Kinetic and Mechanistic Aspects of the Redox Dissociation of Tetraphosphorus Decasulphide in Solution *

Michel C. Démarcq
Institut National des Sciences Appliquées, Laboratoire de Chimie Organique, 20 Avenue Albert Einstein, F-69621 Villeurbanne Cedex, France

The kinetics of the redox dissociation of P_4S_{10} dissolved in 1-chloronaphthalene has been studied at 110—150 °C. Phosphorus-containing reaction products are P_4S_9 and smaller amounts of phosphorus polysulphides. The reaction is conveniently monitored by means of a simple hydrolysis test. The initial kinetics are quasi-first order, the rate being almost unaffected by dilution. The reaction is insensitive to the presence of oxygen or to the addition of sulphur, but catalysis by iodine and bromine compounds has been observed. A mechanism is proposed which involves, as a first step, the rate-determining fission of P_4S_{10} into two molecules of metastable P_2S_5.

Tetraphosphorus decasulphide P_4S_{10} dissociates almost instantly upon melting (561 K) with loss of sulphur and production of P_4S_9 (*ca.* 35–40%, P basis), P_4S_7 ($\leqslant$ 3%), and up to *ca.* 20–22% of polysulphides P_mS_y ($y/m > 2.5$).[1–3] The whole process may be written according to equation (1), where m, x, and y are variable and r is usually very small. Nothing is known of the kinetic order and mechanism of this reaction. An associative process (kinetic order $\geqslant$2) is suggested by the work of Förthmann and Schneider[4] who demonstrated, on the basis of observed deviations from the Trouton and Eötvös rules, that molten P_4S_{10} was an associated liquid, with, in the range 575—750 K, a mean molecular weight (m.m.w.) of about 3.9 times that of the vapour. The old statement that the vapour of P_4S_{10} is fully dissociated to P_2S_5 (m.w. 222)[5] is no longer accepted,[1,6] but nevertheless recent determinations have confirmed the above order of magnitude of the m.m.w. of this vapour (255[7] for the saturated vapour at 699 K). Accordingly, the m.m.w. of liquid P_4S_{10} should be about twice that of P_4S_{10}. The associated state of molten P_4S_{10} was attributed by Förthmann and Schneider[4] to the existence of P=S ··· S=P interactions between P_4S_{10} molecules. The P=S ··· S=P short contacts, arranged in chains of eight sulphur atoms, actually occur in the crystal of the same sulphide (Figure 1).[8] Similar interactions in the liquid, if any, could be regarded as preliminary steps to bi- (or pluri-) molecular sulphur transfer reactions, such as equation (2).

$$p\,P_4S_{10} \rightleftharpoons q\,P_4S_9 + r\,P_4S_7 + \Sigma(s\,S_x) + \Sigma(t\,P_mS_y) \quad (1)$$

$$2\ {>}P{=}S \longrightarrow {>}P{=}S\cdots S{=}P{<} \longrightarrow {>}P{:} + {>}P{=}S{=}S,\ etc. \quad (2)$$

However, since no examples are known of the hypothetical structure >P=S=S,† the ability of P_4S_{10}, as such, to co-ordinate additional sulphur atoms remains questionable; no ion P_4S_{11}, or heavier ones, were actually observed in the mass spectra of dissociated melts of P_4S_{10}, even at low potential[10,11] or using the field desorption technique.[12] In order to test the above possibility, an attempt was made to determine the kinetic order at the onset of the redox dissociation of P_4S_{10} in solution.

Results

The solvent chosen was 1-chloronaphthalene, which proved to be inert under the experimental conditions (110—150 °C), see Experimental section. When monitoring the reaction by ^{31}P n.m.r. spectroscopy, the sole species detected were P_4S_{10}, P_4S_9, and small signals (apparent overall content $\leqslant$10% of that of P_4S_9) at δ 23.35, 55.62, 56.05, 56.67, and 56.9 p.p.m. assigned to phosphorus polysulphides.[3] The latter could not always be distinguished easily from the neighbouring signals of P_4S_{10} (very strong singlet) or P_4S_9 (second-order system, with 14 lines) or from the background noise, especially at short reaction times; for a heating time of 18 min at 140 °C (Figure 2), the polysulphide at δ 56.67 p.p.m. was the only distinct one. Therefore, a precise integration of the n.m.r. spectra proved difficult and burdensome.

