Infrared Spectra of P_4S_{10}, P_4S_9, and P_4S_7 in Solid Argon

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Introduction

The recent observation by Andrews and co-workers of P_4S_9 absorptions in the infrared spectra of P_4S_{10} sublimates trapped in a matrix of solid argon led these authors to conclude that some decomposition must accompany evaporation of solid P_4S_{10} at temperatures as low as 175 °C.[1] This statement is in conflict with the observation of Démarcq and Lamalle that pure solid P_4S_{10} sublimes undissociated under reduced pressure below about 260 °C.[2] In order to resolve this disagreement, new matrix experiments were done with freshly purified samples of P_4S_{10}, P_4S_9, and P_4S_7 and IR spectra were recorded.

Experimental Section

The matrix isolation technique was the same as reported previously.[1] The original Fluka sample of P_4S_{10} was subjected to the purification procedure described by Démarcq.[3] Another sample of P_4S_{10}, purified in the same way, was supplied by Démarcq, as well as specimens of pure P_4S_9[3] and P_4S_7. The samples were loaded into a stainless steel Knudsen cell, which was evacuated and heated to 70–80 °C under vacuum overnight before use.

Results

Figures 1a and 2a illustrate the matrix infrared spectra of the vapor effusing from solid P_4S_{10} at 170 °C and trapped in solid argon. The spectra were virtually identical for the purified Fluka sample, the sample provided by Démarcq, the sample collected in a second subsequent matrix experiment, and a sample evaporated from a quartz Knudsen cell. Spectra similarly obtained with P_4S_9 and P_4S_7 are shown in Figures 1b/2b and 1c/2c, respectively.

The above spectra are dominated by the characteristic absorption peaks of P_4S_{10} at 707.8 and 540.8 cm^{-1}, of P_4S_9 at 711.3, 553.0, and 499.0 cm^{-1}, or of P_4S_7 at 725.7 and 717.2 cm^{-1}. Assignment proposals are listed in Table I and correlated with literature data in terms of frequency shifts Δ(matrix–crystal) and Δ(matrix–solution). In line with a recent low-temperature Raman study on P_4S_{10},[10] all these shifts, but one, are positive. They are largest for $P{=}S$ stretching vibrations, especially as regards the shifts Δ(matrix–crystal) for P_4S_7, while the shift Δ(matrix–solution) of this sulfide appears normal. This anomaly might originate in the existence in solid P_4S_7 of specific $P{=}S\cdots P^{III}$ intermolecular association.[11,12]

