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Peroxides

XII.☆ Gas–liquid and high-performance liquid chromatographic analysis of aliphatic hydroperoxides and dialkyl peroxides

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ABSTRACT

The chromatographic resolution of 1-alkyl hydroperoxides and di-1-alkyl peroxides by either gas–liquid chromatography and/or high-performance liquid chromatography (HPLC) was investigated. The chromatographic methods developed were applied to the compositional analysis of hydroperoxides and dialkyl peroxides in reaction mixtures and to purity determinations. The effect of aliphatic peroxide structure based on the conformations imposed by the dihedral angle of the peroxide bond has strong implications for peroxide resolutions in HPLC compared to their non-peroxy analogues. Comparison of the chromatographic data for peroxide content with that obtained by iodometry show that the methods developed are suitable for peroxide determinations.

INTRODUCTION

Numerous methods of peroxide determination have been devised to cover the range of reactivities shown by diverse peroxide structures. For an aliphatic series of derivatives, the order of increasing O–O bond strength parallels the following decreasing order of reactivity [2,3]: peroxy acid [R–C(O)–O–O–H]; diacyl peroxide [R–C(O)–O–O–C(O)–R]; hydroperoxide (R–O–O–H); perester [R–C(O)–O–O–R]; dialkyl peroxide (R–O–O–R). This peroxide sequence depicts a decreasing reactivity in liberating iodine from iodide ion [4], and increasing stability based on polarographic half-wave potential ($-E_{1/2}$) and energy of activation (E_a) for decomposition [3]. Because of this wide difference in reactivity, no general analytical method for all peroxide classes has appeared in the literature.

Gas–liquid chromatography (GLC) has been a sensitive method of peroxide determination [5], although the relatively low thermal stability of the peroxygen bond has limited the utility of GLC analysis of peroxides to members of low molecular mass, generally below 10 carbon atoms [5–11] and at column temperatures below 100°C. Hydroperoxides are stable to about 90°C [12] but readily decompose to alkyl alcohols and carbonyl compounds (aldehydes from primary alkyl hydroperoxides and ketones from secondary and tertiary alkyl hydroperoxides). This sensitivity of hydroperoxides to thermal de-

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composition has been used in their analyses by pyrolysis GLC [13]. Alternatively, hydroperoxide decomposition has been avoided by reduction to alcohol prior to GLC determination. On the other hand, dialkyl peroxides are the most stable to thermal effects as illustrated by the GLC elution of 2,5-dimethyl-2,5-di(*tert.*-butylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(*tert.*-butylperoxy)hexane [14] at 138°C. Like hydroperoxides, dialkyl peroxides undergo thermal decomposition at elevated temperatures which permit their analysis by pyrolytic GLC [15,16].

High-performance liquid chromatography (HPLC) is a mild method usually conducted at room temperature that assures the peroxide's structural integrity. Because of this major advantage over GLC in the analysis of thermally sensitive, non-volatile and higher-molecular-mass compounds, HPLC has been actively studied for peroxide structures [17–21] and, most importantly, has been accepted as the method of choice for lipid peroxide analysis.

In the course of our recent developments of alkyl hydroperoxide [22] and dialkyl peroxide [23] syntheses, we found limited published literature on chromatographic analyses of homologous series of long chain aliphatic peroxides. This void may have resulted from the compounds' unavailability or by the failure or inadequacies of earlier synthetic methods [24–26] of preparation. The success of our peroxide syntheses was dependent on instituting concurrent GLC and HPLC examinations of reaction products to assess their relative advantages and limitations. The suitability of these chromatographic methods for quantitating hydroperoxides could be independently confirmed by iodometry whereas their accuracy for dialkyl peroxides lacked this independent verification.

The initial goal of this study was to update GLC and HPLC methods using high-resolution columns for the direct determination of hydroperoxides and dialkyl peroxides in complex reaction mixtures. Because of thermal and surface sensitivities of hydroperoxides, GLC and HPLC can give unreliable quantitation that necessitate an independent method of analytical verification. Iodometry has been well established for hydroperoxide determinations [5] but it measures total hydroperoxide content whereas chromatographic methods measure the separated components.