For the routine work it was found to be more expedient to use a method based on the observation that P_4S_{10} is considerably more resistant to hydrolysis than each of the products of its redox dissociation[3] (see Experimental section). The results obtained at 140 °C are presented in Figure 2 and Table 1. Despite the uncertainty (±*ca.* 15 s) of the zero time (the sample of crystalline P_4S_{10} does not dissolve instantly), it is clear that the initial rate is little affected by dilution. This speaks strongly against a bi- (or pluri-)molecular mechanism such as equation (2) and suggests that the redox dissociation of P_4S_{10} is proceeding by a unimolecular process.

Data obtained at 110, 120, 130, and 150 °C are also detailed in Table 1, along with the least-squares estimation of the activation parameters. Above 150 °C the reaction rate was too fast to measure with accuracy and the inertness of 1-chloronaphthalene less certain; below 110 °C, P_4S_{10} was insufficiently soluble. Kinetic data at 22 °C could be obtained however, using CS_2 as a solvent (Table 1); the rate of dissociation (*ca.* 0.12% d^{-1}) is of the same order as the extrapolated value of the rate in 1-chloronaphthalene (0.105%).

The initial rate of 140 °C in 1-chloronaphthalene is unaffected by the presence of oxygen or by the addition of sulphur. On the other hand, a slight catalysis by iodine was noticed (Table 1). Likewise, the substitution of a mixture of 1,4-dibromobenzene and 1,2-dichloronaphthalene, although not affecting the initial rate substantially, resulted in subsequent noticeable, however irregular, rate increases. These observations point to the possibility of a catalysis by iodine or bromine radicals. Note that, like P_4S_{10}, but unlike $PSCl_3$, $PSBr_3$, and, even more markedly, PSI_3 lose sulphur quite readily, affording PBr_3[13] (see

---

* *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

† By contrast, thiosulphinylanilines R–N=S=S, afforded by the reaction of P_4S_{10} with R–N=O, are established products.[9]

