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Hydroperoxide decomposing ability and hydrolytic stability of organic phosphites containing hindered amine moieties (HALS-Phosphites)

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The hydroperoxide decomposing ability and the hydrolytic stability of some HALS-Phosphite stabilisers and some of their hydrolytic transformation products have been investigated by means of ^{31}P NMR spectroscopy. All HALS-Phosphites, including those bearing sterically hindered phenolic substituents proved to be efficient hydroperoxide decomposers. HALS-Phosphites with tertiary HALS moieties are more effective than comparable compounds with secondary HALS groups. The hydrolytic stability of HALS-Phosphites is much higher than those of common phosphites. The path of hydrolysis of HALS-Phosphites was established. In a first step the phenolic moieties are substituted followed by a fast removal of one hindered piperidine group to give the corresponding hydrogen phosphonates. These compounds are hydrolytically stable due to their betaine structure with increased electron density at the phosphorus atom. © 1998 Elsevier Science Limited. All rights reserved

1 INTRODUCTION

Trivalent organic phosphorus compounds are an important class of antioxidants and components of highly effective stabiliser formulations. The activity of different phosphites and phosphonites as melt and thermal stabilisers for synthetic macromolecular compounds is an extensively investigated and well documented area. The efficiency of these antioxidants is mainly due to their ability to decompose hydroperoxides formed during oxidation of polymers in a non-radical way. Trivalent phosphorus compounds with sterically hindered phenolic substituents are also able to act as primary, radical chain breaking antioxidants.[1]

In order to understand the underlying chemistry of the antioxidant performance, Rüger *et al.*[2] and König[3] extensively examined in model studies the cumene hydroperoxide decomposing activity of phosphorous acid esters. The results for hydroperoxide decomposition by phosphites were summarised by Schwetlick.[1] The order of reactivity reveals that phosphonites and aliphatic phosphites react faster than aromatic phosphites. Furthermore the reactivity diminishes with increasing steric demand of the alkyl or aryl substituents. The lowest hydroperoxide decomposing ability is shown by sterically hindered arylposphites.

It is well known that in the presence of small amounts of water phosphites undergo a fast hydrolysis. This fact has been discussed controversially in respect to the performance of phosphites as polymer stabilisers. On one hand hydrolysis has to be considered as a limiting factor for commercial applications of phosphites as polymer antioxidants. Acidic products formed during hydrolysis can cause corrosion of the processing equipment and lead to catalysis of the hydrolysis.[4,5] Furthermore the storage and handling of these compounds may become difficult because the

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product mixtures tend to cake. Poor thermal stability can accompany the hydrolytic instability of phosphites and leads to the formation of 'black specks' during processing of the polymer.[6] Therefore it has been stated that the development of phosphite antioxidants has to be focused on the improvement of hydrolytic stability as well as performance.[5]

On the other hand active stabilising species such as hindered phenols can be released by hydrolysis of phosphites. It has been suggested that these phenols are the species responsible for the antioxidant activity of phosphites at higher temperatures. They can form synergistic mixtures with the parent phosphites or phosphorus containing hydrolysis products.[7–12] Therefore it was emphasised that a high hydrolytic stability may not always lead to maximum performance. Release of antioxidatively acting secondary compounds (mainly phenols) from the phosphites by hydrolysis in combination with the other stabilising mechanisms can contribute to an overall better performance.[13]

Acidic conditions cause an enhancement of the reaction rate of hydrolysis. The acid-catalysed hydrolysis involves a protonation step at the phosphorus atom followed by the nucleophilic attack of water to produce equivalent amounts of alcohol/phenol and phosphonates. Basic hydrolysis directly leads to the formation of the anion of the hydrogen phosphonates.[14] In neutral environment hydrolysis of an aliphatic phosphite, such as tri-*n*-propyl phosphite, was found to obey a third order rate law involving two water molecules as reported by Aksnes *et al.*[15] The authors also showed that traces of Lewis base, such as pyridine, have a marked retarding influence on the rate of hydrolysis. The hydrolytic behaviour of commercially used phosphites during processing and thermooxidation was investigated by Linger *et al.*[16] and Klender[6] and by us.[17]

Klender[18] proposes three methods to increase hydrolytic stability of phosphites for application as polymer stabilisers:

- internal or external addition of basic components to the phosphite;
- increase of steric hindrance around the phosphorus atom;
- reduction of electron density on the phosphorus atom.

Looking for new highly efficient stabilisers with an improved hydrolytic stability we developed phosph(on)ites containing hindered phenolic and HALS-moieties (HALS-Phosphites) which show a remarkable stabilising effect against thermal and light ageing.[19–22] The efficiency of these compounds, containing the antioxidising moieties in one molecule, is often higher than those of the corresponding mixtures of the individual compounds.

In order to get more information about the behaviour of HALS-Phosphites during their application we extended the investigations on their hydroperoxide decomposing efficiency. Furthermore it became of importance to examine the hydrolytic behaviour of the HALS-Phosphites and the antioxidative activity of their transformation products. To find out which hydrolysis products are formed during the autoxidation process the independent synthesis of the expected intermediates and the examination of their sensitivity towards water was required.

2 EXPERIMENTAL

2.1 Materials

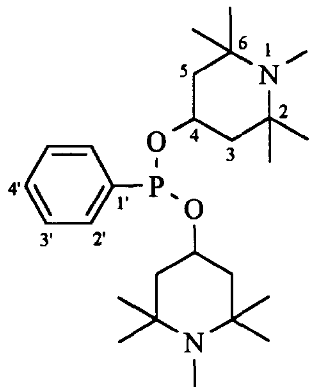
The structures and abbreviations used are given in the Appendix. The following compounds are commercially available:

2,4,8,10-Tetra-*tert*-butyl-6-fluoro-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocine (**Fp-9**, Albe-marle Corp.); triphenylphosphine (**Ae_3**, Fluka Chemie AG); dichlorophenylphosphine (E. Merck, Darmstadt); 2,6-di-*tert*-butyl-4-methylphenol (BHT, Fluka Chemie AG); bis(2,4-di-*tert*-butyl-phenyl)pentaerithritol diphosphite (Ultranox 626, General Electric Comp.); tris(2,4-di-*tert*-butylphenyl)phosphite (Irgafos 168, Ciba–Geigy Corp.).

$AdCl_2$, **Ads_2**, **Adt_2**, **Aes_2**, **Ac_3** and **Act_2**, were synthesised according to Refs 19–23 and **AdH_2** according to Ref. 24 The synthesis of **As_2H** and **AsH_2** is described in Ref. 25

2.2 Synthesis of bis(1,2,2,6,6-pentamethyl-4-piperidinyl) phenylphosphonite (Aet_2)

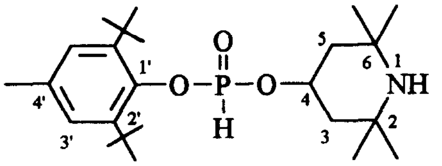
A solution of 17.9 g (0.1 mol) dichlorophenylphosphine in 100 ml dried toluene was added dropwise under stirring and cooling to a mixture of 34.2 g (0.2 mol) dried 1,2,2,6,6-pentamethyl-4-piperidinol and 22.2 g (0.22 mol) triethylamine in 200 ml dried toluene. The solution was refluxed for 10 h. Triethylamine hydrochloride precipitated was filtered off and the solvent was removed *in vacuo*. The remaining product was purified by recrystallisation from *n*-hexane (m.p.: 75°C; yield: 58%).



