This salt lost no weight when it was stored under vacuum over anhydrous calcium chloride for 24 hours.

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A Qualitative Test for Silicon in Organosilicon Compounds and for Germanium in Organogermanium Compounds

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Silicomolybdic acid was first described by Parmentier[1] in 1882. Sixteen years later a method for the detection of silicic acid in water by the use of the yellow silicomolybdate solution for a colorimetric determination was reported.[2]

Feigl and Krumholz[3] first described the use of benzidine in conjunction with silicomolybdic acid as a sensitive spot test for silicon; the benzidine becomes oxidized to "benzidine blue" and simultaneously the silicomolybdic acid is reduced to "molybdenum blue." It has been reported that 0.001 mg. of silica in a concentration of 1:50,000 can be detected by this method. The benzidine–molybdic acid test has been used to detect silica in minerals,[4] silicon in steel[5] and silicic acid in limestone and related materials.[6]

Germanates react similarly with molybdic acid to form the insoluble germanomolybdic acid which like its silicon analog will oxidize benzidine to "benzidine blue" with the concurrent formation of "molybdenum blue."[7] The quantitative methods for germanium in organogermanium compounds have been reviewed recently.[8]

A qualitative test for silicon in organosilicon compounds has been reported,[9] the compound being oxidized to silica with concentrated sulfuric acid plus either glacial acetic acid or 70% nitric acid. Another qualitative test[10] for silicon in organic compounds involves treatment with sodium fluoride and sulfuric acid; the resulting silicon tetrafluoride vapors are allowed to contact an asphalt-covered rod which has been previously dipped in water. A white deposit of silica indicates the presence of silicon.

The benzidine–molybdic acid test recently has been applied to organosilicon compounds.[11] The organosilicon compound was decomposed to the soluble silicate by fusion on a platinum loop with sodium carbonate and sodium peroxide; subsequent reaction with ammonium molybdate and benzidine resulted in the blue coloration when neutralized with ammonia.

The benzidine–molybdic acid test has been employed in this Laboratory; several modifications and refinements have been made and the method has been extended to include organogermanium compounds. Although a platinum loop is more convenient and available than a small platinum spoon, the spoon has several advantages over the loop. Liquids may be tested with greater facility, a smaller amount of the organosilicon (or organogermanium) compound is required and no transferal of the fused mixture is necessary when employing the platinum spoon. Sodium acetate was found more practical than ammonia for neutralizing the acidic solution. Commercially available sodium peroxide contains iron as an impurity which causes a brown color on neutralization with ammonia and thus masks the blue color which is characteristic of a positive test for silicon or germanium. Only with some sulfur-containing organosilicon compounds was any difficulty encountered in obtaining a positive test; with certain of these compounds a large excess of sodium peroxide was necessary in order to ensure complete oxidation of the sulfur atom. If the sulfur is not completely oxidized, the resulting sulfide will reduce the ammonium molybdate solution to "molybdenum blue" and therefore give a positive test in the absence of silicon. A variety of organosilicon and organogermanium compounds has been tested, a positive result being obtained in every case.

Experimental

Approximately 0.02 g. of the organosilicon (or organogermanium) compound, 0.01 g. of sodium peroxide[12] and 0.06 g. of sodium potassium carbonate (1:2 fusion mixture) are mixed thoroughly. If the sample to be tested is a liquid, it is best to mix the materials on a small piece of platinum foil, possibly a platinum crucible lid; 2 or 3 drops of the liquid should be used, and if the liquid is relatively volatile, the mixture should not be made up until the bead is ready to be prepared. A platinum loop (approximately 4 mm. in diameter), which has previously been rid of any silicate by fusion with sodium potassium carbonate, is heated and brought into contact with the mixture. After a bead has been formed, it is heated in a bunsen or meeker burner flame for approximately 1 minute. The mixture should not be heated too rapidly at first or some spattering may occur. After placing about 1 ml. of water in a platinum crucible, the bead is immersed in the water, and the solution is warmed to boiling in order to dissolve the fused mixture; glassware cannot be used since the boiling mixture may dissolve sufficient silica to give a positive test. On a piece of filter paper are placed 2 or 3 drops of ammonium molybdate solution. The 2 drops of the solution to be tested are added to the ammonium molybdate on the filter paper. If the test is run rapidly, the solution will still be warm; however, if the solution has cooled, the filter paper should be warmed gently following the addition of the molybdate and test solutions. Subsequently, 1 drop of benzidine solution and 2–5 drops of

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(1) F. Parmentier, *Compt. rend.*, **94**, 213 (1882).

(2) A. Jolles and F. Neurath, *Z. angew. Chem.*, **11**, 315 (1898).

