Interaction between trialkyl phosphites and aminoxyl radicals: a model study for polymer stabilization

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Received (in Cambridge) 4th March 1999, Accepted 7th May 1999

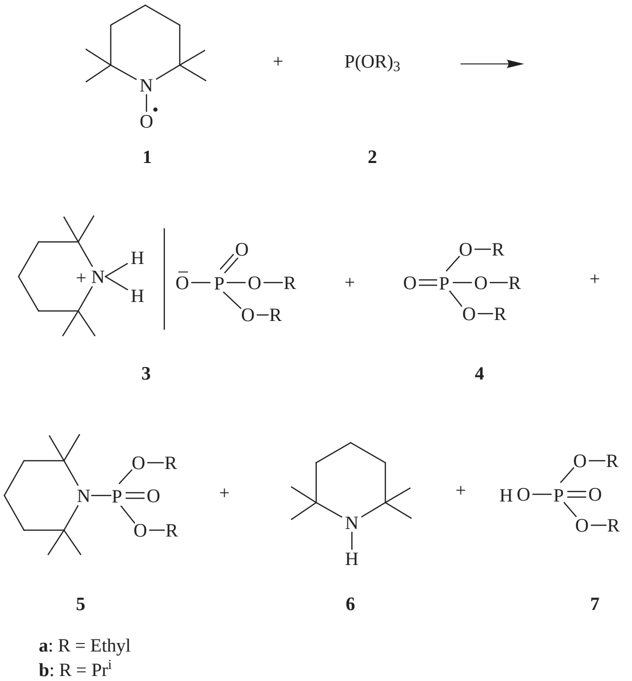
2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) and its bis-1-oxyl analogue react with triethyl and triisopropyl phosphite forming tetramethylpiperidine phosphite which is the main product of the reaction together with dialkyl phosphates. Minor products are tetramethylpiperidinyldialkyl phosphate and tetramethylpiperidine. The reaction mechanism was elucidated by observing the intermediate formation of the phosphoranyl radical which evolves forming the isolated products. The rate of this reaction is considerably lower compared to the stabilization reaction observed between phosphites and hydroperoxides during polymer oxidation. Thus the former reaction could be considered negligible in terms of polymer stabilization under the conditions studied.

Introduction

Alkyl and aryl phosphites are widely used for the stabilization of polymers and other organic materials against oxidation. Their efficiency is attributed to their reaction with hydroperoxides, thus inhibiting the formation of free radicals from the latter which could propagate the oxidation process[1,2] and to the entrapment of alkoxy and alkylperoxy radicals.[2–4] In addition, phosphites may form complexes with transition metals therefore reducing their catalytic effect,[2] and at high temperatures such as those during processing, phosphites could be capable of reacting directly with molecular oxygen.[5] It is a common commercial practice to use phosphites in combination with other stabilizers such as phenols, and/or aromatic and aliphatic sterically hindered amines (SHA) in order to obtain high stabilization effects during the processing and manufacturing of polymers. Sometimes, however, a combination of phosphites with other stabilizers, in particular with SHA gives rise to antagonistic effects.[6,7] The degree of antagonism depends on the chemical composition of the additives, their molar ratio in the mixture and the conditions of polymer oxidation.[6] The nature of this antagonistic effect is most likely due to the transformation products formed from the phosphites and their unfavourable interactions with the transformation products of SHA. Nevertheless, there is very little information in the literature on product analysis to reveal the nature of the complex interactions between phosphites and SHA or with their corresponding aminoxyl radicals which are the main transformation products of SHA. To our knowledge, only diphenylaminoxyls have been studied with triethyl phosphite.[8] However, the reactivity of aliphatic aminoxyls such as TEMPO is different from that of aromatic ones.[9,10] Therefore, in this work, the reactions of triethyl and triisopropyl phosphites with TEMPO and with bis(2,2,6,6-tetramethyl-1-ylooxy-piperidin-4-yl) sebacate (BTS) † were studied in decane and in dodecane in the absence of oxygen.

