

A New Vanadium Monosulfide

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The phase relations in the vanadium sulfur system have been studied by Blitz and Köcher¹ and by Klemm and Hoschek² and more recently by Pedersen and Grøn-vold.³ These, and other recent as yet unpublished results, were recently reviewed by Jellinek.⁴

In the neighborhood of the VS phase region a number of superstructures of the NiAs like VS phase were found on the high sulfur side, but no phases were found to exist between the VS phase and the V₃S phase.

In the residue of a ca. 1500°C vaporization of VS in a tungsten crucible conducted by one of us (H.F.F.) at the University of Kansas, Lawrence, Kansas, a new phase was discovered by Guinier powder diffraction. It was found that this phase was formed by arc-melting VS with a small amount of vanadium metal, and it was accordingly concluded that this new phase resulted from preferential sulfur loss of the samples.

A single crystal was selected from the residue of the vaporization run and data were collected from zero, first and second layer Weissenberg photographs around two of the orthorhombic axes. The diffraction spots were irregular in shape, probably due to a rather imperfect crystal, but attempts to obtain a better crystal were unsuccessful.

The centrosymmetric space group of a predominant substructure was found to be *Pnma* and the structure was determined to be roughly isostructural with TiSe.⁵ Very faint spots were observed on the rotation photographs which suggested doubling of the *a* and *b* axes. No indication of this superstructure was found in the Guinier diffraction patterns or in the substructure zero, first and second layer Weissenberg photographs (around *a* and *b* axes).

A least squares treatment of intensity data obtained by the multiple film technique resulted in the substructure parameters for vanadium: $x = 0.500 \pm 0.003$, $y = 0.250$, $z = 0.239 \pm 0.005$, and for

sulfur: $x = 0.234 \pm 0.003$, $y = 0.250$, $z = 0.296 \pm 0.007$, and in the temperature factor for vanadium: $1.4 \pm 0.2 \text{ \AA}^2$ and for sulfur: $1.3 \pm 0.3 \text{ \AA}^2$. The *R* value was 0.20.

The density of a sample with S/V = 0.90 by combustion analysis was found to be 4.680 g cm⁻³. This corresponds to 3.98 VS_{0.90} units per unit cell indicating that the sulfur deficiency results in sulfur vacancies in the ideal VS_{1.00} structure.

The homogeneity range of VS_{1-x} was determined by an examination of the lattice parameter variation with varying composition. The samples were synthesized from the elements in sealed silica tubes at temperatures which were increased from room temperature to 700°C during one week and were annealed for about one day at 1000°C. The vanadium used in the syntheses was analyzed by combustion analysis and was found, assuming the principal impurity to be oxygen, to be VO_{0.022}. The lattice parameters were determined by a least squares treatment of the sin²θ's from Guinier diffraction patterns.⁶ Typical lattice parameters determined were those for VS_{0.85}: $a = 5.860 \pm 0.001 \text{ \AA}$, $b = 3.304 \pm 0.007 \text{ \AA}$, $c = 5.826 \pm 0.005 \text{ \AA}$.

It was found that the *a* lattice parameter of VS_{1-x} varied between 5.862 Å and 5.827 Å as the composition varied from VS_{0.85} to VS_{1.05}. It was found that the *a* lattice parameter was $5.861 \pm 0.01 \text{ \AA}$ for S/V = 0.85, 0.81, 0.75, 0.70 and that the powder pattern produced by a sample with S/V = 1.10 was that of the "VS" phase only. All analyses were by combustion and are thought to be accurate to within ± 0.01 in S/V. These results indicate that the VS_{1-x} homogeneity range is very wide ($0.85 \leq S/V \leq 1.05$) and that the VS_{1-x}-VS two phase region is very narrow. A precise reinvestigation of this region is now being undertaken by one of us (H.F.F.) using extremely pure vanadium and higher annealing temperatures.

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Acetylene Compounds of Potential Pharmacological Value III*. 4-Dialkylamino-2-butynyl Esters of Benzoic Acid

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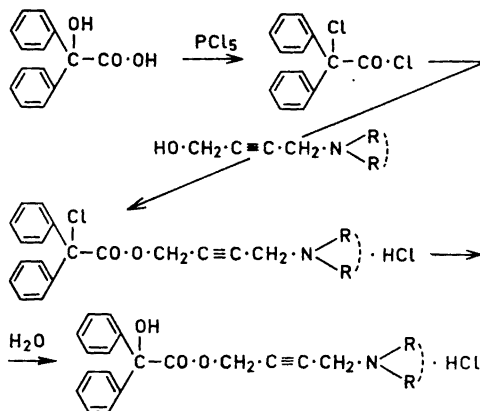
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In the first paper of this series¹ a number of 4-dialkylamino-2-butynyl esters of diphenylacetic acid, of 1-phenylcyclopentane-1-carboxylic acid, and of phenothiazine-10-carboxylic acid were synthesised for pharmacological tests on anticholinergic activity and ability to inhibit tremors induced by Tremorine (1,4-dipyrrolidino-2-butyne). As amino esters of benzoic acid often have pronounced anticholinergic activity, we decided to include some 4-dialkylamino-2-butynyl esters of this acid in our investigations.

These esters were prepared in good yield according to a method proposed by King and Holmes² for the synthesis of amino esters of benzoic acid, as outlined in the following scheme.

These compounds could also be obtained by trans-esterification of methyl benzoate with the appropriate 4-dialkylamino-2-butyne-1-ol, but this procedure gave much lower yields.

Pharmacology. The hydrochlorides of the 4-alkylamino-2-butynyl benzoates (II, V, VIII, IX) were tested with respect to anticholinergic activity and ability to inhibit tremors induced by 1-(2-oxopyrrolidino)-4-



pyrrolidino-2-butyne (oxotremorine). The diethylamino ester II exhibited a strong anticholinergic effect, having about 70 % of the activity of atropine sulphate. The pyrrolidino ester V was also effective in this respect, having 35 % of the activity of atropine sulphate. The piperidino and morpholino esters had only weak activity. The compounds II and V were quite active in the oxotremorine test; a detailed report on this investigation will be published elsewhere. The methobromide III was tested for ganglion-blocking activity. It was about 1–2 times as active as hexamethonium bromide in inhibiting nicotine-induced contractions of the rabbit's ileum.

As the diethylamino ester II bears a certain structural resemblance to the psychopharmacological agent benactyzine (β -diethylaminoethyl benzoate), this compound was compared with chlorpromazine with respect to its ability to block conditioned reflex in rats. However, it had little or no effect in this test.

The tests for tremorolytic activity has been carried out by Prof. D. J. Jenden and Dr. R. George, University of California, Los Angeles. All other pharmacological investigations have been performed in the research laboratories of AB Astra, Södertälje, under the direction of Dr. A. Åström.

Experimental. 4-Dialkylamino-2-butynyl esters of α -chlorodiphenylacetic acid. Equimolecular amounts (0.04 mole) of α -chlorodiphenylacetyl chloride³ and the appropriate 4-dialkylamino-2-butyne-1-ol were mixed, whereupon an exothermic reaction started immediately; the temperature was kept below 50° by external cooling. After a few minutes, the reaction

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