(3) F. Feigl and P. Krumholz, *Mikrochemie, Preg. Festschrift*, 77 (1929); F. Feigl and P. Krumholz, *Ber.*, **62B**, 1138 (1929). See also E. van Dalen and G. de Vries, *Anal. Chim. Acta*, **4**, 235 (1950).

(4) F. Feigl and H. Leitmeier, *Tschermak's mineral. petrog. Mitt.*, **40**, 1 (1929) [*C. A.*, **24**, 4479 (1930)].

(5) G. Thanheiser and M. Waterkamp, *Arch. Eisenhüttenw.*, **15**, 129 (1941) [*C. A.*, **36**, 6943 (1942)].

(6) N. A. Tananaev and A. M. Shapovalenko, *J. Applied Chem. (U.S.S.R.)*, **11**, 352 (1938) [*C. A.*, **32**, 5724 (1938)].

(7) A. S. Komarovskii and N. S. Poluektov, *Mikrochemie*, **18**, 66 (1935).

(8) H. H. Krause and O. H. Johnson, *Anal. Chem.*, **25**, 134 (1953).

(9) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950). For the quantitative determination of silicon in organosilicon compounds see H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 968 (1951); and H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, *ibid.*, **72**, 5767 (1950).

(10) A. P. Kreshkov and V. A. Bork, *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R.*, **3**, 354 (1951) [*C. A.*, **47**, 2646 (1953)].

(11) A. P. Kreshkov and V. A. Bork, *Zhur. Anal. Khim.*, **6**, 78 (1951) [*C. A.*, **45**, 6125 (1951)]; see also A. P. Kreshkov and V. A. Bork, *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R.*, **3**, 361 (1951) [*C. A.*, **47**, 2646 (1953)].

(12) If the organosilicon or organogermanium compound being tested contains sulfur, the amount of sodium peroxide should be two or three times the sample weight.

sodium acetate solution are added; the appearance of a blue color indicates a positive test.

A platinum spoon can be advantageously substituted for the loop, using a short heavy piece of platinum wire fused in a glass rod as a handle. After use of the spoon, any fused mixture remaining within is dissolved in dilute hydrochloric acid, and the spoon is then rinsed with distilled water. The spoon is dried, amost filled with sodium potassium carbonate and again fused. After dissolving the carbonate mixture as described above, the spoon is again ready for use.

Instead of sodium acetate, ammonia vapor can be used to neutralize the free mineral acid. The advantages of employing sodium acetate for this purpose are enumerated in the introductory section of this article; however, the use of ammonia vapor does somewhat increase the sensitivity of the test.

If a blue color is obtained upon addition of the solution containing the fused carbonate mixture to the ammonium molybdate, one of the elements has not been completely oxidized and the test should be repeated using a larger excess of sodium peroxide. It is advisable to run a blank test with the wire (or spoon) and the reagents to assure the initial absence of silicates. A saturated sodium acetate solution on standing will dissolve sufficient silica from a glass container to give a weakly positive test; therefore, the sodium acetate reagent should either be stored in a polyethylene bottle or be freshly prepared.

Concentrated sulfuric acid may be employed (with a platinum spoon) to decompose the organosilicon compound to silica,[9] the sensitivity might be slightly increased; however, the use of sodium peroxide is much more convenient.

Other reagents[13] have been suggested as replacements for benzidine to reduce the molybdenum compound and include pyrrole, 2,4-diaminophenol hydrochloride, hydroquinone, *p*-hydroxyphenylglycine, 1-amino-2-naphthol-4-sulfonic acid, 3,7-diaminodibenzofuran and stannous chloride.

In connection with obtaining some idea of the sensitivity of the test under the above-described conditions, 0.1 g. of tetraphenylsilane (and tetraphenylgermane) was fused with sodium potassium carbonate and the fusion mixture was diluted with water to a volume of 10 ml. Aliquots of this solution were then diluted to various concentrations and a test made of these solutions. With the tetraphenylsilane using sodium acetate for neutralization, solutions as dilute as 0.0125 g. of the original sample in 10 ml. gave a positive test; using ammonia vapor for neutralization, solutions diluted to 0.0063 g./10 ml. still gave a positive test. With tetraphenylgermane using sodium acetate, solutions as dilute as 0.0031 g./10 ml. gave a positive test; using ammonia vapor, solutions diluted to 0.0016 g./10 ml. gave a positive test.