Results

1. Reaction between triethyl phosphite and TEMPO



Scheme 1

Triethyl phosphite and TEMPO were reacted in decane at 150 °C for 2.5 h under nitrogen. From the reaction mixture, products **3a** and **7a** were isolated by column chromatography (Scheme 1); the presence of 2,2,6,6-tetramethylpiperidine **6**, triethyl phosphate **4a** and compound **5a** in the reaction mixture was demonstrated by GC-MS and the products were identified by comparison with authentic samples. Traces of another aminoxyl radical showing an EPR spectrum similar to that of TEMPO were also isolated; this unidentified product has a molecular weight considerably higher and a R_F much lower than those of TEMPO. Salt **3a** is the main product and its structure was identified by NMR and IR spectroscopy. Salt **3a** was also treated with an aqueous solution of NaOH (0.1%) and then extracted with hexane: the presence of **6** in hexane solution was identified by comparing its GC-MS spectrum with an authentic sample.

Fig. 1 shows the kinetics of consumption of TEMPO and triethyl phosphite plotting 1/[TEMPO] *vs.* time and 1/[phosphite] *vs.* time. Assuming that the reaction follows second order

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† This and following aminoxyl radicals have been named according to IUPAC recommendations as set out in *Pure Appl. Chem.*, 1993, **65**, 1388.

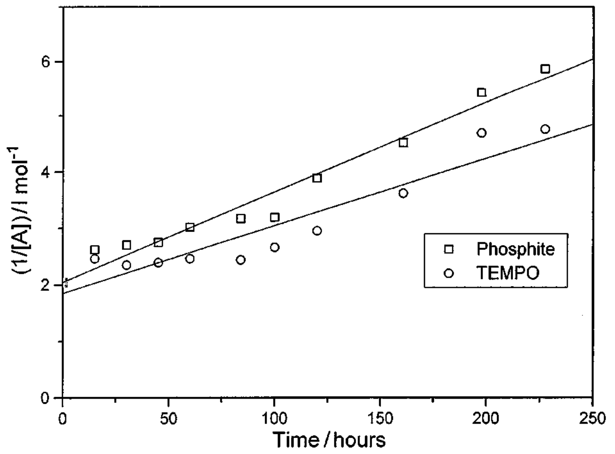


Fig. 1 Consumption of TEMPO and triethyl phosphite in decane at 150 °C plotting 1/[A] *vs.* time; the initial concentrations of reagents are 0.49 mol l^{-1}.

kinetics, we obtain eqn. (1), where k is the rate constant of the

$$1/[A] = 1/[A]_o + kt \qquad (1)$$

reaction, $[A]_o$ and $[A]$ are the initial and current concentrations of the reagents, respectively. The apparent rate constant of the reaction determined from the slopes of the lines in Fig. 1 using eqn. (1) are equal to 1.4×10^{-4} and 1.8×10^{-4} l mol^{-1} s^{-1} (Table 1). Fig. 2a shows the consumption of TEMPO and triethyl phosphite at different initial concentrations of triethyl phosphite. The rate constants of the reaction in these cases were calculated by eqn. (2) where $[B]_o > [A]_o$.

$$\log([B]/[A]) = 0.443([B]_o - [A]_o)kt + \log([B]_o/[A]_o) \qquad (2)$$

Fig. 2b shows the kinetic data for this reaction from which k can be calculated. As shown in Table 1, the rate constants are slightly dependent on the initial concentrations of the reagents. Fig. 3 shows the kinetics of the formation of triethyl phosphate at different initial concentrations of triethyl phosphite. The rate of phosphate formation increases with phosphite concentration and the amount of triethyl phosphate is about 0.28 mol l^{-1} after 3 h during which TEMPO practically disappears.

No consumption of triethyl phosphite was observed in the same reaction conditions in the absence of TEMPO. TEMPO was only slightly consumed (5–10%) under the same conditions without phosphite.

