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Melting Point Intervals of Sulfur Allotropes

MALCOLM THACKRAY
Australian Atomic Research Establishment, Lucas Heights, New South Wales, Australia, 2232

The intervals between the melting points of the four allotropes of cyclooctasulfur (designated α, β, γ, and δ) were measured by a microtechnique in sealed capillaries. New melting point values resulting from this work were β 120.14°, α 115.11°, γ 108.60°, and δ 106.0° C, all appreciably higher than currently accepted values.

AT least four allotropes of sulfur, consisting of different spatial arrangements of the ring molecule of cyclooctasulfur, S_8, and designated α, β, γ, and δ, are known to exist (*5*). The accurate determination of their melting points is of considerable importance for checking the accuracy of vapor pressure equations (*6*) and in theories describing the rates of crystal growth and the polymorphic transformations of sulfur (*2, 7*).

The currently accepted melting points (*5*) are β 119.3°, α 112.8°, and γ 106.8°. The melting point of δ-sulfur is not known.

Factors giving rise to low precision in these measurements include the following:

All the melting points are above 95.6° C and only β-sulfur is stable above this temperature. If nucleation occurs, all other forms transform rapidly to β in the region of their melting points. There is no record of δ-sulfur ever having been preserved in this temperature range and preservation of γ-sulfur in macroscopic amounts rarely occurs.

Naturally occurring sulfur is frequently contaminated with hydrocarbons, which are very difficult to remove (*1, 8*).

Liquid and gaseous sulfur contain species other than S_8 and crystals obtained from the melt or by sublimation are not initially pure cyclooctasulfur and have lowered melting points.

Sulfur crystallized from solvents is usually contaminated with solvent.

Atmospheric constituents, especially oxygen, are strongly adsorbed on sulfur.

Sufficient information is now known of the behavior of sulfur to overcome most of these difficulties. Bacon and Fanelli (*1*) and Von Wartenburg (*8*) have demonstrated methods for removing hydrocarbons, and vacuum distillation of the residue gives very pure sulfur. This can then be converted quantitatively to cyclooctasulfur by heating in an inert atmosphere for several days at about 100° (*4*).

By sealing large numbers of small crystals into fine capillary tubes and observing them on a microscope hot stage, several melting points could be observed in the same tube after appropriate thermal treatments. The intervals between these melting points could be determined with high precision. These intervals should correspond with the differences between the melting points of the various allotropes. By taking the accepted melting point of β-sulfur, the stable modification, as an internal standard, more accurate melting points for the other allotropes could be calculated. This has been done (second row of Table I). The determination of absolute melting points by any other method when using the microscope poses something of a dilemma when one comes to quote the results, because all substances in microcrystalline form melt over an appreciable range of temperature. When the crystals are in contact in a vertical capilliary tube as in most macromethods, the first crystal to melt pulls all the others together by surface wetting and this is taken as the melting point. Most melting points in the literature were obtained by this method. When the crystals are all separate from each other and observed under a microscope, however, it is more logical to take the last crystal to melt as representing the true melting point. The difference between these two types of measurement can be appreciable and for the sake of consistency no "final" melting points are given in this paper. The values given in the third row of Table I are "first" melting points. Although the hot-stage thermometer was checked only at the boiling point and ice point of water and calibrated with the standard substances quoted, measurements

Table I. Derived Melting Points of Sulfur Allotropes

Premise	M.P. β	M.P. α	M.P. γ	M.P. δ
Currently accepted	119.3	112.8	106.8	
Assuming current β MP correct	119.3	(114.3)[a]	(107.8)[a]	(105.2)[a]
Assuming mean measured β MP correct	120.14	115.11	108.60	106.0

[a] Values in parenthesis obtained by subtracting measured temperature intervals from "accepted" melting point of β-sulfur.

on two very different types of hot stage agreed well and results suggest that even the accepted melting point of β-sulfur is too low. The interval method proved that the melting points of the other allotropes are too low.

EXPERIMENTAL

Purification of Sulfur. BDH laboratory-grade sulfur was recrystallized from carbon disulfide and then freed from solvent and hydrocarbons by the method of Bacon and Fannelli (*1*) (repeated boiling with magnesium oxide with oven filtration through sintered glass). The product was distilled in vacuum onto a cold finger at 0°. The cold finger, still under static vacuum but no longer cooled, was placed in an oven at 105° for five days. The temperature was reduced slowly to ambient before nitrogen was allowed into the tube.

