Radical Cations with a Sulphur–Phosphorus 2σ–1σ* Three-electron Bond in Solution

Hartmut Hungerbühler, Shambhu N. Guha and Klaus-Dieter Asmus*

Hahn-Meitner-Institut Berlin, Bereich S, Abteilung Strahlenchemie, Glienicker Strasse 100, D-1000 Berlin 39, Germany

A transient radical cation with an intramolecular sulphur–phosphorus 2σ–1σ* three-electron bond is generated during the oxidation of 1-(diethylphosphino)-3-(methylthio)propane **1** in aqueous solution; it shows an optical absorption at λ_{max} = 385 nm.

It is well established that one-electron oxidized sulphur atoms in organic sulphides generally show a high tendency to be stabilized in S.·.S or S.·.X 2σ–1σ* three-electron bonds by coordination with a second sulphur[1–5] or heteroatom.[6–11]

While numerous experimental data are available for systems with X = halogen, oxygen, nitrogen and selenium,[6–11] no experimental reports exist until now on the stabilization effect of phosphorus in solution. Theoretical calculations suggest though that cationic species of the type $(H_3P.\cdot.SH_2)^+$, for example, should also exhibit a considerable degree of thermodynamic stability.[12,13] Some evidence is also provided in solid matrices.[14]

In this communication we now report on the first experimental verification of a three-electron bonded, $(S.\cdot.P)^+$-type radical cation generated intramolecularly in the ·OH-induced oxidation of 1-(diethylphosphino)-3-(methylthio)propane **1** in aqueous solution. It has been identified on the basis of time-resolved optical absorption and conductivity measurements using the radiation chemical technique of pulse radiolysis.[15] As the pK_a of **1**, with respect to the protonation at phosphorus, was determined to be ≈6.8 by titration in aqueous solution, experiments have been performed with both the protonated and unprotonated species at pH 4.0 and 8.6, respectively.

Figs. 1 (spectrum) and 2(*a*) (absorption–time trace) show optical fingerprints of the transient species obtained upon pulse radiolysis of an N_2O saturated 2 × 10^{-4} mol dm^{-3} aqueous solution of **1** at pH 8.6 recorded immediately after the application of a 1 μs pulse. The absorption band with λ_{max} = 385 nm is assigned to the radical cation **2** formed according to Scheme 1, *i.e.* to a species which contains an intramolecular 2σ–1σ* bond between the sulphur and phosphorus atoms. This assignment is based on the previous information available for similar intramolecular S.·.S or S.·.X species[1,2,7–10] and, with respect to the essential aspects, this is outlined in the following.

Simultaneous time-resolved conductivity measurements at pH 8.6 [Fig. 2(*b*)] show an increase in conductivity revealing the formation of an OH^-–cation pair with kinetic characteristics which correspond to those of the optically absorbing transient.

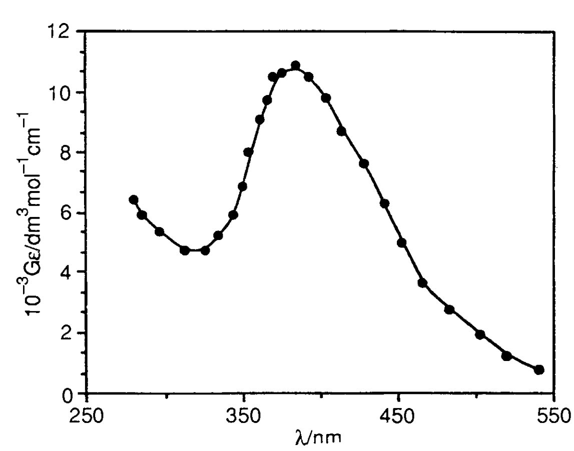


Fig. 1 Absorption spectrum recorded immediately after a 1 μs pulse in an irradiated N_2O-saturated 2 × 10^{-4} mol dm^{-3} aqueous solution of **1** at pH 8.6. (G = 1 equals 0.1 μmol g^{-1}.)