2. Reaction between triisopropyl phosphite and TEMPO

Triisopropyl phosphite and TEMPO were reacted in decane at 150 °C for 2.5 h under nitrogen. Compounds **3b** and **5b** were isolated after column chromatography. Compounds **6** and phosphate **4b** were identified by comparison with authentic samples by analysis of the reaction mixture by GC-MS. In this case, an unidentified aminoxyl showing the same properties as those described in the reaction with triethyl phosphite was also isolated.

Fig. 4 shows the kinetics of consumption of triisopropyl phosphite and TEMPO plotting 1/[TEMPO] *vs.* time or (1/[phosphite]) *vs.* time. The rate constants calculated from the slopes of the plots are close to the values obtained with triethyl phosphite (Table 1).

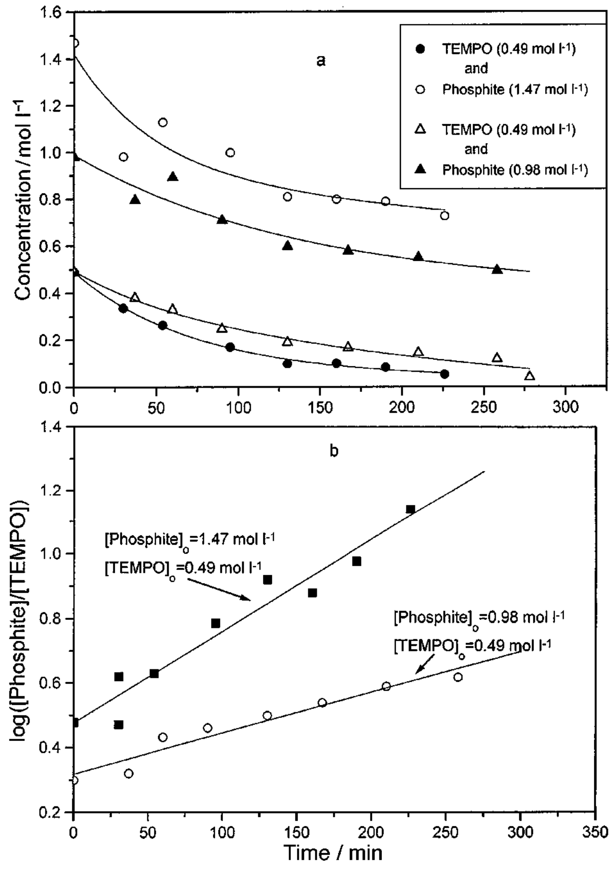


Fig. 2 (a) Consumption of TEMPO and triethyl phosphite at different initial concentrations of reagents, in decane at 150 °C; (b) kinetic curves obtained from eqn. (2) plotting log [Phosphite]/[TEMPO] *vs.* time.

3. Reaction between triethyl phosphite and the bis-TEMPO analogue (BTS)

Triethyl phosphite and BTS **8** were heated in decane at 150 °C in a nitrogen atmosphere for 2 h at equimolar concentrations (Scheme 2). Triethyl phosphate **4** and Tinuvin 770 **9** were compared with authentic samples, while the spectroscopic data of the mono-aminoxyl **10** were compared with those of an authentic sample synthesized *via* the oxidation of BTS with *m*-chloroperbenzoic acid. The disappearance of phosphite **2** and the appearance of phosphate **4** were evaluated by analysis of the reaction mixture using GC-MS, while the disappearance of bis-aminoxyl **8** was followed by EPR. In this case, we were unable to isolate and identify the phosphate of the piperidinium salt of Tinuvin 770.

