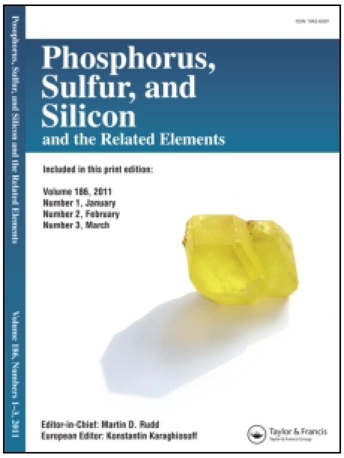

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SULFUR-CENTERED RADICALS IN UV-IRRADIATED PHOSPHORODITHIOATES

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SULFUR-CENTERED RADICALS IN UV-IRRADIATED PHOSPHORODITHIOATES

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Some bis(dialkoxythiophosphoryl) disulfides and bis(dialkyl phosphorodithioato) ammonium and potassium salts have been irradiated in pure solid state by mercury high pressure lamp at 77 K. Depending on the sample methyl and sulfur-centered radicals are produced. The sulfur radicals are identifed as thio radicals [$(RO)_2P(S)S^{\cdot}$].

Keywords: Phosphorodithioates; UV-irradiation; sulfur-centered radicals

INTRODUCTION

Sulfur-centered radicals have been proposed as possible intermediates in the decomposition of more complex sulfur-containing compounds, e.g. phosphorodithioates, which are used as antioxidants. This provokes the intend to study by EPR the different paramagnetic species formed after irradiation of pure compounds or their solutions. It has been found that after UV-irradiation of some O,O'-dialkyl hydrogen phosphorodithioates at 77 K an intense signal of sulfur radicals appears[1]. The signal has been attributed to the radical $(RO)_2P(S)S^{\cdot}$ on the basis of principal values of g-factor and on the hyperfine interaction with one phosphorus nucleus.

When photolysed solid samples of bis(dialkoxythiophosphoryl) disulfides $[(RO)_2P(S)S]_2$ (R = Et and R = ^{i}Pr) were studied, an EPR signal with three broad lines was detected[2]. This signal was attributed to dithioradical $(RO)_2P(S)SS^{\cdot}$. The author's statement is that for this radical any

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phosphorus splitting would be expected to be small, and therefore, not resolved in the EPR spectrum.

However when other phosphorodithioate compounds were studied after UV-irradiation in solid powder state the results call in question the formation of dithioradical, as assumed previously. The most probable structure of the obtained radical seems to be the thio radical $(RO)_2P(S)S^{\cdot}$. Here we report these data.

EXPERIMENTAL

The ammonium salts of O,O'-dimethyl and -diethyl hydrogen phosphorodithioates were commercially available (from Merck and Aldrich respectively) and were used without further purification. The other salts were prepared according the procedure described in [3] . The disulfides were prepared by oxidation of the ammonium salts with aqueous solution of iodine and potassium iodide[4].

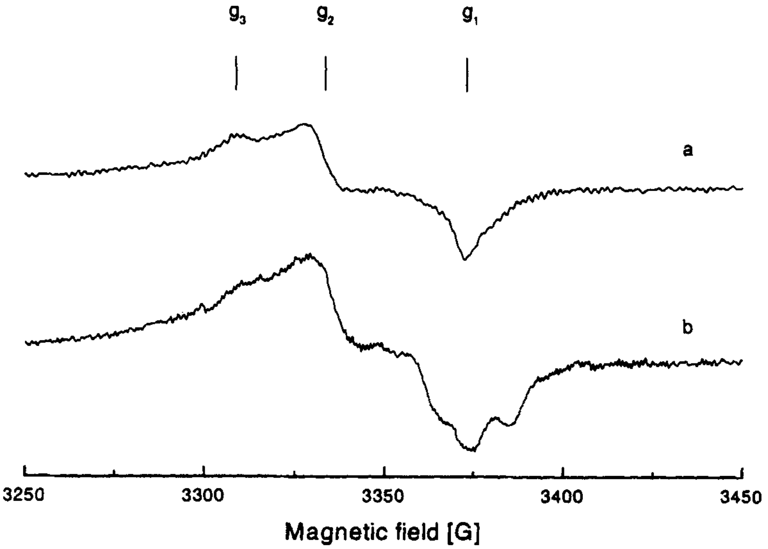

FIGURE 1 EPR spectra at 77 K of UV-irradiated: a) $(EtO)_2P(S)SNH_4$ and b) $(MeO)_2P(S)SNH_4$

