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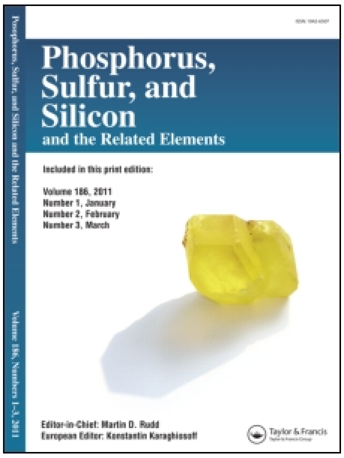

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# REDOX DISSOCIATION OF MELTED TETRAPHOSPHORUS DECASULFIDE†

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$P_4S_{10}$ suffers a fast oxido-reductive dissociation when melted, losing one of its four terminal S atoms to yield $P_4S_9$, which is characterized by nmr, ir and Raman spectroscopy. This dissociated state is largely retained in the cooled melts, which appear to be made up of unaltered $P_4S_{10}$ crystals embedded in an amorphous matrix containing the dissociation products; such melts give rise easily to supersaturated solutions in $CS_2$, from which crystals of pure $P_4S_9$—form I separate on standing.

The same holds true for commercial "$P_2S_5$," for which a definite positive correlation was found between the P and $P_4S_9$ contents.

Examples of redox dissociation of other P/S compounds are quoted for the sake of comparison.

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## INTRODUCTION

It has long been known, since the pioneer work by Stock,[1] that the vapor of $P_4S_{10}$ dissociates at much lower temperatures than that of $P_4S_3$ and $P_4S_7$; at 600°C, not much above its normal boiling point, the mean molecular weight of $P_4S_{10}$ is roughly halved and this lead Stock to the conclusion that $P_4S_{10}$ vapor was wholly dissociated into $P_2S_5$. This statement remained prevalent until Raman studies recently showed that the vapor phase dissociation of this sulfide went actually with the loss of sulfur;[2,3] Eq. (1)[3] and (2)[4] have been claimed to describe this phenomenon:

$$P_4S_{10} \xrightarrow[\text{184–520 mm Hg}]{\text{426–680°C}} P_4S_7 + 3/n\,(S_n) \qquad (1)$$

$$P_4S_{10} \xrightleftharpoons[\text{250–1400 mm Hg}]{\text{527–927°C}} P_4S_5 + 5/2\,(S_n) \qquad (2)$$

## RESULTS

We now report that $P_4S_{10}$ is already dissociated in the liquid state and that this dissociation is largely retained in the cooled solid.

Simple evidence is as follows: if pure $P_4S_{10}$ is twice melted and cooled in a differential scanning calorimeter, the second melting happens at 8° lower than the first one. Likewise, a fusion enthalpy of 11.37 Kcal/mole was found for $P_4S_{10}$ at the first

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† Presented in part at the International Conference on Phosphorus Chemistry, Halle (GDR), September 17–21, 1979.

TABLE I

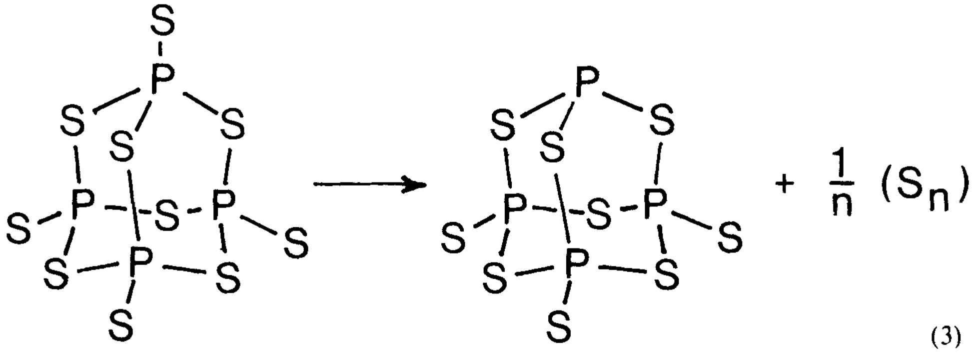
Vapor pressure (mm Hg) *vs* temperature (K)

| P sulfide | log $p$ | $p$ at 561 K[a] |
|---|---|---|
| solid $P_4S_{10}$ | $-7547/T + 12.09$ | 0.043[b] |
| same, after melting at 320°C and cooling | $-8714/T + 15.55$ | 1.04[b] |
| liquid $P_4S_{10}$ [5] | $-4660/T + 8.8$ | 3.11[c] |
| solid $P_4S_9$ | $-7630/T + 12.76$ | 0.144[b] |