Fig. 5a shows the consumption of BTS and triethyl phosphite and the formation of triethyl phosphate during the reaction at 150 °C. The following kinetic features may be observed: (i) the higher values of the effective rate constants calculated from the slopes (Fig. 5b) using eqn. (1) compared to those obtained from the reaction between TEMPO and trialkyl

Table 1 Kinetic parameters of the reaction between phosphites and aminoxyls in decane (150 °C, nitrogen)

Reaction	$[NO]_o$/mol l^{-1}	$[Phosphite]_o$/mol l^{-1}	$k_{NO}/10^4$ l mol^{-1} s^{-1}	$k_{phosphite}/10^4$ l mol^{-1} s^{-1}
TEMPO + triethyl phosphite	0.49	0.49	1.4	1.8
TEMPO + triethyl phosphite	0.49	0.98	1.1	
TEMPO + triethyl phosphite	0.49	1.47	1.2	
TEMPO + triisopropyl phosphite	0.49	0.49	1.0	1.2
BTS + triethyl phosphite	0.25	0.25	6–7	4.0

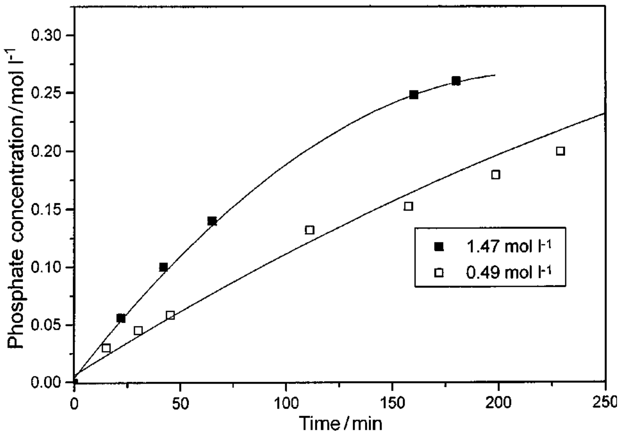
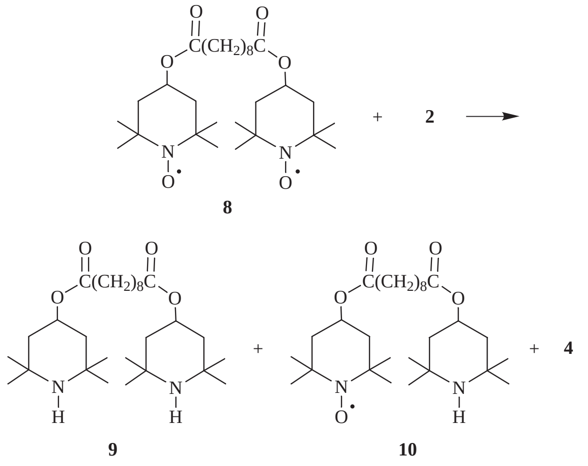


Fig. 3 The formation of triethyl phosphate during the reaction between triethyl phosphite and TEMPO at different initial concentrations of phosphite; $[\mathrm{TEMPO}]_o = 0.49$ mol l^{-1}, $T = 150$ °C.



Scheme 2

phosphites; (ii) the higher consumption of BTS compared to phosphite. In this case, the presence of two active aminoxyl groups in the same moiety could facilitate the reaction due to the higher probability of collisions. On the other hand, the reactivity of the second aminoxyl group may change once the first one has reacted with the consequence of becoming chemically modified.

4. Interaction between phosphites and sterically hindered amines

Sterically hindered amines do not react directly with phosphites. In fact, when equimolar concentrations of triethyl phosphite and 2,2,6,6-tetramethylpiperidine were heated together in decane at 150 °C under nitrogen for 3 h, there was no consumption of the reagents. The same was observed when equimolar concentrations of triethyl phosphite and Tinuvin 770 were heated in dodecane at 210 °C under nitrogen for 4 h.

It is well known that during polymer stabilization, sterically hindered amines are oxidized to their corresponding aminoxyls by peroxy radicals. Consequently, the interaction between aminoxyls and phosphites could be of importance since it could give some insights into the nature of the antagonistic effects sometimes observed when phosphites and amines are used in combination for stabilizing polymers. Therefore, in order to simulate the real behaviour of amines during stabilization, and the effect of phosphites, the following experiment was performed in decane in the presence of oxygen. A solution of Tinuvin 770 (0.05 mol l^{-1}) was air saturated and then heated at boiling point for 4 h, after which the presence of the corresponding aminoxyl was detected by EPR. Part of this solution (1.5 ml) was then introduced into a glass tube and triethyl phosphite (0.04 ml) was added to it, while another 1.5 ml was introduced into a second glass tube but without phosphite addition. Oxygen was then carefully removed from both solutions and the tubes were sealed and heated at 150 °C for 30 min. After this treatment, the concentration of aminoxyl in the solution containing phosphite was 1/6 compared to the initial concentration, while the aminoxyl in the solution without the phosphite had completely disappeared (see Discussion).