Preparation and Use of Capillary Tubes. Thin-walled capillaries of approximately 0.5-mm diameter and 2- to 3-cm-length were prepared from clean glass and silica. The vacuum around the cold finger was released with nitrogen and a few crystals were transferred rapidly to an agate mortar and ground to a fine powder. A little of the sulfur powder was introduced as quickly as possible into each capillary tube, which was then sealed. Exposure to the atmosphere ranged from about 5 to 20 minutes. Shaking the capillaries caused the sulfur crystals to distribute uniformly around the inner walls of the tube. These tubes were viewed in a horizontal position on the microscope hot stage; a large number of crystals were always in the field of view. The effective viewing area could also be increased by traversing the hot stage in the longitudinal direction of the tube. Prolonged heating of macrocrystals at 105° is sufficient to destroy any of the more labile allotropic forms which may have condensed from the vapor during vacuum distillation and, as is usual with sulfur, only two melting points—those of α and β—were observed in the first melting.

The movement of interfaces is so rapid in pure cyclooctasulfur at all temperatures above about 105° that there is no possibility of a crystal's reaching the melting point in a partially transformed state and these melting points are perfectly sharp and reproducible. To observe the melting points of forms other than α and β, it is necessary to induce the drops, formed during the first melting, to solidify. The drops supercool very readily and slow cycling between ambient and liquid nitrogen temperature is necessary to induce crystallization. Even this treatment fails if the tubes have been overheated (above approximately 140°) in such a manner as to produce appreciable amounts of polymerized sulfur.

Even careful melting of sulfur produces some polymer and lowers subsequent melting points by about 0.3°, and it is necessary to heat the capillaries at about 100° for several days before re-use. Since such treatment has a very different effect on the polymer content of drops which are still liquid and, as these might solidify after removal from the oven, no capillaries can be heat-treated until microscopic examination reveals that all drops have solidified.

Hot Stages and Microscope. The first part of the work was performed with a locally made hot stage consisting of an electrically heated copper block 2 inches in diameter by 0.5-inch thick, drilled radially to hold a mercury-in-glass thermometer cemented in position with molten salicylic acid. A deep groove was machined in the top of the copper block just above the thermometer pocket and the capillary tubes were placed in this and covered with silicone oil. The block was insulated underneath and at the side with cork and on top by means of a circular glass cover. The glass cover was held about 1 mm above the upper copper surface by the surrounding cork annulus. The heated block could be traversed with a mechanical stage and the capillary was viewed in reflected polarized light using a Wild M20 microscope with a ×10 objective. The temperature of the block could be raised at any desired rate by means of a Variac.

Use of Mettler FP2 Hot Stage. During the second part of the work a Mettler FP2 hot stage became available. This instrument provides three linear heating rates with instant arrest of heating and maintenance of the sample at the achieved temperature. Push-button digital recording of observed transition temperatures is also provided. Although the capillary tube had to be rested on a microscope slide in air, it was so closely surrounded by the heating elements that no temperature lag effects were ever observed at the slowest heating rate of 0.2° per minute (employed for the results quoted). The samples were again observed in reflected polarized light.

RESULTS AND DISCUSSION

The observed melting point intervals were as follows:

LOCALLY MADE HOT STAGE

Melting Point Interval	No. of Measurements
$\beta - \alpha = 5.01° \pm 0.52$	10
$\alpha - \gamma = 6.50° \pm 0.48$	7
$\beta - \gamma = 11.29° \pm 0.53$	8

FP2 HOT STAGE

Melting Point Interval	No. of Measurements
$\beta - \alpha = 5.03° \pm 0.13$	24
$\alpha - \gamma = 6.50° \pm 0.30$	10
$\beta - \gamma = 11.55° \pm 0.30$	8
$\beta - \delta = 14.1$	1

Only one crystal was observed to melt well below the 2σ limit of the γ modification, referred to here as δ. A fortunate circumstance allowed its melting point to be determined with reasonable precision. This solidified drop, which melted before all the others, changed shape slightly in melting and came into contact with a crystal of β-sulfur, which again caused it to solidify. This permitted the temperature interval to the β melting point to be observed with great care on the same drop of sulfur and proved that the low melting point was not the result of impurity.

