TABLE II

TRANSFERENCE NUMBERS

Expt. no.[28]	Mole ratio	(Na+)	pH	n_{Na^+}	$1 - n_{Na^+}$	n_{SiO_2}	n_{OH^-}	Hydrolysis,[25] %	N (no. of SiO_2/ion)
4	1:2	1.0	12.12	0.42	0.58	0.45	0.13	1.38	1
5	1:2	0.5	11.96	.34	.66	.33	.33	1.88	1
6	1:2	0.1	11.46	.45	.55	.47	.08	2.85	1
7	1:3	1.0	11.29	.40	.60	.68	..	0.192	1.1
8	1:3	0.5	11.27	.45	.55	.78	..	.36	1.4
9	1:4	1.0	10.86	.53	.47	1.17	..	.071	2.2
10	1:4	0.1	10.75	.44	.56	1.23	..	.57	2.2

that in the dilute solutions of sodium silicate used in light-scattering measurements, it is probable that all the silicate species are in solution as monomeric silicic acid.[24,31]

The silica in solutions appears to be colloidal under two conditions. In alkaline solutions above pH 10.6 low molecular weight silicate species are brought into solution by peptization.[31] Also in concentrated solutions of silicic acid the monosilicic acid behaves as if it were aggregated into $[Si(OH)_4]_n$ particles where n is probably a small number.[15]

Acknowledgments.—To Professor J. J. Hermans for suggesting this approach to the problem and for his many suggestions during the course of the study. To Dr. J. Lorimer for helpful discussions. To Miss Joyce van den Berge and Mr. U. Verstrijden for assistance in performing the experiments. Thanks are also due the Foundation for Fundamental Research on Matter (FOM) supported by the Netherlands Organization for Pure Research (ZWO) under whose auspices this research was performed.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE TITANIUM ALLOY MFG. DIV. OF THE NATIONAL LEAD CO.]

The Synthesis and Properties of Zirconium Disulfide[1]

BY ABRAHAM CLEARFIELD

RECEIVED MAY 7, 1958

Historic methods for preparing zirconium disulfide were re-examined and new and refined methods for obtaining a pure product have been developed. The reaction of carbon disulfide with zirconia yields a mixture of zirconium disulfide and zirconium sulfoxide, ZrOS, in the temperature range 850–1200°. Above 1200° only zirconium disulfide is obtained. This has been correlated with the presence of different forms of zirconia in the two temperature ranges. The air oxidation of the disulfide was examined by means of differential thermograms and high temperature X-ray diffraction patterns.

Published information on the sulfides of zirconium is meager and much of what is reported is conflicting. Therefore, a study of the zirconium–sulfur system was undertaken. The present paper describes the synthesis and some properties of zirconium disulfide.

Zirconium disulfide has been synthesized by a variety of methods. Frémy[2] claimed to have prepared it by the action of carbon disulfide on zirconia at red heat. No analysis was given and it is questionable that his product was oxygen-free. A number of workers obtained zirconium disulfide by combination of the elements.[3–5] Of these only Biltz[3] used reasonably pure metal. Biltz and his co-workers also treated zirconium tetrachloride with hydrogen sulfide in a heated tube. They derived a pure product only after reheating the initially obtained material in a hydrogen sulfide atmosphere. Paykull[6] had been unsuccessful with this reaction because he did not rigidly exclude oxygen. VanArkel and DeBoer[7] passed zirconium tetrachloride and sulfur vapors over a hot wire and obtained pure zirconium disulfide but in poor yield. Finally, Hägg and Schönberg[8] reported its preparation by the action of hydrogen sulfide on zirconium metal in the temperature range 550–900°.