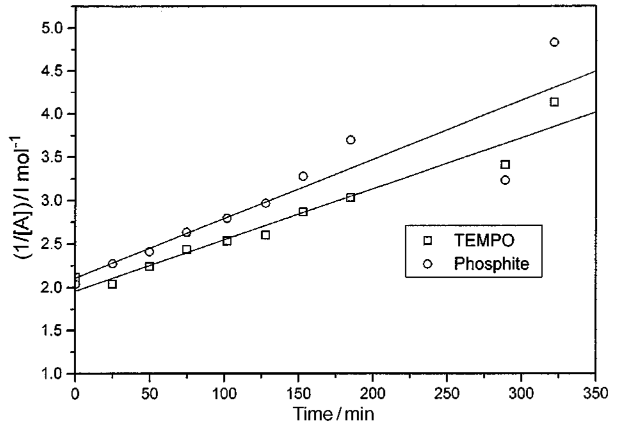


Fig. 4 Consumption of triisopropyl phosphite and TEMPO at 150 °C in decane plotting 1/[A] *vs.* time; the initial concentrations of reagents are 0.49 mol l^{-1}.

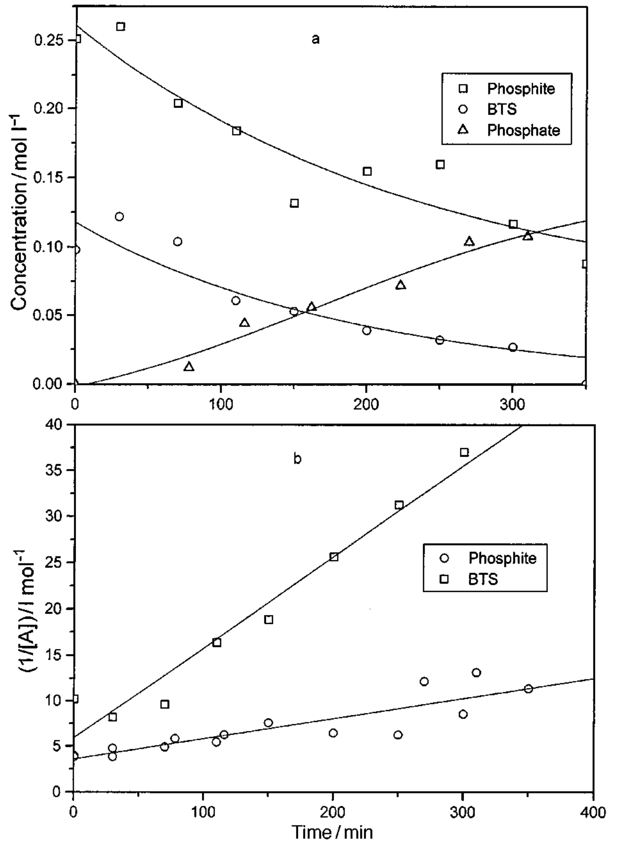
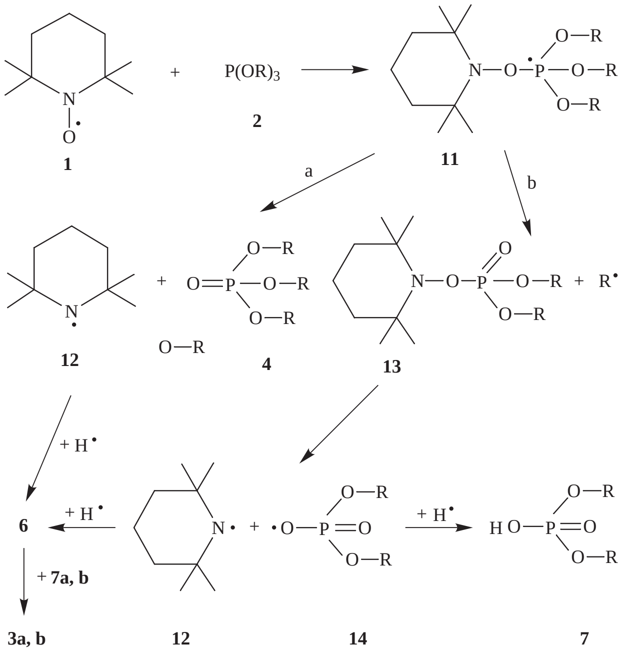


