Kinetic Study of the Homogeneous Methanolysis of Tetraphosphorus Decasulphide

Paul Bourdauducq
Société Atochem, Centre de Recherches Rhône-Alpes, F-69310 Pierre Bénite, France
Michel C. Démarcq *
Institut National des Sciences Appliquées, Laboratoire de Chimie Organique, 20 Avenue Albert Einstein,
F-69621 Villeurbanne Cedex, France

The rate of the homogeneous methanolysis of pure P_4S_{10}, dissolved in CS_2, has been measured at 0, 15, 25, and 35 °C for various $MeOH : P_4S_{10}$ molar ratios. The sole product detected was $(MeO)_2PS_2H$. At not too low concentrations, the reaction is virtually first order in $[P_4S_{10}]$ and second order in $[MeOH]$, owing probably to an autocatalytic process. The multistep reaction is kinetically controlled by the initial attack on P_4S_{10}; this is tentatively explained by the rigidity and geometry of the P_4S_{10} cage molecule and/or by the spontaneous formation of reactive dithioxophosphoranes $ZP(=S)_2$ [$Z = MeO-$ or $>P(S)S-$] from all alcoholysis intermediates. Calculated activation parameters are discussed. Novel data on the solubility of P_4S_{10} are reported.

The chemical literature is devoid of any kinetic report of the homogeneous alcoholysis or hydrolysis of tetraphosphorus decasulphide. Our purpose was to fill this gap. A prerequisite to such an investigation was the proper choice of an inert solvent. Novel data[1] point to the following solubility sequence at 20 °C (concentration, in mg P_4S_{10} per kg of solvent): CS_2 (2 450) $\gg$ PhMe (290) $>$ $C_6H_3Cl_3$ (ca. 270)[2a] $>$ CH_2Br_2 (216) $>$ PhH (164) $>$ n-hexane (64) $>$ CCl_4 (48) $>$ CH_2Cl_2 (42) $>$ Et_2O (<22). Clearly, carbon disulphide, long recognized as a solvent for phosphorus sulphides, is still the best although the solubility in this solvent is only moderate even at higher temperatures (Figure 1).[1,3] Substantial concentrations are attainable if use is made of high-boiling solvents, such as poly-chloro or -bromo arenes,[3,4] but heating at temperatures above ca. 100 °C always leads to some redox dissociation of P_4S_{10},[1] with consequent errors in the measured rates, since the P_4S_9 generated is much more reactive with alcohols[1] and water[5] than is P_4S_{10}.

Experimental

Recrystallized P_4S_{10} was evaluated by d.t.a. (one peak) and ^{31}P n.m.r. spectroscopy. A trace of P_4S_9 was the sole impurity detected; that its content (<2%) could be neglected for our purpose was further evidenced by comparing the blank tests with P_4S_{10} and P_4S_9 (see below) and by duplicate kinetic measurements (Figure 2, $n = 2$) using P_4S_{10} further recrystallized from CS_2.

A weighed amount of P_4S_{10} was dissolved in pure dry carbon disulphide (100 cm³), then equilibrated in a thermostat. After adding a known volume of methanol, aliquots of 10 cm³ were taken at intervals and immediately frozen by pouring into stirred glycerol–water (1:4, 90 cm³) at ca. −10 °C; this operation was intended to extract, more or less completely, the reaction product $(MeO)_2PS_2H$ and residual methanol,† thus virtually stopping the alcoholysis in the CS_2 phase. The solubility of P_4S_{10} in water was regarded as negligible. The stirred emulsion, kept at ≤0 °C, was then quickly titrated with standard alkali to the first inflexion, using a recording potentiograph. One equivalent of strong acidity was taken as

Figure 1. Solubility of P_4S_{10} in carbon disulphide (concentrations in g solute per 100 g solvent). $\bigcirc$, This work; $\bullet$, ref. 3. Data between ca. 0 and 46 °C (normal b.p.) obey the equation: $\log_{10} c = 3.225 - 1124/T$

corresponding to 0.25 mol of alcoholysed P_4S_{10}, assuming the classical, but often approximate, equation (1) to be valid.

$$P_4S_{10} + 8 ROH \longrightarrow 4 (RO)_2P(S)SH + 2 H_2S \quad (1)$$

This was borne out by ^{31}P n.m.r. analysis of the CS_2 solution, which showed $(MeO)_2PS_2H$ to be the sole detectable phosphorus-containing reaction product, even at intermediate stages of methanolysis. For the sake of comparison, the heterogeneous reaction of P_4S_{10} for 7 h at 24 °C, with a large excess of MeOH, was found to generate only 78% of the expected amount of strong acidity.