Experimental

Materials.—Pure zirconium dioxide was prepared by addition of glycolic acid (3 moles) to a solution of zirconyl chloride (1 mole) and calcining the precipitated triglycolatozirconic acid at 900–1000°. A typical sample contained 0.001% Al, 0.002% Ba, 0.02% Ca, 0.002% Cu, 0.001% Fe, 2% Hf, 0.01% Mg, 0.002% Na, 0.01% Si, 0.002% Ti. Zirconium tetrachloride was resublimed from a fused salt ($KCl-ZrCl_4$) melt as described by Horrigan.[9] The zirconium metal powder was Titanium Alloy P grade (−200 mesh) and contained 1–2% oxygen. Zirconium Hydride was obtained from Metal Hydrides, Inc. Traces of oxygen were removed from argon (originally 99.9% pure) by bubbling it through alkaline pyrogallol and drying by passage through tubes containing P_2O_5. Gaseous impurities in tank hydrogen sulfide (99.8% pure) were minimized by inverting the tank and drawing off liquid H_2S. Reagent grade carbon disulfide was used without further purification.

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[1] Portions of this paper have been presented at the 131st National Meeting of the American Chemical Society, Miami, Florida, April 9, 1957.

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[4] J. J. Berzelius, *Ann. Phys.*, **4**, 125 (1825).

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[8] G. Hägg and N. Schönberg, *Arkiv. Kemi.*, **26**, 371 (1954).

[9] R. V. Horrigan, *J. Metals*, **7**, AIME *Trans.*, **203**, 1118 (1955).

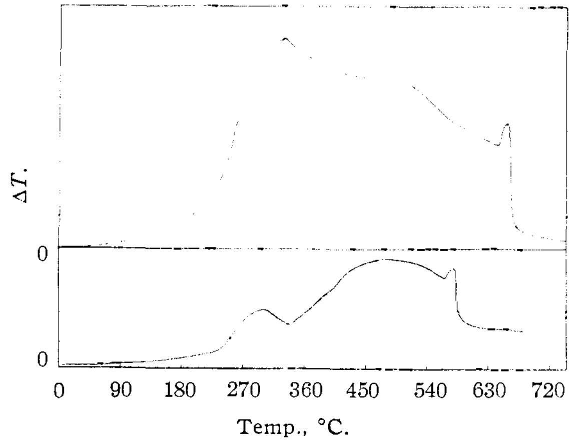

Fig. 1.—Differential thermograms in air of zirconium disulfide: top, heating rate 12.5°/min.; bottom, 7°/min.

Apparatus and Procedure.—The vessel for the reaction between $ZrCl_4$ and H_2S consisted of a Vycor tube 10'' long and 1.5'' in diameter composed of two sections connected by a 45/50 ground glass joint. Two inlet tubes were ring sealed into the male portion of the reaction vessel and ran parallel to and almost the entire length of the inside of the reaction vessel. One of the inlet tubes was connected through a T to tanks of argon and hydrogen sulfide. The other was connected to a 250-ml. round-bottom flask by means of a 24/40 ground glass joint. Zirconium tetrachloride was placed in the flask and slowly sublimed into the reaction chamber while a steady flow of hydrogen sulfide was maintained. The reaction vessel was kept at 600–650° by means of a split ring resistance wire furnace. An exit tube was provided to carry off the excess gases. Zirconium disulfide deposited on the walls of the reaction vessel as bright violet crystals. Yields were never better than 60%, based on the quantity of zirconium tetrachloride used. The principal difficulty lay in controlling the rate of flow of tetrachloride vapor. If the rate of flow was too rapid, some tetrachloride was expelled before reaction occurred. If the flow rate was too slow, the hydrogen sulfide worked its way back into the bulb (A) and formed a sulfide coating on the lumps of zirconium tetrachloride. This retarded the further sublimation of the tetrachloride. A small amount of an orange-red substance always formed in the cooler portions of the reaction tube. It could not be identified from its X-ray pattern, being poorly crystallized, but in appearance it resembled the zirconium trisulfide described by Biltz.[8]

The reactions of zirconia, zirconium carbonitride[10] and zirconium metal with hydrogen sulfide or carbon disulfide were carried out in a zircon combustion tube which was held horizontally in a Lindberg tube furnace. The inlet to the combustion tube was connected to both the argon and hydrogen sulfide tanks by means of a T tube. Carbon disulfide was introduced into the reaction chamber by closing off the H_2S end and allowing the dry argon to bubble through a gas washing bottle filled with carbon disulfide. Temperatures were measured by placing a platinum *vs.* platinum–13% rhodium thermocouple above the charge inside the furnace. Before each run the apparatus was evacuated and filled with argon. The charge was then brought to the operating temperature (while maintaining a flow of argon) and then the sulfiding agent was admitted.

