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The Determination of Small Amounts of Organic Hydroperoxides in the Presence of Hindered Amine Light Stabilizers and their Nitroxyls

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ABSTRACT

A method for the quantitative determination of hydroperoxide (ROOH) in the presence of hindered amine light stabilizers (HALS) and/or their nitroxyl free radical derivatives has been elaborated. The method is based on the quantitative reduction of hydroperoxides by triphenyl phosphine. The resulting compounds (alcohols) are then determined by GLC using the internal standard technique. The method has been tested on the hydroperoxides derived from 2,4-dimethylpentane. Its sensitivity and reproducibility appear to be comparable with other methods for ROOH determination but, unlike the latter, it has the advantage that its results are not influenced by the presence of HALS and/or their nitroxyl radical derivatives in the analyzed medium.

INTRODUCTION

Hindered amine light stabilizers (HALS) based on 2,2,6,6-tetramethylpiperidine derivatives (I) represent a relatively new group of extremely

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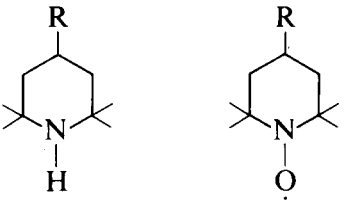
efficient polymer protecting additives whose mechanism of action is still under active investigation.[1]



(I) (II)

It has been shown that a multitude of pathways is involved in the protective mechanism conferred by these additives, but the interactions of HALS (I) and their nitroxyl radicals (II) with radicals present in oxidizing systems, or even with ROOH alone, seem to be of particular importance.

For this reason, the analytical determination of ROOH in the presence of (I) and/or (II) is rendered very difficult, if not impossible. It has been shown by Toda *et al.*[2] that nitroxyl radicals are also able to liberate iodine from potassium iodide by a redox reaction. Thus, the presence of nitroxyls in peroxidized systems must inevitably affect the results of all the iodometric methods for ROOH determination. Although Grattan *et al.*[3] have drawn attention to this fact, it does not seem to be generally recognized.[4-6] The presence of HALS and nitroxyls has been shown to interfere quite seriously also with ferric thiocyanate methods.[7]

Among other sensitive analytical methods for ROOH determination, summarized in the excellent monograph by Swern,[8] the chemical reduction methods appear to be of particular interest. For instance, the reduction of peroxidic compounds by tert-phosphines was reported[9] to be quantitative, unambiguous and fast for almost every peroxidic compound:

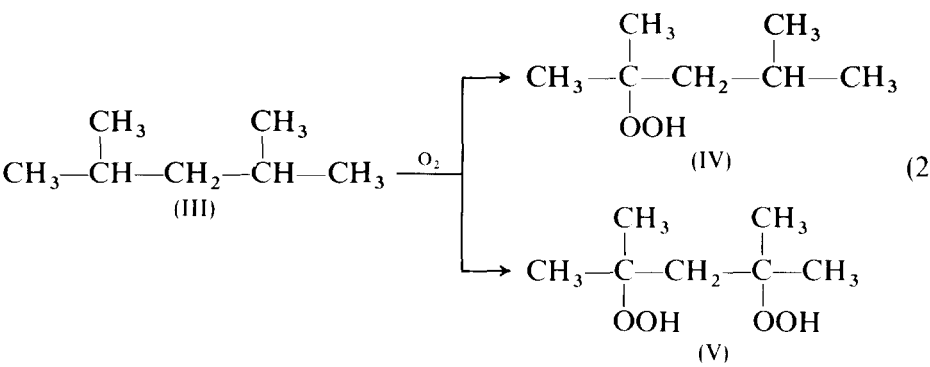
$$P(R)_3 + R'—O—O—R'' \rightarrow OP(R)_3 + R'—O—R'' \qquad (1)$$

where R = alkyl, aryl; and R′, R″ = H, acyl, alkyl or aralkyl.

