

Table 1. CRYSTALLOGRAPHIC DATA ON NIOBIUM, TANTALUM AND TUNGSTEN PHOSPHIDES

Phosphide	Structure type	a (Å)	b (Å)	c (Å)	β°
Nb ₃ P	Ti ₃ P	10.128		5.091	
NbP	NbAs	3.354		11.377	
NbP ₂	NbAs ₂	8.8715	3.2663	7.5194	119.097°
Ta ₃ P	Ti ₃ P	10.154		5.012	
Ta ₃ P ₄	(orthorhombic)	14.420	11.547	3.400	
TaP	NbAs	3.319		11.341	
TaP ₂	NbAs ₂	8.8608	3.2677	7.4382	119.308°
W ₃ P	α -V ₃ S (?)	9.858		4.300	
WP	MnP	5.732	3.249	6.222	
α -WP ₂	NbAs ₂	8.5022	3.1695	7.4660	119.367°
β -WP ₂	MoP ₂	3.106	11.161	4.973	

The unit cell dimensions were determined in Guinier-Hägg type focusing cameras using copper $K\alpha$ radiation with silicon ($a = 5.4305$ Å) as the internal calibration standard.

For NbP₂, TaP₂ and α -WP₂ a least-squares refinement of the powder diffraction data indicated standard deviations for a and c of 0.0007 Å, for b 0.0002 Å and for β 0.005°. The relative accuracy of the unit cell dimensions for the remaining phases is estimated to be higher than 0.03 per cent.

Obviously be retained from the high-temperature range owing to the rapid cooling process in the arc furnace, it disappears completely from W₃P-containing samples on annealing at temperatures between 800° and 1,000° C, and the only remaining phases are tungsten and tungsten monophosphide. Hsu *et al.* reported that their W₃P phase was unstable above 900° C. This suggests that the energetic conditions prevailing during electrolysis permit the formation of metastable W₃P, which can then be recovered only at moderately high temperatures without extensive decomposition.

The Nb₃P and Ta₃P phases remain unchanged after prolonged heat-treatment at 1,000° C, and it therefore appears likely that their formation at low temperatures is prevented by reaction kinetic factors only.

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Photochemistry of the *S*-Nitroso Derivatives of Hexane-1-thiol and Hexane-1,6-dithiol

S-NITROSOHEXANE-1-THIOL, CH₃(CH₂)₅SNO, and di-(*S*-nitroso)hexane-1,6-dithiol, ONS(CH₂)₆SNO, were prepared by the method reported by Saville¹. Their electronic spectra in hexane solution were measured and were found to be similar to the spectrum of *S*-nitrosotoluene- α -thiol². The relevant data are presented in Table I.

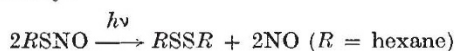
Table I. ELECTRONIC SPECTRA OF THE *S*-NITROSO DERIVATIVES OF THIOLS

Thiol	λ_{\max} (Å)	ϵ_{\max} (M ⁻¹ cm ⁻¹)	λ_{\max} (Å)	ϵ_{\max} (M ⁻¹ cm ⁻¹)
Toluene- α -thiol	5600	26	3400	1030
Hexane-1-thiol	5500	21	3400	940
Hexane-1,6-dithiol	5500	42	3400	1830

Assignment to transitions: $n \rightarrow \pi^*$ $n_o \rightarrow \pi^*$

As can be seen from the data in Table I, the ϵ values for the di- and mono-*S*-nitrosated hexane thiols bear a ratio to each other of very nearly two as would be expected from their structures.

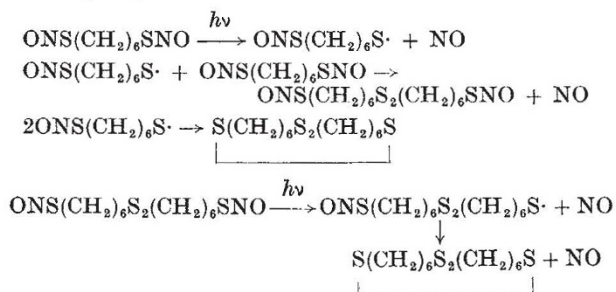
Irradiation at 3650 Å of the mono compound in methanol solution causes photolysis according to the stoichiometry:



The reaction mechanism is similar to that reported for the photolysis of *S*-nitrosotoluene- α -thiol².

Irradiation of the di-nitrosated compound at 3650 Å caused photolysis, and the products were a wax-like solid and nitric oxide. The solid product had a melting point of 35° C and a molecular weight (Rast's method) of 285. Elemental analysis was consistent with the empirical formula (CH₂)₆S₂. From these data it would appear that the solid product was largely 1,2,9,10, tetrathiacyclohexadecane.

The mechanism of the photolysis probably includes the following steps:



Work is proceeding on this and similar systems in order to elucidate a general mechanism for the photolysis of compounds containing two SNO groups.

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Effects of Solvents on Acetylcholine Conformation

In earlier communications¹⁻³ we reported the results of our investigations with acetylcholine and related substances. These led us to conclude that the acetyl group is activated primarily by an inductive influence of the quaternary nitrogen. This conclusion was based in large measure on the carbonyl stretching frequencies which were observed for acetylcholine and its homologues in ethanol, as well as on their rates of hydroxylaminolysis in water.

In a recent communication, Canepa and Mooney⁴ challenged these data and conclusions. They reported the carbonyl stretching frequencies for acetylcholine in water and ethanol and called attention to the well-known influence of the solvent on the carbonyl stretching frequency. They suggested that the solvent hydrogen-bonding to the carbonyl group could explain the observed difference in the energies of absorption between acetylcholine and ethylacetate and, more particularly, they dismissed the possibility of an inductive onium effect. In a subsequent paper Canepa⁵ proposed that the conformation of acetylcholine in the crystal and in water involved an interaction between the quaternary nitrogen and the unshared electrons on the ester oxygen. Although no data are offered which support his conclusions for the behaviour of acetylcholine in aqueous solution, he insisted that the bond angles encountered in the crystal allow an interaction between the positive-charged onium nitrogen and the ester oxygen.

We have undertaken to examine some of the points raised by these publications and wish to report the results of our investigations of acetylcholine and related homo-