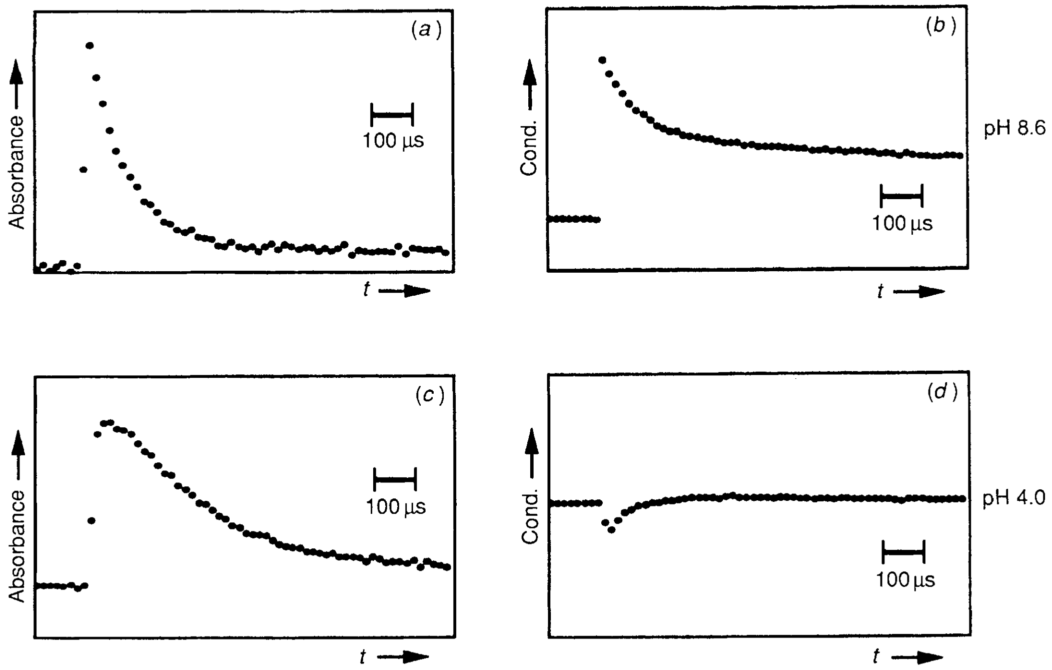
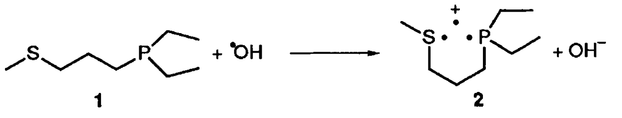
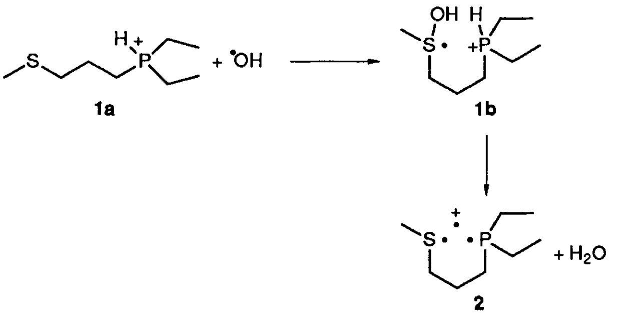


Fig. 2 Absorption-time traces (at λ_{max} = 385 nm) of a pulse-irradiated N_2O-saturated 2 × 10^{-4} mol dm^{-3} aqueous solution of **1** at pH 8.6 (*a*) and pH 4.0 (*c*); corresponding conductivity-time traces at pH 8.6 (*b*) and pH 4.0 (*d*)

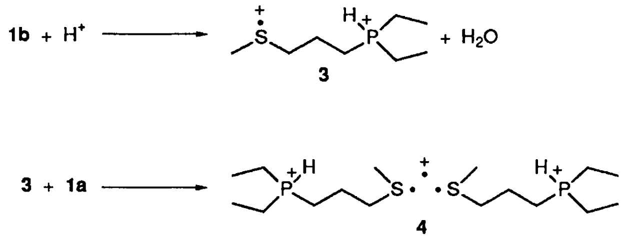


Scheme 1 pH 8.6



Scheme 2 pH 4.0

For protonated phosphorus at pH 4.0, the 385 nm band was also observed. In this case the growth of the absorption is somewhat delayed [Fig. 2(*c*)] and reaches its maximum a few µs after the pulse. The proposed mechanism is displayed in Scheme 2 and resembles the features of the ·OH induced oxidation of the nitrogen analogue, 3-methylthiopropylamine.[10] Accordingly, the ·OH radical adds to sulphur, and with the help of the phosphino proton it is subsequently eliminated as a water molecule. This intramolecular process is responsible for the slight delay in the formation of **2**. The lifetime of **2** in acid solution ($t_{1/2}$ = 150 µs) is longer than in a basic environment ($t_{1/2}$ = 70 µs). Time-resolved conductivity measurements at pH 4.0 [Fig. 2(*d*)] show practically no signal change upon the formation of **2**. This is in accord with Scheme 2 which indicates that one type of cationic species is just replaced by another type of cation with similar specific conductivity.