$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): $\delta = 151.9$.
^1H NMR ($CDCl_3$, 200.1 MHz): $\delta = 0.89$, 0.98, 1.10, 1.13 (4s, 6H each, *cis,trans*-2,6-Me), 1.49–1.71 (m, 6H, *cis,trans*-3,5-H), 1.90 (m_c, 2H, *cis,trans*-3,5-H), 2.2 (s, 6H, 1-Me), 4.21 (m_c, 2H, 4-H), 7.30–7.40 (m, 3H, 2′-H or 3′-H, 4′-H), 7.50–7.61 (m, 2H, 2′-H or 3′-H).
^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 20.8$ (*cis* or *trans*-2,6-Me), 28.0 (1-Me), 32.8 (*cis* or *trans*-2,6-Me), 48.6 (C-3, C-5), 56.0 (C-2, C-6), 70.1 (d, $^2J_{PC} = 11.6$ Hz, C-4), 128.0 (d, $^3J_{PC} = 5.5$ Hz, C-3′), 129.7 (d, $^2J_{PC} = 6.6$ Hz, C-2′), 130.1 (C-4′), 141.6 (d, $^1J_{PC} = 16.5$ Hz, C-1′).

2.3 Synthesis of *rac*-(±)-2,6-di-*tert*-butyl-4-methylphenyl (2,2,6,6-tetramethyl-4-piperidinyl) phosphite (AdsH)

Initially 7.8 g (0.05 mol) dried 2,2,6,6-tetramethyl-4-piperidinol were slowly added as a solid to a stirred and ice cooled solution of 16 g (0.05 mol) **AdCl$_2$** and 10.1 g (0.1 mol) triethylamine in 200 ml toluene. The mixture was stirred at 100°C for 5 h. After completion of the reaction 0.8 g (0.05 mol) water were added and it was stirred for another 30 min at 100°C. The hydrochloride precipitated was filtered and the solvent of the filtrate was evaporated *in vacuo*. The residue was treated with 200 ml *n*-hexane to give a white precipitate which was proved to be the hydrochloride of **AdsH**. It was filtered and again dissolved in 200 ml toluene. 10 g (0.1 mol) 1-methylpiperidine were added. 1-Methylpiperidine hydrochloride formed was filtered off and the solvent was removed from the filtrate. After drying in vacuum racemic **AdsH** was obtained analytically pure. M.p. 107–111°C, yield: 72%.



^{31}P NMR (acetone-d_6, 121.5 MHz): $\delta = 1.6$ (dd, $^3J_{PH} = 8.2$ Hz, $^1J_{PH} = 716$ Hz).
$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): $\delta = 2.6$.
^1H NMR ($CDCl_3$, 200.1 MHz): $\delta = 1.21$ (s, br., 12H, *cis,trans*-2,6-Me), 1.44 (s, 18H, tBu), 1.92-2.11 (m, 4H, *cis,trans*-3,5-H), 4.81–5.12 (m_c, 1H, 4-H), 7.08 (s, 2H, 3′-H), 7.33 (d, $^1J_{PH} = 705$ Hz, PH).
^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 21.4$ (4′-Me), 28.8 (*cis* or *trans*-2,6-Me), 31.9 (*cis* or *trans*-2,6-Me), 34.5 (tBu-Me), 35.4 (C-tBu), 45.7 (C-3, C-5), 51.9 (C-2, C-6), 73.2 (C-4), 127.5 (C-3′), 133.4, 142.1, 144.9 (C-1′, C-2′, C-4′).

The melting points were determined on a Boëtius melting point apparatus. ^1H NMR (TMS internal reference), ^{13}C NMR (TMS internal reference) and ^{31}P NMR spectra (85% H_3PO_4 external reference) were recorded on a Bruker AC-200 P spectrometer. ^{13}C NMR peaks were assigned by means of Distortionless enhancement by polarisation transfer (DEPT).

2.4 Hydroperoxide decomposition by phosphites

The experiments were carried out directly in the NMR tube. The fate of the phosphorus compounds was followed by ^{31}P NMR spectroscopy. 0.5 ml of an 0.2 M solution of cumene hydroperoxide (CHP) in *o*-dichlorobenzene was added to a mixture of 0.5 ml of a 0.2 M solution of the phosphorus compound in *o*-dichlorobenzene and 0.55 ml deuterobenzene ([CHP] = [P-compound] = 0.065 mol l^{-1}). The degree of conversion was determined by the ratio of its ^{31}P NMR peak intensity to the total of all peak intensities.

2.5 Hydrolysis of the phosphites

The reaction was carried out in a thermostatted, magnetically stirred, double-walled vessel at 70°C. As a solvent a mixture of isopropanol/water with changing ratios (see legend of the figures), depending on the solubility of the phosphorus compound, was used. In all cases at least a 100-fold excess of water in respect to the phosphorus compound was used. The concentration of the phosphorus compound was 0.1 mol l^{-1}. Samples of 1 ml were taken from the mixture. For NMR measurements acetone-d$_6$ was added. The degree of conversion was determined by the ratio of the ^{31}P NMR peak intensity of the phosphite used to the total of all peak intensities.

In addition, hydrolysis experiments at higher temperature (150°C) of **Ads$_2$** and, for comparison, of Irgafos 168 were carried out in a 100 ml three-necked flask equipped with magnetic stirrer, thermometer, gas inlet tube and condenser. The vessel was thermostatted in an oil bath. As media, a commercial paraffin blend (PAREX, chain length C_{14}–C_{22}) and a polyether alcohol (SYSTOL T151, BASF Schwarzheide GmbH) were used. The experiments were carried out in oxidising (O_2) and non-oxidising (N_2) atmosphere. The initial concentration of phosphites was 0.2 M. A three-fold molar excess of water was added to the reaction mixture and a gas stream (O_2 or N_2) saturated with water was blown through the solution.

The conversion of the phosphorus species was followed by means of ^{31}P NMR spectroscopy using benzene-d$_6$ as NMR solvent. The release of hindered phenols was proved by means of HPLC.

The behaviour of **Ads$_2$** (0.1 M) in *o*-dichlorobenzene, in pure dodecane and in dodecane with a peroxide initiator (Triganox) at 160°C in oxygen atmosphere were studied directly in the NMR tube. The concentrations of phosphorus components were again followed by means of ^{31}P NMR spectroscopy.

3 RESULTS AND DISCUSSION

3.1 Hydroperoxide decomposition by phosphorus compounds

The hydroperoxide decomposition of different HALS-Phosphites and HALS-Phosphonites was first examined in model studies. The ascertained reaction rate constants in general confirm the expected gradation of activities. In all cases only oxidation products were obtained. While the concentration of the phosph(on)ites was decreasing a simultaneous increase of the concentration of the corresponding phosph(on)ates in the same ratio was observed.

The phosphonites **Aes$_2$**, **Aet$_2$** and the phosphine **Ae$_3$** are extremely active hydroperoxide decomposers. Under the conditions used they are readily transformed into the corresponding phosphonates and the phosphine oxide, respectively, within 30 s. Therefore no rate constant of the oxidation could be determined by means of the method used.