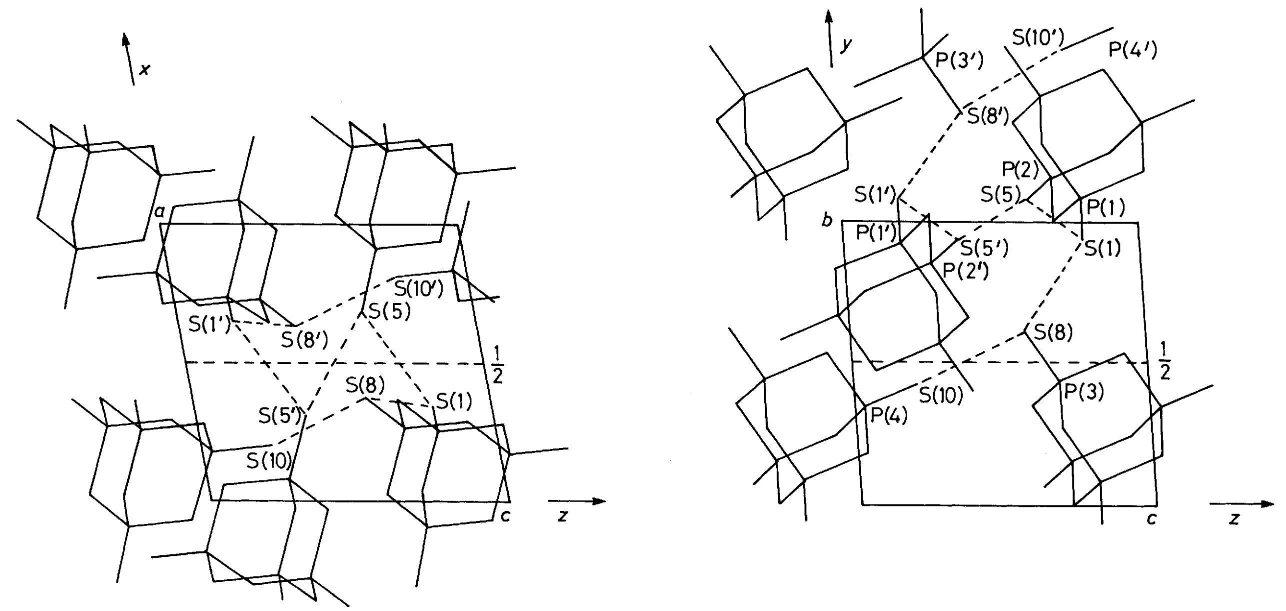


Figure 1. Details of the P=S ··· S=P short contacts in the triclinic crystal of P_4S_{10} (quoted from ref. 8 or calculated from the data therein). Distances (Å): P(4)–S(10) 1.910, P(3)–S(8) 1.916, P(1)–S(1) 1.890, P(2)–S(5) 1.907, S(10) ··· S(8) 3.413, S(8) ··· S(1) 3.578, S(1) ··· S(5) 3.643, and S(5) ··· S(5′) 3.471. Angles (°): P(4)S(10)S(8) 163.0, P(3)S(8)S(10) 100.0, P(3)S(8)S(1) 100.0, P(1)S(1)S(8) 147.3, P(1)S(1)S(5) 107.1, P(2)S(5)S(1) 129.0, P(2)S(5)S(5′) 163.0, S(10)S(8)S(1) 134.5, S(8)S(1)S(5) 70.7, and S(1)S(5)S(5′) 67.7. Dihedral angles (°): P(4)S(10)-S(8)P(3) 126.2, P(3)S(8)S(1)P(1) 114.3, P(1)S(1)S(5)P(2) 98.2, S(10)S(8)S(1)S(5) 91.3, and S(8)S(1)S(5)S(5′) 67.4. The middle of S(5) ··· S(5′) is a centre of symmetry

Table 1. Kinetics of the redox dissociation of P_4S_{10} in solution

Solvent	Temperature/ °C	Initial concentration/ %, w/w	Iodine (%, w/w of P_4S_{10})	$10^4 k_1$/ s^{-1}	Activation parameters
1-Chloronaphthalene	140	1	none	1.90 ± 0.12	
	140	0.4	—	1.77 ± 0.12	$E_a = 82.3 \pm 2.6$ kJ mol^{-1}
	110	0.4	—	0.26 ± 0.03	$\Delta H^\ddagger = 79.8 \pm 2.6$ kJ mol^{-1}
	120	0.4	—	0.535 ± 0.06	
	130	0.4	—	1.075 ± 0.10	$\Delta S^\ddagger = -125.8 \pm 6.5$ J K^{-1} mol^{-1}
	150	0.4	—	3.025 ± 0.25	
	140	0.4	1.7	2.52 ± 0.12	
	140	1	4.5	see Figure 2	
Carbon disulphide	22	0.222	none	*ca.* 1.4×10^{-4}*	
p-$C_6H_4Br_2$:o-$C_6H_4Cl_2$	140	1	—	1.86 ± 0.2	
(4:1)	140	0.4	—	1.62 ± 0.2	

* Experiment lasting 64 d and affording 7.9% of dissociated products, as determined by selective hydrolysis. The formation of P_4S_9 (*ca.* 4%) was confirmed by ^{31}P n.m.r. spectroscopy.

Experimental section) or PI_3[14] respectively.† It also appears from Figure 2 that the extent of dissociation of P_4S_{10} at equilibrium grows with dilution. This implies that the latter process results in a decrease of the mean molecular weight, *i.e.* in equation (1): $q + r + \Sigma s + \Sigma t > p$. No simple kinetic law was found to fit the curves in Figure 2.