By contrast, dialkyl peroxides have been difficult to analyze iodometrically [5,27]. However, the reverse option of using GLC and HPLC methods would provide a criterion that would validate the results of iodometry. In fact, the results of the current study has made possible the development of a newly modified iodometric method [1].

As this study progressed, we observed unexpected effects of peroxide structure on the chromatographic separation of peroxides from their oxy-analogues. Accordingly, this paper composites the details of our chromatographic results on the even-membered homologous series of primary hydroperoxides (hexyl to hexadecyl) and primary dialkyl peroxides (dihexyl to dihexadecyl), a comparison of the chromatographic and iodometric results, and the correlation of the separation of peroxides and their oxy-analogues that together provide new insights on peroxide separations and analyses.

EXPERIMENTAL[a]

Materials

Hydroperoxides were prepared by either of two methods [22]: (a) the perhydrolysis of alkyl triflates or (b) the perhydrolysis of alkyl mercuric tetrafluoroborates. The crude preparations were analyzed directly and pure hydroperoxides isolated by semi-preparative HPLC. Primary dialkyl peroxides were obtained by phase transfer reaction of potassium superoxide with primary alkyl bromides [23] and the peroxides purified as described. *tert.*-Butyl myristate [2] and *tert.*-butyl permyristate [28] were prepared and purified as described. Di-*tert.*-butyl peroxide, 98% (Aldrich, Milwaukee, WI, USA) and dicumenyl peroxide, 98% (Akzo, Chicago, IL, USA) were used as received. HPLC-grade solvents (Burdick & Jackson, Muskegon, MI, USA) were used throughout the investigations.

[a] Reference to a brand or firm name does not constitute an endorsement by the US Department of Agriculture over others of a similar nature not mentioned.

Methods

Gas–liquid chromatography. The instrument was a Hewlett-Packard (Avondale, PA, USA) Model 5830A gas chromatograph equipped with a capillary inlet system and a flame ionization detector (200°C). The quartz capillary columns were 12 m × 0.2 mm coated with 0.33-μm methyl silicone fluid (HP-101) and a 4 m × 0.2 mm coated with 0.33-μm 5% cross-linked phenyl methyl silicone fluid (HP-5). Initial column temperature for the 12-m column was 50°C for hexyl hydroperoxide and 80°C for octyl hydroperoxide, decyl hydroperoxide, and dodecyl hydroperoxide (injector port, 140°C). The carrier gas was helium with a linear velocity of 22.5 cm s^{-1} at a split ratio of 60:1. Dodecyl hydroperoxide was also analyzed on a 4-m column at 40°C (injector port, 140°C) tetradecyl and hexadecyl hydroperoxides at 110°C (injector port, 160°C) with helium at linear velocity of 12 cm s^{-1}. All components in reaction mixtures were resolved by temperature programming at 2°C min^{-1} except for hexadecyl hydroperoxide at 5°C min^{-1} to a final temperature of 150°C, and the important components were identified by comparison with available standards. For differentiation of dialkyl ethers from dialkyl peroxides, the former were prepared by the alcohol alkylation method of Barluenga *et al.* [29].

High-performance liquid chromatography. The HPLC solvent delivery systems used were a Beckman (San Ramo, CA, USA) Model 110A solvent delivery module equipped with an Altex 210 loop injector with either a 20-μl or 100-μl sample loop and a Waters differential refractometer detector, Model R401 (Waters Assoc., Milford, MA, USA) and a Hewlett-Packard Model 1090 solvent delivery module equipped with a Rheodyne Model 7125 loop injector with a 20-μl loop and a Tracor (Austin, TX, USA) Model 945 flame ionization detector operated at 80°C. The HPLC columns used were a 25 cm × 4.6 mm I.D. stainless-steel column prepacked with 5-μm silica (Zorbax SIL, DuPont, Wilmington, DE, USA) or 5-μm ODS (Altex Ultrasphere, Deerfield, IL, USA) for analytical HPLC. Semipreparative isolation of 1-alkyl hydroperoxides was made on a Dynamax (Rainin, Woburn, MA, USA) prepacked 8-μm silica column, 25 cm × 10 mm I.D. The integrator/recorder was a Hewlett-Packard Model 3396A. Samples were dissolved in mobile phase at 5 mg ml^{-1} for analytical HPLC and 100 mg ml^{-1} for semi-preparative HPLC. Response factors to the refractive index and flame ionization detectors were obtained on the purified peroxides over the range of 0.05–0.5 mg. Hydroperoxides were eluted isocratically from the silica columns with hexane–isopropanol (98:2, v/v) at a flow-rate of 1 ml min^{-1} (analytical) or 3 ml min^{-1} (semi-preparative HPLC). Dialkyl peroxides were analyzed isocratically on the ODS column with acetone–acetonitrile (70:30, v/v) at a flow-rate of 0.8 ml min^{-1}.