TABLE I

ORGANOSILICON COMPOUNDS TESTED[a]

- Tetraphenylsilane
- Triethylsilane
- Triethylchlorosilane
- Diphenyldichlorosilane
- Triphenylchlorosilane
- Ethyl silicate
- Tri-1-naphthyl-*p*-tolylsilane
- Tri-*o*-tolyl-*p*-anisylsilane
- Triphenylphenoxysilane
- Triphenylbenzyloxysilane
- Triphenyl-*n*-tetradecylsilane
- Triphenyl-*n*-hexadecylsilane
- Tetra-β-phenylethylsilane
- Diphenyldibenzylsilane
- Tri-γ-phenylpropylphenylsilane
- Diphenyldi-*n*-tetradecylsilane
- Hexaphenyldisilane
- Decaphenyltetrasilane
- Octaphenyltrisilane
- 1,1,1-Trimethyl-1,1,1-tri-*o*-tolyldisiloxane
- Diphenyldi-*n*-dodecylsilane
- Trimethylphenylsilane
- Tri-*n*-hexadecylphenylsilane
- 2-Trimethylsilyldibenzothiophene-5-dioxide
- 3-Trimethylsilyldibenzothiophene-5-dioxide
- 4-Trimethylsilyldibenzothiophene-5-dioxide
- 3-Nitro-4-trimethylsilyldibenzothiophene-5-dioxide
- N-(*p*-Triphenylsilylphenyl)-α,α'-dimethylpyrrole
- Triphenyl-(phenylethynyl)-silane
- Tetra-(phenylmercaptomethyl)-silane
- Hexaphenyldisilazane
- Hexabenzyldisiloxane
- *p*,*p*'-Di-(trimethylsilyl)-biphenyl
- Trimethyltriphenylmethylsilane

[a] All of the compounds listed gave a positive test for silicon. Tetraphenyltin and tetraphenyllead were tested and did not give a positive test.

TABLE II

ORGANOGERMANIUM COMPOUNDS TESTED

- Tetraphenylgermane
- Hexaphenyldigermane
- Triphenylgermane
- Triphenylchlorogermane
- Triphenylbromogermane
- Triphenyliodogermane
- Triphenylbenzylgermane
- Triphenyl-β-phenylethylgermane
- Triphenyl-*n*-octadecylgermane
- Tetra-*n*-dodecylgermane
- Tetra-*n*-tetradecylgermane
- Triphenyl-(triethylsilyl)-germane
- Triphenyl-(triphenylsilyl)-germane
- Hexaphenyldigermoxane

The organosilicon and organogermanium compounds which have been tested are listed in Tables I and II.

Reagents.[14]—**Ammonium Molybdate Solution.**—Five grams of ammonium molybdate is dissolved in 100 ml. of cold water and poured into 35 ml. of nitric acid (sp. gr. 1.42).

Benzidine Solution.—Five-hundredths of a gram of benzidine or benzidine hydrochloride is dissolved in 10 ml. of glacial acetic and diluted with water to 100 ml.

Sodium Acetate Solution.—A saturated solution is used.

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(13) F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand and Co., Inc., New York, N. Y., 1947, 4 vols.

(14) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., Inc., Houston, Texas, 1946, p. 252.

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Mutarotation of *cis*-2-Phenyl-4-carboxy-5-hydroxymethyl-2-oxazolines

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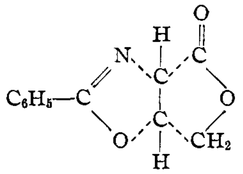
Lactones of two *cis*-2-phenyl-4-carboxy-5-hydroxymethyl-2-oxazolines recently were described.[1] One (αD +254°) was assigned the L-configuration and the other (II, αD −251°) the D-configuration.[2] When I reacted with a base and was then hydrolyzed by acid the amino acid D$_s$-*threo*-α-amino-β,γ-dihydroxybutyric (where C_α is used to indicate configuration and not C_β as used formerly[1]) was obtained. If our assignment of the configuration of I is correct, inversion occurred at C_α. Elliott[4] has reported that bases invert C_α of oxazolines prepared from threonine and allothreonine and that the equilibrium favors the trans (*threo*) compound. If the reaction by bases is a mutarotation and I and II are indeed enantiomers, the rate of the reversible reaction



L-*cis*-oxazoline (I)

$$\mathrm{L}[C\alpha] \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{D}[C\alpha]$$

is given by

$$k_1 + k_2 = \frac{2.3}{t} \log \frac{a_0 - a_\infty}{a_t - a_\infty}$$

This is the well-known expression describing the mutarotation of sugars.

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(1) E. E. Hamel and E. P. Painter, THIS JOURNAL, **75**, 1362 (1953).

(2) In drawing the projection formula of I the convention suggested in the A.C.S. report[3] was followed. While no convention exists for oxazolines I is intended to show the configuration at both optical centers is the same as in L-glyceraldehyde. I is compound VII in a former paper.[1]

(3) *Chem. Eng. News*, **30**, 4524 (1952).

(4) D. F. Elliott, *J. Chem. Soc.*, 62 (1950); 589 (1949).