BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1423—1424 (1971)

ESR Studies of the $(RO)_2PSS$ Radicals in UV-Irradiated *O,O′*-Dialkyl Dithiophosphate Glasses

Mitsuo SATO, Michiyasu YANAGITA, Yuzaburo FUJITA, and Takao KWAN
Faculty of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku, Tokyo

(Received October 22, 1970)

ESR studies have been reported on γ-irradiated phosphate crystals such as KH_2PO_4, where the formation of the phosphate radical, PO_4^{2-}, was observed, and its electronic nature has been discussed.[1-3] For example, according to Subramanian *et al.*,[3] the phosphate radical showd an isotropic ^{31}P ($I=1/2$) hyperfine splitting in the range of 20—40 gauss, leading one to suggest that 0.6—1.1% spins are localized on the phosphorus 3*s* orbital.

We have investigated the UV-irradiation of *O,O′*-dialkyl dithiophosphate glasses and found that dithiophosphate radical species are formed. The radical showed electronic characteristics quite similar to those of the phosphate radicals, the results will be reported in this note.

Experimental

Four kinds of *O,O′*-dialkyl dithiophosphate $(RO)_2PSSH$, where R is CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9 were synthesized by the reaction of phosphorus pentasulfide with the corresponding alkyl alcohols; they were purified by subsequent distillation under reduced pressure.

Each sample was placed in a quartz tube, 4 mm id, carefully degassed, and then immersed in a quartz Dewar vessel filled with liquid nitrogen. The sample was then irradiated at the temperature of liquid nitrogen with the light of a low-pressure mercury lamp (Ushio Electric Co. UL-200W). After the irradiation, the sample was transferred, without warming, to a Dewar vessel kept inside the microwave cavity; electron-spin resonance measurements were then made with an X-band spectrometer (JES P-10) operated at 100 kHz field modulation.

Results and Discussion

Upon the UV irradiation of *O,O′*-dialkyl dithiophosphates, the ESR signals of the radical species shown in Fig. 1 were observed, along with that of

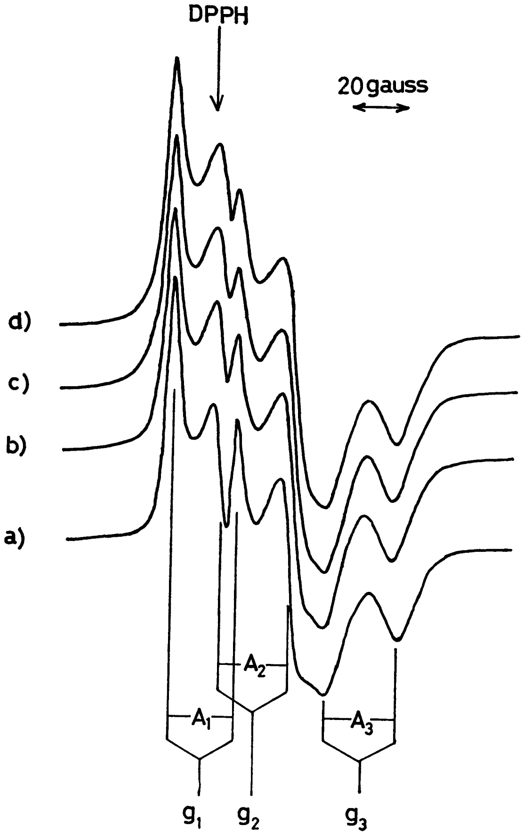

Fig. 1. ESR spectra of dialkyl dithiophosphate radicals. (a) $(CH_3O)_2PSS$, (b) $(C_2H_5O)_2PSS$, (c) $(n$-$C_3H_7O)_2$-PSS, (d) $(n$-$C_4H_9O)_2$ PSS

---

[1] W. E. Hughes and W. G. Moulton, *J. Chem. Phys.*, **39**, 1359 (1963).

[2] R. A. Serway and S. A. Marshall, *ibid.*, **45**, 4098 (1966).

[3] S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc., A.*, **1970**, 1239.

Table 1. ESR constants of dithiophosphate radicals

Radical species	g_1	g_2	g_3	A_1 (gauss)	A_2 (gauss)	A_3 (gauss)
$(CH_3O)_2PSS\cdot$	2.0027	2.0147	2.0407	24.7	25.8	26.1
$(C_2H_5O)_2PSS\cdot$	2.0023	2.0150	2.0400	24.0	26.2	26.1
$(n\text{-}C_3H_7O)_2PSS\cdot$	2.0026	2.0154	2.0397	24.3	27.1	25.8
$(n\text{-}C_4H_9O)_2PSS\cdot$	2.0022	2.0149	2.0397	24.0	26.2	25.8

hydrogen atoms. The spectra were almost identical for all the compounds employed, and the signal intensities increased with the time during 20 minutes' irradiation with little variation in the line shape. Thus, it can be considered that a very similar sort of radical was produced by the liberation of hydrogen atoms. No other photolytic reactions were detectable at least under our experimental conditions.