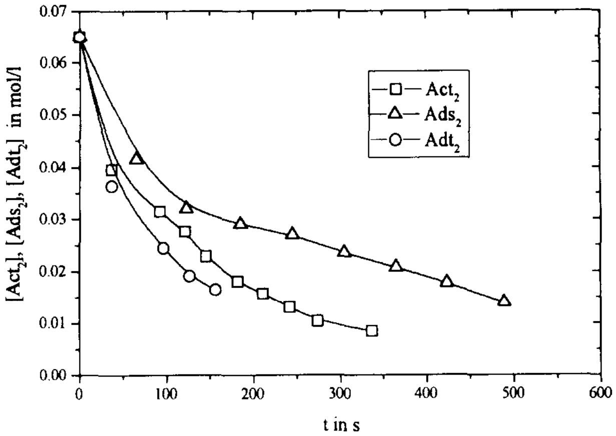


Fig. 1. Concentration of **Act$_2$**, **Adt$_2$** and **Ads$_2$** during oxidation with cumene hydroperoxide in *o*-dichlorobenzene at 25°C ([**Act$_2$**]$_0$ = [**Adt$_2$**]$_0$ = [**Ads$_2$**]$_0$ = [cumene hydroperoxide]$_0$ = 0.065 mol l^{-1}).

The HALS-Phosphites **Act$_2$**, **Ads$_2$** and **Adt$_2$** show a considerable lower hydroperoxide decomposing ability. Among them **Act$_2$** and **Adt$_2$** have almost the same reactivity whereas **Ads$_2$** is less reactive (Fig. 1).

Adt$_2$ containing the tertiary HALS-moiety reacts faster with hydroperoxides than the corresponding compound **Ads$_2$** containing the secondary HALS moiety (Table 1, Fig. 1). This effect could possibly be explained by a preceding acid-base-interaction or complexation of the hydroperoxide with the amino function, which preorganises the reactive centres for the nucleophilic attack of the phosphorus. Tertiary and secondary amines should have a different tendency to give such complexes.

The commercially used phosphorus stabilisers decompose hydroperoxides in a comparatively slow reaction obeying a second order rate law. The determined rate constants for **Ac$_3$**, **Fp-9** and **Ultranox 626** are in the same order of magnitude, whereas the reactivity of **Irgafos 168** with hydroperoxide is pronouncedly lower. The high steric demand of *tert*-butyl groups in **Irgafos 168** causes a

Table 1. Rate constants of the stoichiometric reaction of P(III)-compounds with cumene hydroperoxide in *o*-dichlorobenzene at 25°C ([P-compounds]$_0$ = [ROOH]$_0$ = 0.065 mol

Phosphorus compound	$10^3 \times k$/l mol^{-1} s^{-1}
Act$_2$	306
Adt$_2$	283
Ads$_2$	88
Ac$_3$	58
Ultranox 626	51
Fp-9	48
Irgafos 168	6.7

decrease in the reactivity of the phosphorus in this compound (Fig. 2, Table 1).

Besides phosphorous acid triesters we also examined the behaviour of the possible hydrolysis products **AdH_2** and **AdsH** in the reaction with cumene hydroperoxide (CHP). Even after two days at 25°C, only the phosphorus containing educts were detected. No oxidation products were observed by ^{31}P NMR spectroscopy. However, it was shown by iodometric titration that CHP was completely decomposed. These results can only be reasonably explained by a catalytic decomposition of CHP by these compounds.

3.2 Hydrolysis of phosphorus compounds

Linger *et al.*[16] and Klender[18] investigated the hydrolytic behaviour of the compounds **Ads_2**, **Adt_2** synthesised by us and several commercially applied phosphite stabilisers by following the pH value of the reaction solution and by moisture pick up respectively. In order to get more information on the fate of the phosphorus compounds under hydrolytic conditions we examined the hydrolysis of **Ads_2**, **Adt_2**, and of the phosphonate **AdsH** and the hydrogen phosphonate **AdH_2** by means of ^{31}P NMR spectroscopy.

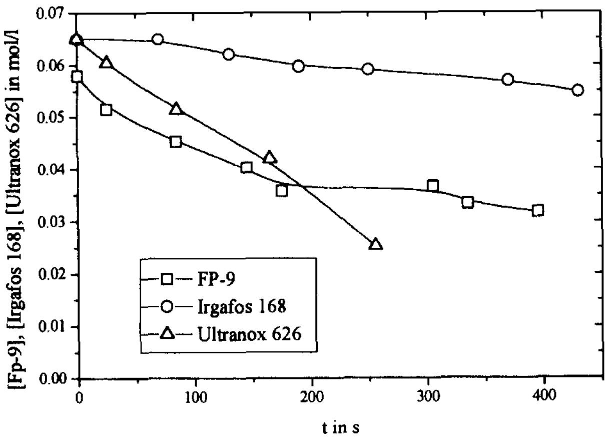


Fig. 2. Concentration of **Fp-9**, **Ultranox 626** and **Irgafos 168** during oxidation with cumene hydroperoxide in *o*-dichlorobenzene at 25°C ([**Fp-9**]$_0$ = [**Ultranox 626**]$_0$ = [**Irgafos 168**]$_0$ = [cumene hydroperoxide]$_0$ = 0.065 mol l^{-1}).

For the identification of the reaction products four possible hydrolysis products (**AdsH**, **As_2H**, **AsH_2**, **AdH_2**) of the HALS-Phosphite **Ads_2** were synthesised independently.

The new unsymmetric, racemic phosphonate **AdsH** was obtained by reaction of **$AdCl_2$** with 2,2,6,6-tetramethyl-4-piperidinol (1:1 ratio) and subsequent partial hydrolysis in 72% yield.

Under the conditions used, the HALS-Phosphites **Ads_2** (Fig. 3, Table 2) and **Adt_2** (Fig. 4, Table 2) exhibit a comparatively high hydrolytic stability. After a reaction time of 3 days at 70°C in isopropanol/water a conversion of less than 10% was observed. Thereby **Ads_2**, the phosphite with the secondary HALS moiety, reacted slightly faster. Both phosphites give rise to only one hydrolysis product with an ^{31}P NMR shift of 0.6 ppm (acetone-d_6) for the hydrolysis of **Ads_2** and −0.4 ppm for the hydrolysis of **Adt_2**, respectively. These peaks represent the hydrogen phosphonates **AsH_2** and **AtH_2**. The product **AsH_2** could

Table 2. Rate constants of the hydrolysis of P(III)-compounds in isopropanol/water at 70°C, ([P-compound]$_0$ = 0.1 mol^{-1}

Phosphorus compound	k/h^{-1}
Ads_2	0.0019
Adt_2	0.0017
AdsH	0.2015
AdH_2	0.0088

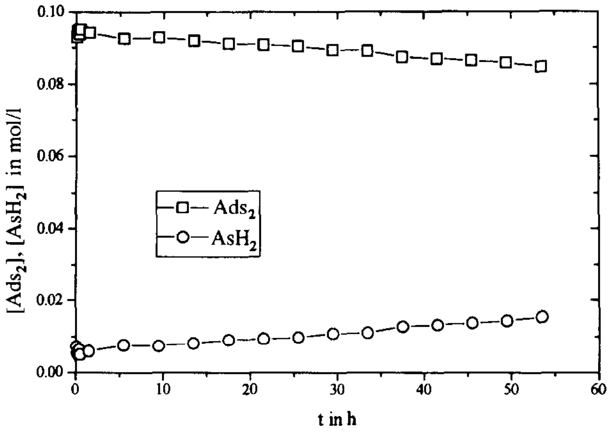


Fig. 3. Hydrolysis of **Ads_2** in isopropanol/water (4:1) at 70°C measured by ^{31}P NMR spectroscopy ([P-compounds]$_{total}$ = 0.1 mol l^{-1}).