[a] mp of pure $P_4S_{10}$.
[b] Extrapolated from the solid side.
[c] Extrapolated from the liquid side.

melting but only 8.23 at the remelting. Vapor pressure data point to the same conclusion (Table I): when reaching the mp, solid $P_4S_{10}$ displays a sudden increase in $p$, which is largely kept after cooling.

We further established that the dissociation of liquid $P_4S_{10}$ involves the loss of one of its four terminal S atoms and the formation of $P_4S_9$ (Eq. 3)



(3)

$P_4S_9$ can be characterized by several spectral methods.

Thus, $^{31}P$ nmr spectra of $P_4S_{10}$ melts, dissolved in $CS_2$, were found to be the mere superimposition of those of $P_4S_{10}$ (an $A_4$ system with $\delta$, 56.3) and $P_4S_9$ (an $AB_3$ system with $\delta$ (A), 57.3; $\delta$ (B), 62.9, $^2J_{AB}$ 96 Hz).[6]

Likewise, ir spectra in solution display only the specific absorption bands of both sulfides, *viz.*, in $cm^{-1}$, 533 (s) and 692 (s) for $P_4S_{10}$ and 492 (m), 547 (s), 695 (s) and 715 (w) for $P_4S_9$; absorption at 547 $cm^{-1}$ was found to obey the BEER law within limits, thus providing a convenient means to determine $P_4S_9$ in such mixtures.

The ir bands of $P_4S_9$ at 492 and 547 $cm^{-1}$ are still visible, although broadened, in the solid spectra (KBr mulls) of neat melts of $P_4S_{10}$; this confirms that $P_4S_9$ does actually exist as such in the latter and not only in their $CS_2$ solutions. This is further substantiated by solid Raman spectroscopy,[7,8] with the strongest specific frequencies of $P_4S_9$ showing at 309 and 389 $cm^{-1}$.‡

All these methods point to $P_4S_9$ being the only new P sulfide produced, at least at not too high temperatures. Surprisingly, only crystalline $P_4S_{10}$ is visible however, by

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‡ Similar frequencies (304 and 381 $cm^{-1}$) have been observed also by Gardner[2] in the Raman spectrum of liquid $P_4S_{10}$.

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TABLE II

Heating experiments on pure $P_4S_{10}$

| Heating temperature, °C | Heating time mn | Cooling | $P_4S_9$ in cooled sulfide,[a] % |
|---|---|---|---|
| 300 | <1 | in liquid $N_2$ | 16 |
| 314 | 120 | ibid | 33 |
| 394 | 10 | ibid | 30 |
| 320 | *ca* 5 | air cooled | 29 |
| 250 | 240 | ibid | nil |
| 250[b] | 240 | ibid | 36 |

[a] ir method.

[b] Dissolved in 10 parts trichlorobenzene (mixed isomers).

X rays or tda, in solidified melts of $P_4S_{10}$; but, if these are briefly shaken with $CS_2$, the solution at once filtrated, then allowed to stand overnight at the same temperature, crystals of pure $P_4S_9$-form I[9] are obtained (*ca* 4% of the initial $P_4S_{10}$). A conclusion follows: cooled melts of $P_4S_{10}$ contain unchanged $P_4S_{10}$ that is mainly crystallized and $P_4S_9$, that is amorphous and consequently gives rise easily to supersaturated solutions.

