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AN ESR STUDY OF THE PHOTOREACTION OF NITROALKANES WITH TETRAPHENYLBIPHOSPHINE AND TETRAETHYLPYROPHOSPHITE

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Abstract—Some paramagnetic species formed in the photoreactions of nitroalkanes with P-compounds have been characterized by ESR. The observed radicals are mostly nitroxides whose structures are consistent with the trapping of P-centred radicals by intermediate nitroso compounds.

The reactions of P-centred radicals with compounds containing unsaturated bonds such as C═C,[1] C═O,[2] and C═N[3] have been extensively investigated by ESR spectroscopy. There have, however, been relatively few reports of free radical reactions of nitroso compounds[4] with P-compounds and we are unaware of any previous studies involving the nitro group. The latter is known[5] to be an efficient spin trap for silyl radicals. We have used ESR spectroscopy to characterise paramagnetic species formed during the photochemical reactions of nitroalkanes RNO_2 (R = Me, Et, n-Pr, i-Pr, t-Bu) with tetraphenylbiphosphine (TPBP) and tetraethylpyrophosphite (TEP), both in the presence and absence of di-t-butylperoxide (DTBP).

EXPERIMENTAL

The nitroalkanes, TPBP, and TEP were commercially available samples. The ESR spectra were recorded on a Bruker ER200 spectrometer equipped with an NMR gaussmeter and microwave frequency counter for precise measurement of g-factors and hyperfine coupling constants. Samples were photolysed within the cavity of the spectrometer using a high pressure 1 kW mercury lamp.

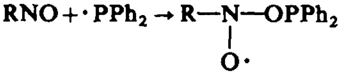
RESULTS AND DISCUSSION

We shall consider the reactions of nitroalkanes with TPBP and TEP separately since they lead to different paramagnetic species via different mechanisms.

Reactions with tetraphenylbiphosphine

Photolysis of deoxygenated benzene solutions of the five aforementioned nitroalkanes and TPBP at, or slightly below, room temperature led in all cases to the detection of ESR spectra characterised by similar nitrogen hyperfine couplings (11.0–11.6 G) and g-factors (2.0066). The spectra also exhibited an additional splitting with the multiplicity expected for the number of β-protons present in the alkyl group R; a further doublet, consistent with the presence of a single ^{31}P nucleus was also resolvable. The magnitude of this splitting decreased with increasing size of R from 4.5 G when R = Me to near zero when R = t-Bu. The spectral parameters of these species (Ia–Ie) are collected in Table 1. For the two cases, R = i-Pr and R = t-Bu, the ESR spectra demonstrated the formation of an additional radical species (IId, e) with $a_N \simeq 10$ G and $a_P \simeq 12$ G (Table 1). The intensity of this signal increased upon prolonged irradiation.

Our initial aim in these experiments was to observe direct addition of phosphinyl radicals to the aliphatic nitro compounds. By analogy with the known behaviour of silyl radicals, we might expect to form an alkylphosphinyloxynitroxide (III).



$$RNO + \cdot PPh_2 \rightarrow R{-}\underset{\displaystyle O\cdot}{\underset{|}{N}}{-}OPPh_2 \qquad (1)$$

(III)

However, these radicals would be expected[6] to exhibit a larger ^{14}N hyperfine coupling constant than is observed for either species I or II, and we reject such an assignment. Further support for this view comes from experiments using nitroso compounds (*vide infra*).

Since the observed radicals do not appear to be directly derived from the nitroalkanes, we must consider an alternative pathway. The most likely route

Table 1. ESR spectral parameters for paramagnetic species observed during the photolysis of RNO_2 with TPBP in benzene at room temperature

Radical	R	a_H	a_N	$a_{^{31}P}$	g
Ia	Me	11.61	11.61	4.53	2.0066
Ib	Et	8.40	11.30	2.72	2.0065
Ic	n-Pr	8.11	10.98	2.68	2.0067
Id	i-Pr	3.26	11.24	0.98	2.0066
Ie	t-Bu	—	11.30	n.r.†	2.0066
IId	i-Pr	2.48	10.01	12.12	2.0068
IIe	t-Bu	—	10.51	11.59	2.0066

† $a_{^{31}P} < 0.1$ G at 298 K; $a_{^{31}P} = 0.31$ G at 363 K.

