Methyl Phosphono- and (Thiophosphono)dithioformate as Radical Trapping Agents

Jocelyne Levillain,† Serge Masson,† Andrew Hudson,‡ and Angelo Alberti*,§

Contribution from Laboratoire de Chimie des Composés Thio-organiques, ISMRA, F-14050 Caen, France, School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, U.K., and ICoCEA—CNR, I-40064 Ozzano Emilia, Italy

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Abstract: The addition of a number of alkyl, alkoxy, thiyl, and organometallic radicals to the title compounds has been investigated by means of EPR spectroscopy. In all cases the reactions resulted in the regiospecific thiophilic attack of the radical at the thiocarbonyl group of the substrates, leading to rather persistent spin adducts. The only exception to this behavior was provided by manganese decacarbonyl, which only reacted with the thiophosphono derivative, yielding a dinuclear adduct for which, by analogy with previous studies, a cyclic structure has been proposed.

Introduction

Phosphonodithioformates (or phosphomethanedithioates) are functionalized dithioesters easily prepared from dialkyl phosphite and carbon disulfide.[1] Previous studies[2-4] related to the addition of nucleophiles (organometallics, trialkyl phosphites, thiolates) to the thiocarbonyl group of these compounds have shown that the phosphonyl moiety favors the thiophilic attack and stabilizes the resulting sulfur-substituted carbanions. The same thiophilic attack and stabilization could, of course, be expected for the addition of radicals to the phosphonodithioformates. We now report the results of an electron paramagnetic resonance (EPR) spectroscopic study of the addition of a variety of free radicals to methyl (diethylthiophosphono)dithioformate (**1**) and methyl (diethylphosphono)dithioformate (**2**).

Results and Discussion

Reactions with Organic and Organometallic Radicals. (Thiophosphono)- and phosphonodithioformates contain two unsaturated groups which might, in principle, undergo radical addition, *i.e.* at the C=S double bond and the P=S or P=O double bond. While radical addition to the latter groups to form phosphoranyl radicals has never been reported, thiocarbonyl compounds, such as thiones or thioaldehydes, are known to readily undergo addition by a variety of different radicals, ranging from nucleophilic carbon-centered radicals such as $(CH_3)_3^{\bullet}$ to electrophilic alkylthiyl and alkoxy radicals.[5,6] Indeed the organometallic thioketone (thiobenzoyl)triphenylsilane was recently reported to be an extremely efficient radical scavenger, only its insolubility in water preventing it from being the "philosopher's stone" among diamagnetic scavengers desired by the *trappist* community.[7]

Reaction of compounds **1** and **2** with radicals generated by *in situ* photolysis of dialkyl or diaryl mercurials yields EPR spectra characterized by coupling of the unpaired electron with a single phosphorus nucleus and the three equivalent protons of a methyl group. The magnitude of the ^{31}P splitting lies within the expected range for a phosphorus atom adjacent to a π-radical center on carbon.[8,9] Moreover, the methyl, benzyl (Figure 1), and *tert*-butyl radicals exhibit additional interaction with three, two, and nine equivalent protons, respectively. The hyperfine splittings (Table I) are thus consistent with formation of adducts **A**. Further confirmation for this assignment is provied by the observation of coupling to six equivalent protons in the methyl adducts **A** (X = Me), as expected if the two methyl groups are equivalent.

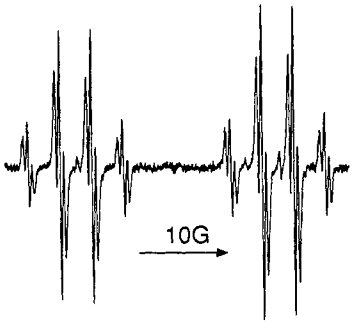
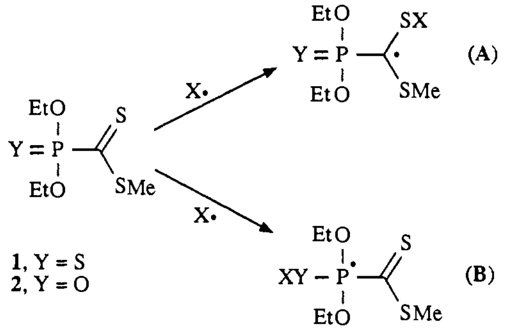


Figure 1. Room temperature EPR spectrum of the benzyl adduct of (thiophosphono)dithioformate **1**.



Oxygen- and sulfur-centered radicals, produced by photolysis of peroxides and disulfides, also react with **1** and **2** to give adducts **A** (X = O^{t}Bu, SMe, SPh). The assignment is supported by the observation of additional hyperfine structure of appropriate magnitude[6] from protons in the methyl and *tert*-butyl groups.

The ease of trapping of *tert*-butoxy radicals posed problems when we attempted to add silyl and germyl radicals, since these are generated by the reaction of *tert*-butoxyl with a silane or germane. Previous work has shown[6] that the rate of addition of alkoxyls to thiones is very fast, and not unexpectedly the spectrum

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† ISMRA.
‡ University of Sussex.
§ ICoCEA—CNR.