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† The distribution ratio $c(H_2O):c(CS_2)$ of methanol is not available but is presumably fairly high; values of 125 and 77 have been found for the systems H_2O CCl_4 and $H_2O-C_6H_6$ respectively.[6]
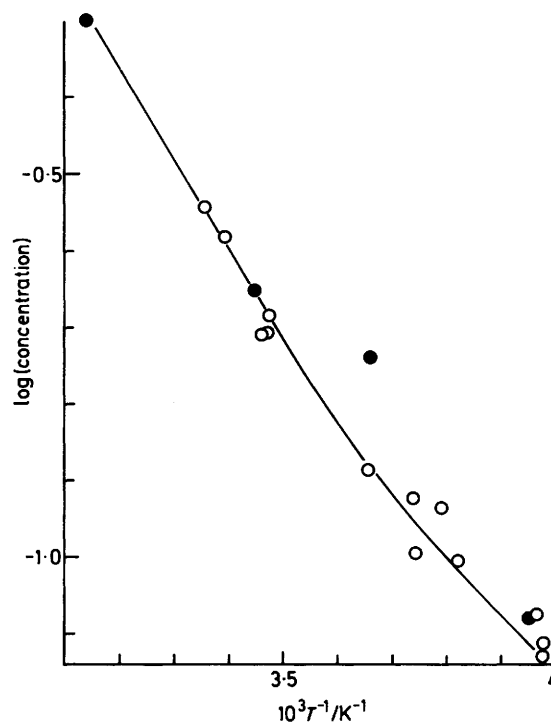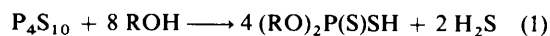
That our procedure results in no hydrolysis was ascertained by a blank test with P_4S_{10} without methanol, when no alkali was consumed at the titration step.

Comparative measurements with P_4S_9 indicated that, even with no excess of methanol, all of this sulphide reacted in less than 3—4 min at 25 °C: only ca. 3 equivalents of strong acidity were generated per mol of P_4S_9, due to the concomitant production of $(MeO)_2P(S)SH$ and $(MeO)_2P(S)H$. On the other hand, a blank test without methanol resulted in complete hydrolysis of P_4S_9, with the production of ca. 4 equivalents of strong acidity per mol. Hence, while the described procedure appears to be fairly well suited to the kinetic study of P_4S_{10}, it would surely be inappropriate in the case of P_4S_9.
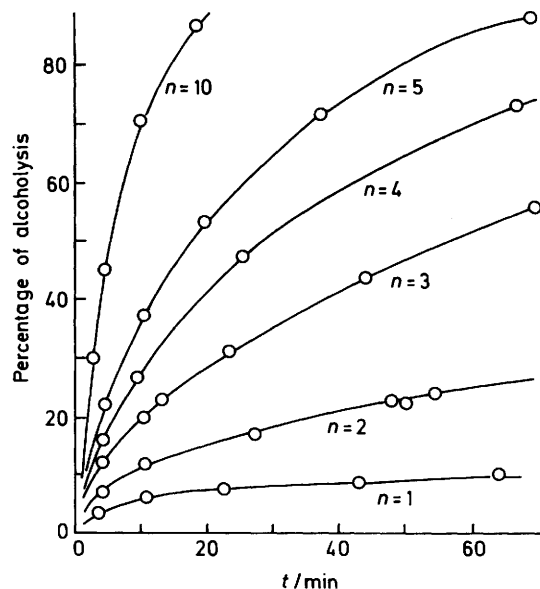
Results