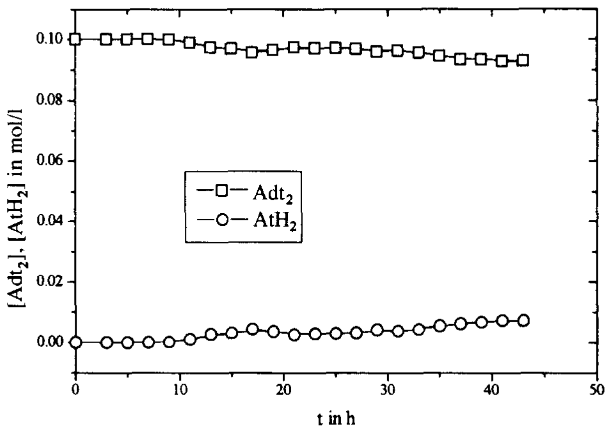


Fig. 4. Hydrolysis of **Adt_2** in isopropanol/water (4:1) at 70°C measured by ^{31}P NMR spectroscopy ([P-compounds]$_{total}$ = 0.1 mol l^{-1}).

be identified by its $^{31}P,^{1}H$-coupling pattern which shows a duplet for $^{3}J_{PH}$ (Fig. 5). Assuming the formation of **As$_2$H** a triplet would have been obtained (see **As$_2$H**: ^{31}P NMR (acetone-d$_6$, 121.5 MHz): $\delta = 4.3$ (td, $^{3}J_{PH} = 8.1$ Hz, $^{1}J_{PH} = 704$ Hz))[25] (see also Fig. 6). The coupling constants for $^{3}J_{PH}$ and $^{1}J_{PH}$ are in agreement with those of the isolated compound **AsH$_2$** (**AsH$_2$**: ^{31}P NMR (acetone-d$_6$, 121.5 MHz): $\delta = 0.6$ (dd, $^{3}J_{PH} = 9.1$ Hz, $^{1}J_{PH} = 623$ Hz)) (synthesis of **As$_2$H, AsH$_2$**[25]).

The phosphonates **AdsH** just like **As$_2$H** can be excluded as product of this reaction because both hydrolyse much more rapidly under these conditions as discussed below. **AsH$_2$** however proved to be very stable towards hydrolysis.

Assuming a similar behaviour for **Adt$_2$** the final stable product of its hydrolysis should be **AtH$_2$**.

It is known that aryl moieties are split off from phosphites by hydrolysis prior to alkyl moieties.[26] So it is even possible to use this behaviour for the

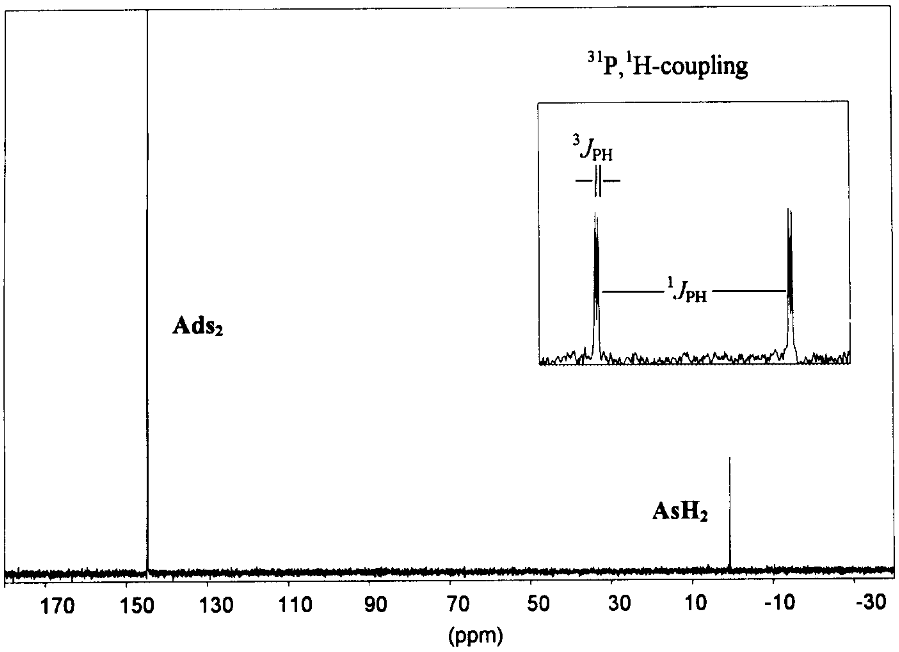


Fig. 5. $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra (acetone-d$_6$) of **Ads$_2$** after 20 h in isopropanol/water (3:2) at 70°C.

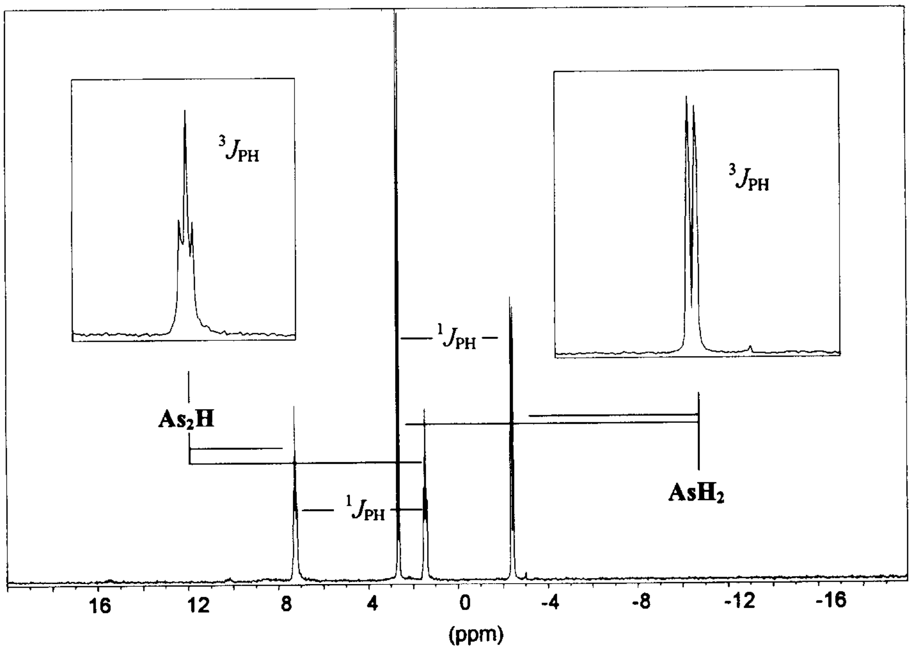
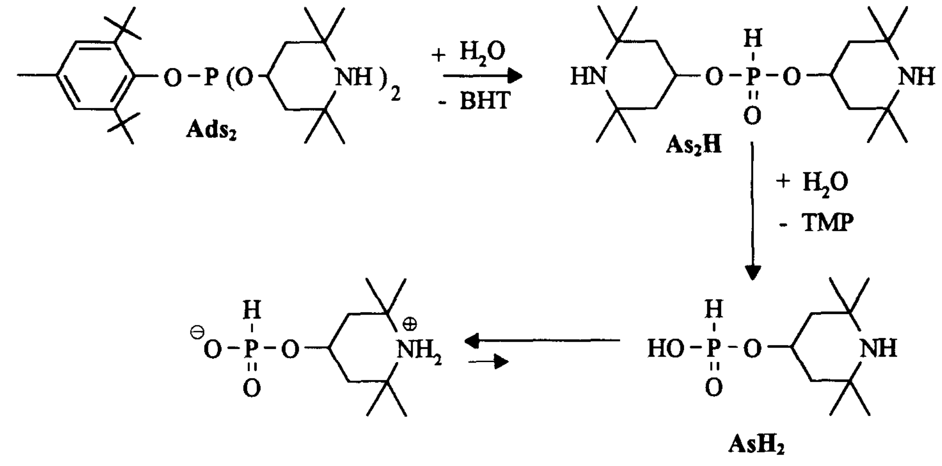


Fig. 6. ^{31}P NMR spectrum (acetone-d$_6$) of **As$_2$H** after 2 h in isopropanol/water (3:2) at room temperature.