For these reasons, phosphine, specifically triphenylphosphine (TPP), methods have been developed for the microdetermination of organic peroxides. The majority of them are based either on the determination of the disappearance of phosphine[10,11] or on appearance of the phosphine oxide.[12] However, both these approaches require strictly anaerobic conditions because the phosphine solutions oxidize slowly in the presence of air. Moreover, the determination, based on the consumption of phosphine, requires the presence of a comparable concentration of the phosphine reactant with respect to that of peroxide, the accuracy of the determination being decreased when a large excess of phosphine is used. But none of these approaches can discriminate between the types of the analyzed peroxides; their results give only the overall concentration of O—O groups in the system. To reach this goal, additional analytical methods must be used.

Thus, Swern[8] recommended that the TPP method of peroxide analysis be improved by analyzing the resulting stable products of peroxide reduction via well established chemical and/or instrumental methods. The facile reduction of hydroperoxides by TPP has indeed been used for the identification of hydroperoxides resulting from the peroxidation of various hydrocarbons.[13-16] There are several pieces of evidence that this reduction can be boosted by strong acids and certain metals[17] and that it can also be inhibited, or at least retarded, by certain impurities.[18] But, up to now, no information whatsoever is available concerning the influence of stabilizers and/or their oxidation products upon the reliability of hydroperoxide analysis when carried out through their reduction by TPP. This lack of information is particularly true in the case with which we are dealing, i.e. the influence of HALS and their nitroxyl free radical derivatives. Grattan *et al.*[3] proposed the use of the TPP method for the analysis of hydroperoxides when nitroxyl radicals (II) were present, but without any experimental details.

The purpose of this communication is to report on the use of the TPP method as applied to the analysis of hydroperoxides (IV) and (V) derived from 2,4-dimethylpentane (III), in order to find the optimum conditions and to check the influence of HALS and their nitroxyls on the results.



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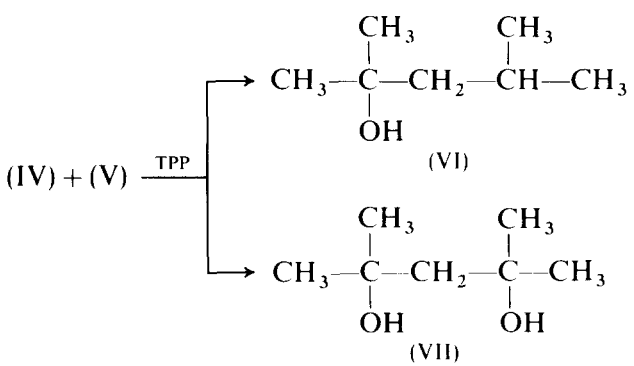

(3)

The alcohols (VI) and (VII) were determined by gas–liquid chromatography (GLC).

In previous work, the same procedure was used in order to establish the inhibition effect of HALS and nitroxyls in the ^{60}Co γ-radiation-induced oxidation of this alkane at 25°C (Marchal and Anton[19]).

EXPERIMENTAL

Reagents

2,4-dimethylpentane (Elf, 99·5% by GLC) was purified prior to use by filtering through a glass column (ϕ 15 mm) packed with Al_2O_3 (Alumina Woelm W 200 basic), the length of the packing being 200 mm. The first 20 ml of filtrate was discarded: the packing was not used for more than 250 ml of liquid. The purified hydrocarbon did not exhibit any measurable absorption in a 1 cm path length cell at $\lambda \simeq 245$ nm. It was stored in an amber flask at -18°C. The absolute measurement of ROOH concentration in the purified material showed that it contained less than 5×10^{-6}M ROOH. The determination was carried out using the ferric thiocyanate procedure.[20]

Azo-bis-isobutyronitrile (AIBN) (Fluka, purum $\simeq$ 98% N) was recrystallized twice from diethylether and stored in the dark at -18°C.

Di-tert-butylperoxide (Fluka) was employed without further purification.

Tert-butyl hydroperoxide was synthesized[21] and then purified by preparative GLC using all glass apparatus. Iodimetric assay 98·7%.