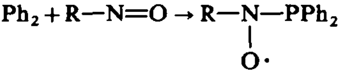
involves the intermediate formation of a nitroso compound. Nitro compounds are known to undergo deoxygenation by P (III) compounds to give the corresponding nitroso derivatives.[7]

$$\mathrm{RNO_2 + PR_3 \rightarrow RNO + OPR_3} \qquad (2)$$

These highly reactive spin traps might also be derived by photolysis of the nitro compound. We have, therefore, also examined the reaction of t-BuNO with TPBP. The ESR spectrum exhibited the presence of the two species formed in the reaction with t-$BuNO_2$ and three additional lines due to di-t-butylnitroxide. It would thus appear that the paramagnetic species I and II result from the reaction of TPBP with nitrosoalkanes rather than the starting nitroalkanes.

The most obvious reaction sequence would involve photolytic homolysis of the P—P bond followed by addition of the resulting phosphinyl radicals to the N=O bond.

$$\mathrm{P_2Ph_4 \rightarrow 2\cdot PPh_2} \qquad (3)$$



$$\mathrm{\cdot PPh_2 + R{-}N{=}O \rightarrow R{-}\underset{\displaystyle O\cdot}{\underset{|}{N}}{-}PPh_2} \qquad (4)$$

(II)

By analogy with related C-centred radicals,[8] alkylphosphinylnitroxides would be expected to exhibit significant ^{31}P coupling constants. Only radicals IId and IIe are consistent with this requirement. Such an assignment is supported by the literature data on related radicals.[4a,c]

The identification of the radicals Ia–Ie which exhibit only a small ^{31}P coupling constant is less straightforward. We have already rejected the possible formation of an alkylphosphinyloxynitroxide (III). This view is reinforced by the observation that the same radical is formed starting from either t-$BuNO_2$ or t-BuNO. Addition of the phosphinyl radical $\dot{P}Ph_2$ to the O atom of the nitroso group to give phosphinyloxyaminyls can also be eliminated. Radicals of this type typically[9] exhibit a ^{14}N splitting of *ca* 15 G, a g-factor close to 2.0047 and a larger coupling to the alkyl protons than we find for species Ia–Ie.

$$\mathrm{R{-}N{=}O + \cdot PPh_2 \rightarrow R{-}\dot{N}OPPh_2} \qquad (5)$$

We consider it possible that species Ia–Ie are actually formed by an electron transfer mechanism. A similar process has already been proposed to account for the formation of the nitrosodurene radical anion in the reaction of nitrosodurene with triarylphosphines.[10] It is noteworthy that the t-$BuNO^{\dot{-}}$ radical anion produced by reduction of 2-methyl-2-nitrosopropane with potassium t-butoxide in toluene[11] has a N-splitting (11.5 G) and g-factor (2.0064) very close to those of radical Ie obtained by photolysis of t-BuNO or t-$BuNO_2$ in the presence of TPBP. We tentatively suggest the formation of radical ion-pairs in which the counterion is a substituted phosphonium cation.

$$\mathrm{R{-}NO^{\dot{-}}\,\overset{+}{P}Ph_2XY}$$

(Ia–Ie)

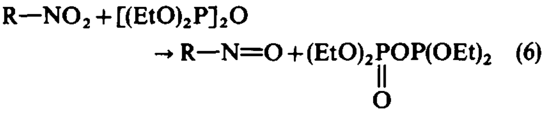
These species could account for the rather small ^{31}P splittings and their decrease with increasing size of the alkyl group R. A more bulky R would decrease contact between the radical anion and the phosphonium cation.