Scheme 1. Hydrolysis of **Ads$_2$**.

synthesis of alkyl hydrogen phosphonates from mixed diaryl alkyl phosphites by partial hydrolysis.[27] In our case the sterically hindered phenol should be an excellent leaving group due to the weakness of the P–O-bond caused by tension from the bulky substituents in the neighbourhood.

The phosphonates (**As$_2$H**, **At$_2$H**) obtained from the first hydrolytic step of **Ads$_2$** or **Adt$_2$** cannot be detected by ^{31}P NMR spectroscopy. This can be explained with their rapid further hydrolysis to hydrogen phosphonates.

In a separate experiment it could be shown that **As$_2$H** in an isopropanol/water mixture readily hydrolyses to give **AsH$_2$** (^{31}P NMR data see above) even at room temperature within 5 h (Fig. 6). At 70°C **As$_2$H** is completely converted to **AsH$_2$** within 1 h.

The monoester **AsH$_2$**, however, proved to be extremely stable against hydrolysis under neutral conditions. Neither H_3PO_3 nor any other transformation products could be obtained during 90 h at 70°C in an isopropanol/water mixture. This can be attributed to a stable betaine structure of this compound which decreases the electrophilicity at the phosphorus atom and therefore reduces the ease of water attack. According to these results the following pathway of hydrolysis of HALS-Phosphites is proposed (Scheme 1).

These results seem to be in contrast to investigations by Klender[6] for the hydrolysis of **Irgafos 168** which was also followed by ^{31}P NMR spectroscopy. In this case all possible hydrolysis products (phosphonates, hydrogen phosphonates and phosphorous acid) were found. This can be attributed to the fact that no stable salts of hydrogen phosphonates can be formed in this system in the absence of bases.

The proposed pathway of HALS-Phosphite hydrolysis also shows that no acidic products are formed in this process. Thus no decrease of the pH value into acidic regions should be observed even though hydrolysis has proceeded to the hydrogen phosphonates.

A similar hydrolytic behaviour is shown by the unsymmetric phosphonate **AdsH** which was completely converted after 2 h at 70°C (Fig. 7, Table 2). First a hydrolysis product with a ^{31}P NMR shift of 0.2 ppm was detected which can be identified as **AsH$_2$** (Fig. 8, see also ^{31}P NMR data above). This is in agreement with the statement above that aryl moieties are split off first from the phosphorous acid derivative during hydrolysis. Only slightly delayed another peak appears in the ^{31}P NMR spectrum at −2.1 ppm. After 20 h the two hydrolysis products do not change their ratio any more. The second peak shows a $^1J_{PH}$- but no $^3J_{PH}$-coupling and does therefore not contain the piperidine moiety (Fig. 8). Presumably it belongs to the

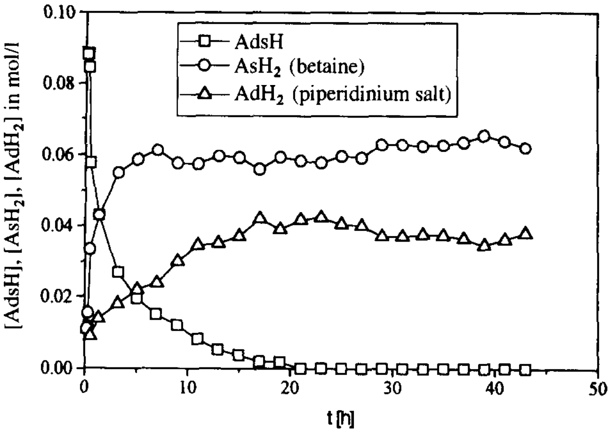


Fig. 7. Hydrolysis of **AdsH** in isopropanol/water (3:2) at 70°C measured by ^{31}P NMR spectroscopy ($[\text{P-compounds}]_{\text{total}} = 0.1\,\text{mol}\,\text{l}^{-1}$).