Discussion

The above results indicate that the redox dissociation of P_4S_{10} in solution involves a unimolecular (dissociative) mechanism. Due to the high dissociation energy D(P=S) in P_4S_{10} (285 or 308 kJ mol^{-1} [15]), it seems unlikely that this sulphide could be directly converted into P_4S_9 by a one-step elimination of atomic sulphur. A multistep mechanism, rate-controlled by an initial dissociation-step, is more plausible; specifically, the formation of P_2S_5, as a metastable reactive intermediate, by collapse of the cage structure of P_4S_{10}, deserves consideration, especially since $P_2S_5^+$ appears as a strong peak in the mass spectrum of pure P_4S_{10}[11,16] (Table 2).

Nascent P_2S_5 in reaction (3) is depicted as a bis(dithioxophosphorane) $(S{=})_2P{-}S{-}P({=}S)_2$ (**1a**). The viability of compounds $RP({=}S)_2$ has been demonstrated at least in one case ($R = 2,4,6\text{-}Bu^t{}_3C_6H_2$).[17] Nonetheless, tautomers such as (**1b**) to (**1d**) are conceivable too; the alternative (**1e**) would probably involve too high an angular strain. Structure (**2**), similar to (**1c**),

---

† The sequence of thermodynamic thiophilicity $PCl_3 > PBr_3 > P_4S_9 > PI_3$ has been confirmed by sulphur-exchange experiments [PZ_3/PSZ'_3 mixtures (Z = halogen) allowed to stand for several weeks at room temperature, either neat or in CS_2], monitored by ^{31}P n.m.r. spectroscopy.

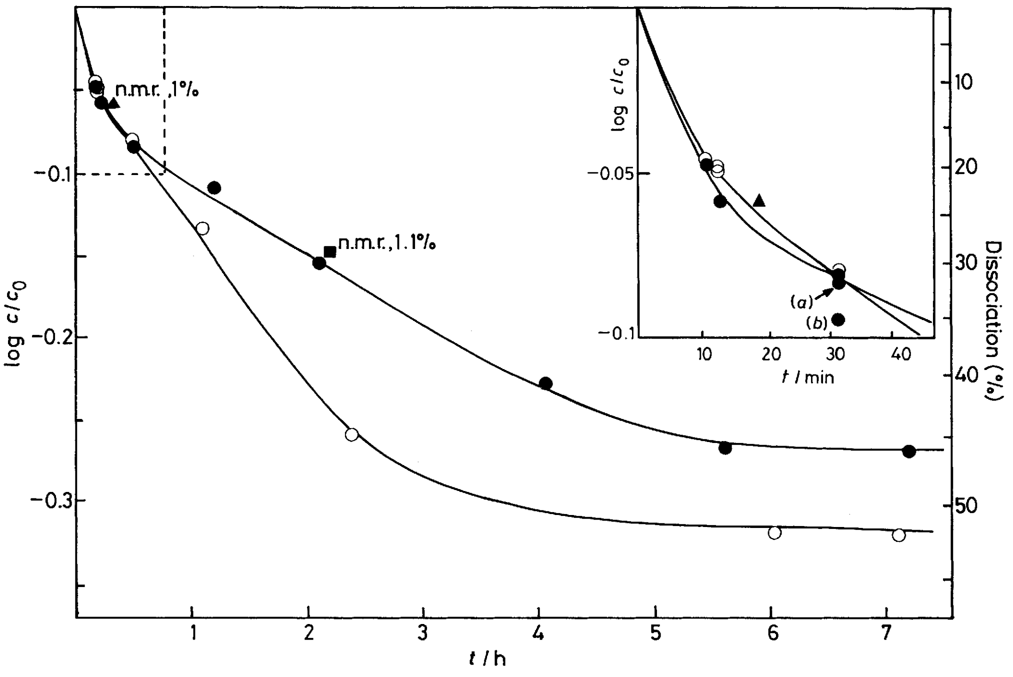
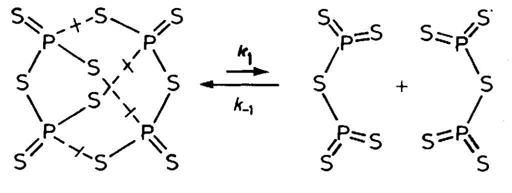