Iodometry. Iodometric analysis of hydroperoxides by the Wheeler method [4] is the liberation of iodine by iodide reduction of easily reducible peroxides in acetic acid–chloroform solution. The method was recently modified for its application to dialkyl peroxides by incorporating catalysis with perchloric acid or ferric ion in acetic acid at 80–100°C [1].

RESULTS AND DISCUSSION

Hydroperoxides

We have recently developed two new methods of preparing alkyl hydroperoxides, each of which has its advantages [22]. In one method, 1-alkyl hydroperoxides were obtained by perhydrolysis of primary alkyl mercuric tetrafluoroborate which produced primary hydroperoxide with minor amounts of positional hydroperoxide isomers (3%), dialkyl ether and dialkyl peroxide in addition to aldehyde and alkanol. In these studies GLC analysis of the reaction products on a 12-m capillary column was found to be highly efficient for the resolution of hydroperoxides from their reaction co-products. For example, Fig. 1 illustrates the resolution of 1-, 2- and 3-hexyl hydroperoxide isomers and the longer retention time co-products, dihexyl ether and dihexyl peroxide. Alternatively, perhydrolysis of a primary alkyl triflate (trifluoromethanesulfonate) forms the primary hydroperoxide with no formation of positional isomers. Although triflate and hydroperoxide have similar GLC reten-

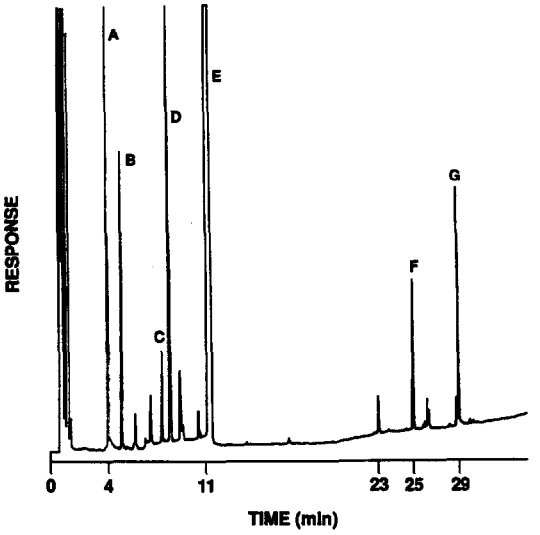


Fig. 1. Reaction products from hexyl hydroperoxide synthesis via perhydrolysis of alkyl mercuric tetrafluoroborate as separated by GLC, 12-m HP-101 capillary column. Conditions as in text. Peaks: A = R_6OH; B = R_6Br; C = 3-R_6OOH; D = 2-R_6OOH; E = 1-R_6OOH; F = R_6OR_6; G = R_6OOR_6.

tion times they are resolvable with triflate having the longer retention time.

Chromatographic determinations of the homologous hydroperoxide series up to 12 carbon atoms at column temperatures not exceeding 90°C established 10 carbon atoms to be the limit in chain size of hydroperoxides for which there is little or no decomposition. Brief contact at higher temperatures volatilizes samples onto the column but injection port temperatures should not exceed 130°C. The effect of temperature on peroxide content was observed on two dodecyl hydroperoxide preparations using a short column (4 m) having the following parameters and giving the results shown in parentheses (injection port temperature, column temperature, peroxide eluate temperature) (% peroxide by iodometry, % peroxide by GLC, % peroxide decomposed): (1) (160°C, 60°C, 91°C) (97%, 20%, 77%), and (2) (140°C, 40°C, 61°C) (75%, 67%, 8%). The milder temperature conditions in No. 2 resulted in mild decomposition compared to No. 1, indicating the injection port temperature should be lower than 140°C.