Table 2. ESR spectral parameters for the nitroxides $RN(\dot{O})P(O)(OEt)_2$ observed during photolysis of RNO_2 with TEP in benzene at room temperature

Radical	R	a_H	a_N	$a_{^{31}P}$	g
IVa	Me	11.03	9.39	13.40	2.0068
IVb	Et	7.55	9.19	13.21	2.0068
IVc	n-Pr	7.42	9.20	13.42	2.0068
IVd	i-Pr	2.34	9.30	13.21	2.0068
IVe	t-Bu	—	9.85	12.93	2.0068

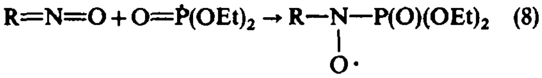
Reactions with tetraethylpyrophosphite

The room temperature photolysis of benzene solutions of the nitroalkanes containing TEP and DTBP led in all cases to the formation of nitroxides IVa–IVe with $a_N \simeq 9.5$ G, $a_P \simeq 13$ G and $g \simeq 2.0068$. Further structure due to primary protons of the alkyl groups was also resolvable. Since in the case of R = t-Bu the same spectrum is obtained starting from the nitroso compound[12] in place of t-$BuNO_2$, we assign these radicals the general structure $RN(\dot{O})P(O)(OEt)$. A possible reaction sequence could be



$$\mathrm{R{-}NO_2 + [(EtO)_2P]_2O \rightarrow R{-}N{=}O + (EtO)_2\underset{\displaystyle O}{\underset{\|}{P}}OP(OEt)_2} \qquad (6)$$

$$\mathrm{t\text{-}BuO\cdot + [(EtO)_2P]_2O \rightarrow O{=}\dot{P}(OEt)_2 + t\text{-}BuOP(OEt)_2} \qquad (7)$$

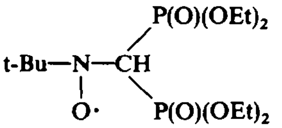


$$\mathrm{R{=}N{=}O + O{=}\dot{P}(OEt)_2 \rightarrow R{-}\underset{\displaystyle O\cdot}{\underset{|}{N}}{-}P(O)(OEt)_2} \qquad (8)$$

(IV)

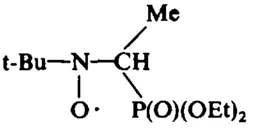
Since less intense ESR spectra of the same nitroxides can be observed in the absence of DTBP it is possible that phosphonyl radicals are also formed by reaction of TEP with a photoexcited state of the nitroalkane.

Prolonged irradiation of these systems led to the formation of persistent radicals. The ESR spectrum ultimately obtained from nitromethane exhibits coupling to N (13.93 G), a single proton (1.43 G) and two equivalent ^{31}P nuclei (40.55 G). The g-factor is 2.0060. We identify the radical as the previously reported[13] β-disubstituted dialkylnitroxide (Va).



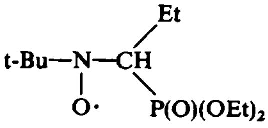
(Va)

Nitroethane (Fig. 1) and 1-nitropropane gave persistent radicals with large coupling to a single ^{31}P nucleus. We assign these to the structures Vb and Vc by analogy with radical Va.



(Vb)

a(1N) = 12.94
a(1H) = 1.46
a(3H) = 0.45
a(1P) = 37.21
g = 2.0058



(Vc)

