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Melting Point of Carbon Tetrachloride

BY A. K. DUNLOP

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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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[1] D. D. Tunnicliff and Henry Stone, *Anal. Chem.*, **25**, 73 (1955).

[2] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

[3] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926).

[4] E. L. Skau, *J. Phys. Chem.*, **37**, 609 (1933).

[5] H. L. Johnston and E. A. Long, THIS JOURNAL, **56**, 31 (1934).

[6] L. Deffet, *Bull. soc. chim. Belg.*, **44**, 41 (1935).

[7] D. R. Stull, THIS JOURNAL, **59**, 2726 (1937).

[8] L. A. K. Staveley and A. K. Gupta, *Trans. Faraday Soc.*, **45**, 51 (1949).

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

The Preparation of Fluorocarbon Carboxylic Acid Cyanide Dimers

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

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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]

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

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.

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	..

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).

TABLE II

MOLECULAR WEIGHT OF TRIFLUOROACETYL CYANIDE DIMER

T, °C.	33	33	33	33
Pressure, mm.	77	46	27.5	9
Mol. wt.	245	246	246	268

The authors wish to thank the Minnesota Mining & Manufacturing Company for their sponsorship of this work and for the supply of fluorocarbon carboxylic acids.

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The Preparation of Fluorocarbon Carboxylic Acid "Thiocyanates"[1]

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

RECEIVED SEPTEMBER 27, 1954

In a previous communication it was demonstrated that fluorocarbon carboxylic acid chlorides react with silver cyanide to yield fluorocarbon carboxylic acid cyanide dimers. It has now been determined that these acid chlorides also react readily with silver thiocyanate to yield fluorocarbon carboxylic acid thiocyanates.

These new thiocyanate derivatives are readily hydrolyzed by water and alcohols to yield, respectively, acids and esters plus thiocyanic acid.

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

TABLE I

Compound	B.p., °C.	d^{25}_4	Sulfur anal. Theory	Sulfur anal. Found	Mol. wt. of vapor Theory	Mol. wt. of vapor Found
$CF_3CO(SCN)$	72–74	1.369	20.64	20.82	155	154
CF_3CF_2CO-(SCN)	87	1.503	15.61	15.84	205	205
$CF_3(CF_2)_2CO$-(SCN)	106	1.644	12.55	13.13	255	256

Since all of these compounds were prepared by the same method, trifluoroacetyl thiocyanate will serve as an example.

Experimental

Trifluoroacetyl Thiocyanate.—Approximately 0.05 mole of trifluoroacetyl chloride was transferred to a heavy-wall Pyrex glass vial containing 13.3 g. (0.08 mole) of dry silver thiocyanate. The vial was sealed and placed in a waterbath for two days with the temperature maintained at 60–80°. The vial was then cooled in liquid air, opened and attached to a vacuum manifold system and the liquid contents transferred to another vial. The second vial was 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. 72–74°, was 4.8 g. (0.03 mole).

Analysis.—The analysis of these compounds was performed by the usual Parr bomb gravimetric analysis for sulfur. The molecular weight of the vapor was calculated from vapor density measurements under the conditions of room temperature (approximately 30°) and the vapor pressure of the compound at that temperature.

Acknowledgment.—The authors are grateful to the Minnesota Mining and Mfg. Company for both the sponsorship of this work and the supply of fluorocarbon carboxylic acids.

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[1] The term "thiocyanate" is used in a general or generic sense as evidence of detailed structure is not available to distinguish between $CF_3\overset{O}{\overset{\|}{C}}SCN$ and $CF_3\overset{O}{\overset{\|}{C}}NCS$. Even for the organic analog of this substance the structure is not known with certainty, *e.g.*, A. E. Dixon and J. Taylor, *J. Chem. Soc.*, **93**, 696 (1908). Even if it were, it would be fallacious reasoning to assign a structure to the fluorocarbon derivatives by analogy.

Properties of Pure Normal Alkanes in the C_{17} to C_{36} Range

BY A. A. SCHAERER, C. J. BUSSO, A. E. SMITH AND L. B. SKINNER

RECEIVED OCTOBER 4, 1954

Although physical properties of some normal alkanes above n-$C_{20}H_{42}$ have been reported in the literature, the actual purity of these compounds is either not given or is estimated from melting curves. Melting curves are, of course, not reliable in view of the formation of solid solutions by adjacent members of this series. Also, there is a particular lack of data on the odd-number carbon normal alkanes of higher molecular weight.

In connection with some studies on properties of petroleum waxes we have prepared a series of pure normal alkanes, in the range n-C_{17} to n-C_{36}, which includes several of the odd-number carbon members. The pure compounds were obtained through a combination of various fractionation processes and the product purity established by high temperature mass spectrometric analysis.

In view of the fact that some of our data on the physical constants of these compounds vary somewhat from those reported by earlier investigators it was felt desirable to publish our results.

Experimental

Preparation of Pure Normal Alkanes.—The normal alkanes were isolated from a commercial crystalline type paraffin wax prepared from an East Texas lubricating oil distillate. The first step consisted of a urea extraction to eliminate the more highly branched isoparaffins and the cyclic compounds. The urea reactive portion was then distilled, at reduced pressure, into narrow fractions using a 90 cm. by 4 cm. i.d. vacuum jacketed column packed with protruded stainless steel packing. Each of the narrow boiling fractions was redistilled several times with heart cuts only being retained. Between each redistillation these heart cuts were contacted with an equal volume of 100% sulfuric acid, 30 minutes at 140°, followed by crystallization from toluene solution.

Purity at the completion of the first few cycles was estimated from automatic differential thermal analysis[1] data but products from subsequent cycles were submitted for high temperature mass spectrometric analysis. Purification cycles were repeated until a purity of 99% v.[2] or better was achieved.

Melting and transition temperatures are plotted in Fig. 1.

Heats of Fusion and Transition.—Heats of fusion and transition, shown in Table I and plotted in Fig. 2, were determined using an adiabatic calorimeter with electrical heating. The values obtained are accurate to within 2%.

Volume Contraction on Solidification and Transition.—Volume changes were determined with a conventional all glass dilatometer using mercury as the displacement liquid.

X-Ray Analysis.—These hydrocarbons were also examined at room temperature with X-rays using both single

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[1] C. J. Penther, S. T. Abrams and F. H. Stross, *Anal. Chem.*, **23**, 1459 (1951).

[2] M. J. O'Neal, Jr., and T. P. Wier, Jr., *ibid.*, **23**, 830 (1951).