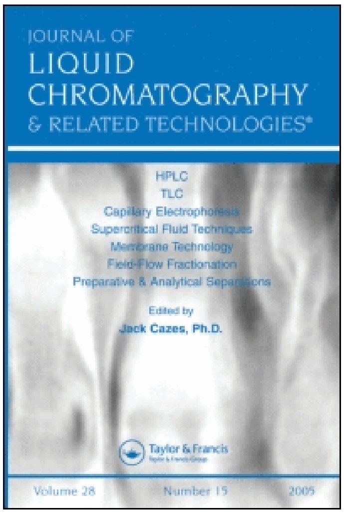

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

QUANTITATIVE DETERMINATION OF ORGANIC PERESTERS

Stefan Baj[a]; Anna Chrobok[a]
[a] Institute of Organic Chemistry and Technology, Silesian Technical University, Gliwice, Poland

To cite this Article Baj, Stefan and Chrobok, Anna(2000) 'QUANTITATIVE DETERMINATION OF ORGANIC PERESTERS', Journal of Liquid Chromatography & Related Technologies, 23: 4, 551 — 556

To link to this Article: DOI: 10.1081/JLC-100101471

URL: http://dx.doi.org/10.1081/JLC-100101471

J. LIQ. CHROM. & REL. TECHNOL., 23(4), 551–556 (2000)

QUANTITATIVE DETERMINATION OF ORGANIC PERESTERS

Stefan Baj, Anna Chrobok

Institute of Organic Chemistry and Technology
Silesian Technical University
44-100 Gliwice, Poland

ABSTRACT

This work presents a method for qualitative and quantitative analysis of selected organic peresters. The method is based on RP-HPLC measurements, using a mixture of acetonitrile and water as a mobile phase. This technique appears to be fast, simple, and precise. The obtained results were found to be highly reproducible. The relative standard deviations are within the range of 0.1-0.7 %.

INTRODUCTION

The widest applications of organic peresters are those in the plastics industry as the initiators of free-radical polymerizations and crosslinking agents.[1-3] Moreover, they are utilized as the bleaching and oxidizing agents, as well as the pharmaceutical additives.[2]

One of the basic methods for the production of organic peresters involves the reaction of alkyl hydroperoxides with acid chlorides. For the synthesis of peresters to be performed successfully it is essential to follow the changes in concentration of substrates and products versus time, as well as to determine purity of the obtained products. For this purpose the high performance liquid chromatography (HPLC)[4-7] could be supposed to be the most advantageous analytical technique.

www.dekker.com

The gas chromatography (GC) is not suitable for the analysis of peresters due to their low volatility and thermal instability. The thin-layer chromatography (TLC) and conventional column chromatography are the time-consuming techniques characterized by relatively low separation efficiency. The results obtained from NMR spectroscopy are not satisfactory as far as the precision is concerned. IR spectroscopy, polarographic analysis, and iodometric titration allow us to analyze only a part of the compounds under study.

Previously we described a method for the analysis of organic peroxides by means of HPLC.[8,9]

The present work provides the results of our study on the application of RP-HPLC to the qualitative and quantitative analysis of peresters, as well as to the separation of post-reaction mixtures obtained in the synthesis of these peresters. This method was verified for several selected peresters giving satisfactory results.

EXPERIMENTAL

Materials

Valeric chloride, butyric chloride, benzoyl chloride, and tetrabutyl-ammonium hydrogensulfate were commercial materials (Merck, Darmstadt); cumyl hydroperoxide (technical product) was purified;[10] tert-butyl hydroperoxide was prepared according to the known procedure described elsewhere.[11] Acetonitrile and water used as eluent for HPLC were HPLC grade (Merck, Darmstadt).

Preparation of Peresters. General Procedure

Into a thermostatted three-necked 250-mL flask equipped with a thermometer, stirrer and dropping funnel, a 96.3% solution of cumyl hydroperoxide ($1.11 \cdot 10^{-2}$ mol) in 20 mL of hexane and tetrabutylammonium bisulfate ($1.11 \cdot 10^{-3}$ mol) as the catalyst were introduced. Then, a 60% aqueous solution of NaOH, Na_2CO_3 or $NaHCO_3$ ($1.11 \cdot 10^{-2}$ mol) was added dropwise, followed by adding a solution of acid chloride ($1.11 \cdot 10^{-2}$ mol) in 20 mL of hexane while stirring. Afterwards, a content of the flask was still stirred for a period of 30 min. to 4 h depending on the reaction rate. Finally, 20 mL of H_2O was added to the post-reaction mixture, and the formed layers were separated. The organic layer was washed with three 20-mL portions of H_2O and left to dry over anhydrous $MgSO_4$. After hexane had been distilled off under vacuum, cumyl or tert-butyl perbenzoate, perbutyrate or pervalerate were obtained.

