Acknowledgments.—This work was carried out under Task Assignment Re2d-02-1 of the Bureau of Ordnance.

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Melting Point of Carbon Tetrachloride

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RECEIVED NOVEMBER 29, 1954

An incidental determination of the melting point of carbon tetrachloride gave a result appreciably higher than previously published values.

The carbon tetrachloride used was a heart cut, b.p. 76.8°, obtained by distilling Baker Analyzed product through a 40-plate Oldershaw column at 20:1 reflux ratio. The purity of the heart cut, determined independently in a 5-ml. calorimeter,[1] was found to be 99.98 mole %. A calorimeter, similar to that employed by Rossini,[2] containing a 50-ml. sample, and a 25 ohm platinum resistance thermometer calibrated two months previously by the National Bureau of Standards were used in the melting point determination.

The data obtained on two separate samples are given in Table I along with previous literature values.

TABLE I

MELTING POINT OF CARBON TETRACHLORIDE

Sample 1, m.p. °C.	−22.782°
Sample 2, m.p., °C.	−22.782
Sample 2, f.p., °C.	−22.796, −22.793
Average	−22.788
Corr. for impurity	+ 0.036
Final value	−22.75 ± 0.03°
Timmermans, Martin[3]	−22.95
Skau[4]	−22.85
Johnston, Long[5]	−22.87
Deffet[6]	−22.95
Stull[7]	−22.79
Staveley, Gupta[8]	−22.96

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The Preparation of Fluorocarbon Carboxylic Acid Cyanide Dimers

BY R. H. PATTON AND J. H. SIMONS

RECEIVED SEPTEMBER 27, 1954

It has been found that fluorocarbon carboxylic acid chlorides react readily with silver cyanide to yield a new fluorocarbon derivative.

These new cyanide derivatives are readily hydrolyzed by water and alcohols to yield, respectively, acids and esters plus hydrogen cyanide. They also react vigorously with silver fluoride or mercuric fluoride to yield the acid fluoride of the original fluorocarbon carboxylic acid and silver or mercuric cyanide.

A few of the physical properties of these compounds are given in Table I.

The determined molecular weights of these compounds as well as the fact that they are independent of pressure at constant temperature indicate that the substances exist in the vapor as "dimers" of the simple formulas. The analogous organic compounds are known to exist in two forms convertible one into the other. For example, the first member of the series[1]

TABLE I

Compound	B.p., °C.	d^{25}_4	CN anal., % Theory	CN anal., % Found	Mol. wt. of vapor dimer Theory	Mol. wt. of vapor dimer Found
$(CF_3COCN)_2$	83–84	1.440	21.14	20.92	246	246
$(CF_3CF_2COCN)_2$	106–108	1.532	15.03	14.77	346	346
$(CF_3(CF_2)_2COCN)_2$	136–138	1.606	11.66	11.52	446	444
$(CF_3(CF_2)_4COCN)_2$	190–193	1.719	8.05	7.63	646	..

$$2CH_3COCN \longrightarrow CH_3COOC(CN)_2CH_3$$

where the monomer has a boiling point of 93° and the dimer 210°. Melting point of the dimer is 69°. It is obvious that the fluorocarbon derivatives are different from the organic ones as the monomer was not obtained, the vapor density indicates no equilibrium between monomer and dimer, and the reaction with water and metallic fluorides produces either the parent acid or acid fluoride. Although the molecular weights indicate the compounds to be non-reversible dimers, the chemical reactions indicate that these do not have structures analogous to the organic analogs.

Since all of these compounds were prepared by the same method, the preparation of the dimer of trifluoroacetyl cyanide will serve as an example. The only difference among the preparations was the reaction time, which ranged from three days for the first member to three weeks for the last member.

Experimental

Trifluoroacetyl Cyanide Dimer.—Approximately 0.05 mole of trifluoroacetyl chloride was transferred to a heavy-wall glass vial containing 10.7 g. (0.08 mole) of dry silver cyanide. The vial was sealed and placed in a water-bath for three days with the temperature maintained at 80–95°. The vial was then cooled in liquid air, opened and attached to a vacuum manifold system and the contents transferred to another vial. The second vial was then removed from the manifold system and the contents transferred to a small fractionating apparatus, avoiding as much as possible contact with atmospheric moisture. The product was then fractionated. The yield of colorless, mobile liquid, b.p. 83–84°, was 5.0 g. (0.04 mole).

Analysis.—Since these compounds hydrolyze readily in water, advantage was taken of this by using the usual gravimetric cyanide analysis of the hydrolyzed solution of these compounds.

Vapor Density.—The molecular weight in the vapor was calculated by measurements of the vapor density. This was done by weighing a known volume of the gas at a known temperature and pressure. A bulb of measured volume carrying a stopcock and ground joint was attached to a vacuum system, exhausted, and filled with the gas under investigation at a measured pressure and temperature. The bulb was then removed and weighed. Table II shows the molecular weight of the methforyl compound at constant temperature with varying pressure.

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(1) H. Hubner, *Ann.*, **120**, 335 (1861).