The kinetic curves obtained at 25 °C are displayed in Figure 2. Despite the cleanness of the reaction, no simple kinetic law is obeyed. At not too low concentrations of both reactants, the kinetic order is close to 3 however, namely $v = k_3[P_4S_{10}]$-
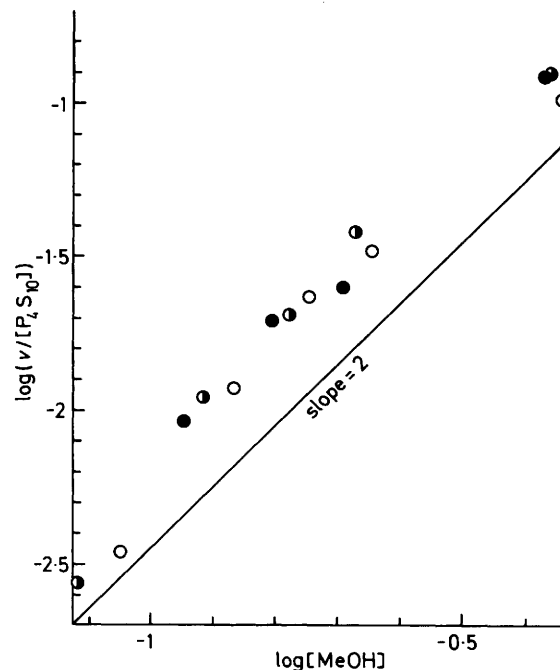
Figure 2. Rate of the homogeneous methanolysis of P_4S_{10} at 25 °C as a function of the $MeOH:P_4S_{10}$ molar ratio. Solvent: CS_2. Initial concentration of P_4S_{10}: 5.63×10^{-3} mol l^{-1}. $8n = [MeOH]:[P_4S_{10}]$ at zero time

Figure 3. Determination of the kinetic order with respect to MeOH. $v = -d[P_4S_{10}]/dt$; concentrations in mol l^{-1} and time (t) in min. Initial concentration of P_4S_{10}: 5.63×10^{-3} mol l^{-1}. Temperature: 25 °C. Estimated rates at 0 (◯), 30 (◑), and 50% (●) methanolysis respectively. The calculated order with respect to [MeOH], obtained by the least-squares method, is 2.086 ± 0.092 (taking account of all of the points) or 1.948 ± 0.048 (excluding the two lowest points and the upper open circle, believed to be less reliable). A more approximate figure of 0.893 ± 0.080 was obtained similarly for the order with respect to $[P_4S_{10}]$, using a plot of log $(v/[MeOH]^2)$ vs. log $[P_4S_{10}]$

Table. Least-squares estimation of the kinetic constants

$\theta_c/°C$	$\dfrac{10^3[P_4S_{10}]_0}{mol\ l^{-1}}$	$n = \dfrac{[MeOH]_0{}^a}{8[P_4S_{10}]_0}$	Third order[b] $\dfrac{10^3 k_3/}{l^2\ mol^{-2}\ min^{-1}}$	Third order[b] $\dfrac{10^2 \Psi_0/}{l^2\ mol^{-2}}$	Second order[c] $\dfrac{10^4 k_2/}{l\ mol^{-1}\ min^{-1}}$	Second order[c] $\dfrac{10^2 \varphi_0}{l\ mol^{-1}}$
25	5.63	1 (6)	691 ± 190	$1\,684 \pm 689$	292 ± 83	74 ± 16
		2 (10)	528 ± 35	750 ± 175	430 ± 33	69 ± 17
		3 (9)	777 ± 32	398 ± 109	929 ± 48	60 ± 16
		4 (5)	725 ± 36	234 ± 118	$1\,149 \pm 74$	48 ± 24
		5 (7)	762 ± 10	135 ± 48	$1\,469 \pm 27$	46 ± 13
		10 (5)	584 ± 22[d]	32 ± 34	$2\,446 \pm 83$	18 ± 13
		3—5 (mean value)	755 ± 26	255 ± 92		
25	3.94	3 (5)	428 ± 50	304 ± 147	389 ± 48	29 ± 14
35	5.63	3 (6)	861 ± 51	362 ± 213	$1\,019 \pm 74$	56 ± 31
15	5.63	3 (6)	701 ± 33	269 ± 113	852 ± 54	40 ± 18
0	3.38	3 (6)	235 ± 30	265 ± 99	187 ± 25	22 ± 8