Figure 2. Kinetics of the redox dissociation at 140 °C of P_4S_{10} dissolved in 1-chloronaphthalene at two initial concentrations, c_0 = 1 (●) and 0.4 (○) % w/w. The concentration (c) of P_4S_{10} has been determined by selective hydrolysis (see text), with the exception of two points obtained by ^{31}P n.m.r. spectroscopy. An expanded view of the initial part of the curves is shown in the top right window. Points (a) and (b) correspond to experiments with added sulphur (S : P_4S_{10} wt. ratio = 2.64 : 1) or iodine (I : P_4S_{10} = 0.045 : 1) respectively

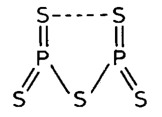
Table 2. Compared ion abundances (partial data) in the mass spectra of P_4S_{10} (pure or dissociated) and P_4S_9[a]

m/z	Ionic species	Pure P_4S_{10}	Dissociated P_4S_{10}[b]	P_4S_9
63	PS^+	100	100	100
222	$P_2S_5^+$	21.3	26.4	12.9
254	$P_2S_6^+$	0.9	6.1[c]	0.4
286	$P_2S_7^+$	0.0	1.0	0.0
318	$P_2S_8^{+}$[d]	0.0	1.1	0.0
350	$P_2S_9^{+}$[d]	0.0	0.1	0.0
382	$P_2S_{10}^{+}$[d]	0.0	0.0	0.0
414	$P_2S_{11}^{+}$[d]	0.0	0.0	0.0
446	$P_2S_{12}^{+}$[d]	0.0	0.0	0.0
316	$P_4S_6^+$	0.2	0.3	0.7
348	$P_4S_7^+$	1.5	1.7	3.8
380	$P_4S_8^+$	1.5	1.4	1.4
412	$P_4S_9^+$	3.1	4.2	7.8
444	$P_4S_{10}^+$	2.7	2.1	0.3

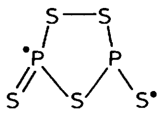
[a] 70 eV, direct introduction, source temperature 200 °C, isotopic satellites omitted. [b] Molten P_4S_{10}, quenched, in a nitrogen atmosphere, on a cold stainless-steel surface (film thickness *ca.* 0.8 mm). [c] A peak at m/z 256 (ion abundance 1.7) is chiefly due to the satellite $P_2(^{32}S)_5(^{34}S)^+$, and, to a slight extent, to S_8^+. [d] After deduction of the calculated ion abundances of the satellites $P_4(^{32}S)_{n-1}(^{34}S)^+$ (n = 6—10).



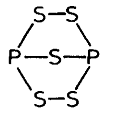
(3)



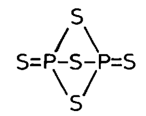
(1b)



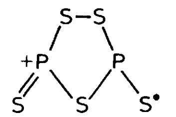
(1c)



(1d)



(1e)



(2)

has been suggested by Penney and Sheldrick[16] for the radical cation $P_2S_5^+$.

It is further postulated that the initial, rate-determining step (3) is followed by a series of sulphur-transfer reactions, such as (4a), (4b),. . . , *etc.*, between P_4S_{10}, a very reactive sulphur-donor,* and P_2S_5, a metastable species, with production of polysulphides P_2S_{5+n}. A concomitant exchange of sulphur between primary polysulphides, *e.g.* as in equation (5), is also likely to take place,

$$P_4S_{10} + P_2S_5 \xrightarrow{k_2\ \text{fast}} P_4S_9 + P_2S_6 \qquad (4a)$$

$$P_4S_{10} + P_2S_6 \longrightarrow P_4S_9 + P_2S_7 \ldots, \textit{etc.} \qquad (4b)$$

---

* In CS_2 at 25 °C, PPh_3 desulphurises P_4S_{10} to P_4S_9 in a matter of seconds, affording $PSPh_3$ quantitatively;[18] hours or days are required with S_8 in apolar solvents.[19]

$$2P_2S_6 \longrightarrow [P_4S_{12}\,?] \longrightarrow P_2S_7 + P_2S_5\ (\longrightarrow \tfrac{1}{2}\,P_4S_{10}) \quad (5)$$

via perhaps condensed molecules $(P_2S_{5+n})_i$ ($i \geqslant 2$). Ultimately, S-rich polysulphides could expel elemental sulphur [equation (6)].