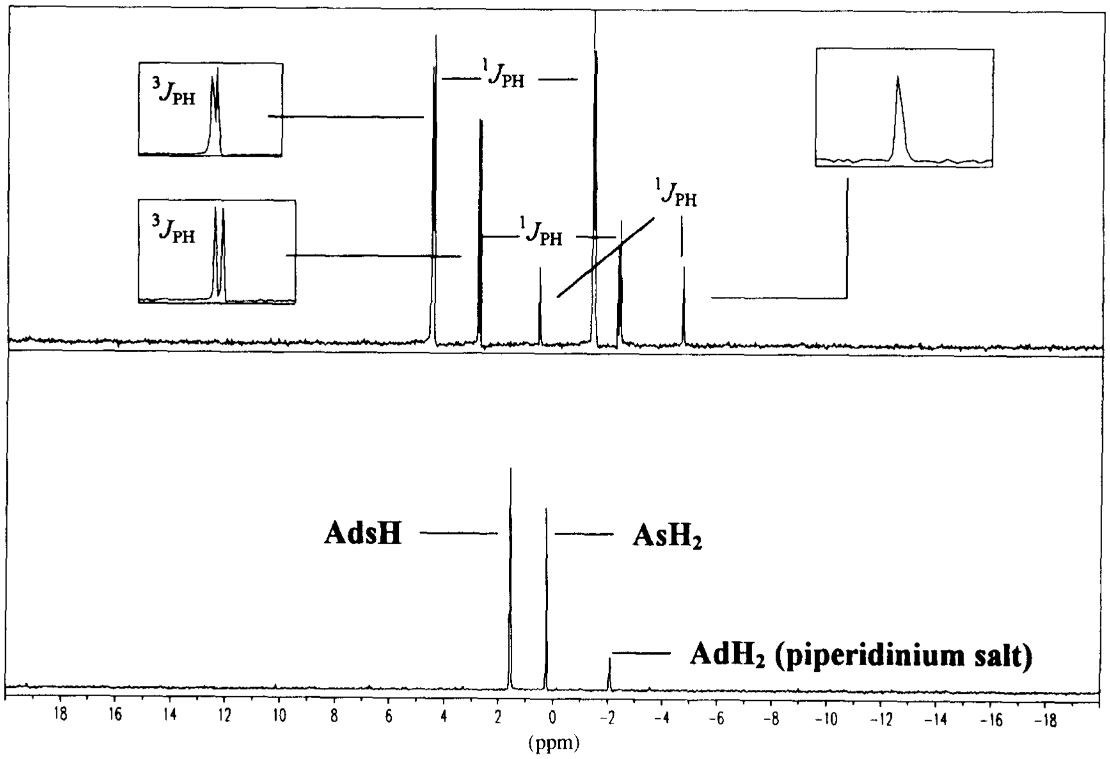


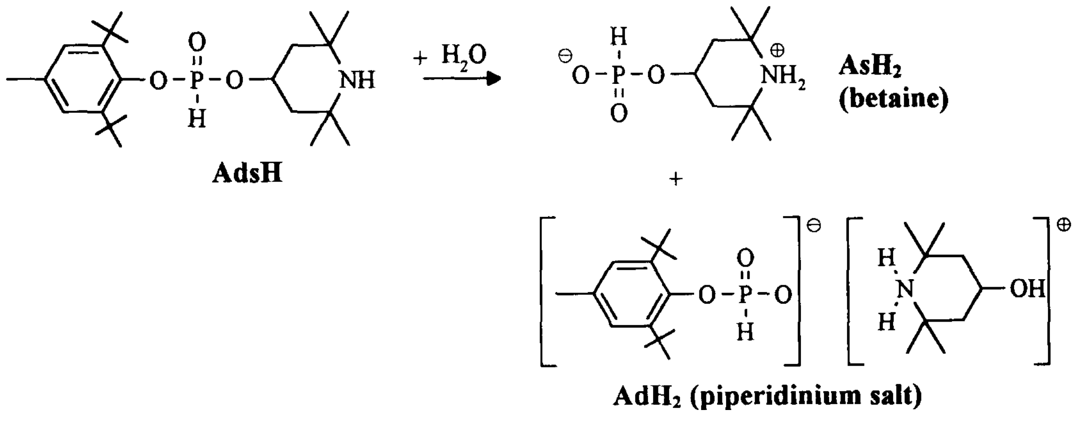
Fig. 8. $^{31}P\{^1H\}$ and ^{31}P NMR spectra (acetone-d_6) of **AdsH** after 40 min in isopropanol/water (3:2) at 70°C.

piperidinium salt of **AdH_2**. This assumption seems probable because **AsH_2** itself does not give any further reaction products under these conditions as proved above. Formation of H_3PO_3 or its salts can be excluded on that route. It should therefore be possible that to a certain degree the piperidine moiety is split off first from **AdsH** resulting in the formation of **AdH_2** which forms a salt with the released piperidine moiety. This salt should be stable against further hydrolysis for the same reasons as it was discussed above for the betaine structure of **AsH_2**. This would explain the stable ratio of the two products after a certain reaction time. The proposed mechanism is given in Scheme 2.

In the case of **AdH_2**, a slow hydrolysis to phosphorous acid (^{31}P NMR: $\delta = 4.98$) with a rate comparable to those of the hydrolysis of **Ads_2** and **Adt_2** was observed (Fig. 9, Table 2). This reaction as well as the hydrolysis of **AdsH** are not important for the description of the reaction of HALS-Phosphites with water as both **AdH_2** and **AdsH** are no intermediates of the hydrolysis of **Ads_2** as discussed above.

The pseudo first order rate constants for some derivatives of HALS-Phosphites are summarised in Table 2.

In order to adapt the model investigations more to the real polymer processing conditions we also



Scheme 2. Proposed route of the hydrolysis of **AdsH**.

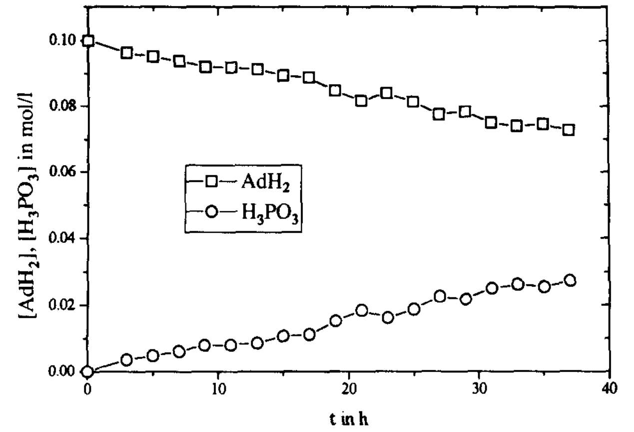


Fig. 9. Hydrolysis of **AdH$_2$** in isopropanol/water (3:2) at 70°C measured by ^{31}P NMR spectroscopy ([P-compounds]$_{total}$ = 0.1 mol l^{-1}).

examined the reaction behaviour of **Ads$_2$** at higher temperatures (> 150°C) in various media. In earlier studies by Winkler[28] and Schwetlick[7] it was postulated that water produced during the autoxidation process of the polymer is responsible for the hydrolysis of the phosphite stabilisers.

When we carried out the reaction in the inert solvent *o*-dichlorobenzene at 160°C in an open system, small amounts of two hydrolysis products were detected by ^{31}P NMR (Fig. 10). Again **AsH$_2$** is very likely the main reaction product (product 1, **AsH$_2$**: ^{31}P NMR (C_6D_6, 121.5 MHz): $\delta = 1.5$ (dd, $^3J_{PH} = 9.1$ Hz, $^1J_{PH} = 697$ Hz)). The difference in the chemical shift and $^1J_{PH}$ coupling constant in comparison to the isolated product are probably due to the different NMR solvent used (^{31}P NMR data in acetone-d$_6$ (see above). The second product shows a triplet for the $^3J_{PH}$ coupling additional to its $^1J_{PH}$ coupling and is therefore assigned to **As$_2$H** even though the coupling constants are smaller than for the isolated product (data for **As$_2$H** in acetone-d$_6$, (see above) (product 2, **As$_2$H**: ^{31}P NMR (C_6D_6, 121.5 MHz): $\delta = 3.4$ (td, $^3J_{PH} = 9.1$ Hz, $^1J_{PH} = 684$ Hz)). In contrast to reaction conditions with excess of water in the present case **As$_2$H** can accumulate. Lack of water suppresses the further hydrolysis to give **AsH$_2$**. Therefore **As$_2$H** can be detected by ^{31}P NMR spectroscopy.

This reaction behaviour leads to the conclusion, that at high temperatures which are required for polymer processing, hydrolysis of the stabiliser can occur in the low oxidisable medium caused by trace amounts of water from the atmosphere.

By use of an oxidisable reaction medium, for instance dodecane, only a slow oxidation of the phosphites was observed. By addition of a peroxide-based initiator (Triganox P) to a solution of **Ads$_2$** in dodecane oxidation to **Bds$_2$** was accelerated by factor 20 in comparison to the uninitiated system (Fig. 11). In both cases oxidation proceeds much faster than hydrolysis. Only after a long reaction time were traces of hydrolysis products observed.

Using a paraffin blend (PAREX, chain length C_{14}–C_{22}) as reaction medium also no hydrolysis of **Ads$_2$** was detectable either in oxidising or in nonoxidising atmosphere at 150°C. In the presence of oxygen only oxidation to **Bds$_2$** occurred, followed by a slow substitution of the reaction product under release of BHT (Fig. 12). Under nitrogen, no significant degradation of the phosphite was observed within 100 h.