[a] $n = 1$ corresponds to the theoretical proportions [equation (1)]. The number of experimental points considered is given in parentheses. [b] k_3 and Ψ_0 are the parameters of the regression line ($\Psi = k_3 t + \Psi_0$), obtained from the plot in Figure 4 or similar ones ($n \neq 1$). For $n = 1$, the integral function was $\Psi' = (1/128)a^{-2} [(1 - p)^{-2} - 1] = k_3 t + \Psi_0'$, with a, p, and t as in Figure 4. In ideal third-order kinetics (first order with respect to $[P_4S_{10}]$ and second order with respect to [MeOH]), $\Psi_0(\Psi_0')$ should be zero and k_3 invariant. [c] k_2 and φ_0 are the parameters of the regression line ($\varphi = k_2 t + \varphi_0$), obtained from a plot of the integral function φ vs. time, with $\varphi = [8a(n - 1)]^{-1}[\ln(1 - p/n) - \ln(1 - p)]$ ($n \neq 1$). For $n = 1$, φ was replaced by $\varphi' = (1/8a)[(1 - p)^{-1} - 1] = k_2 t + \varphi_0'$. In ideal second-order kinetics (first order with respect to $[P_4S_{10}]$ and to [MeOH]), $\varphi_0 (\varphi_0')$ should be zero and k_2 invariant. [d] Probably less reliable, owing to the high initial rate (Figure 2).

[MeOH]^2 (Figures 3 and 4 and Table). For an initial P_4S_{10} concentration of 5.63×10^{-3} mol l^{-1}, the best fit is obtained when the initial methanol concentration is 3—5 times the stoicheiometric value [equation (1)], with $k_3 = 0.755 \pm 0.026$ l^2 mol^{-2} min^{-1} at 25 °C and activation parameters $E_a = 7.7 \pm 2.4$ kJ mol^{-1}, $\Delta H_0^{\ddagger} = 5.2 \pm 2.4$ kJ mol^{-1}, and $\Delta S_0^{\ddagger} = -264 \pm 8$ J K^{-1} mol^{-1}. The reaction rate was insensitive to an initial addition of a dialkyldithiophosphoric acid.

Discussion

It has been shown on many occasions, even though with specimens of uncertain purity, that the heterogeneous alcoholysis of P_4S_{10} generates, in addition to the main product $(RO)_2P(S)SH$ [equation (1)], a number of secondary products such as $P(OR)_3S, (RO)_2P(S)SR, (RO)_2PSOH, (RO)_2P(S)H,$ and $(RO)_2$-