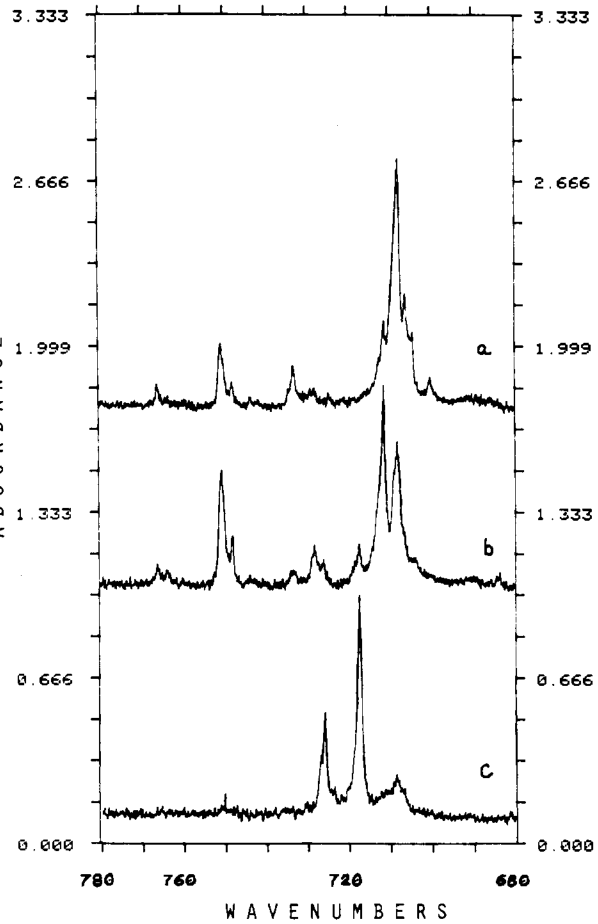

Figure 1. Infrared spectra in the 780–680-cm^{-1} region for phosphorus sulfides in solid argon at 12 ± 1 K: (a) P_4S_{10} vapor at 170 ± 3 °C codeposited with argon for 3 h; (b) P_4S_9 vapor at 178 ± 3 °C codeposited with argon for 5 h; (c) P_4S_7 vapor at 205 ± 3 °C codeposited with argon for 4 h.

The assignment of the 750.5-cm^{-1} band to P_2S_5, assumed to have a S_2PSPS_2 structure,[1] finds support in the infrared spectrum of the dithioxophosphorane 2,4,6-$Bu^t_3C_6H_2PS_2$,[13] which displays a strong band at 788 cm^{-1}, assignable to antisymmetric $\nu[P({=}S)_2]$. Other high-frequency absorptions at 765.8 and 748.3 cm^{-1} are similarly believed to belong to $P({=}S)_2$ molecular species.[1]

Discussion

P_4S_{10}. The appearance in Figures 1a and 2a of P_4S_9 bands at 711.3, 553.0, and 499.0 cm^{-1} confirms that P_4S_{10} tends to desulfurize on sublimation under vacuum, at temperatures as low as 170 °C; the yield of P_4S_9, lower than in previous work,[1,14] was estimated at about 10%, under the assumption of comparable extinction coefficients for the 707.8- and 711.3-cm^{-1} bands.

In order to explain the initial first-order kinetics observed for the redox dissociation of P_4S_{10} in solution, Démarcq has suggested a mechanism involving a rate-controlling fragmentation to P_2S_5 (eq 1) followed by a fast sulfur abstraction from P_4S_{10} by P_2S_5 (eq 2).[3] In the vapor phase, step 1a is expected to take place as well, but due to the low vapor pressure of solid P_4S_{10} (1.1 × 10^{-5}

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(13) Personal communication from Dr. J. Navech to M.C.D., who expresses his thanks.

(14) The larger yields of P_4S_9 found previously[1] are explained by impurity of the commercial sample of P_4S_{10}.[7,15]

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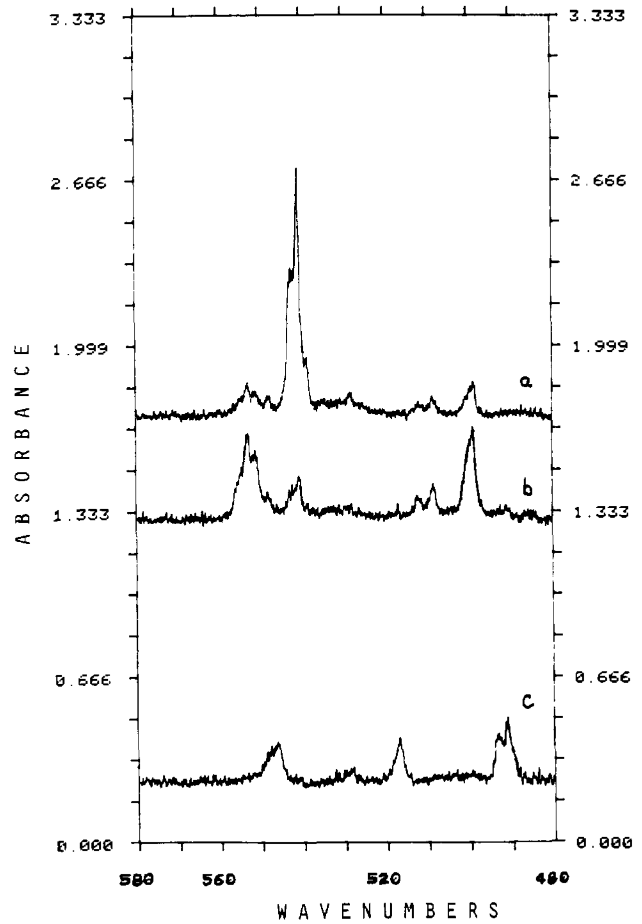

Figure 2. Infrared spectra in the 580–480-cm^{-1} region for phosphorus sulfide samples described in Figure 1.