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Table I. Room Temperature Spectral Parameters[a] for the X• Adducts of Dithioformates **1** and **2**

compd	X	*a*(P)	*a*(CH_3)	*a*(other)	*g*
1	CH_3	21.50	2.31	2.31(3H)	2.0060
	$CH_2C_6H_5$	21.72	3.40	0.51(2H)	2.0060
	$C(CH_3)_3$	23.25	4.05	0.55(9H)	2.0060
	C_6H_5	21.91	4.21		2.0060
	$OC(CH_3)_3$	16.15	3.04	0.29(9H)	2.0055
	SCH_3	20.00	4.20	1.04(3H)	2.0061
	SC_6H_5	19.27	4.13		2.0059
	$Si(C_6H_5)_3$	22.26	3.89		2.0060
	$Ge(C_6H_5)_3$	24.01	3.43		2.0061
	$Sn(C_6H_5)_3$	21.97	3.15		2.0055
	$Pb(C_6H_5)_3$	21.81	3.47		1.9997
2	CH_3	22.13	2.38	2.38(3H)	2.0060
	$CH_2C_6H_5$	22.34	3.26	0.73(2H)	2.0060
	$C(CH_3)_3$	24.29	4.31	0.54(9H)	2.0061
	C_6H_5	24.53	2.40		2.0060
	$OC(CH_3)_3$	18.67	3.28	0.39(9H)	2.0054
	SCH_3	22.25	4.39	1.00(3H)	2.0060
	SC_6H_5	21.61	4.35		2.0059
	$Si(C_6H_5)_3$	22.51	3.71		2.0061
	$Ge(C_6H_5)_3$	24.07	3.53		2.0062
	$Sn(C_6H_5)_3$	21.99	2.57		2.0064
	$Pb(C_6H_5)_3$	22.48	2.98		2.0019

[a] Coupling constants in gauss = 10^{-4} T. [b] Tentative assignments due to very weak and confused signals.

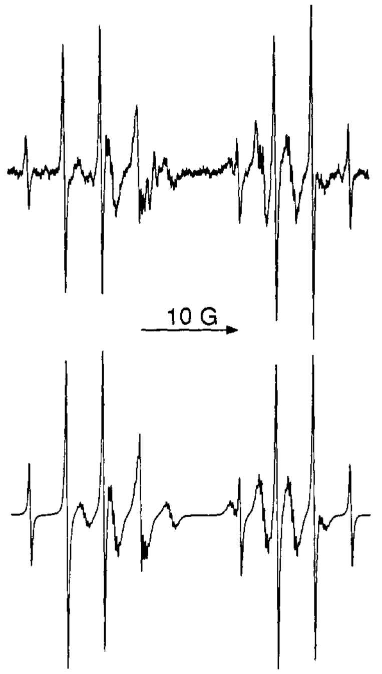


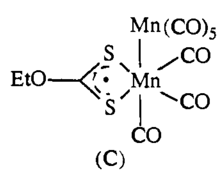
Figure 2. Experimental (top) and simulated (bottom) EPR spectra of a mixture of the *tert*-butoxyl and triphenylsilyl adducts of (thiophosphono)dithioformate **1** recorded in benzene at room temperature.

obtained on photolysis of a benzene solution containing **1**, triphenylsilane, and di-*tert*-butyl peroxide clearly shows (Figure 2) the presence of both adducts. In the presence of excess peroxide only the *tert*-butoxyl adducts of **1** and **2** were observed. Because *tert*-butoxyl reacts more rapidly with germanes than with silanes, it was possible to obtain "clean" spectra of the triphenylgermyl adducts by using a low concentration of the peroxide. The same method proved successful to obtain the triphenyltin adducts using triphehylstannane as a source of triphenylstannyl radicals. However, attempts to add tributylstannyl radicals, formed by photolysis of hexabutylditin, led to te observation of a series of complex spectra consisting of several overlapping signals which have not yet been assigned.

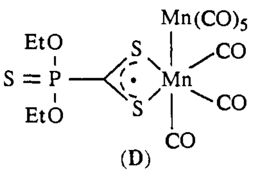
The addition of lead-centered radicals was more straightforward because, although two species were observed on irradiation of solutions of **1** or **2** and hexaphenyldilead in benzene, in each case one spectrum proved to be identical with that of the adducts produced using diphenylmercury as a source of phenyl radicals. It would appear that under our experimental conditions both metal–metal and metal–carbon bond homolysis is occurring. The spectra assigned to the lead adducts are characterized by a low *g* factor (1.9997), similar in magnitude to values previously reported for adducts of lead radicals to thiones.[6,10]

Reaction with Dimanganese Decarbonyl. In previous studies using thiocarbonyl compounds, it has proved possible to trap metal-centered radicals derived from metal carbonyls.[6,11] Thus, photolysis of $Mn_2(CO)_{10}$ gives adducts of $^{\bullet}Mn(CO)_5$ characterized by a sextet splitting from a single ^{55}Mn nucleus. However, quite different behavior was observed when we attempted to add $^{\bullet}Mn(CO)_5$ radicals to **1**. When a solution of $Mn_2(CO)_{10}$ and **1** in benzene was irradiated for a short time (*ca.* 10 s), an EPR spectrum was observed which grew in intensity after the cessation of photolysis and persisted for at least 30 min. The spectrum, which exhibited a marked asymmetric line width effect with the sharpest lines at high field, could be analyzed in terms of coupling to two nonequivalent ^{55}Mn nuclei (10.2 and 3.8 G) and a single nucleus with spin $^1/_2$ (13.3 G). The *g* value was 2.0122.