$P(S)S_nP(S)(OR)_2$, for example refs. 7—9; $(MeO)_2P(S)SMe$ is especially important when $R = Me.$[9,10a] None, or only undetectable amounts, of these species was afforded in our experiments. In accord with previous reports[5,11,12] and in contrast to the behaviour of $P_4O_{10},$[2b,10b,13,14] the absence of any intermediate fragment, retaining P–S–P bonds, of the stepwise cleavage of P_4S_{10} was noticeable; hence, alcoholysis, like hydrolysis,[5] of the latter is kinetically controlled by the initial attack on the P_4S_{10} molecule. This finding could simply reflect the rigidity of this cage molecule and its large intracyclic S–P–S angle (109.5°), which should hamper the formation of an activated complex, or intermediate phosphorane, with the alcohol. Another (or complementary) key could be that subsequent alcoholysis steps take place through a specific rapid route, involving the unimolecular formation of reactive dithioxo-phosphoranes (1) by an elimination process.
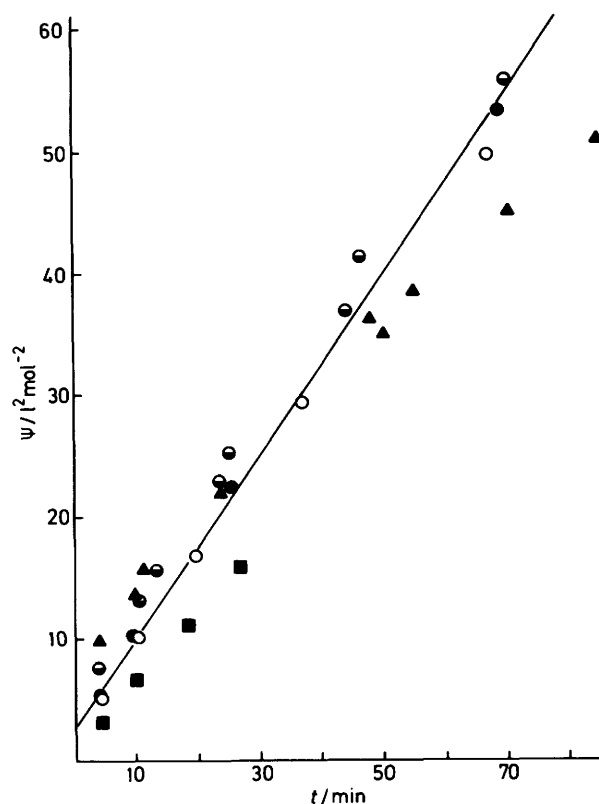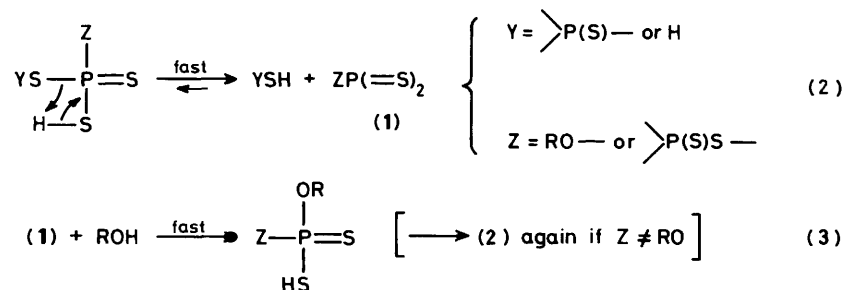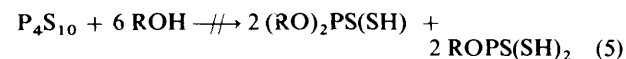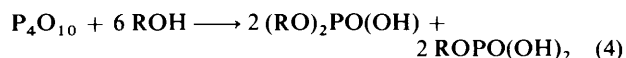
$$YS-\underset{\underset{H-S}{|}}{\overset{\overset{Z}{|}}{P}}=S \xrightarrow[\longleftarrow]{fast} YSH + ZP(=S)_2 \qquad (1)$$

$$\left\{ \begin{array}{l} Y = \text{>P(S)— or H} \\[2ex] Z = RO\text{— or >P(S)S —} \end{array} \right. \qquad (2)$$

$$(1) + ROH \xrightarrow{fast} Z-\underset{\underset{HS}{|}}{\overset{\overset{OR}{|}}{P}}=S \quad [\longrightarrow (2) \text{ again if } Z \neq RO] \qquad (3)$$

Figure 4. Plot of Ψ vs. time at 25 °C, for $a = 5.63 \times 10^{-3}$ mol l^{-1} and $n = 2$ (▲), 3 (◒), 4 (●), 5 (○), and 10 (■). Ψ is the integral function $[8a(n-1)]^{-2}[\ln(1-p/n) - \ln(1-p) - (n-1)(n-p)^{-1} - n^{-1} + 1]$, where $a = [P_4S_{10}]$ and $n = [MeOH] : 8[P_4S_{10}]$, both at zero time, and $100p$ = percentage of alcoholysed P_4S_{10}. Third-order kinetics, namely $[P_4S_{10}]$ and $[MeOH]^2$, implies that Ψ and time are linearly related ($\Psi = k_3t$). Shown is the mean regression line for $n = 3$—5

Support for this proposal can be found in the instability of compounds $ROPS(SH)_2$[15] and $(RS)_2PS(SH).$[16] Dithioxophos-phoranes (1; $Z = RS$) do actually form, as dimers $(RSPS_2)_2$, together with the tetrathiophosphate $P(SR)_3S$, when P_4S_{10} reacts with thiols.[16–19] In that case, however, further thiolysis of $(RSPS_2)_2$ to yield $(RS)_2P(S)SH$, in a similar way to reaction (3), is impeded by the reverse reaction.[16]