2,2,6,6-tetramethylpiperidine-1-oxyl (TMPO) and bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidinyl)sebacate (Tinuvin 770—dinitroxyl) were prepared according to the method due to Rozantsev.[22]

Peroxidation of 2,4-dimethylpentane

First process

2,4-dimethylpentane–2,4-dihydroperoxide (V) was prepared by AIBN initiated peroxidation of 2,4-dimethylpentane (III). 200 ml of (III) containing 200 mg of AIBN were heated under reflux at 55°C for 85 h while air was slowly bubbled through the liquid. After cooling to 0°C, the crystals which separated from the mixture were washed with ice-cool pure (III) and left drying at room temperature. Thus, approximately 200 mg of solid derivatives (at ambient temperature) were obtained. The —OOH concentration in this product found by SCN^- assay[20] was 36·7% (this corresponds to 91% of theoretical, assuming that only (V) was present in the crystals).

Second process

The mixture of 2,4-dimethylpentane–2,4-dihydroperoxide (V) with 2,4-dimethylpentane–2-hydroperoxide (IV) were prepared as described above, but this time, 200 mg of di-tert-butyl peroxide was used as initiator at 80°C for 70 h. After that, the reaction mixture was concentrated to *ca* 20 ml in a rotary evaporator at 25°C. The concentrate was left overnight in an open dish at room temperature. The resulting oil-like liquid was transferred and weighed out into a volumetric flask (87·8 mg/25 ml) and filled up to the mark with pure 2,4-dimethylpentane. This was used as a model mixture for all further experiments. The SCN^- assay showed the presence of $1{\cdot}23 \times 10^{-2}$M —OOH.

The main difference between the two methods of peroxidation of 2,4-dimethylpentane is in the nature of the initiating radicals. While, in the first case, the isobutyronitrile peroxy radicals were selectively attacking tert-hydrogens in (III) giving rise to the formation of (IV) and (V), the alkoxy radicals, produced in the second method, abstracted hydrogens from (III) with much less selectivity to form a rather complex mixture of peroxidized species. The non-selectivity of alkoxy radicals has recently been demonstrated in an elegant experiment by Felder.[23]

Another difference, clearly distinguishing the two methods, was the temperature at which the oxidation was carried out. The temperature of 55°C, in the first case, was sufficiently gentle not to destroy the hydroperoxides formed. To achieve a reasonable rate of initiation in the second case it was, however, necessary to increase the temperature to 80°C. At this temperature (IV) and (V) were probably already being destroyed to form the corresponding alcohols whose presence can be seen in the chromatogram of the raw mixture (Fig. 1a). Other peroxidized species, i.e. those derived from primary and secondary hydrogen abstractions, are destroyed even more easily at this temperature.[8] The resulting oil obtained in method 2 was thus a more complex mixture also containing non-peroxidic compounds (probably of alcohol character). This was also confirmed by the SCN^- assay (see above) which showed that only *ca* 50% of the theoretical amount of (III) was converted to 2,4-dihydroperoxide (V). As will be shown below, however, it is possible to distinguish between the individual 2- and 2,4-hydroperoxides (IV) and (V) using the TPP treatment and even to establish their absolute concentrations knowing the GLC responses of the corresponding alcohols (VI) and (VII).

Procedure for the reduction of the hydroperoxides using triphenylphosphine

Triphenylphosphine (TPP) reagent was prepared by weighing out 0·5 g ($1{\cdot}9 \times 10^{-3}$ mole) of TPP into a 10 ml volumetric flask. To this, 5 ml of