The hydroperoxide preparations for syntheses up to decyl hydroperoxide were conveniently monitored by GLC to determine reaction completeness. The isolated hydroperoxide products were then analyzed by GLC and iodometry for comparison. Since iodometry measures the sum of all isomeric peroxides present and GLC resolves hydroperoxide isomers, the isomer correction to be added to the GLC value of primary hydroperoxides amounts to about 2–3%. The GLC values for primary hydroperoxides and the

TABLE I

ANALYSIS OF 1-ALKYL HYDROPEROXIDES BY IODOMETRY, GLC AND HPLC

Primary 1-alkyl	% Hydroperoxide				
	Iodometric value[a]	GLC[b]	HPLC[c]		
			RP/FID	NP/FID	NP/RID
Hexyl	79	81			
Octyl	81	79	51		
Decyl	81	78		66	87
Dodecyl	82	67	56	60	
Tetradecyl	80	48	77		72
Hexadecyl	81	18[d]	80	58	75

[a] Ref. 22, values based on % (w/w) active oxygen.
[b] 12-m HP-101 capillary column, see Experimental.
[c] RP = Reversed phase; NP = normal phase; FID = flame ionization detection; RID = refractive index detection; results based on % (w/w) from calibration curves of purified hydroperoxides.
[d] 4-m HP-5 capillary column, see Experimental.

iodometric data for the series up to decyl (Table I) were in reasonable agreement to within 3% average. For longer chain hydroperoxides, dodecyl and larger, significant thermal decomposition was observed for each GLC value compared to the corresponding iodometric value (Table I).

Since hydroperoxide reaction products beyond decyl could not be quantified by GLC, the longer-chain hydroperoxides were determined by HPLC in two instruments separately equipped with refractive index (RID) or flame ionization (FID) detection systems and interchangeable reversed-phase (RP) or normal-phase (NP) columns. The hydroperoxides also were determined iodometrically for comparison with the HPLC chromatographic quantitations. The selected data presented in Table I are typical for the series of hydroperoxide preparations. RP/FID was effective only for non-volatile compounds which were not thermally evaporated on the heated evaporative belt that functions for solvent removal prior to sample entry into the detector. The RP/FID values were low compared to the iodometric results but the former increased in value with increasing chain length which indicated their relative degree of volatility. The iodometric and reversed-phase HPLC values for hexadecyl hydroperoxide were in good agreement.

The homologous series of alkyl hydroperoxides and their corresponding alcohols were chromatographed isocratically in reversed-phase HPLC. The two series are graphically presented in Fig. 2 where log k' (capacity factor) *vs.* carbon number of alkyl residues depict the linearity in their order of elution. In this series, the alcohol has the longer retention time for each hydroperoxide–alcohol analogue pair. The alcohol and hydroperoxide series were obtained under identical conditions for comparison whereas literature data reported for the alcohols [30–32] were unusable for this purpose.

An example of a normal-phase HPLC separation of a hydroperoxide preparation is given in Fig. 3A showing alcohol as more strongly retained than hydroperoxide. Normal-phase hydroperoxide values with either FID or RID were low for all examples examined, although RID

