

compounds among the VI A group elements.

The polarographic pattern conclusively proves that the S—S bridge in the diphenyl disulphides has a lower bond energy than the aliphatic disulphides. X-Ray investigations of the diphenyl diselenide⁶ have verified a dihedral angle of 82°. Bergson⁷ also emphasizes, that to a certain extent there will exist a delocalization of the lone-pair electrons with π -symmetry on sulphur and selenium. The disulphide and diselenide molecules must, as a first approximation, be regarded as consisting of two "insulated" π -electron systems which may separately interact with single sulphur or selenium atoms. As a result the bond energies of the S—S and Se—Se bridges will decrease to such an extent that a currentless fission of these bonds and subsequent formation of mercury compounds can take place. The rates of these reactions are high enough to be without measurable influence on the rates of the electron transfer processes, studied by the slower d.c. polarographic methods. They will therefore proceed under reversible conditions.

Experimental. The substances investigated were recrystallized samples and their analytical data was in accordance with the literature. The polarograms were recorded on a Radiometer Polariter P 04. The capillary constant was $m^{1/2} t^{1/2} = 2.120 \text{ mg}^{1/2} \text{ sec}^{-1/2}$. The electrocapillary curves were registered with an automatic equipment.⁸

The author is much indebted to Professor Arne Fredga for kindly supplying the samples used in this investigation and for valuable discussions.

1. Nygård, B. *Acta Chem. Scand.* **15** (1961) 1039.
2. Hall, E. M. *Anal. Chem.* **25** (1953) 556.
3. Colichman, E. and Love, D. *J. Am. Chem. Soc.* **75** (1953) 5737.
4. Karchmer, J. H. and Walker, M. T. *Anal. Chem.* **26** (1954) 271.
5. Kapoor, R. C., Asthana, M. and Nigam, H. L. *J. Polarog. Soc.* **10** (1964) 41.
6. Marsh, R. E. *Acta Cryst.* **5** (1952) 458.
7. Bergson, G. Some New Aspects of Organic Disulphides, Diselenides and Related Compounds, *Abstr. of Uppsala Diss. in Science* 1962.
8. Nygård, B., Johansson, E. and Olofsson, J. *J. Electroanal. Chem. In press.*

Received June 20, 1966.

New Phases in the Zr-P and Zr-As Systems

TORSTEN LUNDSTRÖM

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The existence of the three phases ZrP_2 , ZrP , and a subphosphide in the Zr-P system was reported by Strotzer *et al.*¹ on the basis of tensimetric analysis and X-ray work. Two polymorphs of ZrP were described by Schönberg² and by Irani and Gingerich.³ However, Bachmayer *et al.*⁴ mentioned only the hexagonal β - ZrP . Recently, Hulliger⁵ published X-ray data for ZrP_2 , ZrAs and ZrAs_2 , were characterized by Trzebiatowski *et al.*⁶ In the present paper, two new zirconium phosphides and one arsenide are described.

A master alloy with the approximate composition $\text{ZrP}_{1.2}$ was prepared in the following way. Turnings of zirconium (claimed purity 99.9 %, less than 0.03 % oxygen) and red phosphorus (better than 99 % purity) were enclosed under a slight over-pressure of argon in a zircalloy cylinder equipped with a tight-fitting screw lid. The cylinder was then sealed under vacuum in a silica capsule and heated for three days at 860°C. The synthetic technique described should greatly reduce the possibilities for oxygen contamination of the product. The reaction product, containing mainly β - ZrP and some ZrP_2 , was arc-melted under pure argon with the addition of various amounts of zirconium metal. The zirconium arsenide was synthesized by heating zirconium turnings and arsenic (Johnson, Matthey & Co., spectrographically standardized) in evacuated and sealed silica capsules, an inner alumina crucible being used to prevent direct contact between the metal and silica.