The differential thermal analysis apparatus employed is similar in design to those described in the literature.[11] The furnace is capable of maintaining a uniform heating rate of 7° per min. or 12.5° per min. The thermal reference standard was α-alumina. The high temperature X-ray furnace is similar in design to those developed by Sowman and Andrews[1] but modified slightly for use with the Norelco 90° diffractometer.

Results

Synthesis of ZrS_2.—Monoclinic zirconia[12] reacted with carbon disulfide in the temperature range 850–1100° to yield a mixture of zirconium disulfide and zirconium sulfoxide, ZrOS. The observations on four preparations at 1000° are summarized in Table I. The amounts of each constituent were estimated from the peak heights of their most intense X-ray reflections. In the temperature range 1100–1200° the results were erratic. Sometimes a mixture of products was obtained and in other experiments only zirconium disulfide was obtained. However, from 1200–1300°, complete conversion to zirconium disulfide occurred in 1–2 hours in every case. This temperature coincides with the monoclinic–tetragonal inversion of zirconia. Furthermore, zirconia stabilized in the cubic form (with CaO) yielded only zirconium disulfide throughout the temperature range 850–1300°. Thus, with the monoclinic oxide (below 1200°) it is believed that two reactions occur simultaneously, producing, respectively, ZrS_2 and ZrOS. The first reaction is several times faster than the second so that ZrS_2 is always the predominant product. The sulfoxide is converted to ZrS_2 by further reaction with carbon disulfide but the reaction is slow. For example, in a separate experiment ZrOS reacted with CS_2 at 1000°. After 16 hours about 85% conversion to ZrS_2 had occurred and after 24 hours about 90–95%. In contrast, cubic zirconia was completely converted to ZrS_2 in 4 hours at 1000°.

TABLE I

REACTION OF MONOCLINIC ZIRCONIA WITH CARBON DISULFIDE AT 1000°

Reaction time (hr.)	Composition of product (% of total) ZrO_2	ZrS_2	ZrOS
4	50	35	15
8	..	75	25
16	..	90	10
24	..	95	5

The zirconium disulfide obtained from the action of CS_2 on zirconia at 1200° was a soft, violet powder. A typical analysis gave: Zr, 59.68%; S, 41.01%. Required for ZrS_2 (including hafnium content): Zr, 58.99%; S, 41.01%. Spectrographic examination revealed these impurities: Al, 0.001%; Cu, 0.0005%; Fe, 0.001%; Si, 0.025%; Ti, 0.002%.

Observations.—Zirconium disulfide was heated in an inert atmosphere to 1400° without decomposition. Differential thermograms obtained in air at heating rates of 7 and 12.5° per minute (Fig. 1), however, show that oxidation begins below 100°.

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(10) This substance is made in the arc furnace and is essentially zirconium carbide but contains appreciable amounts of nitrogen and some oxygen.

(11) W. J. Smothers and Y. Chiang, "Differential Thermal Analysis: Theory and Practice," Chemical Publishing Co., Inc., New York, N. Y., 1958.

(12) Zirconia exists in 3 allotropic modifications. The monoclinic form is stable to about 1200°, the tetragonal from 1200° to approximately 1900° and cubic above 1900°. The monoclinic–tetragonal transition temperature is sensitive to the presence of impurities and the previous thermal history of the sample. W. M. Cohn and S. Tolksdorf, *Z. physik. Chem.*, **B8**, 331 (1930), using oxide containing 2% MgO obtained 1000°, J. P. Coughlin and E. G. King, THIS JOURNAL, **72**, 2262 (1950), using purer material found 1205°. The oxide used in this work inverted at about 1200°. The cubic modification can be stabilized below 1900° by the presence of various solutes in the zirconia, such as alkaline earth oxides or carbon.