There are precedents for this type of behavior in the literature. A species observed during the photochemical reaction of dimanganese decarbonyl with nitrosodurene in toluene exhibited manganese splittings of 9.9 and 3.3 G in addition to a nitrogen splitting of 16.7 G.[12] The spectrum was tentatively assigned to an adduct of the $Mn_2(CO)_9^+$ cation. A spectrum observed[13] during the photolysis of a toluene solution of bis(ethoxy(thiocarbonyl)) sulfide and an excess of dimanganese decacarbonyl also showed two different manganese splittings (6.7 and 2.46 G) as well as coupling to two equivalent protons (2.46 G). The *g* value was 2.0128. The spectrum was provisionally assigned to structure **C**.



(C)



(D)

The similarity of the *g* values and coupling constants suggests that we are dealing with a structurally related species, which we tentatively identify as **D**.

The formation of such a species is certainly not easy to rationalize. If an adduct of type **A** were initially formed through addition of a photogenerated $^{\bullet}Mn(CO)_4Mn(CO)_5^+$ radical, the loss of the methyl group might take place in a fashion analogous to the cleavage of the R–O bond in the adducts formed in the Barton–McCombie reaction;[14] on the other hand, a similar fragmentation does not seem to take place in the other adducts **A**. An electron-transfer process might instead take place with formation of the $[Mn_2(CO)_{10}]^{\bullet +}$ radical cation and of the dithioformate radical anion, whose subsequent fragmentation by loss of a methyl radical would lead to an anion which might then condense with the radical cation affording the adduct **D** and carbon monoxide.

Unexpectedly, the reaction of **2** under similar conditions did not lead to any EPR signals.

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Conclusions

The results of this initial investigation suggest that phosphon- and (thiophosphono)dithioformates may have a useful potential as spin traps. The radical adducts are characterized by substantial hyperfine splittings from ^{31}P and g factors which are sensitive to the nature of the attacking radical. The persistence of adducts from **1** to **2** is not sufficient for these particular compounds to have widespread applications as trapping agents, but it should be possible to increase the lifetime of the adducts by introducing bulky substituents. Alkoxy radicals derived from VOCs (volatile organic compounds) are important intermediates in photochemical smog formation, and the ease of trapping of such species suggests the possibility of developing a method for estimating their concentration in polluted atmospheres. The spectra shown in Figure 2 indicate that it is straightforward, using these dithioformates as trapping agents, to estimate the concentration of alkoxy radicals in the presence of other paramagnetic species, but kinetic studies are required in order to develop a quantitative method.

Experimental Section

Materials. Methyl (*O,O*-diethylthiophosphono)methanedithioate (**1**) and methyl (diethylphosphono)methanedithioate (**2**) were prepared by reaction of *O,O*-diethyl thiophosphite or diethyl phosphite sodium salts with CS_2 followed by methylation, according to the method described by Grisley *et al.*[1] Diethyl phosphite was prepared following a published procedure,[15] whereas group 14 organometallic compounds, mercurials, disulfides, and di-*tert*-butyl peroxide were commercially available.

EPR Experiments. The spectra were recorded on a Bruker ER200D spectrometer equipped with an NMR gauss meter for magnetic field calibration. A Systron Donner 6245A frequency counter was used for the determination of g factors, which were corrected with respect to that of the perylene radical cation in concentrated sulfuric acid. A standard variable temperature accessory was also available to control the temperature inside the EPR cavity. When needed, UV irradiation of the samples was performed by focusing the light of a 1-kW high-pressure mercury lamp into the microwave cavity. Infrared radiation was removed by filtering with an aqueous solution of $NiSO_4$ and $CoSO_4$.

Typical samples consisted of quartz tube (i.d. = 4 mm) containing argon-purged benzene solutions of the dithioformates (*ca.* 10^{-3} M) and the reactants necessary for the generation of the attacking radicals. In particular, carbon-centered radicals such as methyl, benzyl, or phenyl were obtained by *in situ* photolysis of the corresponding mercurials, while thiyl radicals ($MeS^\bullet$, $PhS^\bullet$) and *tert*-butoxyl were generated by photocleavage of the appropriate disulfides or peroxide. Triphenylsily, triphenylgermyl, and triphenylstannyl radicals were obtained by hydrogen abstraction from the corresponding hydrides by $^tBuO^\bullet$ radicals, and triphenylplumbyl was photolytically produced from the corresponding dimer.

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