TABLE I EPR parameters of dialkoxy (thiophosphoryl)thio radicals $[(\mathrm{RO})_2\mathrm{P(S)S}^{\cdot}]$ from photolysed pure solid samples at 77 K

compound	*g*	*A(P) [G]*	*ref.*
$(\mathrm{MeO})_2\mathrm{P(S)SNH_4}$	$g_1 = 1.9877$	$A_1 = 10.3$	this work
	$g_2 = 2.0142$	$A_2 = 26.4$	
	$g_3 = 2.0278$	$A_3 = 39.1$	
$(\mathrm{EtO})_2\mathrm{P(S)SNH_4}$	$g_1 = 1.9980$		this work
	$g_2 = 2.0242$		
	$g_3 = 2.0405$		
$[(\mathrm{MeO})_2\mathrm{P(S)S}]_2$	$g_1 = 1.9904$	$A_1 = 12.0$	this work
	$g_2 = 2.0145$	$A_2 = 25.8$	
	$g_3 = 2.0280$	$A_3 = 37.6$	
$[\mathrm{EtO})_2\mathrm{P(S)S}]_2$	$g_1 = 2.0024$		[2]
	$g_2 = 2.0259$		
	$g_3 = 2.041$		
$[(^i\mathrm{PrO})_2\mathrm{P(S)S}]_2$	$g_1 = 2.0005$		this work
	$g_2 = 2.0245$		
	$g_3 = 2.0395$		
$[(^i\mathrm{PrO})_2\mathrm{P(S)S}]_2$	$g_1 = 2.0022$		[2]
	$g_2 = 2.0251$		
	$g_3 = 2.039$		
$[(\mathrm{MeO})_2\mathrm{P(S)SK}$	$g_1 = 2.001$		this work
	$g_2 = 2.024$		
	$g_3 = 2.040$		

The samples were irradiated at 77 K with a mercury high pressure lamp for 15 min. After irradiation the samples were transferred without warming up in a small quartz dewar for EPR mesurments at liquid nitrogen temperature. EPR spectra were recorded on a X-band Bruker B-ER420 spectrometer with 100 kHz modulation.

RESULTS AND DISCUSSION

Bis(diisopropoxythiophosphoryl) disulfide – $[(^iPrO)_2P(S)S]_2$

Only one radical can be identified from an UV-irradiated solid powder sample of this disulfide. The anisotropic EPR spectrum has parameters $g_1 = 2.0025$, $g_2 = 2.0245$, $g_3 = 2.0395$. When comparing these g-values with the g-values reported in ref. 2 and shown in Table I, it is evident that we are dealing with the same radical. Its EPR parameters are typical for a thio radical in which the unpaired electron is localized on sulfur[5].

The disulfide can produce two different sulfur-centered radicals. One of them is a simple thio radical $(RO)_2\,P(S)S^{\cdot}$ formed via homolytic scision of the bond S-S. The second radical which is possible to be obtained, is the dithioradical $(RO)_2P(S)SS^{\cdot}$, in which the S-S bond is not destructed. Which of these two possibilities is realised after UV-irradiation will be discussed later in this section.

Bis(diethylphosphorodithioate) ammonium – $[(EtO)_2P(S)S]NH_4$

The UV-irradiated commercially available ammonium salt reveals an EPR spectrum which has the same shape and nearly the same principal g-values as the disulfide. The spectrum is shown in Fig. 1. The appearance of this EPR spectrum in the sample can not be due to dithio radical, because such structure does not exist in the salt. The only possible radical, which can be found after UV-irradiation, is the thio radical. For supporting these data other dithiophosphoric salts were investigated.

Bis(dimethylphosphorodithioate) ammonium, $[(MeO)_2P(S)S]NH_4$, and bis(dimethylphosphorodithioate) potassium, $[(MeO)_2P(S)S]K$

The EPR spectra of these two compounds are more complex and at least two different spectra can be distinguish. One of them is characterised with lines much narrower than those in the second one. This is the EPR spectrum of methyl radical $^{\cdot}CH_3$. The parameters of this radical are $g = 2.0018$; $A = 22.9$ G for $[(MeO)_2P(S)S]K$ and $g = 2.0020$; $A = 23.0$ G for $[(MeO)_2P(S)S]NH_4$. The spectrum of the methyl radical is dominant in the irradiated potassium salt.