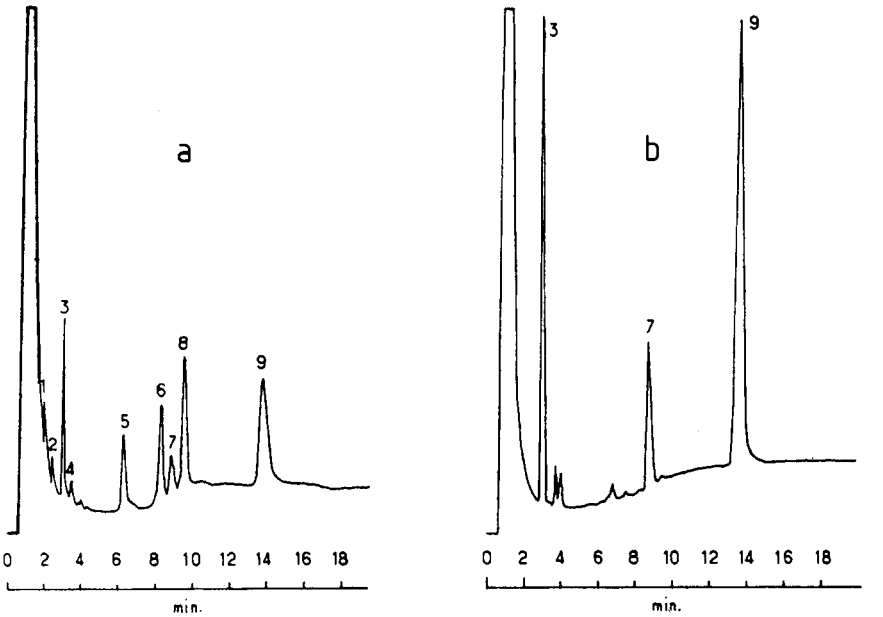

Fig. 1. GLC chromatograms of the products of di-tert-butylperoxide initiated autooxidation of 2,4-dimethylpentane. (a) Before TPP treatment. (b) After TPP treatment.

cyclohexane was added. The latter contained $3{\cdot}52 \times 10^{-2}$M of *ortho*-xylene as the internal standard for GLC. After all the TPP was dissolved, the solution was made up to the mark with pure cyclohexane.

For the reduction of hydroperoxides, 1 ml of hydroperoxides containing 2,4-dimethylpentane was pipetted to a sample vial (Perkin-Elmer) into which 0·1 ml of TPP reagent was added. The vial was then covered with a silicone rubber septum coated with Al foil and closed by using a Perkin-Elmer safety closure. In this way, the samples could be stored for a long time without any loss of material. For GLC analysis, the appropriate quantity was taken off with a syringe through the septum.

Quantitative analysis of resulting alcohols by gas–liquid chromatography (GLC)

Procedure

A Sigma 1 (Perkin-Elmer) gas chromatograph equipped with an automatic integration unit was used for most of the analyses. In some experiments, a simpler Intersmat (IGC 15) instrument was also employed to compare the precision of the subjective and the automatic data treatments. Furthermore, the injection chamber of this instrument was not fully made of glass-teflon as

was the former. This does not seem to be of importance since the GLC experiments were done *after* the hydroperoxides' reduction to alcohols which are not decomposed under these separation conditions. Both instruments were fitted with a FID detector and temperature programming facilities. The separations were carried out using a 2·80 m × 3 mm stainless steel column packed with 5% Ucon Polar 50 HB 2000 on Chromosorb W DMCS 60/80 mesh, nitrogen being used as carrier gas at a flow rate of 20 ml/min. The oven temperature was programmed from 90 to 120°C at a rate of 3°C/min. The injected quantity of 0·6 μl of sample was measured by a Hamilton 1 μl syringe.

Standard solution of 2,4-dimethylpentanol-2 (VI)

This solution was prepared by weighing out 204·6 mg of (VI) (Fluka purum) into a 25 ml volumetric flask and making up to the mark with cyclohexane. Other standards were prepared by appropriate dilution of this stock solution. In this way, the GLC calibration was made within the range $7{\cdot}05 \times 10^{-5}$ to $7{\cdot}05 \times 10^{-2}$M. For the analyses, 1 ml of the appropriate standard was mixed with 0·1 ml of the internal standard solution ($1{\cdot}76 \times 10^{-2}$M *o*-xylene in cyclohexane).

Standard solution of 2,4-dimethylpentane diol-2,4 (VII)

This was obtained from the corresponding dihydroperoxide by weighing out 40·5 mg of (V) into a 50 ml volumetric flask and making up to the mark with 2,4-dimethylpentane. For calibration, 1 ml of this solution was mixed with 0·1 ml of the TPP reagent and treated as described above for the reduction procedure. The reduction appears to be complete after several minutes and the GLC properties of this solution were not changed after several days of standing under laboratory conditions. From the absolute concentration [—OOH] determined by the SCN^- method applied to the initial solution and the small amount of monohydroperoxide (IV) (found by GLC after reduction with TPP), it was then possible to establish the FID response of diol (VII).