The thermograms exhibit three exothermic peaks. The nature of the changes was determined by taking X-ray diffraction patterns at temperatures just below and above the peaks on the thermograms. The pattern for ZrS_2 persists up to the temperature of the first exothermic peak (300–330°) whereupon it is converted to cubic ZrO_2. Analysis of the samples at this point showed that they still contained 2–5% sulfur. The sulfur could not be washed out with CS_2, water or dilute acid. This sulfur stabilizes the zirconia in the cubic form. The broad exothermic region above 360° in the thermograms results from the burning of this sulfur. As soon as enough sulfur is burned out, the cubic zirconia reverts to the monoclinic form, producing the final sharp peaks.

An equimolar mixture of ZrO_2 and ZrS_2 heated in a sealed evacuated Vycor tube yielded ZrOS. Complete reaction was achieved in about 30 hours at 1000°.

Powdered zirconium metal was found to reduce the disulfide to lower sulfides. Heating an equimolar ratio of reactants at 900–1000° for 4 hours yielded a mixture of Zr_3S_4 (90%) and Zr_3S_2 (10%).[13] With increased proportions of zirconium metal the proportion of Zr_3S_2 in the product increased.

Reduction of zirconium disulfide also was accomplished at 900–1000° with magnesium metal. In this case, too, a mixture of Zr_3S_4 and Zr_3S_2 was obtained together with MgS as a by-product.

Zirconium carbonitride was treated with hydrogen sulfide at 1100°, and zirconium metal with carbon disulfide at 800–1000° in the hope of obtaining reduced zirconium sulfides. In both cases zirconium disulfide resulted.

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[13] For a more complete description of these sulfide phases and their X-ray diffraction patterns see H. Hahn, B. Harder, U. Mutschke and P. Ness, *Z. anorg. allgem. Chem.*, **292**, 82 (1957).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. XVII. Halogen Complexes of Pentamethylenetetrazole[1]

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Electron donor properties of a convulsant agent, pentamethylenetetrazole (PMT), were investigated by studying its complexes with iodine and iodine halides. A stable solid complex PMT·ICl was prepared. The stability of these complexes was investigated spectrophotometrically in carbon tetrachloride solution and the formation constant values were, respectively, 2.0×10^3 for PMT·ICl, 1.5×10^2 for PMT·IBr and 7.5 for $PMT \cdot I_2$. The infrared absorption spectra of PMT and of PMT·ICl were determined in the sodium chloride region.

Introduction

Study of the synthesis and pharmacological properties of neurological drugs has been a very active field of research for a number of years. Yet, it is surprising how little information is usually available on the chemical and physico-chemical properties of physiologically active substances, some with a long and a successful clinical history behind them. It seems quite natural to expect, however, that certain of these chemical properties must be in some way related with their action in living organisms. It is with this thought in mind that a detailed physico-chemical study of convulsant and anticonvulsant drugs has been undertaken in this Laboratory.

This study was begun with pentamethylenetetrazole (hereafter abbreviated as PMT). This compound is a well-known convulsant agent which has been quite widely used in shock therapy and as a stimulant in general. Numerous derivatives of PMT and of similar tetrazoles have been prepared and were shown to have a wide spectrum of convulsant and even of depressant activity.[3] Literature search revealed, however, that while reports on PMT's pharmacological and clinical activity are extremely numerous, its chemical properties remain virtually unknown. Several solid metal complexes of PMT with cadmium, copper, mercury and silver have been prepared by pouring together concentrated solutions of PMT and the respective salt, but were not adequately identified or described.[4]

It was of particular interest in this investigation to study the basic or the electron donor properties of PMT. The donor strength of a molecule can be very conveniently determined from the study of its halogen complexes, and actually a basicity scale based on the strength of the iodine complex has been proposed.[5] This is especially true for rather weak bases in which case the determination of their basicity constants K_b with respect to the hydrogen ion may be rather difficult. Also, since complexation with halogens can be carried out in non-aqueous

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[1] Presented before the Medicinal Chemistry Division at the 133rd Meeting of the American Chemical Society, San Francisco, California, April 16, 1958.

[2] On leave of absence from Institute of General Chemistry, University of Pavia, Pavia, Italy.

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[4] (a) J. L. Zwikker, *Pharm. Weekblad.*, **71**, 1170 (1934); (b) A. Dister, *J. Pharm. Belg.*, **3**, 193 (1946).

[5] G. Kortum, *J. chim. phys.*, **49**, C127 (1952).