The second EPR spectrum has broad lines and is very similar to that observed in $[(EtO)_2P(S)S]NH_4$ which was attributed to the thio radical. For better determination of EPR parameters of this spectrum, the methyl radical EPR spectrum was extracted and the manipulated spectrum is shown in Fig. 1.

It should be noticed that the relative intensity ratio for the two radicals is different – in the potassium salt the methyl radical is more intense than the thio radical, while it is vice versa for the ammonium salt. For that reason it is difficult to observe whether the sulfur radical in irradiated potassium salt has hyperfine structure, due to phosphorus interaction.

The observed radicals can be divided into two groups. The first group contains the sulfur-centered radicals whose characteristic spectra have considerable *g*-anisotropy. The second one contains the alkyl radicals which are isotropic and in this series of experiments are represented only by the methyl radical. No other alkyl radicals were recorded. Further we will discuss the formation only of the sulfur radicals.

One question which appears is what is the nature of the sulfur-centered radical. In general two modes of decomposition giving such radicals are possible for disulfides:

$$\mathrm{RSSR} + \mathrm{h}\nu \rightarrow 2\mathrm{RS}^{\cdot} \qquad (1)$$

$$\mathrm{RSSR} + \mathrm{h}\nu \rightarrow \mathrm{RSS}^{\cdot} + \mathrm{R}^{\cdot} \qquad (2)$$

while for acids and salts it is only one:

$$\mathrm{RSH} + \mathrm{h}\nu \rightarrow \mathrm{RS}^{\cdot} + \mathrm{H}^{\cdot} \qquad (3)$$

In earlier publication[2] the radical, formed upon UV-irradiation of bis (diisopropoxythiophosphoryl) disulfide has been assigned to a dithio radical formed by pathway (2). This assignement seems to be logical but the observation of a similar (if not the same) radical after irradiation of bis(diethylphosphorodithioato) ammonium salt rule out this possibility. We believe that most probably this is a radical formed by homolytic cleavage of the S-S bond (1). Similar observations were made for other organic disulfides. It has been found that the primary dialkyl disulfide undergo 1% C-S cleavage and 99% S-S cleavage[6]. A higher yield of C-S cleavage has been reached with tertiary disulfides.

Additional support of the proposed mechanism is the simple shape of the radical. As has been reported in ref. 7 the disulfide radicals $RSS^{\cdot}$ exist in two conformations with slightly differing *g*-values. This reflects in a four-lines pattern of the EPR spectrum, which in our case was not detected.

Of course, if a simple thio radical is formed, we can expect some delocalisation of the unpaired electron on the phosphorus atom which will reflect on the EPR spectra as hyperfine splitting due to this interaction. These EPR spectra would be similar to those observed for irradiated O,O'-dialkyl hydrogen phosphorodithioates. Indeed the observed sulfur radicals in the irradiated bis (dimethoxythiophosphoryl) disulfide and bis (dimethylphosphorodithioato) ammonium salt have EPR parameters close to those reported in ref. 1. The radical in the ammonium salt shows larger anisotropy, although the isotropic hyperfine constant does not change too much (A_{iso} = 25.5 G as reported in ref. 1 for the O,O'-dimethyl hydrogen phosphorodithioate and A_{iso} = 25.3 G for the ammonium salt).

This is not the case for the compounds with ethyl substituents. Although we can expect nearly the same interaction with the phosphorus, the EPR spectrum does not show any phosphorus splitting. This experimental fact is difficult to be explained, having in mind that the thio radicals in the corresponding UV-irradiated dialkyl hydrogen phosphorodithioates show phosphorus splitting[1]. Of course, it should be noticed that even in this case the phosphorus splitting is remarkably low. It corresponds to a percentage s-orbital occupancy of the unpaired electron on phosphorus of *ca.* 0.7%, which probably arises via spin polarization of the S-P bond from unpaired electron density in sulfur *p*-orbitals. Most probably the alkyl substituents play an important role on the electron spin delocalisation in the radical acting on the S-P bond polarization. From the EPR experiment we can conlude that only for R = CH_3 this polarization is high enough that the phosphorus splitting could be recorded. This is the reason that these thio radicals have been assigned previously to dithio radicals.

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