By heating of **Ads$_2$** in a polyether alcohol at 150°C under nitrogen a hydrolysis product with direct P,H-coupling and a chemical shift of 1.4 ppm in ^{31}P NMR and a small amount of the phosphate **Bds$_2$** were observed (Fig. 13). In agreement with the results described above the hydrolysis product

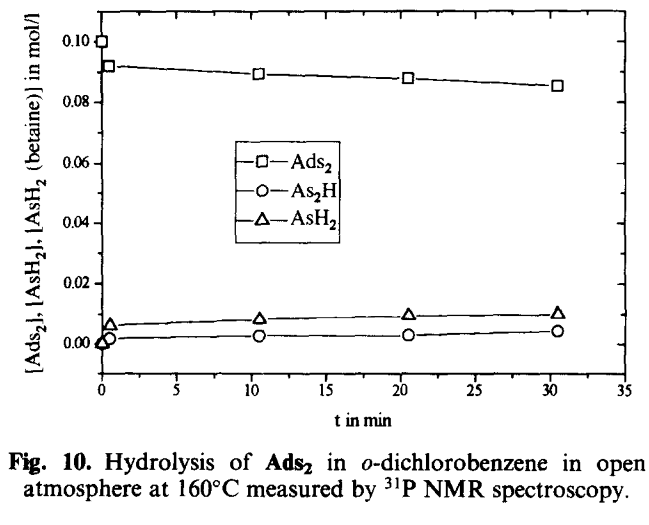


Fig. 10. Hydrolysis of **Ads$_2$** in *o*-dichlorobenzene in open atmosphere at 160°C measured by ^{31}P NMR spectroscopy.

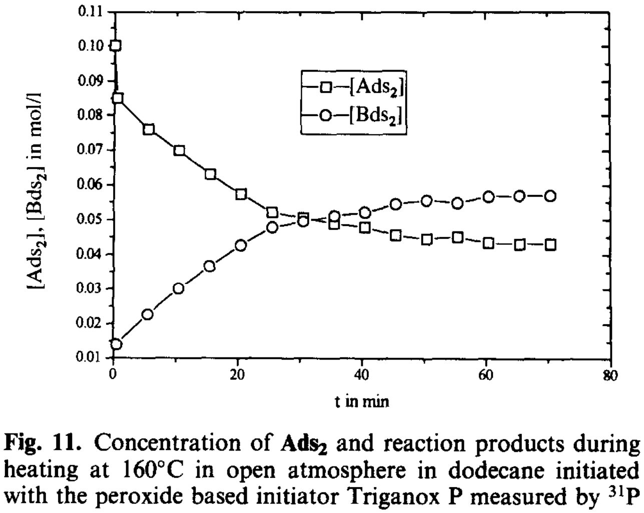


Fig. 11. Concentration of **Ads$_2$** and reaction products during heating at 160°C in open atmosphere in dodecane initiated with the peroxide based initiator Triganox P measured by ^{31}P NMR spectroscopy.

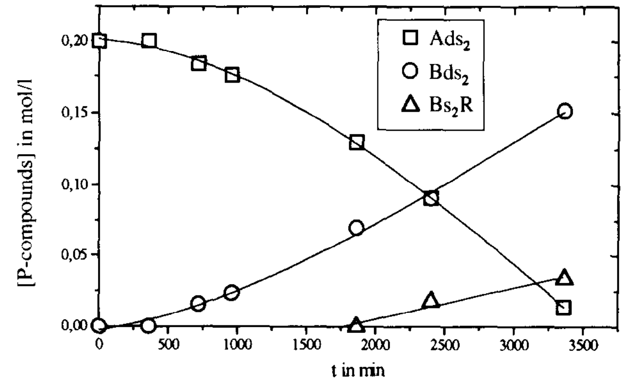


Fig. 12. Concentration of **Ads₂** and reaction products in a paraffin blend (PAREX) at 150°C in water saturated O_2 atmosphere measured by ^{31}P NMR spectroscopy ($[\text{P-compounds}]_{\text{total}} = 0.2\,\text{mol}\,l^{-1}$).

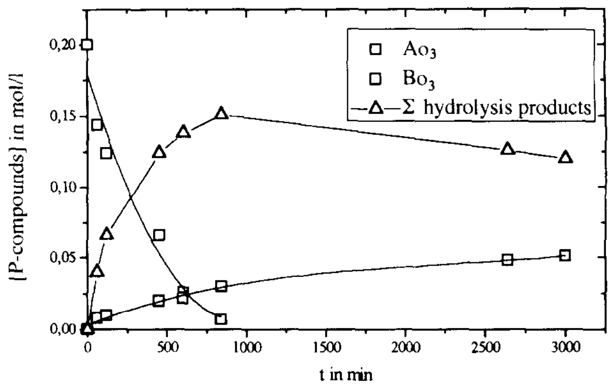


Fig. 14. Concentration of **Irgafos 168** (**Ao₃**) and reaction products in a polyether alcohol (SYSTOL T151) at 150°C in water saturated O_2 atmosphere measured by ^{31}P NMR spectroscopy ($[\text{P-compounds}]_{\text{total}} = 0.2\,\text{mol}\,l^{-1}$).

is assumed to be **AsH₂**. The release of the phenol BHT was detected by means of HPLC.

In oxygen atmosphere in polyether alcohol solution the transformation of the phosphite **Ads₂** was finished after 650 min. No hydrolysis could be observed. The only product detected by ^{31}P NMR spectroscopy was the corresponding phosphate **Bds₂**. In a polyether alcohol, however, hydrolysis of the phosphite can be detected in nitrogen, but not in oxygen atmosphere. In general, the degradation rates of the phosphites are significantly higher in the polyether alcohol than in paraffins caused by faster thermal and oxidative degradation of the polyether alcohol. For comparison Irgafos 168 was examined under identical conditions in polyether alcohol (Fig. 14). In this case, also in oxygen atmosphere hydrolysis occurred in competition to oxidation. The corresponding phosphate **Bo₃** was identified and a mixture of hydrolysis products (phosphonates, hydrogen phosphonates, phosphorous acid, ^{31}P NMR shift 4...7 ppm, direct P,H-coupling) were observed. 2,4-Di-*tert*-butylphenol formed by hydrolysis was detected by HPLC.

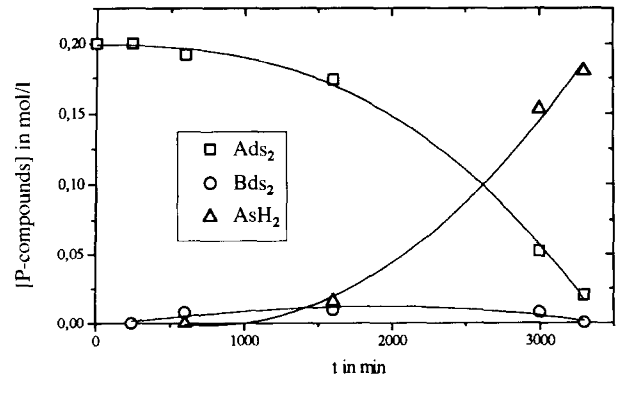


Fig. 13. Concentration of **Ads₂** and reaction products in a polyether alcohol (SYSTOL T151) at 150°C in water saturated N_2 atmosphere measured by ^{31}P NMR spectroscopy ($[\text{P-compounds}]_{\text{total}} = 0.2\,\text{mol}\,l^{-1}$).