Scheme 3 pH 1.0

Our argument is further supported by the study of solutions at pH 1.0. In this case elimination of the hydroxyl function from the adduct **1b** does not occur intramolecularly but instead by reaction with bulk protons (Scheme 3). The result is oxidation of the sulphur function to a cationic radical centre with the phosphine function still being protonated, **3**. Further stabilisation of this species can only occur intermolecularly by association with another substrate molecule to yield the dimer sulphur–sulphur three-electron bonded species **4**. The transient optical absorption recorded shortly after the pulse at this very low pH differs significantly from that at higher pH and shows a pronounced maximum at 470 nm in full accord with other intermolecular $(S\therefore S)^+$ radical cations.[1,2]

Shortening of the bridge between sulphur and phosphorus to two methylene groups yields an intramolecular radical cation analogous to **2**. In this case sulphur–phosphorus interaction leads to a four-membered ring system which is less favourable with respect to orbital overlap. As has been shown for related dithia compounds (intramolecular sulphur–sulphur interaction) such a conformation results in much weaker three-electron bonds, associated with a considerable red-shift in the absorption (the optical transition is, in first approximation, $\sigma \rightarrow \sigma^*$).[1,2,16] The observed λ_{max} = 480 nm for the intramolecular $(S\therefore P)^+$ type radical cation from 1-(diethylphosphino)-2-(methylthio)ethane thus also supports our assignment. (Time-resolved conductivity measurements at pH 4.0 again show no signal change upon the formation of the intramolecular species.)

The other alternative possibilities as candidates for the absorbing transient from **1**, namely intermolecular phosphorus–phosphorus or sulphur–phosphorus interaction, can be excluded. Firstly, no effect was seen of the concentration of **1** on the 385 nm absorption. Further, employing triethylphosphine alone, an absorption band [almost certainly due to the intermolecular $(P\therefore P)^+$ radical cation] is observed at λ_{max} = 370 nm. Although this differs only by 15 nm from that of the proposed species **2**, it cannot be due to the latter since it is generated only at high pH (>7), and there only at high solute concentration. Finally, experiments conducted with solute mixtures of diethyl sulphide and triethylphosphine, *i.e.* with sulphur and phosphorus in two different molecules, revealed only one broad band peaking around 490 nm [probably due to intermolecular $(S\therefore S)^+$ and, at high pH, possibly also $(S\therefore P)^+$ radical cations] but no band around 385 nm.

In conclusion, our pulse radiolysis experiments on the ·OH radical induced oxidation of 1-(diethylphosphino)-3-(methylthio)propane **1** provides a first experimental example of a transient intramolecular $(S\therefore P)^+$ 2σ–$1\sigma^*$ three-electron bonded radical species in solution.

This work has been supported by the International Bureau of the KfA Jülich within the terms of an agreement on scientific cooperation between Germany and the Republic of India. S.N.G. has been on deputation from Bhabha Atomic Research Centre, Bombay.

Received, 26th April 1991; Com. 1/01978C

References

1 K.-D. Asmus, *Acc. Chem. Res.*, 1979, **12**, 436.
2 K.-D. Asmus, in *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*, ed., C. Chatgilialoglu and K.-D. Asmus, NATO ASI Series, Series A: Life Sciences Vol. 197, Plenum Press, New York, p. 155, 1990.
3 B. C. Gilbert, D. K. C. Hodgeman and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1748.
4 W. B. Gara, J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1444.
5 R. L. Petersen, D. J. Nelson and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1978, 225.
6 M. Bonifačić and K.-D. Asmus, *J. Chem. Soc., Perkin Trans 2*, 1980, 758.
7 E. Anklam, H. Mohan and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.*, 1987, 629.
8 E. Anklam, H. Mohan and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1297.
9 R. S. Glass, M. Hojjatie, G. S. Wilson, S. Mahling, M. Göbl and K.-D. Asmus, *J. Am. Chem. Soc.*, 1984, **106**, 5382.
10 K.-D. Asmus, M. Göbl, K.-O. Hiller, S. Mahling and J. Mönig, *J. Chem. Soc., Perkin Trans. 2*, 1985, 641.
11 H. Fujihara, H. Mima, J.-J. Chiu and N. Furukawa, *Tetrahedron Lett.*, 1990, **31**, 2307.
12 T. Clark, *J. Am. Chem. Soc.*, 1988, **110**, 1672.
13 T. Clark, *J. Comput. Chem.*, 1981, **2**, 261; 1982, **3**, 112; 1983, **4**, 404.
14 R. A. J. Janzen, O. M. Aagaard, M. J. van der Woerd and H. M. Buck, *Chem. Phys. Lett.*, 1990, **171**, 127.
15 K.-D. Asmus, *Methods Enzymol.*, 1984, **105**, 167; 1990, **186**, 168.
16 M. Göbl, M. Bonifačić and K.-D. Asmus, *J. Am. Chem. Soc.*, 1984, **106**, 5984.