Reaction sequence (2) + (3) would also account for the fact that no monoester $ROPS(SH)_2$, an unstable species (see above), is produced upon reaction of P_4S_{10} with alcohols, as could have been anticipated by analogy with P_4O_{10}[10b] [equations (4) and (5)].
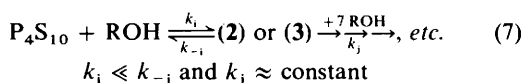
$$P_4O_{10} + 6 ROH \longrightarrow 2 (RO)_2PO(OH) + 2 ROPO(OH)_2 \qquad (4)$$

$$P_4S_{10} + 6 ROH \xrightarrow{\;\;\not\!\!\!\longrightarrow\;\;} 2 (RO)_2PS(SH) + 2 ROPS(SH)_2 \qquad (5)$$

Neutralization is expected to stabilize YS–P(S)Z(SH) intermediates by thwarting elimination process (2). Significantly, the forbidden reaction (5) has been shown to take place when carried out in the presence of a base.[15,20] Likewise, the cognate reaction of P_4S_{10} with NH_3 affords the anion $[P_3S_9]^{3-}$, i.e. a P–S–P retaining fragment, which reacts further with NH_3 to give $[P(NH_2)S_3]^{2-}.$[21]

An extension of scheme (2) + (3) could be that the initial nucleophilic attack of the alcohol brings about cleavage of P_4S_{10} to two molecules of metastable P_2S_5, a presumed bis(dithioxophosphorane) $(S=)_2P–S–P(=S)_2$. Several bases are known to yield substituted derivatives of P_2S_5, i.e. $(^-S)XP(S)–S–P(S)X(S^-)$ (X = F, N$_3$, or pyridinium), upon reaction with $P_4S_{10}.$[22,23]

The order 2 with respect to the alcohol concentration, exhibited by the homogeneous methanolysis of P_4S_{10}, is not exceptional; several other phosphorus derivatives behave likewise, especially $PCl_3S.$[24] Other examples are $P(OPr)_3,$[25] $\overline{O–C_6H_2Me_2\text{-}3,5\text{-}CH_2\text{-}P}(OEt)_3,$[26] and $P(OPh)_5.$[27] This feature
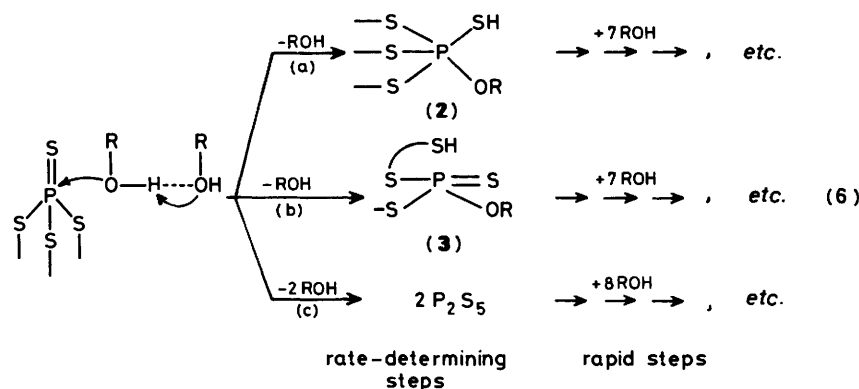
could arise from an autocatalytic effect of the alcohol (a general base) on the rate-determining step, *i.e.* either the formation of a phosphorane (2) [pathway (6a)], or the first actual P–S–P cleavage to intermediate (3) [pathway (6b)], or even a base-catalysed partition to P_2S_5 (see above) [pathway (6c)]. One could also imagine the initial step as simply bi-molecular but rapid and strongly reversible [equation (7)].

$$P_4S_{10} + ROH \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} (2) \text{ or } (3) \xrightarrow{+7\,ROH}_{k_j} , etc. \qquad (7)$$

$$k_i \ll k_{-i} \text{ and } k_j \approx \text{constant}$$

In that case, a classical steady-state treatment gives equation

$$\frac{-d[P_4S_{10}]}{dt} = \frac{k_i k_j [P_4S_{10}][ROH]^2}{k_{-i} + k_j[ROH]} \qquad (8)$$

(8) and third-order kinetics is obtained if $k_{-i} \gg k_j[ROH]$. However this condition does not fit our data, which clearly indicate that decreasing [ROH] results in increased deviation from a third-order law.