Instrumentation

Analytical high performance liquid chromatography was performed on an Alliance liquid chromatograph (Waters 2690 system, produced by Waters Corporation, Milford, Massachusetts, USA) with a Photodiode Array Detector and Differential Refractometer Detector, and 3.9 x 150 mm HPLC Cartridge Column (Nova-Pak C18 60A, 4m) containing dimethyloctadecylsilyl bonded amorphous silica. Solvent system included acetonitrile/water mixtures (70/30, 75/25, 80/20, 85/15, 90/10 v/v; flow rate 1.0 mL/min.). Samples for injection (20μL) were dissolved in the mobile phase.

Quantitative Procedure

Calibration was carried out according to the external standardization method. The experimental data were processed with the aid of an appropriate program (Millennium^{32} Software). For determining the compounds, solutions of the investigated peresters in acetonitrile were used. The 2 - 20 μL injections were made by means of an automatic injection system (Waters 717 plus Autosampler).

RESULTS AND DISCUSSION

In this work we intended to develop a method for the analysis of the post-reaction mixtures composed of acid chlorides, cumyl and tert-butyl hydroperoxides, as well as corresponding peresters, i.e. cumyl and tert-butyl perbenzoate, perbutyrate, and pervalerate.

The analysis of the above substances was performed using a Nova-Pak C18 colum (60A, 4 μm). Water/acetonitrile mixtures of various volume ratios were used as eluents.

Detection of the samples was carried out by means of a PDA detector and differential refractometer. Retention times obtained from the both detectors appeared to be highly reproducible.

The plots in Figure 1 present the relations of ln (k') against composition of the mobile phase for respective chlorides and peresters, using the PDA detector.

The best separation of the examined substances is observed (Fig. 1) when the volume ratio of acetonitrile to water is 70 : 30. Such a composition of eluent, aside from ensuring good separation efficiency of the substances in the

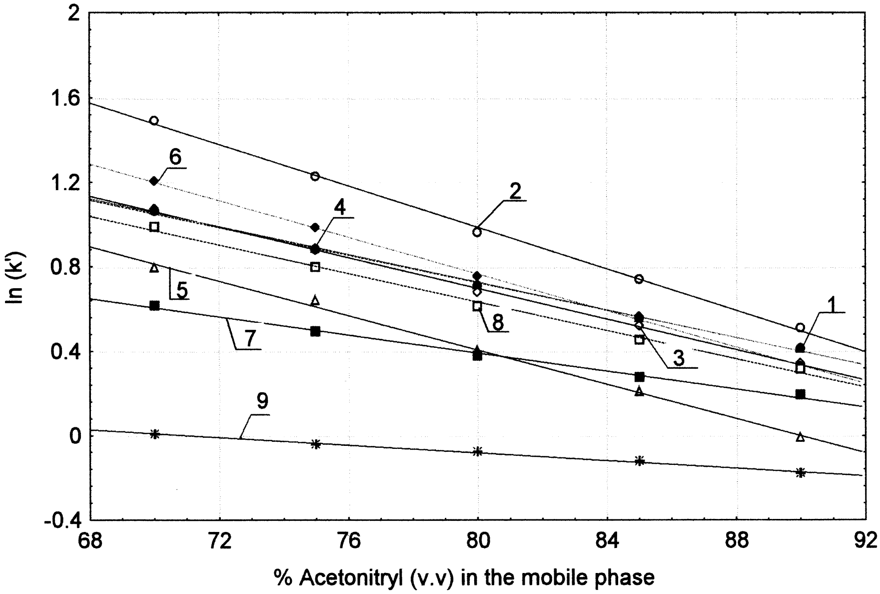

Figure 1. The plots of ln (k') vs concentration of acetonitrile in the mobile phase for the following compounds: 1 - valeric chloride (λ =210 nm), 2 - cumyl pervalerate (λ=210 nm), 3 - tert-butyl pervalerate (λ =210 nm), 4 - butyric chloride (λ =210 nm), 5 - tert-butyl perbutyrate (λ =210 nm), 6 - cumyl perbutyrate (λ =210 nm), 7 - benzoyl chloride (λ =220 nm), 8 - tert-butyl perbenzoate (λ =220 nm), 9 - cumyl perbenzoate (=220 nm).

mixture, meets also the requirement that the retention volume be within the range of 1 < k' < 10.

The retention times and coefficients k' of the analyzed compounds are collected in Table 1.

During injection of the samples, a high reproducibility of the retention time values was observed.