RESULTS AND DISCUSSION

Figure 1a shows a chromatogram of the products of the peroxidation of (III) carried out according to the second process. The model mixture solution of these products in (III), (87·8 mg/25 ml) was injected before treatment. This somewhat complicated system becomes substantially simpler when GLC

analysis is done after the addition of 5 mg of solid TPP to 1 ml of the above-mentioned solution (see Fig. 1b). One can see that the major effect is a huge increase in peaks 3 and 9. This result allows us to assign these peaks, respectively, to 2,4-dimethylpentane-2-ol (VI) and 2,4-diol (VII). This was further corroborated by a comparative GLC experiment carried out with (VI) (Fluka, purum) and with diol (VII) obtained by TPP reduction of crystalline dihydroperoxide (V).

Having established the peak identity formed on TPP treatment, it was possible to suggest a standard method and to carry out the quantitative experiments.

Time dependence of hydroperoxide reduction

Table 1 shows the time dependence of the reduction of hydroperoxides (IV) and (V) by TPP expressed in terms of peak areas of the corresponding alcohols (VI) and (VII).

It follows from these results that the overall reducing reactions are completed in less than 30 min at room temperature. This is further confirmed by the fact that results were not changed by prolonged heating at 60°C. It is worth noting that the reduction of dihydroperoxide (V) proceeds somewhat faster than that of (IV). The reaction time of 30 min was therefore adopted for all further experiments presented in this work.

Reproducibility of the chromatographic determination

In order to establish the reproducibility of the mono- and dihydroperoxides' determination using the above method, a series of several analyses were

TABLE 1

Peak Area A Counts for Alcohol (VI) and Diol (VII) with Respect to Internal Standard Area S as a Function of TPP Reaction Time t at Room Temperature

t (*min*)	A_{VI}/S	A_{VII}/S
2	0·284 3	1·458 6
20	0·369 5	1·435 0
30	0·415 9	1·367 6
220	0·407 8	1·412 0
220[a]	0·411 8	1·403 1

[a] After this period, the sample was heated up to 60°C for 45 min.

TABLE 2

Results of ROOH Reduction by TPP Expressed in Terms of Peak Heights (Manual Measurements) or as Peak Areas (Automatic Integration). H_{VI}, H_{VII} and H_S are Peak Heights Due to the Alcohol (VI), Diol (VII) and the Internal Standard, Respectively, While A_{VI}, A_{VII} and S Represent the Corresponding Peak Areas

Run	H_{VI}/H_S[a]	H_{VII}/H_S[a]	A_{VI}/S[b]	A_{VII}/S[b]
1	0·471	0·409	0·406 1	1·458 5
2	0·468	0·424	0·407 8	1·362 2
3	0·471	0·440	0·415 9	1·327 0
4	0·474	0·409	0·413 8	1·359 4
5	0·478	0·423	0·415 0	1·340 2
6	0·466	0·444	0·411 8	1·367 6
7	0·477	0·446	0·411 8	1·352 4
Average ($\pm\sigma$)	0·472 ($\pm$1%)	0·428 ($\pm$3%)	0·411 8 ($\pm$1%)	1·366 7 ($\pm$3%)

[a] Results obtained with the Intersmat IGC 15 apparatus.

[b] Results obtained with the Sigma 1 Perkin-Elmer instrument by a different operator. Areas expressed in arbitrary units (number of counts).

carried out without changing the experimental procedure and with the same standard hydroperoxides solution. Moreover, the peak areas for (VI) and (VII) were compared with that of the internal standard, in one case, whilst, in the second case, by using the simplest GLC instrument, the peak height ratios only were calculated. These results are summarized in Table 2.

It can be asserted that, under the given conditions, the TPP method of hydroperoxide determination using the GLC finish is sufficiently reproducible, even when an unsophisticated and inexpensive gas chromatograph is employed for the analysis. Nevertheless, for hydroperoxide levels substantially lower than those which were used in the example described, the automatic integration mode would naturally be preferred.

Influence of stabilizers

In order to check the influence of hindered amine light stabilizers (HALS), corresponding nitroxyl free radicals and phenolic antioxidants upon the yields of alcohols produced by ROOH reduction by TPP, further experiments were carried out with and without addition of a well known stabilizer of one or the other type to the analyzed system. The results are given in Table 3.