As shown in Table II, the amount of $P_4S_9$ is already substantial after a matter of seconds just above the mp (288°C); it changes little with the cooling rate or on storage at r.t.; however, annealing causes it to decrease (Figure 1). Likewise, $CS_2$ solu-

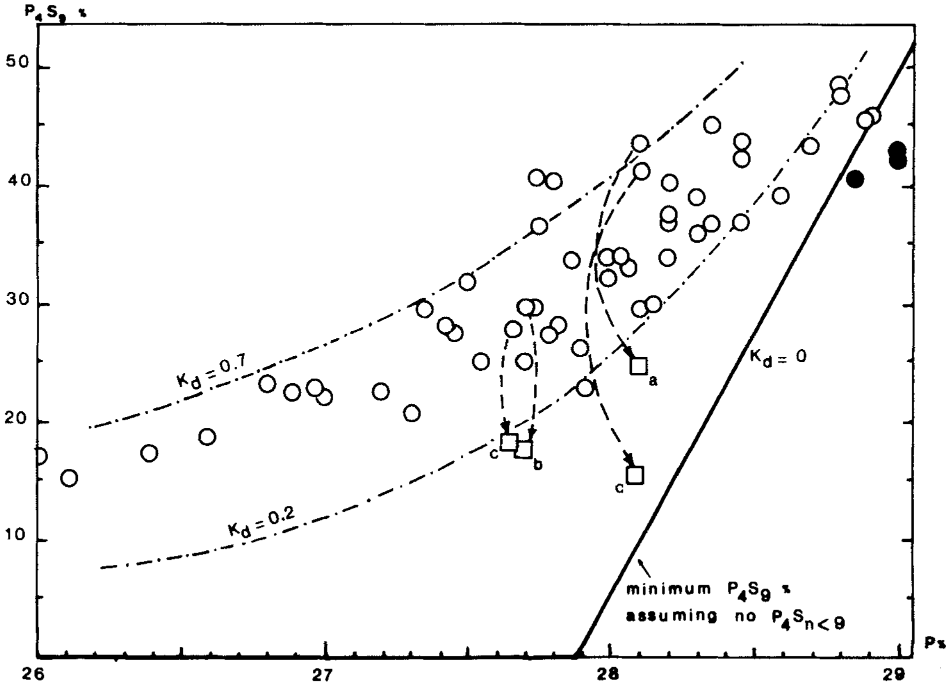

FIGURE 1 $P_4S_9$ *vs* P contents for commercial phosphorus pentasulfide of various origins. Open circles: normal specimens; black circles: anomalous ones (contain crystallized $P_4S_9$ as evidenced by tda and X rays); open squares: annealed, 1 h at 220°C (a), 1 h at 250°C (b) or 16 h at 250°C (c). $K_d$ (see text) is in moles.kg$^{-1}$.

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tions remain stable for days, but evaporation, even *in vacuo*, causes the $P_4S_9$ content to regress.

All that has been said about fused $P_4S_{10}$ holds true, without exception, for commercial phosphorus "pentasulfides," inasmuch as the latter, either distilled or not, are always *in fine* chilled from the liquid state. Schematically, commercial "$P_2S_5$" can be viewed as a conglomerate of crystallized $P_4S_{10}$ with an amorphous phase containing much $P_4S_9$ and "free" sulfur. A plot of the $P_4S_9$ % *vs* the P % is shown in Figure 1 for samples of commercial $P_2S_5$ of various origins; as expected, there is an obvious tendency for both parameters to run parallel. $P_4S_7$ was found absent up to P contents of at least 29% as indicated by the nmr.[10]

As $n$ in Eq. 3 is unknown, a conventional dissociation constant

$$K_d = [P_4S_9][S]/[P_4S_{10}]$$

was derived; results in Table II and Figure 1 are consistent with $K_d = 0.2$ to 0.7 moles.Kg$^{-1}$, at temperatures around 300–320°C.