Table I. Infrared Absorptions of Matrices Prepared by Condensation of P_4S_{10}, P_4S_9, or P_4S_7 Vapors with Argon at 12 ± 1 K

freq, cm^{-1}	rel intensity			assgnt		shift (Δ),[a] cm^{-1}	
	P_4S_{10}	P_4S_9	P_4S_7			matrix–crystal	matrix–solution
765.8	w	w		$HSPS_2$[b]	$\nu[P(=S)_2]$		
750.5	m	s		P_2S_5			
748.3	w	m		P_2S_5[c]			
733.1	w	vw		P_4S_{10} (a_1)	$\nu(P=S)$	18	
728.0	vw	m		P_4S_9 (a_1)		19	13
725.7		vw	s	P_4S_7 (b_1?)		43	16
717.2		m	vs	P_4S_7 (a_1?)		42	19
711.3	m	vs		P_4S_9 (e)		21	16
708			m	P_4S_7[d]		43	
707.8	vs	s		P_4S_{10} (t_2)		18	16
704.3	w	wm		P_4S_8?			
553.0	w	s		P_4S_9 (e)	$\nu(P—S)$	7	6
546.5			m	P_4S_7		6	3
540.8	vs	m		P_4S_{10} (t_2)		11	8
516.9		vw	m	P_4S_7		–4	3
508.4	vw	w		P_2S_5			
499.0	m	s		P_4S_9 (a_1)		9	7
490.8			ms	P_4S_7		16	6

[a] Data from refs 4–8. [b] Appears in PH_3/S_8 discharges, probably due to the P_2S_5 hydrolysis product, $HSPS_2$.[1] [c] This shoulder may be the 748.9-cm^{-1} band previously assigned to P_2S_4;[1,9] however, the absorbance ratio of 748.3 to 750.5 cm^{-1} is about the same in Figure 1a,b and is seemingly insensitive to superheating,[1] which suggests that the former is a matrix site splitting of the latter. [d] The absence of absorption at 540.8 cm^{-1} in Figure 2c demonstrates that the 708-cm^{-1} band in Figure 1c is not due to P_4S_{10} impurity and is distinct from the 707.8-cm^{-1} band of the latter.

Torr at 170 °C[7,16]), the recombination reaction (eq 1b) and the

$$P_4S_{10} \overset{a}{\underset{b}{\rightleftharpoons}} 2P_2S_5 \qquad (1)$$

$$P_4S_{10} + P_2S_n \rightarrow P_4S_9 + P_2S_{n+1} \quad (n = 5, 6, ...) \qquad (2)$$

abstraction step (eq 2) should be much slower than in solution, so that the $(P_2S_5)/(P_4S_{10})$ concentration ratio should rise to relatively high levels (as denoted by the absorption at 750.5 cm^{-1} in Figure 1a), while the time required for this ratio to reach its maximum (steady state) should be increased. Also, the overall reaction rate in the vapor is not necessarily controlled solely by the step 1a, as in solution.[3]

The discrepancy between the present experimental results and those of Démarcq and Lamalle[2] may be rationalized in terms of effective heating time of the vapor. In the first case, P_4S_{10} molecules are allowed to react during their stay inside the Knudsen cell (kept at a constant temperature), before effusing through the orifice (1 mm); in the latter case, they travel directly to the cold finger along a temperature gradient[17] and react only negligibly. The yield of P_4S_9 is expected to be particularly sensitive to the heating time (t) at the very onset of the reaction (before the steady state is reached), since then this yield is approximately proportional to t^2.

Consistent with eqs 1 and 2, it is noteworthy that none of the S_x species ($x \leq 8$) recently identified by their infrared spectra in argon matrices[18] are detectable in Figures 1a and 2a, as well as in previous matrix spectra.[1] Since we lack information on the vibrational behavior of polysulfides P_2S_n ($n > 5$), their localization in Figures 1a and 2a can only be speculative; small peaks at 700.2 and 706.1 cm^{-1}, absent in Figure 1b, are possible candidates.