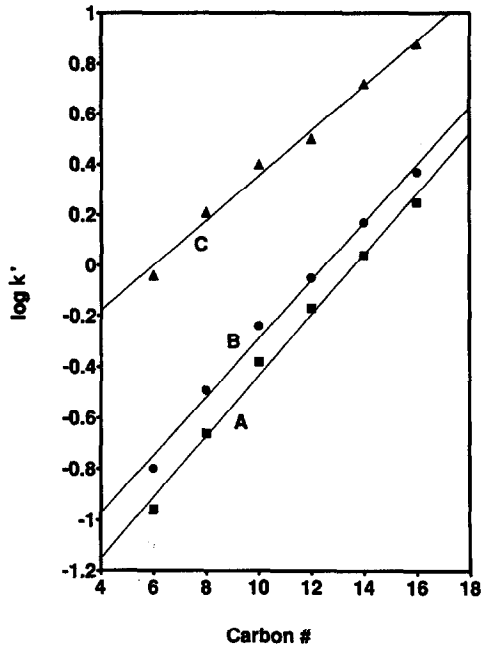


Fig. 2. Plot of log k' *vs.* carbon No. (#) of alkyl chain separated by RP-HPLC. A = Alkyl hydroperoxide; B = alkyl alcohols; C = dialkyl peroxides, where carbon No. is half total carbons of dialkyl peroxide.

gave the higher values. The NP/RID method introduced a large negative peak [33,34] with a corresponding uncertainty in the quantitation. This negative peak arises from solvent and pressure effects. Assuming the negative peak contained no overlapping component of identical retention time, the peroxide results could be

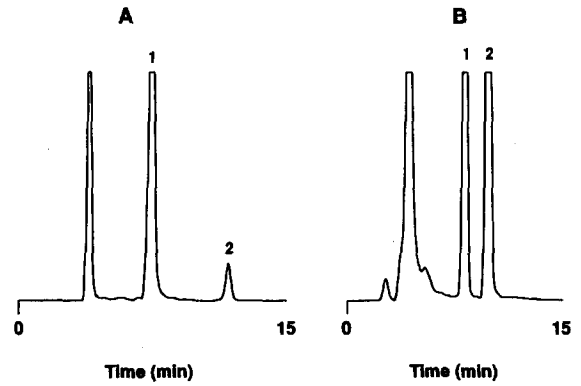


Fig. 3. HPLC–FID: (A) normal-phase (decyl hydroperoxide and decyl alcohol); (B) reversed-phase (didecyl peroxide and didecyl ether). Peaks: (A) 1 = $R_{10}OOH$, 2 = $R_{10}OH$; (B) 1 = $R_{10}OOR_{10}$, 2 = $R_{10}OR_{10}$.

adjusted proportionally. The measured values were within an average 8% of the iodometric values for the few determinations obtained. Consequently, RP/FID offered the best set of determinations for non-volatile hydroperoxides beyond C_{12} chain length and is the method of choice for chromatographic analysis. However, the NP/RID system was useful for isolating pure long-chain hydroperoxides on a semi-preparative scale: for example, a sample of hexadecyl hydroperoxide (70%, 1 g) was purified to 99% (0.5 g).

Dialkyl peroxides

A summary of the analyses of dialkyl peroxide preparations by iodometry, GLC and reversed phase HPLC is presented in Table II. Primary dialkyl peroxides are readily prepared from alkyl bromides by reaction with superoxide anion under phase transfer conditions [23]. In these reactions the major co-products are the dialkyl ether analogues. Quantitation of volatile dialkyl peroxides up to eight carbon atoms per alkyl chain was obtained by GLC (12-m column). The isomeric pair, dihexyl and butyl octyl peroxides, were resolved with the latter unsymmetrical peroxide having the longer retention time (Fig. 4). Dialkyl peroxides and reaction products exceeding eight carbon atoms per chain, although chromatographable by GLC, gave variable results because of the peroxides' thermal decomposition associated with the higher column temperatures needed for the analysis.

TABLE II

ANALYSIS OF DIALKYL PEROXIDES BY IODOMETRY, GLC AND HPLC

Carbon No. per alkyl	% Dialkyl peroxides		
	Iodometric[a]	GLC[b]	HPLC[c]
6	93.8	93.9	
8	89.1	90.1	
10	94.6		95.4
12	32		95.6
14	40		98.8
16	26		99.1
Supplementary dialkyl peroxides			
tert.-Butyl 1-octyl	91.2	90.6	
Dicumenyl	99.4		99.6
Di-*tert.*-butyl	97.2	99.9	

[a] Ref. 1, values based on % (w/w) active oxygen.
[b] 12-m HP-101 capillary column, see Experimental.
[c] By reversed-phase/flame ionization detection: values based on % (w/w) from calibration curves of purified dialkyl peroxides.