Quantitative Analysis

A quantitative analysis was performed with the aid of a PDA detector. External standard calibration gave a linear response for the peak-area ratio for standard concentration in the range of 1 - 20 mg/mL. The correlation coefficients are very high, thus reflecting high precision of the method. The para-

Table 1

Retention Time, k' Values and Parameters of Linear Regression by the Last-Squares for a Plot of Peak Area Versus Mass Injected for the Investigated Compounds*

Compounds	Retention Time (s)	k'	Range (μg)	Slope $a \times 10^{-7}$	Intercept, b	Correlation Coefficient, r
Valeric chloride	149	2.892	1.0-20.0	2956	113960	0.9989
Butyric chloride	140	2.909	1.0-20.0	1089	-35277	0.9998
Benzoyl chloride	102	1.857	0.0-10.0	186359	3790747	0.9974
tert-Butyl pervalerate	141	2.917	1.0-20.0	8954	-6461	0.9998
Cumyl pervalerate	196	4.450	1.0-20.0	150586	247672	0.9988
tert-Butyl pervalerate	115	2.212	1.0-20.0	6876	-3761	0.9999
Cumyl perbutyrate	156	3.333	1.0-20.0	116523	156358	0.9998
tert-Butyl perbenzoate	132	2.683	0.0-10.0	213266	467205	0.9999
Cumyl perbenzoate	152	1.008	0.0-10.0	197644	-89441	0.9976

---

* Number of calibration points for each compound, n = 7; number of replicates of each injection, m = 5.

Table 2

Reproducibility of External Standard Method for the Determination of Investigated Dialkil Peroxides*

Compound	Amount Added (μg)	Mean Amount Found (μg)	S.D. (μg)	R.S.D. (%)	Amount Added (μg)	Mean Amount Found (μg)	S.D. (μg)	R.S.D. (%)
Valeric chloride	8.34	8.52	0.0090	0.11	19.85	20.02	0.0752	0.38
Butyric chloride	4.73	4.83	0.0048	0.10	18.18	18.09	0.0959	0.53
Benzoyl chloride	0.30	0.29	0.0009	0.33	7.20	7.18	0.0206	0.29
tert-Butyl pervalerate	5.08	5.26	0.0086	0.16	19.09	19.52	0.0539	0.28
Cumyl pervalerate	1.02	1.05	0.0042	0.40	10.50	10.32	0.0347	0.34
tert-Butyl perbutyrate	1.86	2.01	0.0098	0.49	12.45	12.56	0.0729	0.58
Cumyl perbutyrate	1.71	1.72	0.0078	0.45	18.10	18.07	0.0630	0.35
tert-Butyl perbenzoate	0.57	0.58	0.0039	0.67	7.08	7.12	0.0097	0.14
Cumyl perbenzoate	2.02	2.04	0.0054	0.27	6.83	6.79	0.0147	0.22

---

* Number of injections for each determination, m = 8.

meters resulting from the least-squares regression for external standard method are given in Table 1.

Relative standard deviations (R.S.D.) of replicate injections are shown in Table 2. The obtained results of the quantitative analysis show the method to be highly sensitive. This method is relatively fast, and enables analysis of peresters with high accuracy.

From Table 2, it follows that the R.S.D. coefficients are very low and are within the range of 0.1-0.7 %. All the obtained results confirm that the method can be successfully used to analyze the studied substances.

REFERENCES

1. Y. Savaki, in **Organic Peroxide**, Wataru Ando, New York 1992.

2. L.A. Singer, **Organic Peroxide, Vol 1**, Wiley-Interscience, New York 1970.

3. I. Thijs, S. N. Gupta, D. C. Neckers, J. Org. Chem., **44**, 4123 (1979).

4. L. Topolova, Kh. Dimitrov, M. Aleksandrova, Izv Akad Nauk SSSR, Ser Khim **19**, 520 (1986).

5. B. J. Baltra, B. de Havedia, Afinidad, **46**, 185 (1989).

6. C. P. Patel, S. Lilly, LC-GC, **6**, 424 (1988).

7. W. Van Tilborg, J. Chromatog., **115**, 616 (1975).

8. S. Baj, Fresenius. Z. Anal. Chem., **350**, 159 (1994).

9. S. Baj, Z. Kulicki, J. Chromatog., **588**, 33 (1991).

10. W. Karminski, Z. Kulicki, Z. Stec, Chemia Stosow., **24**, 17 (1969).

11. L. A. Singer, N. P. Kong, J. Am. Chem. Soc., **20**, 5213 (1966).

Received January 15, 1999
Accepted May 18, 1999
Author's Revisons September 31, 1999
Manuscript 4969