## DISCUSSION

Propensity for the transfer of S atoms appears to be customary with P sulfides; redox disproportionations have been already reported for $P_4S_2$, $P_4S_4$, $P_4S_5$ and $P_4S_9$.[2,11]† The case of $P_4S_{10}$ is unique in that cleavage of P=S bonds can be balanced only by formation of S—S bonds (probably $S_n$ molecules). Similar reactions take place also with other $Z_3PS$ compounds, with Z = SR, Cl, Br,[13-17] as well as for $As_2S_3$:[12]

$$(RS)_3PS + P_4S_{10} \xrightarrow{>175^\circ C} \text{reorganized (poly)thiophosphates} + (RS)_3P + R_2S + R_2S_2;\ddagger \text{ Ref.}^{13} \quad (4)$$

$$(C_2H_5S)_3\,PS \xrightarrow{120\text{-}130^\circ C} (C_2H_5S)_3P + 1/n\,(S_n);\ \text{Ref.}^{14} \quad (5)$$

$$Cl_3PS + CH_3\text{—}CH_2\text{—}CH_3 \xrightarrow{280^\circ C} PrP(S)Cl_2 + HCl\ (+\ PCl_3);\ \text{Ref.}^{15} \quad (6)$$

$$Cl_3PS + 3/2\,(RS)_2Pb \longrightarrow (RS)_3PS + 3/2\,PbCl_2(+\ PCl_3 + R_2S_2);\ \text{Ref.}^{16} \quad (7)$$

$$Br_3PS \xrightarrow{212^\circ C} Br_3P + 1/n\,(S_n);\ \text{Ref.}^{17} \quad (8)$$

A moderate driving force for reactions 3 to 8 could be a $\pi$ or $\sigma$ delocalization of the new-born lone pair on P into the empty $d$ orbitals of the substituent heteroatoms.[6]

The mechanism of reaction (3) and the fate of the lost sulfur will be discussed separately.

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† According to our own results, $P_4S_7$ appears to melt undissociated (no change of mp), in line with its relatively high mp and bp (resp. 308 and 529°C compared to 288 and 513–5°C for $P_4S_{10}$).

‡ The formation of $R_2S$ and $R_2S_2$ was not proved by Maier *et al.* We have repeated some of their experiments and were able to fully characterize by glc/ms the disulfide $Ph_2S_2$ in the thermal dissociation products of $(PhS)_3PS$ and both $Ph_2S$ and $Ph_2S_2$ in those of $(PhS\text{-}PS_2)_2$.

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## EXPERIMENTAL (coworkers: P. Bourcier, B. Blanchon, C. Guillaud, P. Chanfrey)

$P_4S_{10}$ and $P_4S_9$ were recrystallized from pure dry $CS_2$ until pure and checked by ir, tda, nmr, X rays and elemental analysis.

Heating experiments on $P_4S_{10}$ (Table II) were performed in vacuum sealed quartz tubes.

tda and dsc diagrams were recorded at a heating rate of 20°/mn in a DU PONT 900 thermal analyzer.

Fusion enthalpies were measured with a Triflux microcalorimeter of the Thermoanalyse Company; found (Kcal/mole), for $P_4S_{10}$ (1st melting): 11.3, 11.4, 11.42 (mean value 11.37); (2nd melting): 8.1, 8.3, 8.3 (mean value 8.23); for $P_4S_9$ (1st melting): 8.0; (2nd melting): 6.9.

Vapor pressures were determined on degassed specimens by a tga method[18] using a Ugine Eyraud B 60 thermobalance.

nmr spectra were obtained at 40.5 MHz with a Varian XL 100-15 or at 80.76 Hz with a Jeol JNM-FX 200; + shifts are downfield from 85% $H_3PO_4$. ir spectra were recorded with a Perkin Elmer 577 grating spectrometer. The $P_4S_9$ contents were found, with a relative error of *ca* 5%, by means of the equation:

$$P_4S_9\ \% = 456\ A$$

with A = absorbance at 547 $cm^{-1}$ for a 2.5 g/l solution in $CS_2$, using 0.5 mm KBr cells (all spectra compensated for the solvent).

Raman spectra were recorded on a Dilor RTI triple monochromator system with a Spectra Physics 164 $Ar^+$ laser (50 mV at 5165 Å).

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