Powder diffraction films were taken with Guinier-Hägg type cameras using strictly monochromatized $\text{CuK}\alpha_1$ and $\text{CrK}\alpha_1$ radiation. The cell dimensions given in Table 1 are based on silicon as internal calibration standard with $a = 5.43054 \text{ \AA}$. A least-squares refinement of the lattice parameters was made with a program called CELSIUS, written by J. Tegenfeldt⁹ for a CDC 3600 computer. As may be seen from Table 1 the standard deviations indicate a high degree of precision; however, it is possible that systematic errors in some cases are of greater magnitude than those indicated by the standard deviations.

Table 1. Crystallographic data for Zr_3P , ZrP_x , ZrP_2 , and Zr_3As . Cell parameters given at 20°C.

Phase	Structure type	Space group	Cell dimensions and their standard deviations (Å)	Cell volume (Å ³)
Zr_3P	Ti_3P	$P4_2/n$	$\begin{cases} a = 10.7994 \pm 0.0003 \\ c = 5.3545 \pm 0.0003 \end{cases}$	624.5
ZrP_x $0.5 < x < 1$	new	$Pn\bar{m}$ or $Pnn2$	$\begin{cases} a = 16.715 \pm 0.001 \\ b = 27.572 \pm 0.002 \\ c = 3.6742 \pm 0.0003 \end{cases}$	1693.3
ZrP_2	$PbCl_2$	$Pnma$	$\begin{cases} a = 6.4940 \pm 0.0005 \\ b = 8.7434 \pm 0.0005 \\ c = 3.5135 \pm 0.0003 \end{cases}$	199.5
Zr_3As	Ti_3P	$P4_2/n$	$\begin{cases} a = 10.9734 \pm 0.0006 \\ c = 5.4499 \pm 0.0005 \end{cases}$	656.3

Zr_3P and Zr_3As were both found to belong to the Ti_3P [or $\epsilon_1(Fe-P-B)$] type structure,⁷ which now has more than one dozen representatives.⁸ Apparently, Zr_3As is the first arsenide reported to crystallize with this structure type.

The existence of α - ZrP and β - ZrP was corroborated, as well as that of ZrP_2 . The lattice parameters of ZrP_2 were measured in a two-phase specimen containing β - ZrP , and are in good agreement with those obtained by Hulliger.⁵ Lattice parameter variations for β - ZrP were observed, indicating an appreciable homogeneity range.

A new phase, provisionally denoted by ZrP_x , was found in a two-phase sample together with α - ZrP , and in another sample together with a further new phase, more phosphorus-rich than Zr_3P . The crystallographic examination of ZrP_x indicated an orthorhombic symmetry, the space group probably being $Pn\bar{m}$ or $Pnn2$. The composition is at present somewhat uncertain but will be settled more accurately in the course of a single-crystal investigation now being undertaken at this Institute. For identification purposes, powder diffraction data for ZrP_x are given in Table 2. The intensities given are uncorrected peak intensities, obtained with a Philips powder diffractometer,

Table 2. X-Ray data for ZrP_x . $\sin^2\theta$ with $CuK\alpha_1$ radiation. Intensities measured with diffractometer and uncorrected for Lp and absorption.

h	k	$\sin^2\theta_{obs}$ $\times 10^5$	$\sin^2\theta_{calc}$ $\times 10^5$	I_{obs}	
5	2	0	5621	5621	11
3	0	1	6309	6306	30
0	5	1	6350	6346	
2	4	1	6491	6493	17
3	3	1	7013	7008	19
0	6	1	7188	7204	12
2	5	1	7188	7195	
1	10	0	8010	8016	30
5	6	0	8115	8118	25
4	2	1	8115	8105	
3	9	0	8228	8232	33
0	7	1		8219	
6	3	0	8358	8347	45
4	8	0	8399	8392	20
4	4	1	9048	9041	30
1	8	1	9599	9602	25
4	5	1	9746	9743	33
5	2	1	10033	10016	22
2	8	1	10239	10239	40
5	3	1	10436	10406	47
6	6	0		10454	
4	10	0	10205	10202	30
5	9	0	11617	11630	32
4	7	1		11616	

using filtered copper radiation. Only the strong lines with 2θ less than 50° are listed.

