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

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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 water-bath 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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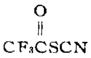
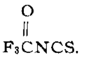
[1] The term "thiocyanate" is used in a general or generic sense as evidence of detailed structure is not available to distinguish between


$CF_3\overset{\overset{O}{\|}}{C}SCN$

and


$CF_3\overset{\overset{O}{\|}}{C}NCS$.

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).