Fig. 5 (a) Consumption of triethyl phosphite and BTS and the formation of triethyl phosphate at 150 °C in decane. The initial concentrations of triethyl phosphite and BTS are 0.25 and 0.125 mol l^{-1}, respectively; (b) consumption of triethyl phosphite and BTS plotting 1/[A] *vs.* time.

Discussion

As stated in the introduction, the only aminoxyl studied to date with triethyl phosphite was the diphenylaminoxyl.[9,10] Since the most widely used light stabilizers are aliphatic secondary amines, which during polymer stabilization give rise to the corresponding aminoxyls, it was of importance to study the interaction of aliphatic aminoxyls such as TEMPO with phosphites, in order to obtain further insights into the mechanistic aspects of the use of SHA and phosphites together.

The results here described show that the main products of the reaction of TEMPO with triethyl/triisopropyl phosphites are the corresponding dialkyl (Et or Pr^i) phosphates **4** and salts **3**. The phosphate and amine **6** may be explained by the interaction of the aminoxyl with phosphite affording the intermediate phosphoranyl radical **11** (Scheme 3).



Scheme 3

It is well documented that phosphoranyl radicals decompose to give phosphate **4** and a radical,[11,12] which in our case is the piperidinyl radical **12** according to path *a* of Scheme 3. However, the intermediate phosphoranyl **11** may also decompose by elimination of an alkyl radical as shown in path *b* and both these possibilities (paths *a* and *b*) are in agreement with the behaviour of phosphoranyls studied by others.[8,13] Following path *b*, phosphate **13** could be formed. This, however, was never isolated because it decomposed at high temperature giving rise to a phosphonyl radical such as **14**, which justifies the formation of dialkyl hydrogenphosphate **7**. The acid **7** was identified in the free form and in salt **3** as the anion, since salt **3** arises from the interaction of amine **6** with acid **7**. The formation of compound **5** which was isolated only in one case, could easily be explained by the interaction of aminyl radical **12** with phosphite **2** in accordance with the literature reports[14] (eqn. (3)).

$$\mathbf{12} + \mathbf{2} \longrightarrow \mathbf{5} + \mathrm{R}^{\bullet} \qquad (3)$$

During this reaction, a second molecule of phosphite is consumed. However, the amount of **5** was very small compared with the products arising from the breakdown of the intermediate phosphoranyl radical **11**, formed in the first step of the reaction described in Scheme 3. This lead us to hypothesize that the first step of the reaction, namely, the bimolecular interaction of aminoxyl with phosphite, is the limiting step of the whole complex reaction which is in agreement with second order reaction kinetics.

In the experiment carried out to simulate the real behaviour of amines during their stabilization, and the effect of phosphites, aminoxyl **8** was formed during the oxidation of decane (used as a model of polymer oxidation) containing Tinuvin 770. This, as expected, confirms that amines give rise to aminoxyls during their stabilization. However, the fate of this aminoxyl depends on whether phosphite is subsequently added or not to the above solution (see Results). In fact, when phosphite is present, aminoxyl **8** is consumed but not completely, since its concentration is 1/6 compared to the initial concentration prior to phosphite addition. But, when phosphite is not added, the aminoxyl completely disappears. In order to explain this unexpected result, we have to take into account that in oxidized decane solution, hydroperoxides are formed. Hydroperoxides and their decomposition products can react with aminoxyl leading to its consumption.[15–17] However, hydroperoxides are also efficiently decomposed through a non-radical pathway by reaction with phosphites to give alcohol and the corresponding phosphate esters.[18] This latter reaction leads to a decrease in the concentration of hydroperoxides in the system containing the aminoxyl and phosphite. As a consequence, less hydroperoxides are available to react with the aminoxyl and therefore less aminoxyl is consumed. In the system in which the phosphite is absent, more hydroperoxides are available for reaction with the aminoxyl leading to its total consumption.