a(1N) = 13.88
a(1H) = 1.76
a(2H) < 0.3
a(1P) = 50.88
g = 2.0060

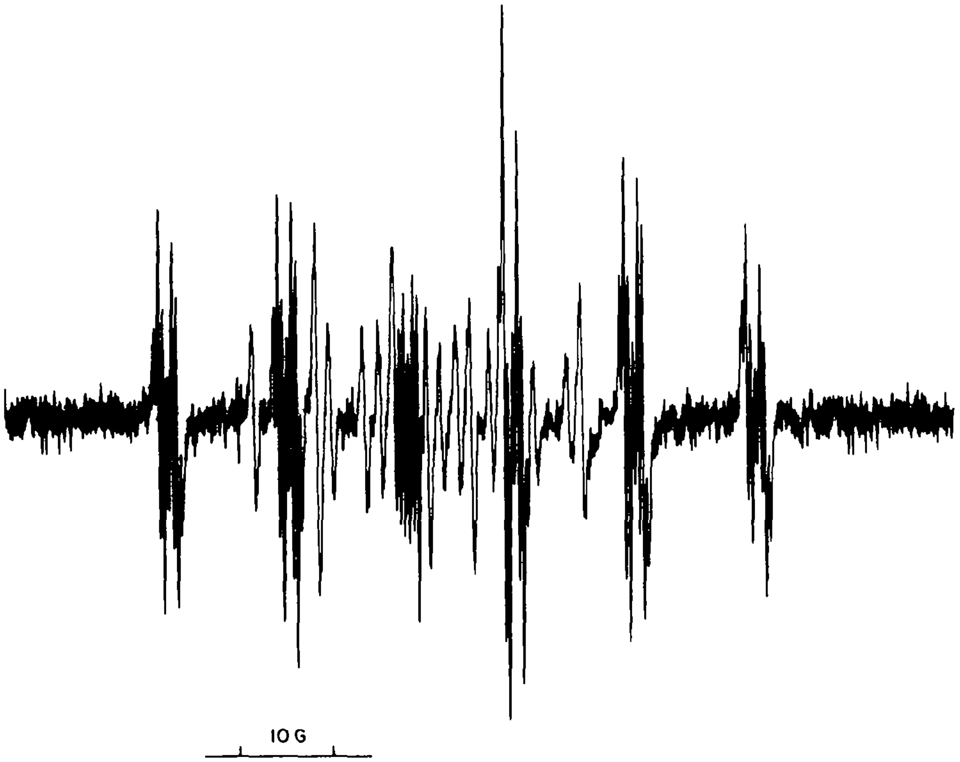
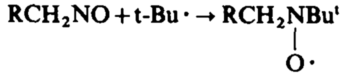


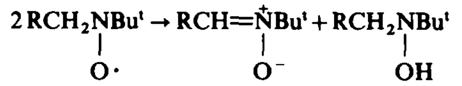
Fig. 1. ESR spectrum observed at room temperature after prolonged irradiation of a benzene solution of $EtNO_2$ containing TEP and DTBP. The broad lines are due to the phosphonyl nitroxide IVb and the sharper lines to radical Vb.

The formation of persistent radicals after prolonged photolysis is often observed in ESR studies and does not necessarily reflect a major reaction pathway. In the present case the following reactions may contribute.

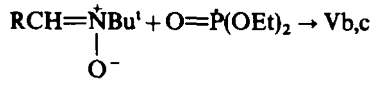
$$t\text{-}BuO\cdot + Bu^tOP(OEt)_2 \rightarrow t\text{-}Bu\cdot + Bu^tOP(O)(OEt)_2 \qquad (9)$$


(10)

$$RCH_2NO + t\text{-}Bu\cdot \rightarrow RCH_2\underset{O\cdot}{\underset{|}{N}}Bu^t \qquad (10)$$


(11)

$$2\,RCH_2\underset{O\cdot}{\underset{|}{N}}Bu^t \rightarrow RCH{=}\underset{O^-}{\underset{|}{\overset{+}{N}}}Bu^t + RCH_2\underset{OH}{\underset{|}{N}}Bu^t \qquad (11)$$


(12)

$$RCH{=}\underset{O^-}{\underset{|}{\overset{+}{N}}}Bu^t + O{=}\dot{P}(OEt)_2 \rightarrow Vb,c \qquad (12)$$

When R=H further disproportionation occurs leading eventually to Va. The intermediate dialkylnitroxides involved in this scheme have not been detected but they are expected to be more transient than the persistent radicals V. The latter are not formed in the absence of DTBP so it would appear that (9) is an essential step in their formation.

CONCLUSIONS

In contrast to silyl radicals, phosphorus centred radicals derived from TPBP and TEP do not give adducts with nitroalkanes detectable by ESR spectroscopy. The observed free radical intermediates are essentially those derived from the corresponding nitroso compounds.

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