In the light of the ESR informations on sulfur radicals[4–7] and on phosphate radicals,[1–3] each spectrum in Fig. 1 can be readily interpreted as due to the $(RO)_2$-PSS radical: a triplet due to the anisotropy in the g factor splits to doublets as a result of the action of three canonical components of a hf tensor. The observed g-values and hf coupling constants are listed in Table 1.

It is shown in Table 1 that the g-values are almost identical for all the compounds within the limits of experimental error, and that the g-value shifts (Δg) from that of a free spin (2.0023) are $\Delta g_1=0.000$, $\Delta g_2=0.013$, and $\Delta g_3=0.038$ for g_1, g_2, and g_3 respectively. Generally speaking, this kind of g-value shift depends upon the magnitude of the spin-orbit coupling of an atom with an unpaired electron and increases rapidly with the atomic number. Also, it depends upon the energy separations between the ground state and excited states of the radical. For example, in carbon radicals, including alkyl and aromatic radicals, the g-value shift is relatively small and usually lies within 0.002. On the contrary, much larger shifts have been observed for sulfur radicals[4–7] ($\Delta g_1=0.001$, $\Delta g_2=0.020$—0.030, $\Delta g_3=0.040$—0.60), and for phosphate radicals,[3] most of which exhibit anisotropy with an axial symmetry ($\Delta g_1=\Delta g_2=0.002$—$0.005$, $\Delta g_3=0.010$—0.050).

The unpaired electron of the dithiophosphate radical may not be involved in the alkyl group, because the observed spectra did not show any hf structure due to protons in the alkyl groups (R), irrespective of the variation in R from the methyl to the n-butyl group. Instead, the hf splitting shown in the spectra may be interpreted most reasonably as that of $^{31}P(I=1/2)$, which is common to all the compounds investigated. The hf coupling constant is almost isotropic, in contrast to the g-factor, and its isotropic component of 25.5 gauss is too small for an unpaired electron to be localized on the phosphorus atom, as will be discussed below.

If the unpaired electron is localized on the oxygen atom, one may expect hf splitting or unresolved hf-line broadening due to the protons in the adjacent alkyl group, as in the case of alkoxy radicals.[8] Since the observed spectra do not show any appreciable change with R, it seems very likely that the unpaired electron is localized mainly on the sulfur atom.

It is assumed that the radical is formed by the scission of the S–H bond and that unpaired electrons are confined mainly on the sulfur atom. The structure of the radical is, then, one with C_{2v} symmetry where two P–S bonds are equivalent, and the orbital for the unpaired electron is a non-bonding $3p(\pi)$-orbital of the sulfur atom with a_2 symmetry.[9]

Although the a_2 orbital of the sulfur atom occupied by the unpaired electron does not give the spin density on the phosphorus atom in the first approximation, it is well known that some spin density arises in the $3s$ orbital of the phosphorus atom *via* the mechanism of spin-polarization[10] or that of configurational interaction of P–S σ-electrons.

The isotropic ^{31}P hf coupling constant (A_P) of 25.5 gauss (72.1 MHz) corresponds to the following spin density (f_{3s}) in the $3s$ orbital of the phosphorus atom:

$$f_{3s}=\frac{A_P}{A_P{}^\circ}=\frac{72.1\ (\mathrm{MHz})}{10178\ (\mathrm{MHz})}\simeq 0.7\%$$

where $A_P{}^\circ$ (10178 MHz) is the calculated hf coupling constant for an electron in the phosphorus $3s$ orbital.[11] As is shown above, the calculated spin density, f_{3s}, for the dithiophosphate radical nearly coincides with those for phosphate radicals (0.6—1.1%[3,12]).

The value of f_{3s} may reflect the extent of the spin polarization and the $3s$ character of phosphorus in the P–S σ-orbital.[10] Thus, it may be suggested that the extent of spin-polarization and the $3s$ character of phosphorus are nearly the same in both dithiophosphate and phosphate radicals.

---

4) J. J. Windle, A. K. Wirsema, and A. L. Tappel, *J. Chem. Phys.*, **41**, 1996 (1964).

5) Y. Kurita and W. Gordy, *ibid.*, **34**, 282 (1961).

6) D. A. Stiles, W. J. R. Tyerman, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **44**, 2149 (1966).

7) M. Yanagita, Y. Fujita, and T. Kwan, *Nippon Kagaku Zasshi*, **91**, 898 (1970).

8) L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **32**, 1107 (1960).

9) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam (1967).

10) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

11) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964): G. W. Chantry, A. H. Horsfield, J. R. Morton, J. R. Lowlands, and D. H. Wiffen, *Mol. Phys.*, **5**, 233 (1962).

12) T. F. Hunter and M. C. R. Symons, *J. Chem. Soc.*, *A*, **1967**, 1770.