Although the original intention of this work was only to record these temperature intervals between allotropes and to take the accepted melting point of β-sulfur at 119.3° as an internal standard, it became obvious as the work progressed that the FP2 hot stage permitted such precise and accurate determination of melting points by this method on other known standards, that a comparative determination of the β melting point was a reasonable extension of the work. The value recorded for the β melting point was 120.14° ± 0.17 from 30 measurements. Since the sulfur was exposed to the atmosphere while the capillary tubes were filled, no claim for high accuracy is made for this value. However, the fact that it is higher than the currently accepted value suggests that a new attempt should be made to measure this constant on pure cyclooctasulfur free from atmospheric contamination.

The results are summarized in Table I.

The melting points of the following highly purified standards were obtained in an identical manner on the FP2 stage: iodine, 113.4–13.7°; benzoic acid, 122.0–22.4°; urea, 132.2–32.8°. They are strictly comparable with those for the melting point of β-sulfur and permit an estimate of its accuracy.

These results agree well with currently accepted values and suggest that the melting point of pure β-cyclooctasulfur free from atmospheric contamination may be well above the currently accepted 119.3°. This would be in agreement with the measurements of Dufraise *et al.* (*3*).

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Phosphorus-31 NMR Data for Some Miscellaneous Compounds

SAMUEL O. GRIM,[1] ANTHONY W. YANKOWSKY, SALVATORE A. BRUNO,
WILLIAM J. BAILEY, EDWARD F. DAVIDOFF, and TOBIN J. MARKS
Department of Chemistry, University of Maryland, College Park, Md. 20742

Phosphorus-31 chemical shifts are reported for 61 organophosphorus compounds, which include six secondary phosphines, seven chlorophosphines, 28 tertiary phosphines, eight quaternary phosphonium salts, seven ylides, and several miscellaneous compounds. The preparation of iodomethyltriphenylphosphonium methyl sulfate and iodomethyltriphenylphosphonium hexafluorophosphate is reported.

Over the past several years we have collected phosphorus NMR data on some miscellaneous compounds which we have not previously reported (Table I). Some experimental results are given for several compounds which will not be reported elsewhere.

An interesting case of metathesis occurred during an attempt to obtain soluble phosphonium salts from a slightly soluble phosphonium iodide.

Iodomethyltriphenylphosphonium iodide (*9*), which is prepared by the reaction of triphenylphosphine and methylene iodide, is not soluble enough to permit measurement of the ^{31}P chemical shift under our conditions. One usual procedure for conversion of iodide salts to compounds of other anions—viz., treatment of the phosphonium salt with freshly prepared silver oxide, filtration, and addition of the acid of the desired anion—failed in this case because of apparent side reactions of the iodomethyl groups. Several other attempts to form a soluble salt by metathesis also failed. However, treatment of iodomethyltriphenylphosphonium iodide with freshly distilled dimethyl sulfate produced the soluble methyl sulfate salt:

$$[(C_6H_5)_3PCH_2I]I + (CH_3O)_2SO_2 \rightarrow [(C_6H_5)_3PCH_2I][CH_3OSO_3] + CH_3I$$

EXPERIMENTAL

Phosphorus-31 NMR measurements were obtained as described elsewhere (*4*) on a Varian DP60 NMR spectrometer. The chemical shifts are reported for 85% H_3PO_4 as the standard. The measurements were made at 22° ± 2° C.

Proton measurements were obtained on a Varian A60A spectrometer.

Iodomethyltriphenylphosphonium Methyl Sulfate. Iodomethyltriphenylphosphonium iodide (5.0 grams, 9.4 mmoles) was placed in a flask under N_2. Methylene chloride (35 ml) was added and the mixture was stirred overnight at room temperature. Most of the solvent was removed under vacuum and addition of ether caused precipitation of the product, which was recrystallized from isopropyl alcohol after treatment with decolorizing carbon. The yield was 3.3 grams (86%) of light yellow crystals (m.p. 179–81°). The proton NMR gave three peaks: a multiplet at 2.08 τ, a doublet at 4.89 τ ($^2J_{PCH}$ = 7.8 Hz), and a singlet at 6.35 τ, of intensities 15.3:2.0:2.9, respectively. The peaks are due to the phenyl, methylene, and methyl groups with the expected ratio of 15:2:3.

Anal. Calcd. for $C_{20}H_{20}IO_4PS$: C, 46.75; H, 3.89. Found: C, 46.88; H, 4.15.

Iodomethyltriphenylphosphonium Hexafluorophosphate. This compound was made from the methyl sulfate salt

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[1] To whom correspondence should be sent.