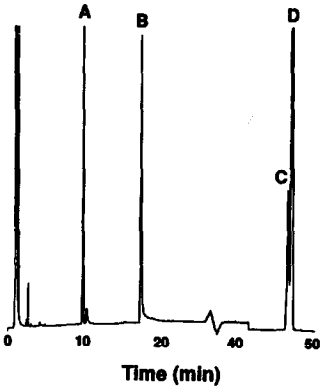


Fig. 4. Reaction products from 1-butyl 1-octyl peroxide synthesis. Peaks: A = 1-hexyl hydroperoxide (R_6OOH); B = 1-octyl hydroperoxide (R_8OOH); C = dihexyl peroxide (R_6OOR_6); D = 1-butyl 1-octyl peroxide (R_4OOR_6). GLC conditions as in text.

Dialkyl peroxide homologues were not resolvable using normal-phase HPLC. The medium- and long-chain homologues were chromatographed by HPLC in the RP/FID system with good resolution using acetonitrile–acetone cosolvents. The homologous even-carbon alkyl chain C_6–C_{16} series, which was chromatographed in reversed-phase HPLC, gave the linear relationship shown in Fig. 2. The nonperoxy analogue, dialkyl ether, similar to alcohol in the hydroperoxide series, was more strongly retained as demonstrated in Fig. 3B.

The synthetic availability of the dialkyl peroxides offered the opportunity to examine them iodometrically [1]. Dialkyl peroxides are unreactive with iodide ion at room temperature but were induced to liberate iodine thermally under complex conditions [27]. A new simplified method using perchloric acid or ferric ion catalysis achieved rapid, quantitative liberation of iodine whose values could be accepted with confidence by comparison with the chromatographic values serving as the standards (Table II) [1]. This

represents the inverse of the hydroperoxide analyses whereby iodometry functioned as the criterion for the chromatographic values.

Table II summarizes these results for which there is good agreement for all the compounds listed except the C_{12}–C_{16} members. The latter failed to achieve quantitation in the heated acetic acid solution because of poor solubility and decomposition within the melted sample globules. The table includes additional representations of dialkyl peroxide structures analyzed iodometrically. Each class of normal to tertiary alkyl peroxide required specific analytical conditions which permitted the arrangement ot an order of increasing stability and decreasing reactivity as follows:

increasing stability

n-dialkyl → *tert*-butyl *n*-alkyl → dicumenyl → di-*tert*.-butyl

decreasing reactivity

Peroxide structural effects

Peroxides have a dihedral angle as a characteristic structural feature that twists the O–O bond into opposing planes that is aptly described as an open book model (Fig. 5A). The dihedral angle leads to conformations in different peroxide structures in which this angle is enlarged or compressed [35].

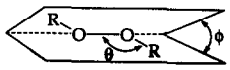
Peroxides and their non-peroxy analogues were resolved in GLC with the former having the longer retention time in accordance with the peroxide's higher molecular mass. Both the alkyl hydroperoxide and dialkyl peroxide were eluted at longer retention times than their corresponding alcohols and dialkyl ethers, respectively. Resolution of the isomeric di-1-hexyl and 1-butyl 1-octyl peroxides, the latter having the longer retention time, may be explained in terms of the dihedral angle inducing the longer octyl chain into conformations engaging Van der Waals interactions more extensively than the hexyl chain, *i.e.*, the longer the chain, the greater the degree of interaction and the longer the retention time.

By contrast in HPLC, alkyl hydroperoxides elute earlier (less retained) than their corresponding alkyl alcohol analogues in both reversed-phase (Fig. 2) and normal-phase (Fig. 3A) chromatography. Primary hydroperoxides dimerize to an intermolecular hydrogen-bonded cyclic structure (Fig. 5B) in contrast to their alcohol counterpart (dimers and polymers) [36] presumably arising from the greater acidity of the hydroperoxide and the increased stability of the pseudo six-membered ring structure. Accordingly, for normal-phase HPLC, the free terminal hydroxyl group of alcohol hydrogen bonds more strongly to silica leading to increased elution volumes.