$$P_2S_{5+n} \longrightarrow \tfrac{n}{x}\,S_x + P_2S_5\ (\longrightarrow \tfrac{1}{2}\,P_4S_{10}) \quad (6)$$

In line with the assumed formation of P_2S_{5+n} as primary polysulphides, peaks corresponding to $P_2S_6^+$, $P_2S_7^+$, $P_2S_8^+$, and $P_2S_9^+$ (the last one less significant) have been observed in the mass spectra (ionizing voltage 70 or 20 eV) of dissociated melts of P_4S_{10}; these peaks are absent or much weaker in the spectra of pure P_4S_{10} or P_4S_9[10,11,16] (Table 2). Ions of polysulphides P_mS_y, with $m > 2$, were not observed (see above).

The presence of low-molecular-weight polysulphides in the dissociation products of P_4S_{10} is also implied by the effect of dilution on the redox equilibrium, as evidenced by Figure 2, where lowering the concentration by a factor of 2.5 results in a 5.9% increase of the extent of dissociation at equilibrium; the calculated theoretical shift would be $<2.7\%$ if only P_4S_9, S_8, and polysulphides P_mS_y with $m \geqslant 4$ were produced [equation (1)]. Finally, the dramatic rise of the vapour pressure (5.7 to 415 Pa) that accompanies the redox dissociation of neat P_4S_{10}, when the latter is melted,[1] as well as the low values of m.m.w. of the vapour in equilibrium with this liquid sulphide,[7] are consistent with the assumed formation of diphosphorus polysulphides, although, in this domain of temperature (>561 K), the content of P_2S_5 is perhaps less negligible.

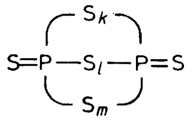
If only the onset of the process is considered, reactions (4b), (4c), . . ., *etc.*, as well as (5) and (6), and the reverse reaction of (4a) may be neglected. The concentration of P_2S_5, the reactive intermediate, should remain very small, so that the system is amenable to a steady-state treatment, according to equation (7).

$$d[P_2S_5]/dt = 2k_1[P_4S_{10}] - k_{-1}[P_2S_5]^2 - k_2[P_4S_{10}][P_2S_5] = 0 \quad (7)$$

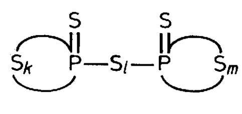
If $k_{-1}[P_2S_5]^2$ is small enough, we obtain $[P_2S_5] \approx 2k_1/k_2$. Then, in accord with the above experimental results, the initial kinetics will be first order [equation (8)].

$$v = -d[P_4S_{10}]/dt = k_1[P_4S_{10}] + k_2[P_4S_{10}][P_2S_5] = 3k_1[P_4S_{10}] \quad (8)$$

Structures suggested for diphosphorus polysulphides are shown in (3) and (4);* (3) is obviously more appropriate to low n values. By contrast, triphosphorus polysulphides are hardly conceivable geometrically, but tetra (and higher) phosphorus polysulphides [*cf.* equation (5) or similar ones] can readily be imagined. Of course, the absence of parent peaks corresponding to such species in the mass spectra of dissociated P_4S_{10} (Table 2) is not sufficient evidence against their presence.



(3)



(4)

The above kinetic results do not necessarily imply that the redox dissociation of neat molten P_4S_{10} obeys the same unimolecular model as in solution. The strongly negative activation entropy (-125.8 J K^{-1} mol^{-1}) found for the dissociation in chloronaphthalene in fact suggests that the activated complex is stabilised by association with the solvent. Since, in the case of neat molten P_4S_{10} the solvent is P_4S_{10} itself, a similar solvation would amount to an increase in the kinetic order. The slight growth of k_1 in Table 1, when the initial concentration changes from 0.4 to 1%, might, if significant, reflect this effect.