Acknowledgements. The author wishes to thank Professor G. Hägg for his never failing interest and Dr. S. Rundqvist for stimulating discussions. This work has been supported by the *Swedish Natural Science Research Council* as well as by *Knut and Alice Wallenbergs Stiftelse*, the donator of the Philips diffractometer.

1. Strotzer, E. F., Biltz, W. and Meisel, K. *Z. anorg. allgem. Chem.* **239** (1938) 216.
2. Schönberg, N. *Acta Chem. Scand.* **8** (1954) 226.
3. Irani, K. S. and Gingerich, K. A. *J. Phys. Chem. Solids* **24** (1963) 1153.
4. Bachmayer, K., Nowotny, H. and Kohl, A. *Monatsh.* **86** (1955) 39.
5. Hulliger, F. *Nature* **204** (1964) 775.
6. Trzebiatowski, W., Weglowski, S. and Lukaszewicz, K. *Roczniki Chem.* **32** (1958) 189.
7. Rundqvist, S. *Acta Chem. Scand.* **16** (1962) 1.
8. Rossteutscher, W. and Schubert, K. *Z. Metallk.* **56** (1965) 813.
9. Tegenfeldt, J. *Institute of Chemistry, Uppsala. Unpublished.*

Received June 20, 1966.

N-Isothiocyanatoamines

I. On the Existence of Monomeric *N*-Isothiocyanatodialkylamines (Dialkylaminoisothiocyanates)

U. ANTHONI, CH. LARSEN and
P. H. NIELSEN

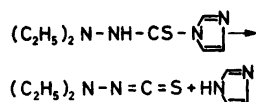
Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

In a recent communication, Podgornaya *et al.*¹ reported that *N*-piperidinedithiocarbamic acid on heating in ethanol will eliminate hydrogen sulfide to give piperidinoisothiocyanate (*N*-isothiocyanatopi-

peridine). This compound was characterized by its m.p. and by N and S analysis. Our work has provided strong evidence that the substance formed is, in fact, *N,N*-pentamethylenehydrazinium *N,N*-pentamethylenedithiocarbazate. A recent postulation² of aminoisothiocyanate being an intermediate in the reaction between dithiocarbamic esters with amines to form thiosemicarbazides prompts us to give a preliminary account of our findings.

We believe this report provides the first recognized case entailing thermal decomposition of thiocarbazoylimidazoles to species exhibiting the properties expected from a monomeric *N*-isothiocyanatoamine. The corresponding *N*-isocyanatoamines have been claimed by a similar method by Staab³ and reported to dimerize immediately.

These studies have primarily been conducted with *N,N*-diethylthiocarbazoylimidazole. This compound has been chosen because of its ready availability and the relative ease of characterisation of the products from the thermolysis reaction:



The *N*-isothiocyanatodiethylamine thus formed may be stored for some time in liquid air, and shows the expected reactions with, for example, amines to form thiosemicarbazides and hydrazines to give thiocarbonylhydrazides.

Further work on this interesting new group of compounds will be presented later in subsequent articles. Without citing specific examples, it can be stated that the application of the method outlined below (as well as thermolysis of dithiocarbazates) offers very promising preliminary results with other (monomeric and dimeric) aliphatic and aromatic *N*-isothiocyanatoamines.

Experimental. The analyses were carried out at the microanalysis department of this laboratory. The infrared spectra ($400-4000\text{ cm}^{-1}$) were recorded using a Perkin-Elmer model 337 grating infrared spectrophotometer.

N,N-Diethylthiocarbazoylimidazole. The preparation of this compound followed essentially the procedure by Staab and Walther⁴ for