In the case of dialkyl peroxides, the dihedral angle about the peroxy bond (Fig. 5A), which exceeds 100°, projects the two alkyl chains at approximately right angles to each other. The alkyl chains are thereby skewed into conformations that diminish their Van der Waals interactions with the octadecyl groups of the bonded stationary phase. The conformations are expressed as a foreshortening of chain length [2] compared to the more linear extension of the non-peroxide analogue. Hence, dialkyl peroxides in HPLC have shorter retention times than their non-peroxide analogues.

The generality of the foregoing relationship may be applied to peroxides of all classes as is further illustrated by the *tert*.-butyl permyristate/*tert*.-butyl myristate pair (Fig. 6) for which the ester was more strongly retained in reversed-phase HPLC. This same relationship would be

A



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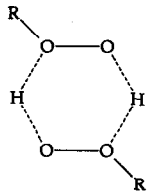

Fig. 5. (A) Structure of peroxides (R=H, alkyl, acyl); ϕ = dihedral angle; θ = R–O–O angle. (B) Cyclic dimer of alkyl hydroperoxide in solution.

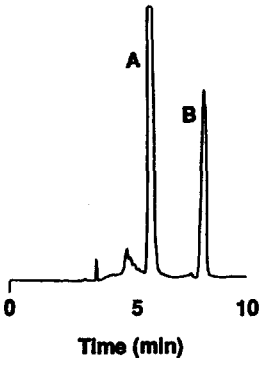

Fig. 6. Reversed-phase HPLC: (A) *tert.*-butyl permyristate; (B) *tert.*-butyl myristate. HPLC conditions as in text.

predicted by extension to diacyl peroxides relative to anhydrides for which peroxide there was foreshortening via the O–O bond skew [2].

Peroxy acids would also be expected to follow this rule. However, peroxy acids are monomeric, intramolecular hydrogen-bonded species [35,37,38] (dihedral angle, 72°) in the liquid and vapor states compared to intermolecular hydrogen-bonded dimers for carboxylic acids so that peroxy acids would be more volatile and less strongly retained in chromatographic separations than their carboxylic acid analogues.

CONCLUSIONS

Alkyl hydroperoxides for chain-size up to C_{10} were analyzable by GLC in 3% average deviation which is of moderate accuracy compared to their iodometric values. Although GLC could be used qualitatively to detect longer chain hydroperoxides, up to C_{16}, thermal decomposition precluded their quantitative analysis. Longer-chain hydroperoxides, C_{10} to C_{16}, were determined by NP-HPLC–RID with 7% average deviation, a fair accuracy which is attributed to the quantitative uncertainties associated with RID. RP-HPLC–FID requires the hydroperoxide to be non-volatile and that the FID thermal evaporative belt be operated below the hydroperoxide's decomposition temperature. Nevertheless, as hydroperoxide chain length increases and volatility decreases, there is a concomitant increase in quantitation so as to provide an excellent determination for hexadecyl hydroperoxide. Among these methods, NP-HPLC–FID was the least useful analytically being consistently low by 15–20%. NP-HPLC–RID, however, provided a useful semi-preparative method for obtaining alkyl hydroperoxides in pure form.

Dialkyl peroxides are more stable than the hydroperoxides. The dialkyl peroxides with average carbon number per alkyl chain up to 8 carbon atoms were accurately determined by GLC whereas the longer chain members were best determined by RP-HPLC–FID. Since previous iodometric methods could not be easily applied as a standard analytical method for dialkyl peroxides, the reverse approach of applying the chromatographic determinations derived in this study to establish accurate peroxide values facilitated the recent development of a new modification of iodometry.

The resolution of long chain dialkyl peroxides is based on chain size and the inherent property of skewness derived from the dihedral angle of the O–O bond. Between two dialkyl peroxide isomers, the one having one chain longer than the longest chain in the other isomer has the longer retention time in GLC. In HPLC, it is proposed that the peroxygen dihedral angle imposes a conformation to the dialkyl peroxide that foreshortens the overall chain length leading to diminished column interactions that shortens its retention time relative to the more extended ether analogue.

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