Experimental

P_4S_{10} was purified by vigorously stirring a solution of commercial 'phosphorus pentasulphide' (5 g) in CS_2 (900 cm^3) with water (100 cm^3) at *ca.* 30 °C for 50 min, in order to hydrolyse all of the redox impurities. The organic layer was decanted off and washed six times with water. The solution was dried with powdered $CaCl_2$, then filtered and allowed to crystallise at -21 °C. The collected crystals were dried at room temperature under reduced pressure. Yield: 1.3 g (Found: P, 27.80. P_4S_{10} requires P, 27.85%). ^{31}P N.m.r. (CS_2): δ 56.3 (s) p.p.m. Impurity: trace of P_4S_9, estimated at *ca.* 0.25% from the results of the hydrolysis test, extrapolated to zero time (see below).

The compound P_4S_9 was conveniently obtained by stirring powdered commercial phosphorus pentasulphide (10 g) with dry carbon disulphide (100 cm^3) for 10—15 min at room temperature; the suspension was rapidly filtered, giving a solution (supersaturated in P_4S_9), which, upon standing overnight at the same temperature, afforded crystals of P_4S_9 form I (monoclinic). Yield *ca.* 0.4 g (Found: P, 29.95. P_4S_9 requires P, 30.05%). ^{31}P N.m.r. (CS_2): A_3B spectrum (14 lines), δ_A 63.1, δ_B 57.3 p.p.m., J_{AB} 96 Hz. Impurity: P_4S_{10} (0.7%). Crystallographic parameters (to date unreported): monoclinic, $a = 26.96$, $b = 24.28$, $c = 8.60$ Å, $\beta = 111.69°$, $Z = 16$. In accord with a previous report,[25] the determination of the structure was found impracticable, due to crystal disorders (*cf.* Acknowledgements). The ^{31}P n.m.r. spectra were obtained at 80.76 or 121.5 MHz.

Redox Dissolution of P_4S_{10} *in Solution* (*Example*).—Pure P_4S_{10} (60 mg) was rapidly dissolved (30—60 s) in dry 1-chloronaphthalene (6 g) under nitrogen, in a tube which was shaken in a thermostat bath at 140 °C. At the end of the heating period, the solution, sometimes opalescent, was rapidly chilled under tap-water, then diluted or redissolved in enough CS_2 (25 cm^3) and analysed by means of the following hydrolysis test or by ^{31}P n.m.r. spectroscopy. Evidence for the inertness of 1-chloronaphthalene towards P_4S_{10} under the experimental conditions (110—150 °C) followed from the observation that the latter n.m.r. spectra were devoid of the characteristic ^{31}P n.m.r. signals of a control solution heated for 1 h at 250 °C (complex spectrum, with strongest lines at δ 66.9 and 70.6 p.p.m.).

Test of Hydrolysis.—The solution of dissociated P_4S_{10} was magnetically stirred with twice distilled water (100 cm^3) for 15 min at 25 °C. The aqueous phase was decanted off, then concentrated to *ca.* 10 cm^3. After dilution with MeOH (50 cm^3), the solution was titrated with KOH to the first pH inflection. The extent of hydrolysis was calculated on the basis of 1 equivalent of 'hydrolysed phosphorus' per equivalent of strong acidity. No additional acidity was extracted by repeated washings with water of the organic solution. The latter solution was found by ^{31}P n.m.r. spectroscopy to contain only P_4S_{10}, which has withstood hydrolysis. Blank tests revealed that, under similar conditions, the extent of hydrolysis amounted to 99.5% for P_4S_9. It was only 0.5 and 1.0% for P_4S_{10} after 15 and 45 min respectively; these data, extrapolated to 0 min, allowed us to estimate the P_4S_9 content of the specimen of P_4S_{10} to *ca.* 0.25%.

---

* Compounds $R(S)P(\text{-}SS\text{-})(\text{-}S_n\text{-})P(S)R$ (R = Me, Bu^t, Br, or S^-; n = 1 or 2)[20–23] and $R(S)\overline{P\text{-}S_n}$ (R = Me or Bu^t; n = 5—7),[24] with cycles as in (3) or (4), are established products.