The reactions between phosphites and hydroperoxides obey a second-order rate law with high rate constant, *i.e.* the k of the interaction of triethyl phosphite with cumyl hydroperoxide is 0.35 l mol^{-1} s^{-1} at 30 °C.[18] It is therefore clear that the rate of the reaction between the phosphite and the aminoxyl is considerably lower (see Table 1) compared to that between phosphite and hydroperoxide and this can be confirmed by the results of the experiment discussed in the preceding paragraph.

Conclusion

The data described in this work demonstrate that aminoxyls react with phosphites giving rise to the phosphates of the corresponding amines as the main products, and the mechanisms of the reactions involved are very complex. On the other hand, the rate constant of the reaction between aminoxyl and phosphite is lower than for the reaction between phosphite and hydroperoxide. Consequently, the role of the former reaction in polymer stabilization could probably be considered negligible, as it should not interfere with the stabilization effect of phosphites.

In addition, the results obtained above have prompted us to investigate the reactivity of TEMPO and other aliphatic aminoxyls with aromatic phosphites in order to gain more information on the stabilizing effects of antioxidants used in polymers. This work is currently under way and will be discussed in a future paper.

Experimental

Triethyl phosphite, triisopropyl phosphite, TEMPO, decane and dodecane were purchased from Aldrich and were of ACS grade; bis(2,2,6,6-tetramethyl-1-ylooxy-piperidin-4-yl) sebacate (BTS) and Tinuvin 770 were supplied by CIBA Specialty Chemicals.

UV spectra were recorded on a Uvikon 944 Plus spectrophotometer, IR solid state spectra were measured on a Nicolet 20SX FT-IR spectrometer and EPR spectra were recorded on a Varian E-4 spectrometer containing a ruby in the cavity. NMR spectra, recorded on a Varian Gemini 200 spectrometer, are referred to SiMe$_4$. Mass spectra were recorded on a Carlo Erba QMD 1000 mass spectrometer in EI mode, equipped with a Fisons GS 8060 gas chromatograph.

The reactions between phosphites and aminoxyls were performed in a three-necked round flask at 150 °C and 210 °C in nitrogen atmosphere under magnetic stirring. The kinetics of the reactions were followed by the consumption of phosphite and aminoxyl and the formation of phosphate, using GC-MS and EPR spectrometry. Quantitative measurements were made using internal standards and with a ruby as a reference, respectively.

Reaction between triethyl phosphite and TEMPO

Triethyl phosphite (2.18 ml, 12.7 mmol) and TEMPO (1 g, 6.4 mmol) were heated together in 5 ml of decane at 150 °C for 2.5 h; the reaction mixture gradually turned dark brown from the original orange colour. The reaction mixture was then chromatographed on a silica gel column eluting first with cyclohexane–ethyl acetate 9 : 1 and then increasing the polarity to cyclohexane–ethyl acetate 6 : 4. The following products were isolated: TEMPO (200 mg), unidentified aminoxyl (traces), compound **7a** (70 mg): δ_H ($CDCl_3$) 1.34 (6 H, t, *J* 7.0, CH_3), 4.1 (4 H, q, *J* 7.0, CH_2), 8.35 (1 H, s, OH); MS (70 eV, EI): *m*/*z* 155 (M^+, 3%), 111 ($M^+ - OCH_2CH_3$, 47), 83 ($M^+ - OCH_2CH_3 - CH_2CH_3$, 91), 65 ($M^+ - 2OCH_2CH_3$, 100). Salt **3a** (650 mg) was extracted with methanol from the dark brown fraction at the top of the column and purified on preparative silica-gel plates by eluting with ethyl acetate–methanol 8 : 2 followed by extraction with methanol: ν_{max}/cm^{-1} 2410 (NH_2^+), 1222 (P=O), 1120–1002 (P–O–C); δ_H ($CDCl_3$) 1.26 (6 H, dt, *J* 7.0 and 0.5, CH_2CH_3), 1.49 (12 H, s, CH_3), 1.68 (6H, s), 3.92 (2 H, q, *J* 7.0, CH_2CH_3), 3.93 (2 H, q, *J* 7.0, CH_2CH_3), 9.2 (2 H, br, NH).

