.

[5] G. W. Schaeffer, T. L. Kolski and D. L. Ekstedt, THIS JOURNAL, **79**, 5912 (1957).