Redox Dissociation of Thiophosphoryl Trihalides.—Pure $PSBr_3$ was heated in a sealed tube at 140 °C for 43 min. The n.m.r. spectrum revealed the formation of PBr_3 (4.3%, P basis). Pure $PSCl_3$ was similarly heated at 150 °C for 64 h: PCl_3 found by n.m.r. spectroscopy, 0.6%.

Acknowledgements

The author is deeply grateful to the Company Atochem (Centre de Recherches Rhône Alpes) for the recording of n.m.r. and mass spectra and to A. Durif and M-T. Averbuch (Laboratoire de Cristallographie du C.N.R.S., Grenoble) for the determination of the crystallographic parameters of monoclinic P_4S_9.

References

1 M. C. Démarcq, *Phosphorus Sulphur*, 1981, **11**, 65.
2 M. C. Démarcq, *Phosphorus Sulphur*, 1987, **33**, 127.
3 M. C. Démarcq, *J. Chem. Res.*, submitted for publication.
4 R. Förthmann and A. Schneider, *Z. Phys. Chem., Neue Folge, Frankfurt am Main*, 1966, **49**, 22.
5 A. Stock and H. von Bezold, *Chem. Ber.*, 1908, **41**, 657.
6 D. W. Muenow and J. L. Margrave, *J. Inorg. Nucl. Chem.*, 1972, **34**, 89.
7 J. Bouix, R. Hillel, H. Vincent, and Y. Monteil, *J. Therm. Anal.*, 1977, **12**, 371.
8 A. Vos and E. H. Wiebanga, *Acta Crystallogr.*, 1955, **8**, 217; A. Vos, R. Olthoff, F. Van Bolhuis, and R. Botterweg, *ibid.*, 1965, **19**, 864.
9 G. W. Kutney and K. Turnbull, *Chem. Rev.*, 1982, **82**, 333; D. R. H. Barton and M. J. Robson, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1245.
10 D. W. Muenow and J. L. Margrave, *J. Inorg. Nucl. Chem.*, 1972, **34**, 89.
11 R. Thamm, G. Heckmann, and E. Fluck, *Phosphorus Sulphur*, 1982, **12**, 319.
12 Atochem, Centre de Recherches Rhône Alpes, unpublished work.
13 J. M. Andrews, J. E. Ferguson, and C. J. Wilkins, *J. Inorg. Nucl. Chem.*, 1963, **25**, 829.
14 K. B. Dillon, M. da G. Craveirinha Dillon, and T. C. Waddington, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 349; M. Baudler, G. Fricke, and K. Fichtner, *Z. Anorg. Allg. Chem.*, 1964, **327**, 124.
15 H. Vincent and C. Vincent-Forat, *Bull. Soc. Chim. Fr.*, 1973, 499; P. G. Perkins, *Inorg. Chim. Acta*, 1983, **73**, 45.
16 G. J. Penney and G. M. Sheldrick, *J. Chem. Soc. A*, 1971, 243.
17 J. Navech, J. P. Majoral, and R. Kraemer, *Tetrahedron Lett.*, 1983, **24**, 5885; R. Appel, F. Knoch, and H. Kunze, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 1004.
18 J-J. Barieux and M. C. Démarcq, *J. Chem. Soc., Chem. Commun.*, 1982, 176.
19 P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, 1956, **78**, 3710.
20 J. Hahn and T. Nataniel, *Z. Naturforsch., Teil B*, 1987, **42**, 1263.
21 F. W. B. Einstein, B. R. Penfold, and Q. T. Tapsell, *Inorg. Chem.*, 1965, **4**, 186.
22 P. C. Minshall and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1378.
23 M. Z. Jandali, G. Eulenberger, and H. Hahn, *Z. Anorg. Allg. Chem.*, 1985, **530**, 144.
24 T. Heinlein and K. F. Tebbe, *Acta Crystallogr., Sect. C*, 1984, **40**, 1596; J. Hahn and T. Nataniel, *Z. Anorg. Allg. Chem.*, 1987, **548**, 180.
25 W. Hilmer, *Acta Crystallogr., Sect. B*, 1969, **25**, 1229.

Received 28*th September* 1988; *Paper* 8/03837F