P_4S_9. The appearance in Figures 1b and 2b of bands at 707.8, 540.8, and 717.2 cm^{-1} is a sign that solid P_4S_9 disproportionates to P_4S_{10} + P_4S_7 on evaporation at 178 °C, as also previously observed for the molten sulfide (about 20% decomposition in 5 s at 260–270 °C).[19]

The height of the P_2S_5 peak at 750.5 cm^{-1} in Figure 1b proves that this species does not solely arise from the dissociation of the byproduct P_4S_{10} but also arises from that of P_4S_9 itself (eq 3). This fragmentation, followed by steps 4 and 1b, could be the way

$$P_4S_9 \rightleftharpoons P_2S_5 + P_2S_4 \qquad (3)$$

$$2P_2S_4 \rightleftharpoons (P_4S_8) \rightarrow {}^1/_2P_4S_7 + {}^1/_2P_4S_9 \qquad (4)$$

the disproportionation to P_4S_{10} + P_4S_7 takes place. A driving force for the above mechanism would certainly be the irreversibility of the second part of step 4, a consequence of the instability of P_4S_8;[19] this would explain the smallness (or absence; see Table I) of the P_2S_4 band at or near 748.3 cm^{-1} in Figure 1b.

P_4S_7. It is clear from Figures 1c and 2c that solid P_4S_7 sublimes undissociated at 205 °C. This observation is in agreement with known behavior of this compound, which was found by ^{31}P NMR spectroscopy to withstand melting (5 min at 330 °C) without decomposition.[8]

P_2S_5. One argument in favor of the identification of the 750.5- and 508.4-cm^{-1} absorber as P_2S_5 is the abundance of the $P_2S_5^+$ ion in the mass spectra of P_4S_{10}.[1] This is contradicted by the work of Muenow and Margrave, who inferred from the high appearance potential of this ion (14.2 eV, compared with 9.6 eV for $P_4S_{10}^+$) that the $P_2S_5^+$ signal is not a molecular peak.[20] The disagreement may be only apparent however, as the data of Muenow et al. may simply mean that the ionization of molecular P_2S_5 requires a high potential. Indeed, while in monothioxophospho-

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(17) In one sublimation experiment performed at about 260 °C under 0.8 Torr,[2] the effective residence time of the vapor in the hot zone was estimated at less than 0.1 s.

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ranes $Z_3P{=}S$, lone p-electron pairs on S back-coordinate chiefly into vacant d orbitals on sp^3 P, in dithioxophosphoranes $ZP({=}S)_2$ they must also overlap with p_π orbitals on sp^2 P.[21] Since p_π–p_π bonds are stronger than p_π–d_π bonds, the energy of p lone pairs on terminal S in $(S{=})_2PSP({=}S)_2$ should be lowered and—bearing in mind that lone pairs on S are major components of the HOMO in P=S compounds (see for instance ref 23)—the first ionization potential should be increased.

Conclusions

The present infrared matrix experiments confirm that P_4S_{10} undergoes redox dissociation in the vapor phase, with production of P_4S_9, at temperatures as low as 170 °C. Previous contradictory results are ascribed to shorter effective heating time of the vapor.

The vapor of P_4S_9 was similarly shown to disproportionate to $P_4S_7 + P_4S_{10}$ at 178 °C, and P_4S_7 was shown to sublime undissociated at 205 °C.

Evidence was obtained for the fragmentations of P_4S_{10} to P_2S_5 and of P_4S_9 to $P_2S_5 + P_2S_4$ in the gas phase. The latter species could act as intermediates in the redox dissociation process of P_4S_{10} and P_4S_9.

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(21) The dithioxophosphorane 2,4,6-$Bu^t_3C_6H_2PS_2$, regarded as a model for P_2S_5, involves a planar CPS_2 moiety (S=P=S = 126°).[22] A planar structure, involving bent P—S—P and intramolecular P=S···S=P interactions, was similarly suggested for P_2S_5.[3]

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