4 CONCLUSIONS

It is shown that HALS-Phosph(on)ites containing tertiary HALS moieties are better hydroperoxide decomposers than comparable compounds with secondary HALS moieties. The hydrolysis of HALS-Phosphites starts with the substitution of the phenolic group by water. The resulting phosphonates hydrolyse faster than the original phosphites, to give the HALS containing hydrogen phosphonates having a betaine structure. These compounds are remarkably stable against further hydrolysis due to their increased electron density at the phosphorus atom.

Besides oxidation reactions a slow hydrolysis of HALS-Phosphites occurred in the low oxidisable medium *o*-dichlorobenzene at higher temperatures (160°C) in an open atmosphere. In oxidisable medium (dodecane, paraffin blend, polyether alcohol) in a water saturated, oxidising atmosphere HALS-Phosphites were almost exclusively oxidised to the corresponding phosphates.

REFERENCES

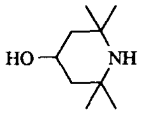
1. Schwetlick, K., in *Mechanisms of Polymer Degradation and Stabilisation*, ed. G. Scott. Elsevier, London, 1990, Ch. 2.
2. Rüger, C., König, T. and Schwetlick, K., *J. Prakt. Chem.*, 1984, **326**, 622.
3. König, T., Dissertation, TU Dresden, 1986.
4. Gächter, R. and Müller, H., *Taschenbuch der Kunststoffadditive*. Carl Hanser Verlag, München, 1983.
5. Minagawa, M., *Polym. Degrad. Stab.*, 1989, **25**, 121.

6. Klender, G. J. in *Polymer Durability—Degradation, Stabilization and Lifetime Prediction*, Advances in Chemistry Series 249, ed. R. L. Clough, N. C. Billingham and K. T. Gillen. ACS, Washington, DC, 1996, p. 397.
7. Schwetlick, K., Piontek, J., Winkler, A., Hähner, U., Kroschwitz, H. and Habicher, W. D., *Polym. Degrad. Stab.* 1991, **31**, 219.
8. Ryšavý, D. and Sláma, Z., *Angew. Makromol. Chem.*, 1969, **9**, 129.
9. Khloplyankina, M. S., Karpuchin, O. N., Buchachenko, A. L. and Levin, P. I., *Neftekhimiya*, 1965, **5**, 49.
10. Bass, S. I. and Medvedev, S. S., *Zh. Fiz. Khim.*, 1962, **36**, 2537.
11. Novoselova, L. V., Zubtsova, L. I., Babel', V. G. and Proskuryakov, V. A., *Zh. Prikl. Khim.*, 1973, **46**, 1329.
12. (a) Zaichenko, L. P., Babel', V. G. and Proskuryakov, V. A., *Zh. Prikl. Khim.*, 1974, 47, 1168; (b) 1974, **47**, 1354; (c) 1976, **49**, 465.
13. Tochácek, J. and Sedlár, J., *Polym. Degrad. Stab.*, 1993, **41**, 177.
14. Westheimer, F. H., Huang, S. and Covitz, F., *J. Am. Chem. Soc.*, 1988, **110**, 181.
15. Aksnes, G. and Aksnes, D., *Acta Chem. Scand.*, 1964, **18**, 1623.
16. Linger, G., Staniek, P. and Stoll, K., Paper presented at the RETEC, Houston, TX, February 1993.
17. Körner, S., Diploma thesis, TU Dresden, 1994.
18. Klender, G. J., *Proceedings of the 11th Bratislava IUPAC/FECS International Conference on Polymers*, Stará Lesná, Slovak Republic, 24–28 June, 1996, p. 85.
19. Hähner, U., Habicher, W. D. and Chmela, Š., *Polym. Degrad. Stab.*, 1993, **41**, 197.
20. Chmela, S., Habicher, W. D., Hähner, U. and Hrdlovic, P., *Polym. Degrad. Stab.*, 1993, **39**, 367.
21. Bauer, I., Habicher, W. D., Rautenberg, C. and Al-Malaika, S., *Polym. Degrad. Stab.*, 1995, **48**, 427.
22. Bauer, I., Habicher, W. D., Körner, S. and Al-Malaika, S., *Polym. Degrad. Stab.*, 1997, **55**, 217.
23. König, T., Habicher, W. D. and Schwetlick, K., *J. Prakt. Chem.*, 1992, **334**, 333.
24. Quin, L. D. and Ionkin, A. S., *Phosphorus, Sulfur Silicon Relat. Elem.*, 1995, **103**, 205.
25. Bauer, I. and Habicher, W. D., *Phosphorus, Sulfur Silicon Relat. Elem.*, in press.
26. Sasse, K., in *Methoden der Organischen Chemie (Houben-Weyl)*, Vol. XII/2, ed. E. Müller. Georg Thieme Verlag, Stuttgart, 1964, p. 8.
27. Tanaka, T., *J. Pharm. Soc. Japan*, 1959, **79**, 721.
28. Winkler, A., Diploma thesis, TU Dresden, 1989.

APPENDIX

Structures of the stabilisers used

TMP



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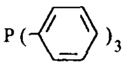

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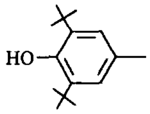

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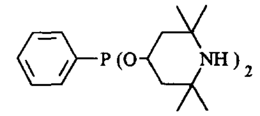
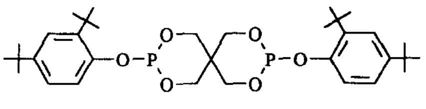


Ultranox 626



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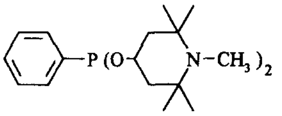
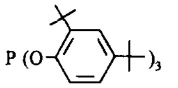
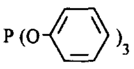


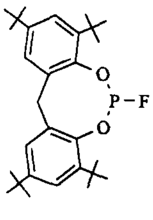
Irgafos 168



Ac$_3$



Fp-9



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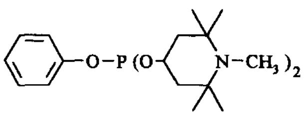
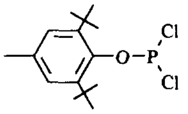


AdCl$_2$



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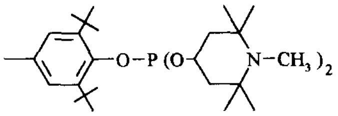

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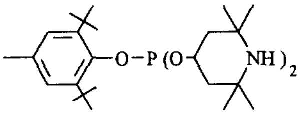
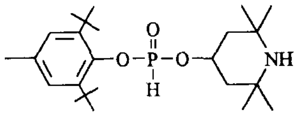


AdsH



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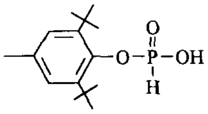
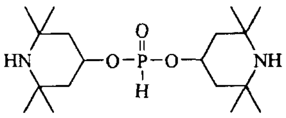
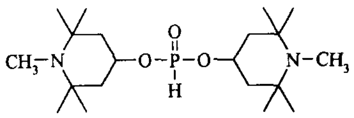


As$_2$H



At$_2$H



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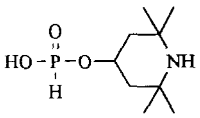

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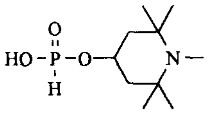

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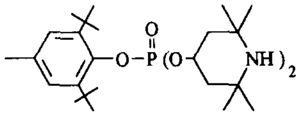

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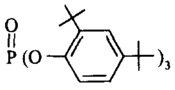

Bs$_2$R