The values found for the activation energy (*ca.* 7.7 kJ mol⁻¹) and enthalpy (*ca.* 5.2 kJ mol⁻¹) are noticeably low (methanolysis of PCl_3S: [24] $E_a = 41$ kJ mol⁻¹). The exothermicity associated with the concerted formation of a hydrogen bond between the two ROH molecules in scheme (6) certainly contributes to the lowering of E_a and $\Delta H^\ddagger$ but is probably not the only factor. The relative slowness of P_4S_{10} alcoholysis is basically linked to its strongly negative activation entropy (-264 J K⁻¹ mol⁻¹), which itself could originate in the angular rigidity of the P_4S_{10} molecule and/or in the termolecular character of the reaction; a comparable negative activation entropy (-196 J K⁻¹ mol⁻¹) has been reported for the third-order methanolysis of PCl_3S.[24]

References

1 M. C. Démarcq, unpublished work.
2 J. R. Van Wazer, 'Phosphorus and its Compounds,' Interscience, New York, 1958, vol. 1, (a) p. 292, (b) p. 278.

3 A. Stock and B. Herscovici, *Chem. Ber.*, 1910, **43**, 1223.
4 R. Barral, M. C. Démarcq, and C. Mai, *J. Chem. Res.*, 1984, (S), 156.
5 J-J. Barieux and M. C. Démarcq, *Rev. Chim. Miner.*, 1984, **21**, 611.
6 I. N. Korenman and Z. G. Chernorukova, *Zh. Prikl. Khim. (Leningrad)*, 1974, **47**, 2523.
7 K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, 1963, **25**, 683.
8 A. E. Lippman, *J. Org. Chem.*, 1966, **31**, 471.
9 L. Nebbia and V. Bellotti, *Chim. Ind. (Milan)*, 1970, **52**, 369.
10 K. Sasse, 'Methoden der Organischen Chemie (Houben-Weyl),' G. Thieme Verlag, Stuttgart, 1964, vol. XII/2, (a) p. 684, (b) p. 879.
11 G. M. Kosolapoff, 'Organophosphorus Compounds,' Wiley, New York, 1950, p. 236.
12 P. Bencze, *Rev. Inst. Fr. Pèt. Ann. Combust. Liq.*, 1970, **25**, 647.
13 H. Adler and W. H. Woodstock, *Chem. Ind. (N.Y.)*, 1942, **51**, 516, 557.
14 Csaba Ujhelyi, *Acta Chim. Acad Sci. (Hung.)*, 1969, **59**, 211.
15 N. I. Zemlyanskii and I. V. Murav'ev, *Dokl. Akad. Nauk SSSR*, 1965, **163**, 654.
16 C. B. Scott, A. Menefee, and D. O. Alford, *J. Org. Chem.*, 1957, **22**, 789.
17 L. Rosnati, *Gazz. Chim. Ital.*, 1946, **76**, 272.
18 L. Maier and J. J. Daly, *Chimia*, 1964, **18**, 217.
19 H. Davy, *J. Chem. Soc., Chem. Commun.*, 1982, 457.
20 B. P. Kotovich, *Khim. Khim. Tekhnol. (cheboksary, USSR)*, 1969, 41.
21 G-U. Wolf and M. Meisel, *Z. Anorg. Allg. Chem.*, 1982, **494**, 49.
22 H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1967, **89**, 1272.
23 M. Meisel and H. Grunze, *Z. Anorg. Allg. Chem.*, 1968, **360**, 277.
24 N. M. Loznikova, Yu. N. Sapozhkov, and K. D. Shvetsova-Shilovskaya, *Zh. Obshch, Khim.*, 1976, **46**, 1761.
25 G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, 1964, **18**, 1623.
26 V. E. Bel'skii, L. A. Khismatullina, T. G. Bykova, A. V. Burykina, and B. E. Ivanov, *Zh. Obshch. Khim.*, 1979, **49**, 344.
27 W. C. Archie and F. H. Westheimer, *J. Am. Chem. Soc.*, 1973, **95**, 5955.