Reaction between triisopropyl phosphite and TEMPO

Triisopropyl phosphite (2.24 ml, 9.1 mmol) and TEMPO (1 g, 6.4 mmol) were mixed in decane (5 ml) and reacted at 150 °C for 2.5 h under the same conditions as above. The following products were isolated after column chromatography on silica gel following the same procedures as above: TEMPO (130 mg), unidentified aminoxyl (traces), compound **5b** (6 mg), δ_H ($CDCl_3$) 1.31 (12 H, dd, *J* 6.2 and 2.8, CH_3), 1.45 (12 H, s, CH_3), 1.56 (6 H, s), 4.6 (2 H, m, *J* 8.0 and 6.2); MS (70 eV, EI): *m*/*z* 305 (M^+, 2%), 165 ($M^+ - [(CH_3)_2CHO]_2P{=}O$, 100); salt **3b** (670 mg); ν_{max}/cm^{-1} 2460 (NH_2^+), 1226 (P=O), 1076 (P–O–C); δ_H (200 MHz; $CDCl_3$) 1.23 (12 H, d, *J* 5.8, CH_3), 1.44 (12 H, s, $CH(CH_3)_2$), 1.66 (6 H, s), 4.42 (2 H, br, $CH(CH_3)_2$), 4.7 (2 H, br, NH).

Reaction between triethyl phosphite and bis(2,2,6,6-tetramethyl-1-ylooxypiperidin-4-yl) sebacate (BTS)

Triethyl phosphite (0.6 ml, 3.5 mmol) and BTS (0.5 g, 0.9 mmol) were mixed in decane (5 ml) and heated at 150 °C for 2 h under the conditions described above. The reaction mixture was then cooled at room temperature and chromatographed on a column of silica gel by eluting with cyclohexane–ethyl acetate (8 : 2). Unreacted BTS (60 mg), mono-aminoxyl **10** (traces) and Tinuvin 770 (**9**) (10 mg) were isolated. BTS and compound **9** were identified by comparison with authentic samples. The fraction containing the mono-aminoxyl **10** was evaporated to dryness and the residue was further chromatographed on a silica plate eluting with methanol. Tinuvin 770 containing traces of pure mono-aminoxyl **10** was extracted with dichloromethane. In this solution, compound **10** was identified by EPR (three well defined lines; $a^N = 14.79$ G) and MS (70 eV, EI): *m*/*z* 496 (M^+, 3%), 342 (M^+ − Tempo, 4), 140 (2,2,6,6-tetramethylpiperidine, 48).

Reaction of Tinuvin 770 with *m*-chloroperbenzoic acid

Tinuvin 770 (0.5 g, 1 mmol) and *m*-chloroperbenzoic acid (0.086 g, 0.5 mmol) were mixed at room temperature in dichloromethane. After 12 h, the reaction solution was washed with 10% aqueous $NaHCO_3$, separated, dried over Na_2SO_4 and then chromatographed on a column of silica gel. Mono-aminoxyl **10** was isolated following the procedure described above. The EPR and MS spectra were identical to those of the product obtained in the reaction of triethylphosphite and BTS.

Acknowledgements

The authors wish to thank Ciba Specialty Chemicals and the University of Ancona for financial support.

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Paper 9/01741K