From these experiments, it can be concluded that none of these three kinds

of free radical scavenger exhibits any influence on the yields of (IV) and (V) hydroperoxide reduction by TPP. All these results are in accordance with the observation of Hiatt *et al.*[18] who excluded a free radical mechanism to explain the reduction of peroxidic species by TPP.

Influence of hydroperoxide concentration

In a separate run, tert-butyl hydroperoxide was added to the solution of peroxidized 2,4-dimethylpentane in such a quantity that the total hydroperoxide content was almost equimolar with the TPP available for the reduction reaction. The results of these complementary experiments are also given in Table 3. They show that, even at these concentrations, the reduction is quantitative within the time limit used for the analysis.

TABLE 3

Influence of Certain Additives on the Yield of ROOH Reduction by TPP. A_{VI}/S, A_{VII}/S are the Ratios of Integrator Counts for VI, VII and Internal Standard Peak Areas, Respectively

Additive	*Concentration (mol liter^{-1})*	A_{VI}/S	A_{VII}/S
None	—	0·404 3	1·358 9
bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate (Tinuvin 770)	$1{\cdot}5 \times 10^{-2}$	0·413 2	1·367 2
bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidinyl) sebacate	$1{\cdot}5 \times 10^{-2}$	0·411 2	1·410 2
2,2,6,6-tetramethyl-1-oxyl-piperidine	$1{\cdot}5 \times 10^{-2}$	0·407 8	1·412 0
2,6-di-tert-butyl-4-methyl phenol (BHT)	$1{\cdot}5 \times 10^{-2}$	0·418 3	1·372
tert-butyl hydroperoxide	6×10^{-3}	0·417 2	1·34

Example of use

Using the standard solution of alcohol (VI) and diol (VII) (see 'Experimental'), the FID responses can be expressed in terms of absolute concentrations.

Thus, as an example, from the results obtained with the simplest GLC apparatus under given conditions, the ratios H_{VI}/H_S and H_{VII}/H_S were unity for concentrations [VI] = $1{\cdot}79 \times 10^{-3}$M and [VII] = $12{\cdot}4 \times 10^{-3}$M, respectively, over the entire concentration range used. Knowing these values of the concentration calibration factors and having shown that the hydroperoxide reduction by TPP is quantitative, it was possible to calculate concentrations of hydroperoxides (IV) and (V) from the averages of H_{VI}/H_S and H_{VII}/H_S

given in Table 2 and, finally, to obtain the corresponding overall concentration of —OOH groups.

$$[IV] = [VI] = 0{\cdot}472 \times 1{\cdot}79 \times 10^{-3} = 0{\cdot}84 \times 10^{-3}\text{M}$$
$$[V] = [VII] = 0{\cdot}428 \times 12{\cdot}4 \times 10^{-3} = 5{\cdot}31 \times 10^{-3}\text{M}$$
$$\sum[\text{—OOH}] = (0{\cdot}84 + 2 \times 5{\cdot}31) \times 10^{-3} = 11{\cdot}46 \times 10^{-3}\text{M}$$

This value compares well with that found using the thiocyanate method ($12{\cdot}3 \times 10^{-3}$M). It should be emphasized again, however, that the latter method is not applicable in the presence of nitroxyls and excessive concentrations of HALS,[20] this disadvantage being overcome by the present procedure.

Sensitivity of the method

The sensitivity limit is imposed by the GLC conditions under which the alcohols (VI) and (VII) can be determined with reasonable accuracy. In our case, this limit was found to be 5×10^{-5}M when using the apparatus equipped with automatic integration.

CONCLUSION

The method for the determination of hydroperoxides using GLC for the separation and quantification of the corresponding alcohols produced by reduction by triphenylphosphine, is simple, sensitive and reproducible. The results are not influenced by the presence of phenolic antioxidants or by the presence of HALS or their nitroxyls, while these do affect the results obtained when common hydroperoxide determination methods are used. This feature is quite useful for investigations required to gain a better understanding of the mechanisms of the stabilization of organic materials by HALS.

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